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A comprehensive review of catalyst deactivation and regeneration in heavy oil hydroprocessing

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ABSTRACT

Catalyst deactivation and regeneration are critical aspects of heavy oil hydroprocessing. This review provides a comprehensive overview of the factors contributing to catalyst deactivation, including coke formation, metal and other heteroelement poisoning, and active metal sintering. We delve into the mechanisms underlying these deactivation processes and discuss their impact on catalyst performance and reactor operations. Furthermore, the review explores various catalyst regeneration techniques, such as combustion and gasification techniques. We evaluate the effectiveness of these methods in removing coke and restoring catalyst activity. Additionally, we discuss strategies for mitigating coke formation, including the development of more coke-resistant catalysts and the addition of solvents and surfactants. Refineries can optimize their operations, improve product yields, and minimize environmental impact by understanding the causes of catalyst deactivation and the effectiveness of different regeneration techniques.

1. Introduction

The world's energy supply remains heavily dependent on fossil fuels, which continue to dominate the global energy mix. Fossil fuels, including crude oil, natural gas, and coal, currently account for over 80 % of global primary energy consumption. Crude oil, in particular, remains the most dominant source, contributing approximately 33 % of the world's total energy demand [1]. This heavy reliance on fossil fuels has major implications for the environment, as their combustion is a primary contributor to greenhouse gas emissions and climate change. Despite the growth of renewable sources in recent years, fossil fuels still provide the majority of the world's energy [2] (Fig. 1). Before the mid-1990s, the average API gravity of discovered crude oil was declining at a rate of 0.15 degrees per year. However, this rate has intensified since then, with a steeper decline of 0.22 degrees per year observed from 1995 onwards [3,4]. This implies a progressive depletion of lighter, higher-

quality crude oil reserves and a corresponding increase in heavier, more viscous crudes. This shift in crude oil characteristics has significant implications for the refining industry, as it necessitates adjustments in processing technologies and infrastructure to handle heavier feedstocks.

Heavy oil constitutes a significant portion of global petroleum reserves, with Canada and Venezuela housing the majority [5]. Despite its abundance, processing heavy oil poses substantial challenges. Heavy oil, unlike lighter crude oils, is characterized by its high content of petroleum macromolecules, including resins and asphaltenes. These components possess a complex aromatic structure and are often associated with impurities such as nitrogen, oxygen, sulfur, and heavy metals. This combination of factors makes heavy oil more challenging to refine into valuable fuels compared to lighter crudes. In contrast, they often undergo polycondensation, forming large, complex molecules that accumulate on equipment surfaces [6,7].

Carbon rejection is a primary method for upgrading heavy oil,

Abbreviations: API, American Petroleum Institute gravity; APPI, Atmospheric pressure photoionization; HDAs, Hydrodeasphaltenes; HDM, Hydrometallization; HDN, Hydrodenitrogenation; HDT, Hydrotreating; HDY, Hydrogenation; MALDI, Matrix-assisted laser desorption/ionization; SARA, Saturates, aromatics, resins, and asphaltenes; SEC, Size exclusion chromatography; VPO, Vapor pressure osmometry; HDS, Hydrodesulfurization.

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encompassing processes like solvent deasphalting, coking, visbreaking, and catalytic cracking. While these methods offer simplicity and versatility, they often yield lower-quality products and limited carbon utilization [8,9]. In recent years, hydrogen addition technologies have gained prominence. By reacting heavy oil with hydrogen under high pressure and temperature in the presence of a catalyst [3,10], these processes achieve higher carbon utilization efficiency and produce valuable products. The added hydrogen can significantly improve product quality by reducing impurities like sulfur, nitrogen, and metals, resulting in cleaner and more desirable fuels.

Despite the advantages coming from hydroprocessing, it is sensitive to catalyst deactivation by coke or metal deposition. This carbonaceous and metal deposit can deactivate catalysts by blocking active sites, leading to reduced product yield and increased operational costs. Additionally, coke buildup can foul reactor internals, causing pressure drops and potential shutdowns [11,12]. The formation of coke also contributes to greenhouse gas emissions, exacerbating environmental concerns. To ensure the economic viability and long-term sustainability of heavy oil upgrading, effective coke mitigation as well as catalyst regeneration strategies are essential.

