

Annotated Bibliography on
Advanced Technologies for Enhancing Heavy Oil Upgrading



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Table of Contents

Introduction:..... 3

Articles' Abstracts: 4

Contact NSTIC for full Text:..... 37

Introduction:

In the face of a global economic downturn, there has been a year-to-year reduction in total liquid fuel consumption. Despite this, liquid fuels, primarily derived from petroleum, continue to serve as the world's primary energy source. This category encompasses heavy oils, which are denser and more viscous forms of petroleum. The process of upgrading heavy oils involves the application of various advanced technologies aimed at enhancing their quality and characteristics, thereby making them more suitable for a wide array of energy-related applications.

Furthermore, the accessibility of heavy oil fields varies significantly, influenced by factors such as well depth, geographic remoteness, and the fluid properties of the oil. These variations present a challenge when attempting to implement a single technology for upgrading the various types of heavy oil. As highlighted by Carrillo and Corredor (2013)¹, there is a growing need for increased production of heavy and extra heavy crude oils in regions like the Gulf of Mexico and Northeastern China, as conventional middle and light oil production declines over the next two decades. This emphasizes the urgency for new technologies and innovations in heavy oil upgrading that can meet the rising energy demands while also addressing environmental concerns within the heavy oil industry.

The primary aim of this annotated bibliography is to support the Petroleum Research Center, particularly the Optimization of Petroleum Refinery Processes (OPRP) program, by providing recently published articles (2019 – 2023) that feature new technologies for enhancing heavy oil upgrading.

E-Resources used: Scopus – American Chemical Society (ACS) – OnePetro.

Contact NSTIC to request full-text articles

¹ Carrillo, J. A., & Corredor, L. M. (2013). Upgrading of heavy crude oils: Castilla. *Fuel Processing Technology*, 109, 156–162.

Articles' Abstracts:

1. Al-Samhan, M., Al-Fadhli, J., Al-Otaibi, A., & Bouresli, R. (2023). Synthesis of micromesoporous zeolite-alumina catalysts for olefin production from heavy crude oil. *International Journal of Chemical Engineering*, 2023

Abstract: Maximizing the production of high-value olefins from heavy crude oil is a crucial topic in the downstream refining industry. However, converting heavier fractions is a major challenge due to the small pore size of the zeolites. Therefore, this work aimed to develop extrudate zeolite catalysts posing adequate micromesoporous pore network and moderate acidity by combining microporous zeolite with the boehmite phase of alumina. These extruded zeolite-alumina catalysts are expected to allow sufficient diffusion of heavy fractions, thus leading to high cracking of heavy oil into valuable olefins. Different zeolite-alumina catalysts of varying alumina content ranging from 25 to 75% (AlZ-25, AlZ-50, and AlZ-75) were prepared in the laboratory to study the optimum zeolite-alumina ratios for maximum olefin production from heavy oil. The catalysts were characterized for their chemical and physical properties using nitrogen adsorption (N_2 adsorption), X-ray diffraction (XRD), inductively coupled plasma (ICP) spectrometry, Fourier transform infrared (FT-IR) spectroscopy, and NH_3 temperature programmed desorption (TPD). A gradual increase in the average pore diameter (APD) of the catalysts was observed due to the alumina ratio with a distinct range of acidity that is in the range of 125 to 375°C, and also the geometry of pores is not the same for all of the supports. Catalytic performance tests were conducted in a fixed-bed reactor at 450°C, 10 bar, and liquid hourly space velocity (LHSV) of 1 h^{-1} . The results revealed that the prepared catalysts were thermally stable and effective in heavy oil conversion to olefins. Moreover, the selectivity of propylene was higher than that of ethylene (P/E) due to the modified textural and acidic properties of the catalysts. The results showed that the catalysts prepared with moderate acidity and adequate mesopores exhibited a considerable effect on the conversion of heavy

crude oil into olefins. Hence, the acidity and mesoporosity of the catalysts play a vital role in determining the catalyst performance.

2. Gharibi, S., Fatemi, S., Mjalli, F. S., & Al-Hajri, R. (2023). CO₂-H₂O assisted co-pyrolysis of petroleum vacuum residue and polypropylene to improve asphaltene reduction and coke suppression: A statistical approach. *Journal of Analytical and Applied Pyrolysis*, 171

Abstract: Non-catalytic co-pyrolysis of petroleum vacuum residue (VR) and polypropylene (PP) was studied under CO₂ and/or steam atmospheres in a batch condition. A statistical approach was performed to analyze the effect of temperature, CO₂ initial pressure, reaction time, PP and water contents using fractional factorial design methodology. A comparison of co-pyrolysis in steam, CO₂, and steam + CO₂ atmospheres showed that CO₂ + steam is a more effective environment for reduction of asphaltene and suppressing coke formation. In detail, steam dominated the pyrolysis process, whereas CO₂ enhanced the thermal cracking reactions, thereby increasing the asphaltene conversion to maltene and decreasing coke formation. Moreover, the results indicated that the addition of PP to VR improved the yield and quality of the liquid product and diminished the coke content. The optimum conditions were the temperature of 380 °C, CO₂ initial pressure of 0.6 MPa, reaction time of 90 min with PP/ VR and water/ VR ratios of 0.23, and 0.25 (g/g), respectively. Pyrolysis of VR under such conditions resulted in the 86% maltene yield, 89.7% asphaltene reduction and 6.3% coke reduction. ¹H NMR analysis showed that paraffins occupy the major content of the liquid (81.07 vol%), followed by aromatics (12.28 vol%) and olefinic compounds (6.65 vol%). In addition, the upgraded oil had a remarkable °API gravity of 35.9 and a low viscosity of 5.27 ± 0.02 cP. Furthermore, heavy metals of Ni and V were removed from the liquid product by

56.1% and 65.6%, respectively. Pyrolysis of VR with PP in the CO₂ + steam environment would be deemed an economically viable and environmentally friendly technique of transforming the abundant low-grade VR feedstocks to valuable liquid fuels at a milder processing condition without using any catalysts.

3. Huang, Z., Zhao, Q., Chen, L., Guo, L., Miao, Y., Wang, Y., & Jin, H. (2023). Experimental investigation of enhanced oil recovery and in-situ upgrading of heavy oil via CO₂-and N₂-assisted supercritical water flooding. *Chemical Engineering Science*, 268, 118378.

Abstract: Exploitation of heavy oil is critical for mitigating the energy crisis. However, conventional thermal recovery methods cannot completely exploit the potential of heavy oil owing to its high viscosity and heavy distillates. A new technology is proposed with reference to CO₂- and N₂-assisted supercritical water (MGA-SCW) injection for heavy oil recovery. In this study, an experimental apparatus was developed to simulate the MGA-SCW flooding process and test its feasibility. MGA-SCW injection remarkably enhanced oil recovery, increased the oil production rate, and improved the oil quality. For MGA-SCW flooding at 25 MPa and 400 degrees C, the recovery factor approached 95 %, and the oil viscosity decreased by 32 %; the light distillate fraction (180-350 degrees C) increased from 11 to 15 %. The dynamic process of MGA-SCW flooding is divided into three stages: pressure difference, thermal, and miscible drives. This technology can be applied to the development and utilization of offshore heavy oil fields.(c) 2022 Elsevier Ltd. All rights reserved.

4. Kholmurodov, T., Mirzaev, O., Affane, B., Tajik, A., Romanova, K., Galyametdinov, Y., . . . Vakhin, A. (2023). Thermochemical upgrading of heavy crude oil in reservoir conditions. *Processes*, 11(7), 2156.

Abstract: The purpose of this study is to enhance the quality of heavy oil through refinement using aquathermolysis with the simultaneous injection of steam and thermally stable nonionic surfactants (NS). To achieve this, the NS R-PPG of the nonionic type was synthesized, and the optimal product structures were characterized using infrared (IR) methods. Furthermore, the thermal stability of the synthesized NS R-PPG was investigated in line with the requirements for surfactants used in heavy oil applications. Subsequently, the study delved into investigating the hydrothermal upgrading of heavy oil with a catalyst, involving the joint participation of steam and surfactants at a temperature of 250 & DEG;C. Additionally, we assessed the improved oil characteristics resulting from the experimental process through SARA analysis, elemental analysis, GC, and viscosity reduction evaluations. The experimental results demonstrated distinct effects concerning the presence and absence of surfactants on heavy oil. Based on these findings, we conclude that surfactants play a crucial role in dispersing asphaltene clusters, thereby facilitating the decomposition process under mild thermobaric conditions, leading to a noticeable increase in the content of light fractions. Furthermore, as per the results of the elemental analysis, surfactants contribute significantly to the desulfurization of heavy oil. Overall, the incorporation of surfactants during hydrothermal upgrading resulted in an irreversible reduction in the viscosity of heavy oil, thereby enhancing its overall quality.

5. Li, H., Li, X., Zhao, D., Zhou, G., & Yo, B. (2023). Preparation of graphene supported ni-fe bimetallic nanocatalyst and its catalytic upgrading and viscosity reduction performance for heavy oil. *Geoenergy Science and Engineering*, 227, 211847.

Abstract: Graphene supported single metal catalyst can improve the dispersion of active components and enhance the viscosity reduction effect of heavy oil. However, there is little research on graphene-supported bimetallic catalysts in the field of heavy oil upgrading and viscosity reduction. In this paper, super heavy oil of Liaohe Oilfield was taken as the research object. Graphene was selected as the carrier material, and nickel and iron chlorides were used as precursors. Graphene-supported nickel-iron bimetallic nanocatalysts were prepared by solvothermal method, and their synthesis feasibility was proved by microscopic characterization. Then the prepared catalyst was used in the evaluation experiment of catalytic upgrading and viscosity reduction performance of Liaohe heavy oil. By analyzing the parameters of oil samples before and after catalytic upgrading and viscosity reduction, the catalytic upgrading and viscosity reduction effect was evaluated and the viscosity reduction mechanism was revealed. The results showed that the viscosity reduction rate of heavy oil with graphene supported Ni-Fe bimetallic catalyst was 42.38%. With the aid of decalin, the viscosity reduction rate of heavy oil could reach 71.43%. At this time, the content of heavy components, the average molecular weight of heavy components and the aromaticity fA of oil samples decreased after catalytic upgrading and viscosity reduction, while the aromatic condensation degree HAU/CA and the branched chain index BI increased, and the modification effect was significant. Among them, the average molecular weight of asphaltene decreased from 2266 to 1444, with the most obvious decrease. The decrease of heteroatom content in asphaltene led to a significant decrease in intermolecular force and hydrogen bonding, which was the main reason for the catalytic upgrading and viscosity reduction of heavy oil by graphene supported Ni-Fe bimetallic catalyst.

6. Medina, O. E., Galeano-Caro, D., Brattekkås, B., Pérez-Cadenas, A. F., Carrasco-Marín, F., Cortés, F. B., & Franco, C. A. (2023). Simultaneous CO₂ adsorption and conversion over ni-pd supported CeO₂ nanoparticles during catalytic n-C₇ asphaltene gasification. *Fuel*, 342 .

Abstract: Shallow heavy oil reservoirs are suitable for the geo-sequestration of CO₂ based on its adsorption and conversion during thermal-enhanced oil recovery processes. This study aims to evaluate multifunctional nanomaterials for CO₂ adsorption and its subsequent transformation into valuable sub-products during the catalytic decomposition of asphaltenes in a steam gasification atmosphere. Three ceria nanoparticles with cubic (C-CeO₂), orthorhombic (O-CeO₂), and spherical (S-CeO₂) shapes were tested in four stages including i) CO₂ adsorption at 30, 50, 100, and 200 °C between 0.084 and 3.0 MPa, ii) dynamic in-situ CO₂ adsorption in the presence of steam between 170 and 230 °C at 3.0 MPa, iii) dynamic in-situ CO₂ adsorption in the presence of steam with adsorbed asphaltenes between 170 and 230 °C at 3.0 MPa and iv) CO₂ conversion at the same conditions. The best nanoparticle morphology was doped with 1 wt% of Ni and Pd (C-CeNiPd) and was tested in the same experiments. Among the most important results, CO₂ adsorption increased in the order S-CeO₂ < O-CeO₂ < C-CeO₂ < C-CeNiPd, regardless of the temperature. When steam was injected, CO₂ adsorption is reduced in all the systems. At 200 °C adsorption decreased by 3.0 %, 2.7 %, 2.5 %, and 2.0 % in processes assisted by S-CeO₂, O-CeO₂, C-CeO₂, and C-CeNiPd, respectively. Nanoparticles with adsorbed asphaltenes presented a high tendency for CO₂ adsorption as well. The nanoparticle with the best morphology (C-CeO₂) adsorbed about 24.3 % (3.92 mmol) of CO₂ at 200 °C, and the yield increased after doping with Ni and Pd, obtaining CO₂ adsorption of 34 %. Finally, for CO₂ conversion, a mixture of gases composed of CO, CH₄, H₂, and light hydrocarbons (LHC) is obtained. The hydrogen production content follows a trend that agrees well with each material's adsorptive capacity and catalytic activity. The maximum %vol of H₂

produced at 200 °C during asphaltene gasification was 31 %, 29 %, 24 %, and 23 % for C-CeNiPd, C-CeO₂, O-CeO₂, and S-CeO₂, respectively.

7. Mikhailova, A. N., Al-Muntaser, A. A., Suwaid, M. A., Zairov, R. R., Kadhim, I. T., Djimasbe, R., . . . Varfolomeev, M. A. (2023). Ferrocene-based catalysts for in-situ hydrothermal upgrading of heavy crude oil: Synthesis and application. *Fuel*, 348, 128585.