This review provides a comprehensive overview of heavy oil characterization, with a particular emphasis on the resin and asphaltene fractions. We delve into the physicochemical evolution of these fractions and their impact on catalyst deactivation. Asphaltenes and resins are known to contribute to coke and metal deposition, which can significantly impair catalyst performance. Furthermore, we explore various catalyst regeneration techniques designed to remove coke and restore

catalyst activity. Finally, we discuss strategies for mitigating coke formation, a crucial aspect of optimizing heavy oil upgrading processes.

2. The physicochemical properties of resin and asphaltene in heavy oil

2.1. The composition of heavy oil

Heavy oils are the residual fractions that remain after atmospheric distillation, typically boiling above 350 °C and having a specific gravity greater than 0.934 [13]. Their complex molecular composition, characterized by low volatility, high polarity, and compositional diversity, makes them difficult to characterize at the molecular level [14]. However, the interest in understanding the properties of heavy oils continues to grow, as upgrading processes for the bottom-of-the-barrel (BOB) fraction have become increasingly important for modern refining operations [15].

For decades, many different techniques have been developed for heavy oil characterization. While Gas Chromatography (GC) is primarily designed for analyzing lighter, volatile compounds, it can be employed to analyze heavier fractions of crude oil through specific techniques such as Pyrolysis-Gas Chromatography (Py-GC) and Thermal Desorption-Gas Chromatography (TD-GC). With Py-GC, the heavy oil samples are thermal decomposed into smaller and more volatile fragments. These fragments are analyzed separately using GC to give an insight into the molecular composition of the original heavy oil [16–18]. On the other hand, in TD-GC, heavy oil samples are thermally desorbed to release

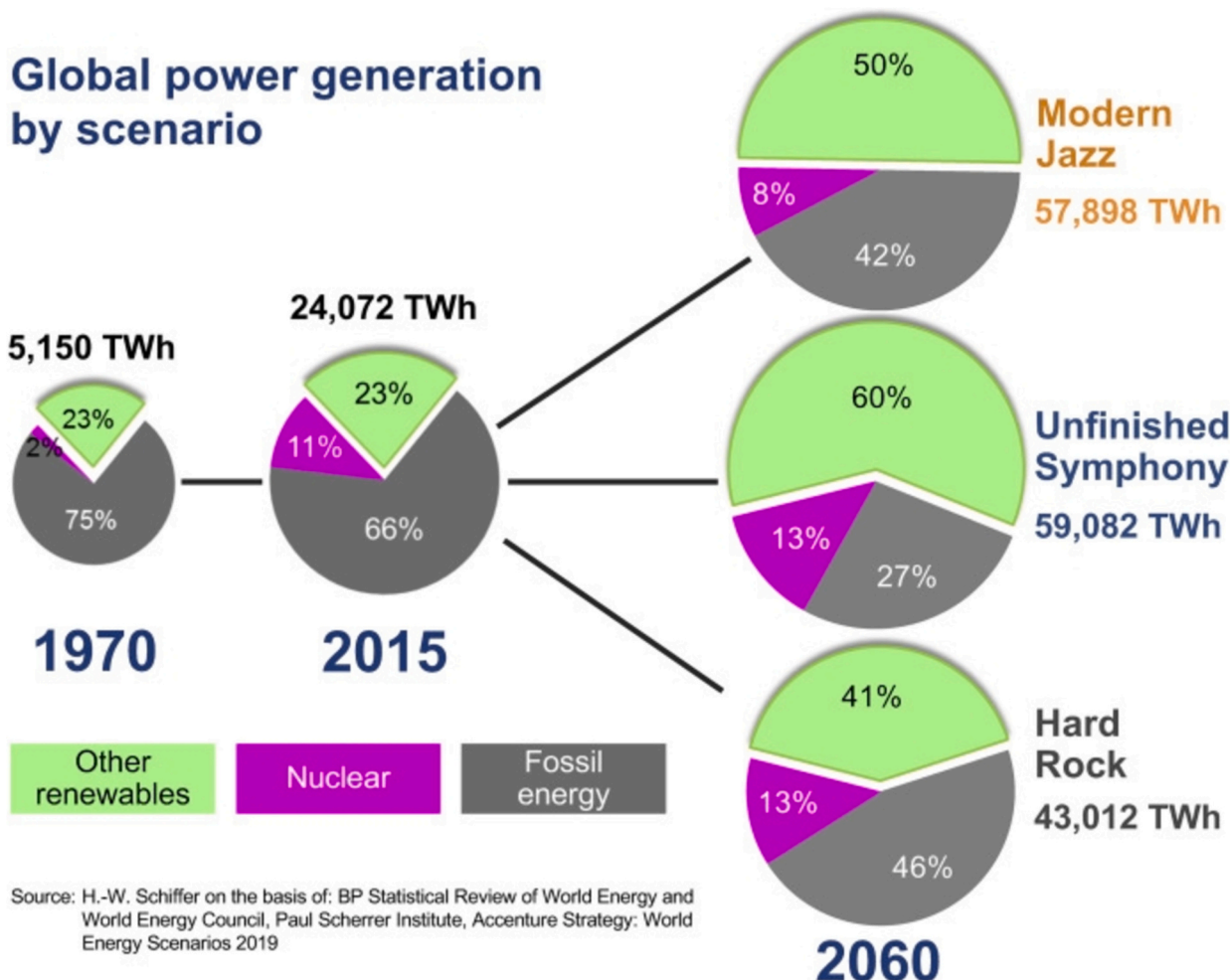


Fig. 1. The global power generation by sources [2] (Reuse with permission).

volatile components. These volatiles are then carried by an inert gas into the GC column for separation and analysis [19]. Using different types of detectors such as total ion chromatogram (TIC), and extracted ion chromatogram (EIC), the structural information of heavy oil could be predicted. However, these methods involve thermal decomposition, which can lead to the formation of artificial products reducing the price of the method. Moreover, for very high molecular weight components, the information obtained may be limited.

Along with the chromatographic methods, spectroscopic techniques are also applied to characterize heavy oil. Nuclear Magnetic Resonance (NMR) provides detailed information about the molecular structure of heavy oil components, including the types of carbon and hydrogen atoms present [20,21]. Infrared (IR) spectroscopy can be used to identify functional groups and molecular structures [20,22]. Meanwhile, Mass Spectrometry (MS) can be used to determine the molecular weight and structure of individual compounds in heavy oil [23]. In contrast to GC methods, the spectroscopic techniques do not destruct the heavy oil molecular and the analysis is generally rapid making them suitable for real-time monitoring and control. However, the complex nature of heavy oil also leads to difficulty in accurate data interpretation. Moreover, this technique might not be sensitive enough to detect trace components in samples.

The most common and applicable method used to investigate the physicochemical properties of this material is based on the polarity of its constituent compounds. Heavy oil is often categorized into saturate, aromatic, resin, and asphaltene (SARA). Different methods have been developed and used for the SARA analysis of crude oils. These methods include gravimetric adsorption chromatography, as outlined in ASTM standards D4124, D3279, D6560, and D2007, which involves separating the oil into saturates, aromatics, resins, and asphaltenes using adsorbents such as n-heptane and clay-gel (Fig. 2) [24]. High-performance liquid chromatography (HPLC) and thin-layer chromatography-flame ionization detection (TLC-FID) are additional techniques used for SARA analysis [25–28].

Table 1 provides a SARA composition overview of various heavy oils from different geographical sources. The composition of heavy oils is heavily influenced by the geological properties of their reservoirs. A common characteristic of these heavy oils is their high content of resins and asphaltenes, as well as significant levels of heteroatoms such as sulfur and metal [29,30]. Resins and asphaltenes are generally the heaviest fractions in crude oils [24,31], and their high abundance in heavy oils often results in low API gravities, as shown in Table 1. Additionally, heavy oils tend to have substantial sulfur content, necessitating desulfurization processes to meet environmental fuel

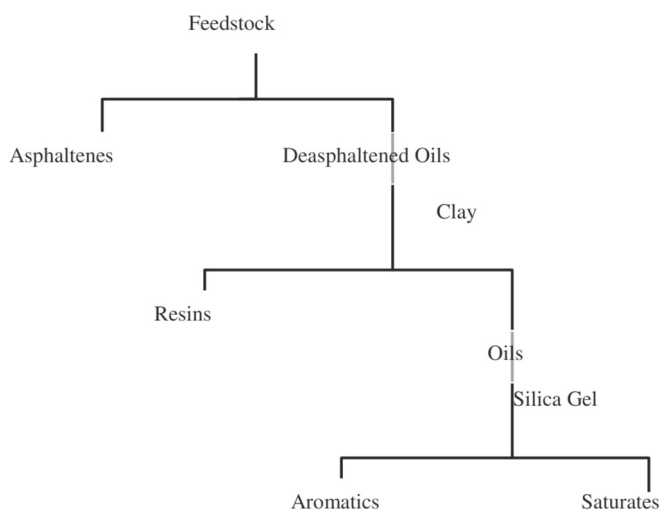


Fig. 2. The saturate, aromatic, resin, and asphaltenes separation from heavy oil [24] (Reused with permission).

specifications [32].