Abstract: In this work, the effect of synthesized Ferrocene-based ligand catalysts, including Mono-, Di- and Tri-Ferrocene, as additives for promoting the catalytic in-situ hydrothermal upgrading of Tatarstan (Russia) heavy crude oil was studied. In addition, the changes in composition of upgraded oil samples as well as the in-situ transformation and characteristics of used catalysts were evaluated in detail using comprehensive analyzing techniques. All of the catalytic and non-catalytic hydrothermal upgrading experiments were carried out under the steam stimulation conditions at 300 degrees C, 72 bar (1044.27 psi) and 24 h of reaction time. The results show that introducing Ferrocene-based ligand catalysts to the upgrading system promotes the in-situ upgrading of heavy crude oil and improves the physical and chemical properties of upgraded oil samples. The maximum viscosity reduction was observed in presence Tri-Ferrocene and reached around 40% compared to non-catalytic hydrothermal upgrading. In addition, the upgrading performance also reflects in increase of H/C ratio, reduction of sulfur content, increase of saturates and aromatics, and decrease of the content of resins and asphaltenes as well as a noticeable change (increase) in the light fractions of C₁₀-C₂₀ are observed for all upgraded oil samples. Mono-Ferrocene as an oil-soluble catalyst mainly transformed to the particles of Fe₃O₄ (Magnetite) and FeS, which can act as active forms of catalysts and accelerate the hydrothermal conversion of heavy crude oil and its heavy

fractions including resins and asphaltenes. These transformations were confirmed using XRD, SEM-EDX and Mo center dot ssbauer analyzing techniques. Generally, the good catalytic performance of used ferrocene-based ligand catalysts as well as their low cost and commercial availability makes them great potential catalysts for improving the efficiency of steam injection for heavy oil production and in-situ upgrading.

8. Namdar, H., Manteghian, M., Jafari, A., & Saviz, S. (2023). Effective parameters on in-situ oil upgrading with nanocatalyst in large scale: Kinetics modeling. *Journal of Analytical and Applied Pyrolysis*, 173, 106073.

Abstract: Thermal enhanced oil recovery (EOR) methods are the main techniques used to produce oil from heavy oil reservoirs. But this methods are associated with environmental challenges and do not reduce viscosity permanently. One of the new methods with less environmental challenges that can permanently improve oil quality and enhanced oil recovery is the in-situ oil upgrading with nanocatalyst. In the present study, effectiveness of the insitu oil upgrading with nanocatalyst in improving the quality of oil and increasing the oil production have been investigated at a large-scale heavy oil reservoir with the aid of STARS simulator. Reactive flow was considered in the simulation by kinetic modelling of a reaction network with 5 pseudo-components. Also, effect of temperature and type of oil have been studied. Details on how to carry out reactions and changes in oil components over time have been investigated. In addition, steam flooding and in-situ oil upgrading with nanocatalyst were compared from the point of view of the amount of released CO₂ gas and the required water. The results show that in-situ oil upgrading with nanocatalyst is a time-consuming process and causes a 40% increase in the cumulative production and 23.58% decrease in the density compared to the steam flooding. There is an optimum temperature (300 degrees C) for the in-situ oil upgrading

process with nanocatalyst at which the maximum amount of oil is produced and has a better recovery on heavier oils. The major part of VR is converted into distillate in the heavier oil, while in the lighter oil, the dominant reaction was conversion of VR to VGO. In addition, in-situ oil upgrading with nanocatalyst reduces the required water and emission of CO₂ compared to the steam flooding method and among the three factors of injection flow rate, temperature, and steam quality, the most effective factor to reduce environmental problems with the help of in-situ oil upgrading with nanocatalyst is injection flow rate.

9. Pirouzfard, V., Mohamadkhani, F., Van Nguyen, N., & Su, C. -. (2023). The technical and economic analysis of processing and conversion of heavy oil cuts to valuable refinery products. *International Journal of Chemical Reactor Engineering*, 21(8), 965-977.

Abstract: Many of the modern refineries are founded on converting/upgrading the heavy bases of low value to lighter products by higher added value like gasoline, jet fuel and diesel fuel. In this work, some process configurations in heavy refinery cracking, converting and treating are technically and economically evaluated. In this purpose, four process configurations for refinery plants are suggested. These processes are evaluated and analyzed to obtain the most optimal configurations with the aim of achieving the most valuable refinery products. The difference of the processes is in heavy residue conversion and processing. These processes are included the Asphalt Air Blowing Unit (AABU, Type 1), Delayed Coker Unit (DCU, Type 2), Heavy Residue Hydro-Conversion (HRH, Type 3) and Solvent De-Asphalting (SDA, Type 4). The units are common in mentioned refineries cases and just ABU, HCU, DCU, HRH and SDA are different. In economic consideration, the payout period is considered as one of the standard methods of assessing the economic projects and economically estimating them. As results, the highest rate of gasoline is recorded in the refinery type of DCU unit and the highest amount of

LPG/C4/C3, kerosene and gasoline production observed in refinery type of HRH unit. The construction of refinery with ABU unit has minimum investment (980 million \$) and highest rate of return (19.4).

10. Ruiz, W., Guillemant, J., Coniglio, L., Rodgers, R. P., Christensen, J. H., Garcia-Montoto, V., . . . Bouyssiere, B. (2023). Bio-oil inorganic analysis: A minireview of current trends, challenges, and future perspectives. *Energy Fuels*, 37(16), 11608-11621.

Abstract: The analysis of the inorganic content of bio-oils has not been widely reported in the literature. In this work, the analytical methods employed for the quantification and speciation of inorganic species in bio-oils are summarized. Total inorganic analysis of bio-oils is commonly performed using inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry techniques; however, other quantitation techniques are compiled and discussed in this review. Additionally, the few studies that have recently been reported on the inorganic speciation of bio-oils by supercritical fluid chromatography–inductively coupled plasma mass spectrometry, gel permeation chromatography–inductively coupled plasma high-resolution mass spectrometry, and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry are also addressed. Cumulatively, the reports suggest that the lack of standard analytical methods in the total inorganic analysis of bio-oils is a major contributor to inaccurate results. Thus, future research with analytical methodologies already applied in crude oils should be adapted to account for the unique bio-oil(s) matrix. Such a strategy offers a path toward more accurate inorganic speciation/quantitation of inorganics in bio-oils, which might be the key to the understanding of production problems, storage stability, and upgrading processes commonly encountered with such samples.; The analysis of the inorganic content of bio-oils has not been

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11. Tan, J., Wang, Z., Chen, S., & Hu, H. (2023). Progress and outlook of supercritical CO₂–Heavy oil viscosity reduction technology: A minireview. *Energy Fuels*, 37(16), 11567-11583.

Abstract: Under the guidance of the carbon peaking and carbon neutrality strategies, the recovery, emission reduction, and effective utilization of industrial CO₂ are particularly important. Supercritical CO₂ viscosity reduction technology effectively improves the flowability and reduces the energy consumption of heavy oil pipeline transportation. This work

reviews the experimental research on supercritical CO₂ viscosity reductions of heavy oil, summarizes the viscosity reduction mechanisms and main influencing factors, describes the research achievements regarding theoretical parameters such as the solubility and viscosity of supercritical CO₂ and the density and viscosity of live oil, introduces engineering applications of supercritical CO₂ in the oil and gas field, analyses the problems involved in corrosion, stability, and solids deposition of crude oil containing dissolved CO₂, and presents the current challenges and perspectives. The main future research directions of this technology involve the mechanism of supercritical CO₂ viscosity reduction, ensuring the stability of supercritical CO₂ and crude oil mixtures during pipeline transportation, designing and establishing oilfield surface engineering facilities for supercritical CO₂ viscosity reduction technology, and improving the protection strategies for CO₂ corrosion. This work can provide a reference for the application of supercritical CO₂ in heavy oil development and pipeline transportation.;

Under the guidance of the carbon peaking and carbon neutrality strategies, the recovery, emission reduction, and effective utilization of industrial CO₂ are particularly important. Supercritical CO₂ viscosity reduction technology effectively improves the flowability and reduces the energy consumption of heavy oil pipeline transportation. This work reviews the experimental research on supercritical CO₂ viscosity reductions of heavy oil, summarizes the viscosity reduction mechanisms and main influencing factors, describes the research achievements regarding theoretical parameters such as the solubility and viscosity of supercritical CO₂ and the density and viscosity of live oil, introduces engineering applications of supercritical CO₂ in the oil and gas field, analyses the problems involved in corrosion, stability, and solids deposition of crude oil containing dissolved CO₂, and presents the current challenges and perspectives. The main future research directions of this technology involve the mechanism of supercritical CO₂ viscosity reduction, ensuring the stability of supercritical CO₂ and crude oil mixtures during pipeline transportation, designing and establishing oilfield

surface engineering facilities for supercritical CO₂ viscosity reduction technology, and improving the protection strategies for CO₂ corrosion. This work can provide a reference for the application of supercritical CO₂ in heavy oil development and pipeline transportation.

12. Zhou, W., Xin, C., Chen, Y., Mouhouadi, R. D., & Chen, S. (2023). Nanoparticles for enhancing heavy oil recovery: Recent progress, challenges, and future perspectives. *Energy Fuels*, 37(12), 8057-8078.

Abstract: Heavy oil is estimated to account for about 70% of the remaining oil reserves and considered as the most promising and readily available oil resource to meet energy demands in the coming decades. However, traditional enhanced oil recovery (EOR) methods for heavy oil face significant challenges, such as high mobility of injected fluids, polymer degradation, surfactant adsorption, significant chemical consumption, considerable energy and water consumption, significant greenhouse gas emissions, high operation costs, and the need for robust facilities. Recently, nanoparticle technology has been launched as a promising alternative technology for heavy oil recovery enhancement due to their unique characteristics of ultrasmall size, large surface area to volume ratio, low costs, and environmental friendliness. This paper presents a comprehensive discussion of the most recent studies about nanoparticle applications for heavy oil recovery and helps researchers gain insights into EOR mechanisms underlying these various applications. Nanoparticle applications for enhancing heavy oil recovery can be summarized into two major categories: nanofluid flooding (i.e., the use of nanoparticles alone) and its hybrids of traditional EOR methods. First, various applications of nanofluid flooding are summarized in terms of incremental oil recovery performance and EOR mechanisms. Second, recent research progress on the hybrids of nanoparticles and traditional EOR methods including thermal, chemical, and gas injection technologies is highlighted.

Finally, the challenges and future perspectives for development and applications of nanoparticles for enhancing heavy oil recovery are identified.; Heavy oil is estimated to account for about 70% of the remaining oil reserves and considered as the most promising and readily available oil resource to meet energy demands in the coming decades. However, traditional enhanced oil recovery (EOR) methods for heavy oil face significant challenges, such as high mobility of injected fluids, polymer degradation, surfactant adsorption, significant chemical consumption, considerable energy and water consumption, significant greenhouse gas emissions, high operation costs, and the need for robust facilities. Recently, nanoparticle technology has been launched as a promising alternative technology for heavy oil recovery enhancement due to their unique characteristics of ultrasmall size, large surface area to volume ratio, low costs, and environmental friendliness. This paper presents a comprehensive discussion of the most recent studies about nanoparticle applications for heavy oil recovery and helps researchers gain insights into EOR mechanisms underlying these various applications. Nanoparticle applications for enhancing heavy oil recovery can be summarized into two major categories: nanofluid flooding (i.e., the use of nanoparticles alone) and its hybrids of traditional EOR methods. First, various applications of nanofluid flooding are summarized in terms of incremental oil recovery performance and EOR mechanisms. Second, recent research progress on the hybrids of nanoparticles and traditional EOR methods including thermal, chemical, and gas injection technologies is highlighted. Finally, the challenges and future perspectives for development and applications of nanoparticles for enhancing heavy oil recovery are identified.

13. Al-Mishaal, O. F., Suwaid, M. A., Al-Muntaser, A. A., Khelkhal, M. A., Varfolomeev, M. A., Djimasbe, R., . . . Hakimi, M. H. (2022). Octahedral cluster complex of molybdenum as oil-soluble catalyst for improving in situ upgrading of heavy crude oil: Synthesis and application. *Catalysts*, 12(10), 1125.

Abstract: Heavy oil resources are attracting considerable interest in terms of sustaining energy demand. However, the exploitation of such resources requires deeper understanding of the processes occurring during their development. Promising methods currently used for enhancing heavy oil recovery are steam injection methods, which are based on aquathermolysis of heavy oil at higher temperatures. Regardless of its efficiency in the field of in situ upgrading of heavy oil, this technique still suffers from energy consumption and inefficient heat transfer for deeper reservoirs. During this study, we have developed a molybdenum-based catalyst for improving the process of heavy oil upgrading at higher temperature in the presence of water. The obtained catalyst has been characterized by a set of physico-chemical methods and was then applied for heavy oil hydrothermal processing in a high-pressure reactor at 200, 250 and 300 degrees C. The comparative study between heavy oil hydrothermal upgrading in the presence and absence of the obtained molybdenum-based oil soluble catalysts has pointed toward its potential application for heavy oil in situ upgrading techniques. In other words, the used catalyst was able to reduce heavy oil viscosity by more than 63% at 300 degrees C. Moreover, our results have demonstrated the efficiency of a molybdenum-based catalyst in improving saturates and light hydrocarbon content in the upgraded oil compared to the same quantity of these fractions in the initial oil and in the non-catalytically upgraded oil at similar temperatures. This has been explained by the significant role played by the used catalyst in destructing asphaltenes and resins as shown by XRD, elemental analysis, and gas chromatography, which confirmed the presence of molybdenum sulfur particles in the reaction medium at higher temperatures, especially at 300 degrees C. These particles contributed to stimulating hydrodesulphurization, cracking and hydrogenation reactions by breaking down the C-heteroatom bonds and consequently by destructing sphaltenes and resins into smaller fractions, leading to higher mobility and quality of the upgraded oil. Our results add to the

growing body of literature on the catalytic upgrading of heavy oil in the presence of transition metal particles.

14. Banerjee, A., Golsztajn, A., & Girard-Lauriault, P. (2022). Plasma chemical synthesis of valuable fuels and chemicals from n-hexane and its mixture with methanol and ethanol. *ACS Sustainable Chemistry and Engineering*, *10*(34), 11358-11366.

Abstract: Among several emerging technologies that are focused on finding sustainable routes for reforming heavy oils and/or alcohols into valuable fuels and complex chemicals, non-thermal plasma shows promise both due to its non-equilibrium nature and its ability to use intermittent renewable electricity. In this work, we investigate its interaction with organic compounds as a “green” process for simultaneously synthesizing hydrogen, cracking heavy oils, and producing more valuable, complex chemicals. A pin-to-plate microsecond-pulsed argon plasma was used at temperatures of 20, 0, and -20 °C. Using 390 kJ/kg of specific energy input, we were able to achieve a conversion efficiency of 771.4 mmol/kW h for the treatment of the hexane–ethanol mixture at 0 °C. It is concluded that the production of H₂ and other lower fuels (gas hydrocarbons) can be increased by the addition of alcohols in our reforming processes. At 0 °C, the production efficiency and selectivity of gas products were found to be higher compared to other temperatures. A low temperature of -20 °C showed the highest production efficiency for liquid products. Product formation was observed to mainly undergo dissociation and dehydrogenation, whose reaction pathway is also discussed.