2.2. Saturated compounds in heavy oil

Saturated hydrocarbons represent a significant fraction of petroleum crude oil and serve as valuable components in transportation fuels and petrochemical feedstocks, such as lubricant oil production. While the molecular composition of saturated hydrocarbons in distillate fractions has been extensively studied [45–47], the characterization of high-boiling-point saturated hydrocarbons in heavy oil remains challenging due to limitations in analytical techniques. To overcome these challenges, researchers have employed advanced techniques like laser-induced acoustic desorption (LIAD) coupled with mass spectrometry. Campbell et al. [48,49] and Duan et al. [50,51] utilized LIAD-CI MS under vacuum conditions with cyclopentadienyl cobalt radical cation or ligated water cluster of Mn + [ClMn(H₂O)⁺] to analyze saturated hydrocarbons. This approach enabled the vaporization and ionization of large and highly branched molecules without significant fragmentation. Nyadong et al. [52] further refined the technique by using O₂ as a carrier/reagent gas. This method facilitated the ionization of straight-chain, branched, and cycloalkanes with minimal fragmentation. The resulting mass spectra predominantly showed [M-H]⁺ ions for straight-chain and branched alkanes, and M⁺ ions for cycloalkanes at lower capillary temperatures (<100 °C). At higher temperatures (>200 °C), [M-H]⁺ ions became dominant for cycloalkanes. The atmospheric pressure operation of this CI method enables easy coupling with FT-ICR MS.

Zhou et al. [53] introduced a novel chemical derivatization method, Ruthenium-Ion-Catalyzed Oxidation (RICO), to analyze saturated hydrocarbons in heavy petroleum fractions using ESI FT-ICR MS. This approach transforms saturates into alcohols, which can be ionized by ESI. Specifically, branched paraffins and naphthenes with tertiary C–H bonds are oxidized to alcohols, while n-paraffins are converted to ketones and subsequently reduced to alcohols using LiAlH₄. This derivatization strategy enables the differentiation between n-paraffins and isoparaffins. By using negative-ion ESI, the method simplifies mass spectra, generating only [M-H]⁻ ions. This simplification, coupled with the continuous and stable ion stream provided by ESI, improves the signal-to-noise ratio and detection dynamic range, facilitating semi-quantitative analysis of heavy saturates. In another approach, Zhou et al. [54] employed a ruthenium-ion-catalyzed oxidation (RICO) to convert saturated hydrocarbons in vacuum residue petroleum fractions into ketones (20 %) and alcohols (76 %). Subsequently, these oxygenated compounds were analyzed using ESI FT-ICR MS. The results revealed the presence of naphthenes with up to 10 rings and carbon numbers approaching 100 in the vacuum residue samples. H. Muller and Q. Saleem [55] recently investigated saturated compounds in heavy petroleum. Their study revealed that saturated compounds comprise approximately 60 wt% of the lightest vacuum gas oil (VGO) sample, while this proportion decreases to around 7.6 wt% in vacuum residue (VR). The average number of naphthenic rings in saturated molecules ranges from 1 to 2 in light VGO to 6 in VR, with some compounds containing up to 12 naphthenic rings.

In summary, saturated hydrocarbons constitute a significant portion of heavy oil, particularly in lighter fractions like vacuum gas oil (VGO). As the boiling point increases, the proportion of saturated compounds decreases, and the complexity of their molecular structures increases. In lighter VGO, saturated compounds typically contain 1–2 naphthenic rings, while heavier fractions, such as vacuum residue, may contain up to 12 naphthenic rings. Despite their high molecular weight, some of these polynaphthenic compounds exhibit compact structures with most carbon atoms residing within the rings.

2.3. Aromatic compounds in heavy oil

All the SARA fraction in heavy oil was investigated by P.S. Ferreira et al. [56]. The monocyclic, bicyclic, tricyclic, and tetracyclic

Table 1
The basic properties of different heavy oils.