15. Bueno, N., & Mejia, J. M. (2022). Numerical verification of in-situ heavy oil upgrading experiments and thermal processes for enhanced recovery. *Fuel*, 313, 122730.

Abstract: Thermal techniques remain to be one of the most successful recovery methods for heavy oil production. Nanotechnology has opened an opportunity to take the advantage of thermal EOR methods to another level, leading to the emergence of in-situ upgrading: a permanent enhancing of thermodynamic properties leading to an increase in the oil recovery and the commercial value of the upgraded oil. Currently, there is not a clear approach to extrapolate the available experimental findings to reservoir conditions, based on the use of a generalized model representing the relevant phenomenology. This study presents a rigorous mathematical description of in-situ upgrading, by coupling the transport equations with kinetic models and an equation of state, allowing for a thermodynamic description of the complex mixtures. The paper introduces the formulation and implementation of the model, presents a benchmark case to compare thermal results, and numerical verification of a recent upgrading experiment is provided. With the calibrated parameters, the model is able to reproduce experimental measurements during the steam and nanocatalyst injection, such as the enhanced oil recovery and the improving of thermodynamic properties such as density (or API gravity) and viscosity. The model also provides additional insights into important time-dependent processes, such as local kinetic reactions, nanoparticle retention on the porous rock, or species distribution, that cannot be measured in the laboratory. The model can be used to design a field-scale deployment strategy for increasing both, recoverable reserves and the quality of upgraded oil.

16. Isa, K. M., & Saad, S. A. (2022). Technologies for biomass thermochemical conversion. *Green energy and technology* (pp. 79-98).

Abstract: In the past few decades, increasing environmental pollution and rapid depletion of conventional fossil fuels has fueled the requirement of alternative renewable sources of fuels. In this context, biomass-based bio-oil has received much interest as a renewable and sustainable alternative to crude petroleum. Thermochemical conversion processes including direct combustion, pyrolysis, gasification, and liquefaction are seen as promising to renewable energy sources. Pyrolysis is a promising route with suitable reactors and a quick process to produce liquid yield. In contrast to the first three options, which require dry biomass, hydrothermal liquefaction (HTL) is suitable for handling wet biomass with varying moisture contents, thus avoiding drying-related throughput. Thermochemical conversion to produce liquid yield using biomass as a feedstock still facing constraints to directly use the produced bio-oil. High oxygenated compounds of bio-oil seek an upgrading process to enhance the quality. However, a number of upgrading processes can be considered to enhance the oil's quality. Solvolysis using hydrogen donor solvents, alcohols and water is also the best option to explore to produce a good quality of bio-oil under thermochemical conversion. Malaysia is blessed with an abundant source of biomass due to agriculture activities, producing a massive amount of waste every year. This gives the advantage of utilizing the thermochemical conversion route as a promising process to convert biomass into a valuable liquid product.

17. Kuzina, D. M., Yuan, C., Nurgaliev, D. K., Emelianov, D. A., Varfolomeev, M. A., Bolotov, A., V., & Minhanov, I. F. (2021). Effect of in-situ combustion process on the magnetic properties and composition of rock. *Socar Proceedings*.

Abstract: In-situ combustion (ISC) is a proved, effective method for enhanced oil recovery (EOR). In our previous work, we studied the feasibility of ISC process for heavy oil recovery in Nurlat Oil Field (Tatneft oil company, Russia) regarding to oil recovery, in-situ oil upgrading, stability of combustion front, etc. In this work, we investigated the effect of ISC process on the rock properties and composition. We found that magnetic minerals can be in-situ formed in rock during combustion process of oils. The formation of magnetic minerals in rock depends on temperature, heating time, and oil environment. Based on the magnetic properties, the samples can be divided into the most heated, less heated, and non-heated ones with hydrocarbons. The changes in the magnetic properties of rock can be used for developing technologies for combustion front monitoring, which is very valuable for controlling ISC process and its adjustment. (C) 2021 "OilGasScientificResearchProject" Institute. All rights reserved.

18. Muhammad, I., & Manos, G. (2022). Catalytic copyrolysis of heavy oil with polypropylene. *ACS Sustainable Chemistry & Engineering*, 10(48), 15824-15837.

Abstract: Catalytic and noncatalytic copyrolysis of plastic and heavy oil was studied using thermogravimetric analysis (TGA), pyrolysis reactor experiments, and GC analysis of the formed liquid. As revealed by the TGA experiments, predegradation as a pretreatment method had further lowered the decomposition temperature of polypropylene– (PP–) bitumen mixtures and reduced the severity of catalyst deactivation by coke. The presence of PP in the copyrolysis had increased the liquid yield and decreased the coke yield. The presence of PP in the copyrolysis had shifted the product distribution from heavier to lighter fractions while copyrolysis using predegradation displayed the highest percentage of C5–C9 and C9–C14 fractions. Based on the performance of the catalysts, C5–C14 was produced in the following

order, HY > 20% USY > APC > K30, while C14–C20 was produced in the reverse order of K30 > 20% USY > APC > HY. In-depth analysis of the percentage product distribution confirmed the availability of synergies during the thermal copyrolysis of PP and Ex-Mwambe heavy oil. Predegradation as pretreatment method has intensified the contact between the two feed constituents, enabling synergistic effects to materialize. The excess percentage of C5–C9 and the insignificant amount of C20+ produced from the thermal copyrolysis affirmed the possibility that the presence of PP facilitates the conversion of waxy hydrocarbons into lighter products. the conversion of waxy hydrocarbons into lighter products. Coke components from predegradation method are more volatile while the coke formed during normal mixing pyrolysis contained a higher percentage of hard coke.; Catalytic and noncatalytic copyrolysis of plastic and heavy oil was studied using thermogravimetric analysis (TGA), pyrolysis reactor experiments, and GC analysis of the formed liquid. As revealed by the TGA experiments, predegradation as a pretreatment method had further lowered the decomposition temperature of polypropylene– (PP–) bitumen mixtures and reduced the severity of catalyst deactivation by coke. The presence of PP in the copyrolysis had increased the liquid yield and decreased the coke yield. The presence of PP in the copyrolysis had shifted the product distribution from heavier to lighter fractions while copyrolysis using predegradation displayed the highest percentage of C5–C9 and C9–C14 fractions. Based on the performance of the catalysts, C5–C14 was produced in the following order, HY > 20% USY > APC > K30, while C14–C20 was produced in the reverse order of K30 > 20% USY > APC > HY. In-depth analysis of the percentage product distribution confirmed the availability of synergies during the thermal copyrolysis of PP and Ex-Mwambe heavy oil. Predegradation as pretreatment method has intensified the contact between the two feed constituents, enabling synergistic effects to materialize. The excess percentage of C5–C9 and the insignificant amount of C20+ produced from the thermal copyrolysis affirmed the possibility that the presence of PP facilitates the

conversion of waxy hydrocarbons into lighter products. the conversion of waxy hydrocarbons into lighter products. Coke components from predegradation method are more volatile while the coke formed during normal mixing pyrolysis contained a higher percentage of hard coke.

19. Nasution, F., Husin, H., Abnisa, F., Tirta Yani, F., & Maulinda, L. (2022). Conversion of pyrolysis vapors derived from non-biodegradable waste plastics (PET) into valuable fuels using nickel-impregnated HZSM5-70 catalysts. *Energy Conversion and Management*, 273.