Oil origin	Saturate (wt%)	Aromatic (wt%)	Resin (wt%)	Asphaltene (wt%)	Metals (ppm)	Sulfur (wt%)	API	Ref
Lukqin Oilfield heavy oil	34.66	25.38	36.71	3.25	–	0.17	16.7	[33]
Liaohe super heavy oil	–	–	26.0	43.2	–	–	12.5	[34]
Tatarstan heavy crude oil	37.91	38.98	15.36	7.75	490.0	4.61	13.35	[35]
Ashalcha heavy crude oil	28.1	31.3	34.3	6.3	–	–	13.94	[36]
Heavy crude oil	28.79	44.32	20.98	5.91	43.3	4.61	13.35	[37]
Bohai oilfield heavy oil	31.37	24.83	41.32	2.48	–	0.79	14.7	[38]
Dead crude oil	27.79	41.19	17.93	13.09	–	6.23	19.0	[39]
Zyuzeevskoye heavy oil	24.6	43.5	21.5	10.4	–	4.53	17.9	[40]
Liaohe heavy oil	21.4	25.7	42.8	10.1	–	0.02	10.2	[41]
Ashal'cha heavy oil	28.79	44.32	20.98	5.91	–	4.52	14.10	[42]
Changqing vacuum residue	48.84	21.40	23.80	5.33	380.0	0.44	17.8	[43]
Ultra-heavy oil	13.5	22.0	15.5	49.0	–	1.3	8.6	[44]

compounds were found to be the main components in the aromatic fraction (Fig. 3). E. Kim et al. [57] used (+) APPI FT-ICR Mass Spectra and estimated the average molecular weight of aromatic compounds about 470–483 Da. Moreover, in contrast with the saturated fraction, the S1 class represents the compounds containing one sulfur atom that was abundant in the aromatic fraction. Meanwhile, it was almost nitrogen-free in this fraction. In another study, S. Akmaz et al. employed a similar mass spectra technique and found a much lower average molecular weight of aromatic compounds of 284 Da. The inconsistency in average molecular weight values reported by the two researches might come from the difference in the origin of oil. Nevertheless, they all agreed that aromatic fractions were nitrogen-free but contained a significant amount of sulfur.

2.4. Asphaltenes in heavy oil

Asphaltenes, a key component of heavy oils, are characterized by their unique solubility behavior. They are insoluble in light aliphatic solvents like $n\text{-C}_5\text{H}_{12}$ or $n\text{-C}_7\text{H}_{14}$ but readily dissolve in aromatic solvents like toluene or benzene [58–60]. This solubility property distinguishes asphaltenes from other oil constituents and plays a significant role in their interactions during refining processes. The presence and quantity of asphaltenes in heavy oils have been directly linked to the generation of high-molecular-weight carbonaceous compounds, often referred to as coke, during upgrading processes [61]. However, the specific chemical composition and structure of asphaltenes also influence their propensity to form coke [62]. Understanding the nature of asphaltenes is crucial for developing effective strategies to mitigate coke formation and optimize heavy oil refining operations.

Asphaltenes are known to possess complex molecular structures, typically comprising one or more polyaromatic core units connected by aliphatic linkages. These core molecular structures often include a range

of different atoms beyond just carbon and hydrogen, such as sulfur, nitrogen, oxygen, and various metal elements [63]. The intricate and diverse nature of asphaltene chemistry, as well as their tendency to self-associate into larger aggregates, presents significant challenges in the study and understanding of asphaltenes. The inherent complexity of asphaltene structures, which incorporate a variety of heteroatoms, contributes to the many difficulties and ambiguities encountered in the field of asphaltene science. This complexity poses challenges when investigating the physical and chemical transformations that occur during the upgrading of heavy oils and bitumen. The properties of asphaltene were summarized in detail elsewhere [64,65].

The molecular weight of asphaltenes can vary significantly, ranging from a few hundred to several thousand Daltons, depending on the origin of the oil and the measurement technique employed. This wide range reflects the complex and diverse nature of asphaltene structures. Vapor pressure osmometry (VPO) analyses have yielded molecular weight estimates for an asphaltene molecule of 700 – 2000 Da. Meanwhile, the aggregated asphaltenes have been found to have molecular weights between 2000 and 30,000 Da [66–71]. These findings underscore the tendency of asphaltenes to self-associate into larger supra-molecular structures. Other analytical methods have provided similar, though sometimes more narrow, molecular weight distributions for asphaltenes. Size exclusion chromatography (SEC) has specified an average asphaltenes MW of around 1700 Da [69]. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has produced values within 786–1280 Da range [72]. Atmospheric pressure photoionization (APPI) has yielded molecular weights between 400 and 900 Da [73], while fluorescence depolarization (FD) studies have suggested asphaltene molecular weights of 500–1000 Da [74].