Abstract: Recycling waste plastics into pyrolytic fuels is a highly promising energy-saving approach. The improvement and enhancement of the resulting fuel quality from heavy oil-derived-waste plastics pyrolysis is in high demand. We performed catalytic reforming of heavy oils-derived polyethylene terephthalate (PET) pyrolysis to simultaneously improve the quality of oils into valuable fuels (gasoline-range hydrocarbon) and reduce the oxygenated compounds. Nickel-impregnated HZSM5-70 catalysts were prepared by the wet-impregnation method. The catalytic process was carried out in a catalytic tubular reactor at a constant feeding rate of 2.5 mL/h. In particular, various processing factors were examined by varying the impregnation loading of nickel (2–10 wt%), catalyst mass (1–5 wt%), and process temperature (400–500 °C). Increasing any of the three process parameters resulted in a relatively similar decrease in the quantity of liquid products and an improvement in the quality of reformed products. The best quality of reformed oils were obtained at 5 % catalyst loading and 10 % nickel loading on the catalyst at 450 °C. FT-IR analyses show that raising process parameters has a substantial influence on increasing aliphatic and aromatic hydrocarbon content, while lowering the quantity of undesired products (acids, alcohols, and ketones) in the oils. GC–MS analysis results confirmed that the relative content/area of liquid products predominantly

contains gasoline-range hydrocarbons (C5-C12), with a total of 33.39 % on blank-run. The hydrocarbons (C5-C12) production from HZSM5-70 and NiO/HZSM5-70 was greatly enhanced to 66.48 % and 85.05 %, respectively, while the oxygenated compounds, including alcohols, acids, and ketones were reduced from 39.38 to 10.75 % (total area). In comparison to HZSM5-70, the NiO/HZSM5-70 catalyst performs more effectively, retaining its catalytic activity after five cycles (~3 % decrease). Thus, the NiO/HZSM5-70 exhibits high catalytic performance and reusability.

20. Schacht-Hernández, P., Quintana-Solórzano, R., Morelos-Santos, O., Soto-Escalante, I., & Ancheyta, J. (2022). In situ upgrading of heavy crude oil: Comparative study of the performance of cu-, fe-, ni-, or zr-containing water-based catalysts. *Energy Fuels*, 36(20), 12580-12590.

Abstract: The world continues experiencing a steady decrease in the availability of conventional light or even medium crude oils, and hence, refineries inevitably face the challenge of processing increasing amounts of (extra) heavy crude oils while preserving their economic targets. This requires changes/improvements in existing refining technologies for converting heavy crude oil, which may be conveniently preceded by an improvement in its flowing properties in the underground reservoir itself. In this context, this research focuses on the use of liquid catalysts containing Cu, Fe, Ni, or Zr for upgrading in situ a heavy crude oil stream (12.6 °API) in a bench-scale batch-stirred reactor operated at 380 °C and 10.8 MPa for 1 h, in the presence of high-purity hydrogen. Upon reaction, the heavy crude oil properties improve while catalysts undergo in situ transformations identifying from the analysis of residual solid recovered from the bottom of the reactor, the formation of some metallic sulfides and oxides (by X-ray diffraction (XRD)), which exhibit Bronsted and/or Lewis-type acidity

(via Fourier transform infrared (FT-IR) spectroscopy). While converting ca. 43% of the heavy crude oil residue fraction ($>524\text{ }^{\circ}\text{C}$), the Zr-containing catalyst, which exhibits relatively strong Bronsted and Lewis acid sites thus increasing the cracking rate, decreases the kinematic viscosity (1444–24 cSt, at $37.5\text{ }^{\circ}\text{C}$) as well as the amount of asphaltenes (28–13 wt %) and sulfur (5.14–2.8 wt %), and increases the content of light and middle distillates (18.9–34.1 wt %) along with the API gravity (12.6–21°). The results indicate that the use of liquid catalyst appears as a promising option on the way to development of an “inside-reservoir technology” for heavy crude oil processing.; The world continues experiencing a steady decrease in the availability of conventional light or even medium crude oils, and hence, refineries inevitably face the challenge of processing increasing amounts of (extra) heavy crude oils while preserving their economic targets. This requires changes/improvements in existing refining technologies for converting heavy crude oil, which may be conveniently preceded by an improvement in its flowing properties in the underground reservoir itself. In this context, this research focuses on the use of liquid catalysts containing Cu, Fe, Ni, or Zr for upgrading in situ a heavy crude oil stream (12.6 °API) in a bench-scale batch-stirred reactor operated at $380\text{ }^{\circ}\text{C}$ and 10.8 MPa for 1 h, in the presence of high-purity hydrogen. Upon reaction, the heavy crude oil properties improve while catalysts undergo in situ transformations identifying from the analysis of residual solid recovered from the bottom of the reactor, the formation of some metallic sulfides and oxides (by X-ray diffraction (XRD)), which exhibit Bronsted and/or Lewis-type acidity (via Fourier transform infrared (FT-IR) spectroscopy). While converting ca. 43% of the heavy crude oil residue fraction ($>524\text{ }^{\circ}\text{C}$), the Zr-containing catalyst, which exhibits relatively strong Bronsted and Lewis acid sites thus increasing the cracking rate, decreases the kinematic viscosity (1444–24 cSt, at $37.5\text{ }^{\circ}\text{C}$) as well as the amount of asphaltenes (28–13 wt %) and sulfur (5.14–2.8 wt %), and increases the content of light and middle distillates (18.9–34.1 wt %) along with the API gravity (12.6–21°). The results indicate

that the use of liquid catalyst appears as a promising option on the way to development of an “inside-reservoir technology” for heavy crude oil processing.

21. Suwaid, M. A., Varfolomeev, M. A., Al-Muntaser, A. A., Abdaljalil, N., I., Djimasbe, R., Rodionov, N. O., . . . Vagizov, F. G. (2022). Using the oil-soluble copper-based catalysts with different organic ligands for in-situ catalytic upgrading of heavy oil. *Fuel*, 312, 122914.

Abstract: Oil-soluble copper-based catalysts with different organic ligands (octanoate, decanoate, oleate, and stearate) were proposed in this work for improving the upgrading processes. All of the upgrading experiments were carried out using a batch reactor at temperatures of 250 and 300 degrees C, and 24 h of reaction time. The changes in the physical properties and chemical compositions of the oil samples before and after upgrading were studied including viscosity, SARA analysis, and GC analysis of evolved gases as well as the distribution of carbon number in saturates. In addition, TG-FTIR and XRD techniques were used to evaluate the in-situ transformation of used catalysts. Used catalysts were mainly transformed into particles of copper oxide, sulfide, and pure metal which acted as a catalytic phase during upgrading of heavy crude oil. Introducing proposed catalysts as additives to the upgrading system resulted in viscosity reduction and reached their maximum value at 300 degrees C in presence of copper-oleate (50.31%). Moreover, an increase in the content of saturates (especially with light alkanes C-10-C-20), decreasing the content of heavy fractions including resins and asphaltenes as well as removal of sulfur were observed. The best catalytic performance was provided by copper oleate. The low cost and availability of proposed catalysts combined with good catalytic performance make them promising and potential catalysts for improving in-situ upgrading of heavy oil.

22. Xiang, L., Li, H., Qu, Q., Lin, F., Yan, B., & Chen, G. (2022). In-situ catalytic pyrolysis of heavy oil residue with steel waste to upgrade product quality. *Journal of Analytical and Applied Pyrolysis*, 167

Abstract: Heavy oil residue (HOR) as a kind of oil-containing wastes (OW) is suitable to be treated by pyrolysis to obtain valuable products. However, the recovered products remain poor quality due to much heavy fractions in feedstock. This paper employed two typical steel wastes, i.e. iron-rich rolling sludge (FOS) and steel slags (SS), for catalytic pyrolysis of HOR to upgrade pyrolytic products. FOS and SS additions both effectively decreased the temperature of HOR pyrolysis stage and the activation energy. Compared with SS, FOS addition enhanced the yield of CH₄ and H₂, leading to higher heating values for pyrolytic gases. However, insufficient FOS couldn't provide enough energy to trigger the conversion of macromolecules as well as the cracking of short-chain alkanes and alkenes. In terms of pyrolytic oil, SS addition greatly improved the content of light fractions and exhibited stronger selectivity in reforming of alkanes into alkenes, while FOS addition promoted aromatization. Furthermore, Fe-doping carbon materials with different valent Fe and abundant defects were obtained through pyrolysis of HOR/FOS and HOR/SS. Combined with their magnetic properties, the separation of materials from contaminants and subsequent cycle utilization could be achieved. Subsequently, the addition of different Fe compounds validated the promotion of zero-valent Fe on aromatization while Fe₂O₃ on alkenes production as well as Fe oxides would offer active oxygen species to participate in the pyrolysis reaction. However, model Fe compounds were hard to simulate catalytic behaviors of FOS and SS in gas production due to the complex components of steel wastes. This paper provides a novel perspective for upgrading all products from HOR pyrolysis and opens a path for simultaneous disposal of multiple solid wastes.

23. Gaya, U. (2021). Recent approaches, catalysts and formulations for enhanced recovery of heavy crude oils. *Periodica Polytechnica-Chemical Engineering*, 65(4), 462-475.

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.

24. Li, Y., Wang, Z., Hu, Z., Xu, B., Li, Y., Pu, W., & Zhao, J. (2021). A review of in situ upgrading technology for heavy crude oil. *Petroleum*, 7(2), 117-122.

Abstract: With the growing demand of oil worldwide, heavy oil has increasingly become vital in the world energy market. However, further development of heavy oil reservoirs are limited by regular enhanced oil recovery (EOR) methods. In situ upgrading technology provides potential for the development of heavy oil and bitumen reservoirs. This study reviews three categories of in situ upgrading methods: solvent-based, in situ combustion (ISC), and catalytic. Solvent-based methods, including cyclic solvent injection, vapor extraction, and hybrid processes, have recently received attention and have been progressed in both laboratory and field applications. However, high solvent costs in relation to the low price of heavy oil have continued to limit the field applications of these techniques. ISC, which may have the potential

to develop particularly harsh reservoirs with extremely viscous crude oil, involves complex reaction mechanisms and consists of three main steps: oxidation, combustion, and gas flooding. Yet, complex operating conditions and a low success rate have restricted its application. Catalytic methods, which have demonstrated the potential to refine and upgrade crude oil in a more economic and environmentally friendly way, are often accompanied by conventional thermal EOR methods, such as steam flooding and ISC, and involve a series of hydroprocessing or hydrotreating reactions, such as hydrocracking, hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, and hydrodemetallization. However, the high cost and complexity of the reaction mechanisms have limited their applications. (c) 2020 Southwest Petroleum University. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

25. Zhao, F., Liu, Y., Lu, N., Xu, T., Zhu, G., & Wang, K. (2021). A review on upgrading and viscosity reduction of heavy oil and bitumen by underground catalytic cracking. *Energy Reports*, 7, 4249-4272.

Abstract: Nowadays, the output of light crude oil is approaching its peak, which has shifted the attentions of petroleum industry to a large quantity of heavy oil and bitumen in order to offset the growing demand of energy and fuels. The heavy oil and bitumen are usually characterized by high viscosity, high density/low API gravity, low yield of low boiling point fuel fraction, and high heteroatom content in comparison with the light oil, requiring in situ upgrading to improve the mobility of heavy oil. before recovery it. One of the methods for upgrading is to add catalysts to the underground reservoir. This paper firstly reviewed various kinds of catalysts, including mineral, water-soluble, oil-soluble, solid acid, ionic liquid (IL)

catalysts, and dispersed and super-dispersed catalysts that reported in domestic and foreign literatures, and secondly described their effectiveness in underground catalytic cracking and upgrading of heavy oil. This critical review suggests that it is necessary to develop the catalytic cracking catalysts of low-cost, high activity, high selectivity, and wide adaptability in order to accommodate a wide range of heavy oil with different properties, especially the ultra-dispersed nano-catalysts. The in situ upgrading technology by injecting super-dispersed nano-catalysts is a promising method to improve the quality of the lowest grade heavy oil components and enhance the recovery of heavy oil reservoirs. Moreover, further research is needed to explore the optimal process of catalyst synthesis, catalytic working conditions and the actual mechanisms of heavy oil with catalysts. (C) 2021 The Authors. Published by Elsevier Ltd.

26. Elahi, S. M., Khoshooei, M. A., Ortega, L. C., Scott, C. E., Chen, Z., & Pereira-Almao, P. (2020). Chemical insight into nano-catalytic in-situ upgrading and recovery of heavy oil. *Fuel*, 278, 118270.

Abstract: In situ upgrading technology (ISUT) is a thermal EOR-upgrading process, which combines hydrogen and nano catalyst for carrying out hydroprocessing reactions downhole at sufficient temperature (320-360 degrees C) and reservoir pressure. The production of light hydrocarbons and gases when ISUT is applied helps improve displacing the oil-in-place to enhance the recovery rate. In addition, the produced liquid has upgraded quality in terms of reduced viscosity and density and improved composition as to become transportable without dilution. In this study, both upgrading and recovery of heavy oil in a bench-scale setup resembling a carbonate reservoir were carefully investigated by using carbonate cores. Phenanthrene and fluorenone were added as chemical markers to closely monitor the expected hydroprocessing reactions. Total hydrodeoxygenation of fluorenone and 25% hydrogenation

of phenanthrene were achieved during the upgrading reactions. As a result of the hydroprocessing reactions, 50 wt% of the asphaltene compounds from the feedstock were broken and converted to mainly saturated hydrocarbons. Post-mortem analysis of the rock after the experiment has shown that light and middle distillate upgraded oil is prone to penetrate into the carbonate pore structure, acting as a solvent to improve oil recovery. The claim of ISUT integrating both quality improvement as well as enhancing the heavy oil recovery is evidenced in this paper.

27. Suwaid, M. A., Varfolomeev, M. A., Al-muntaser, A. A., Yuan, C., Starshinova, V. L., Zinnatullin, A., . . . Chemodanov, A. E. (2020). In-situ catalytic upgrading of heavy oil using oil-soluble transition metal-based catalysts. *Fuel*, 281, 118753.