The molecular structure of asphaltenes is a subject of significant debate and research in the field of petroleum science. Two primary conceptual frameworks have emerged to model asphaltene structures. The continental model depicts asphaltenes as single large aromatic core units with aliphatic side chains [75]. In contrast, the archipelago envisions asphaltenes as comprising multiple aromatic core units connected by bridging alkane chains [76,77]. While some studies have suggested that both continental and archipelago-type structures may coexist in heavy oils and bitumen, more recent evidence indicates that continental model structures are likely the predominant asphaltene arrangement [78–82]. The Yen-Mullins theory (Fig. 4), proposed in 2011, has become the most widely accepted model for asphaltene molecular structure [83]. Key features of this model include:

- Most asphaltene molecules have a continental structure, with a distribution ranging between 500 and 1000 Da and an average weight of 700 Da.
- In a typical molecule, asphaltene consists of one polycyclic aromatic core having seven fused rings on average.

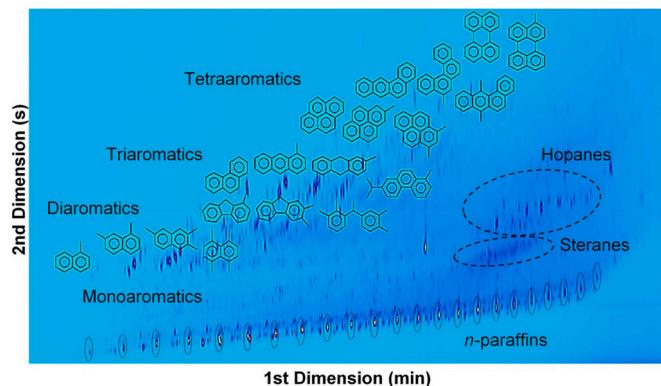


Fig. 3. GCxGC/MS chromatogram of the aromatic fraction [56] (Reused with permission).

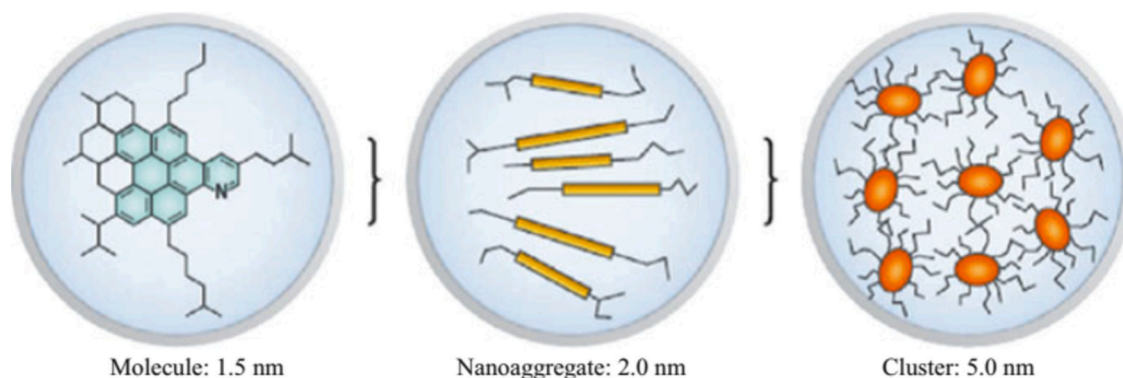


Fig. 4. The asphaltene structure in heavy oil proposed by Mullins [83] (Reuse with permission).

- Asphaltenes in heavy oils exist in three forms: individual molecules, nanoaggregates (small clusters of ~6 molecules), and larger clusters (containing ~8 nanoaggregates).