Abstract: In this study, oil-soluble transition metal-based catalysts (Fe, Co, Ni) are proposed for catalyzing aquathermolysis reactions in steam injection process for heavy oil production to achieve in-situ upgrading of heavy oil. Their catalytic performance and possible mechanism were investigated by autoclave experiments together with a comprehensive analysis of the change in physical and chemical properties of the upgraded oil using SARA analysis, viscosity measurement, GC, GC-MS, FTIR, and ¹³C NMR, etc. Simultaneously, the in-situ transformation of these catalysts was also analyzed by TG-FTIR, XRD, and Mossbauer spectra, etc. to better understand the possible catalytic mechanism. The results showed that the in-situ transformation of these oil soluble catalysts occurred during the thermal treatment process at 250 degrees C and 300 degrees C, and their metal-based complexes, oxide, sulfide, and sometime pure metal were in-situ generated and played a catalytic role for aquathermolysis reactions. These catalysts showed a good catalytic performance at 300 degrees C for heavy oil upgrading in reducing viscosity, increasing saturates content (especially low molecule weight

alkanes), decreasing resins and asphaltenes content, removing sulfur and nitrogen, and decreasing polyaromatics content, etc. by inhibiting the condensation and recombination reactions and promoting thermal decomposition reactions of heavy components (resin, asphaltene, and polycyclic aromatics, long chain alkanes, etc.) and hydrogenation reaction. Nickel gives the best catalytic performance. The low cost and easy access together with its high catalytic activity make its wide application a great potential in catalyzing aquathermolysis reaction in steam injection process for in-situ upgrading and heavy oil recovery.

28. Zhao, Q., Guo, L., Wang, Y., Jin, H., Chen, L., & Huang, Z. (2020). Enhanced oil recovery and in situ upgrading of heavy oil by supercritical water injection. *Energy & Fuels*, 34(1), 360-367.

Abstract: Heavy oil accounts for two-thirds of the world oil resources but contributes only one-seventh of the world oil production due to its high oil viscosity and heavy distillates. Steam injection has been widely used for heavy oil recovery by heating up the reservoir to reduce oil viscosity. However, severe carbon loss to coking causes low recovery efficiency and high energy consumption. Here, we report supercritical water injection for heavy oil recovery. Supercritical water is expected to be both a heat carrier and an organic solvent, thereby not only reducing oil viscosity but also dissolving heavy distillates to avoid coking. To test its feasibility, core experiments were first conducted to simulate the recovery process. Results showed that supercritical water flooding improved oil recovery by 17% and reduced heat consumption by 34% versus classical steam flooding. Further, to clarify its recovery mechanism, a visualization technique and a quantitative method were developed for regulating phase behaviors and upgrading reactions between heavy oil and supercritical water. Results showed that supercritical water has good miscibility with heavy oil, and it is the key to both

enhanced oil recovery and in situ upgrading. High miscibility means formation of supercritical water clusters around organic macromolecules, which makes asphaltene difficult to aggregate and polymerize to form coke but easy to decompose to form maltene and recover. Overall, supercritical water injection has made great advances in enhanced oil recovery, energy saving, and in situ upgrading for heavy oil recovery. The work provides a sound basis for its application in oilfields.

29. Al-Attas, T., Ali, S. A., Zahir, M. H., Xiong, Q., Al-Bogami, S., Malaibari, Z. O., . . . Hossain, M. M. (2019). Recent advances in heavy oil upgrading using dispersed catalysts. *Energy Fuels*, 33(9), 7917-7949.

Abstract: Unconventional feedstocks, such as heavy vacuum residue (VR), have become potential candidates that could be positively exploited to meet the increasing demand of high-value transportation fuels, in view of the growing scarcity in other energy sources. However, such feeds contain extremely high-molecular-weight species, besides many impurities of heteroatom-containing organic compounds that lead to quick fouling, poisoning, and deactivation of catalysts. This causes a significant pressure decrease during the conventional hydrocracking in ebullated- or fixed-bed reactors. In contrast, slurry-phase hydrocracking has the ability to overcome these drawbacks through the enhancement of hydrogenation reactions in the presence of the dispersed catalysts. Slurry-phase processing is a resilient technology, which employs catalysts that are generally categorized as heterogeneous solid supported catalysts and homogeneously dispersed catalysts. The dispersed catalysts are classified into water or oil-soluble types and fine powders. Soluble dispersed catalysts show higher catalytic activity, compared to finely powdered catalysts, because of the in situ formation of infinitesimally minute active metal sites at high surface-area-to-volume ratios. Recent

technologies and studies on heavy oil upgrading that implement the dispersed catalysts have been reviewed. Studies using a combination of two-phase catalysts have also been included.; Unconventional feedstocks, such as heavy vacuum residue (VR), have become potential candidates that could be positively exploited to meet the increasing demand of high-value transportation fuels, in view of the growing scarcity in other energy sources. However, such feeds contain extremely high-molecular-weight species, besides many impurities of heteroatom-containing organic compounds that lead to quick fouling, poisoning, and deactivation of catalysts. This causes a significant pressure decrease during the conventional hydrocracking in ebullated- or fixed-bed reactors. In contrast, slurry-phase hydrocracking has the ability to overcome these drawbacks through the enhancement of hydrogenation reactions in the presence of the dispersed catalysts. Slurry-phase processing is a resilient technology, which employs catalysts that are generally categorized as heterogeneous solid supported catalysts and homogeneously dispersed catalysts. The dispersed catalysts are classified into water or oil-soluble types and fine powders. Soluble dispersed catalysts show higher catalytic activity, compared to finely powdered catalysts, because of the in situ formation of infinitesimally minute active metal sites at high surface-area-to-volume ratios. Recent technologies and studies on heavy oil upgrading that implement the dispersed catalysts have been reviewed. Studies using a combination of two-phase catalysts have also been included.

30. Elahi, S. M., Scott, C. E., Chen, Z., & Pereira-Almao, P. (2019). In-situ upgrading and enhanced recovery of heavy oil from carbonate reservoirs using nano-catalysts: Upgrading reactions analysis. *Fuel*, 252, 262-271.

Abstract: Exploitation of heavy/extra heavy oil is becoming challenging as it conventionally requires injection of steam in high proportions, making it not environmentally friendly. In-situ

upgrading technology (ISUT) is a novel alternative to the current heavy oil and bitumen production methods, which gives the benefits of both oil recovery and upgrading in one single stage. In this method, recovered vacuum residue (VR) from produced oil along with nano-catalyst and hydrogen will be injected in the reservoir, where upgrading reactions take place. For the first time, a comprehensive kinetic analysis of mild hydrocracking reactions inside a carbonate rock is implemented, which considerably enhances predictive simulations of the technology. With the aid of a continuous experimental setup, nano-catalyst deposition into the rock is also assessed in carbonate cores. Furthermore, a five-lumped kinetic model is developed and matched against experimental data with an average error of 6%. Significant viscosity reduction of 99.8% and API gravity increase of 8 degrees API are observed for the most severe condition with 35% VR conversion, while asphaltene stability criterion is met. It is recurrently omitted in most in-reservoir upgrading reports and the literature the essentially relevant information about oil stability limits. Non-catalytic conversion of heavy oils, disregarding the energy source employed, is most certain to produce unstable asphaltenes and/or coke before reaching surface transportability viscosity requirements, with additional mid-long term reservoir impairment consequences. It is included in this paper the required confirmation that the in-situ upgraded oil is fully stable when transportable viscosity values are reached.

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