2.5. Resin in heavy oil

Resins represent the second heaviest fraction in heavy oils, typically comprising 20–40 % of the total weight. In contrast to the extensive research conducted on asphaltenes, the scientific understanding of resins remains relatively limited. Despite this, resins are known to play a crucial role in maintaining the stability of petroleum products. They prevent the phase separation of asphaltene components during oil exploration and refinery [24]. A study by P.M. Spiecker et al. [84] examined the interactions between resins and asphaltenes. Their findings indicate that the addition of resins disrupts the π - π and polar bonding interactions between asphaltene monomers. This, in turn, reduces the size of asphaltene aggregates. Interestingly, the resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions, but only when the number of resin molecules per micelle exceeds the number of asphaltene molecules per micelle. This suggests a delicate balance in the resin-asphaltene relationship and its influence on the stability of the petroleum system. Moreover, this dynamic suggests the possibility of the resin molecules disrupting the aggregation of asphaltene molecules [85,86]. The colloidal suspension of asphaltene in resin and other fractions present in heavy oil is illustrated in Fig. 5.

Petroleum resins and asphaltenes share some common structural characteristics. Both contain similar elements in their carbon skeleton and aromatic heterocyclic compounds with aliphatic substituents [87,88]. However, there are notable differences between the two. Petroleum resins generally have a lower average molecular weight compared to asphaltenes isolated from the same oil sources [83,88]. Typically, petroleum resins have a molecular weight range of 360–400 Da [89], which is significantly lower than the 700–2000 Da range observed for asphaltenes [66–71]. Additionally, the hydrogen to carbon

(H/C) ratios of resins, which vary from 1.2 to 1.7, are on average higher than the 0.9 to 1.2 range observed for asphaltenes [90]. This suggests that resins have a lower degree of aromaticity compared to the asphaltene fraction. Furthermore, the heteroatom is more condensed in asphaltenes than in resins. Asphaltenes often contain 0.4–1.0 % nitrogen and 4.6–8.3 % sulfur, whereas resins have lower concentrations of 0.2–0.5 % nitrogen and 0.4–5.1 % sulfur [91].

Recent solid-state ^{13}C NMR analysis by T. Liang et al. has provided insights into the chemical structure of petroleum resins [92]. The results indicate that the resin structure is composed of an aromatic core with short aliphatic chains and cycloalkanes attached at the periphery. The primary skeleton of the resin molecule is carbon-hydrogen, with the inclusion of three types of heteroatoms: nitrogen, oxygen, and sulfur. Interestingly, oxygen is found to be the dominant heteroatom present. Examination of the functional groups reveals that methyl, methylene, and methine groups have the highest relative proportions. This suggests that the average resin structure contains short chains and cycloalkanes, rather than long aliphatic chains. The relative proportion of aromatic carbon groups is relatively low, accounting for less than a quarter of the total structure. Additionally, the aromatic cluster within the resin structure exhibits a high degree of condensation, implying a low number of protonated aromatic carbons in this region. Based on the collective findings from this research, a 2D molecular structure of resin has been proposed and is depicted in Fig. 6. This detailed characterization of the resin's chemical composition and structural features provides valuable insights into the nature of these important petroleum components.

3. Catalytic hydrocracking reaction mechanism

The general hydrocracking reaction mechanism is summarized in Fig. 7 [93]. Hydrocracking transforms heavy oil molecules into smaller, more valuable products through a combination of thermal and catalytic cracking reactions. These cracking reactions, initiated by both heat and hydrogen radicals, occur at a slower rate compared to thermal cracking

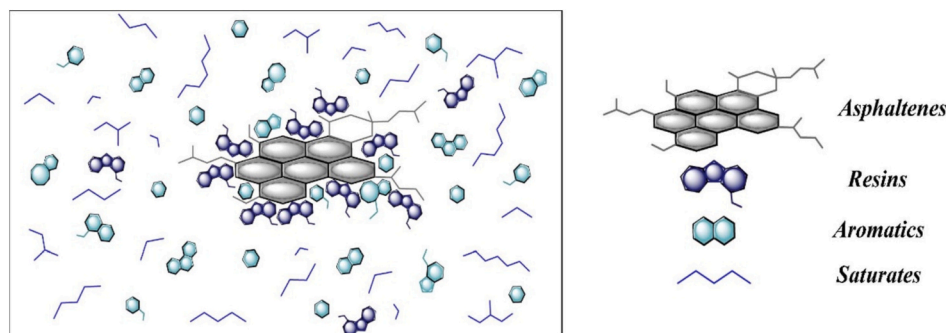


Fig. 5. The resin-asphaltene colloidal structure in heavy oil [85] (Reused with permission).

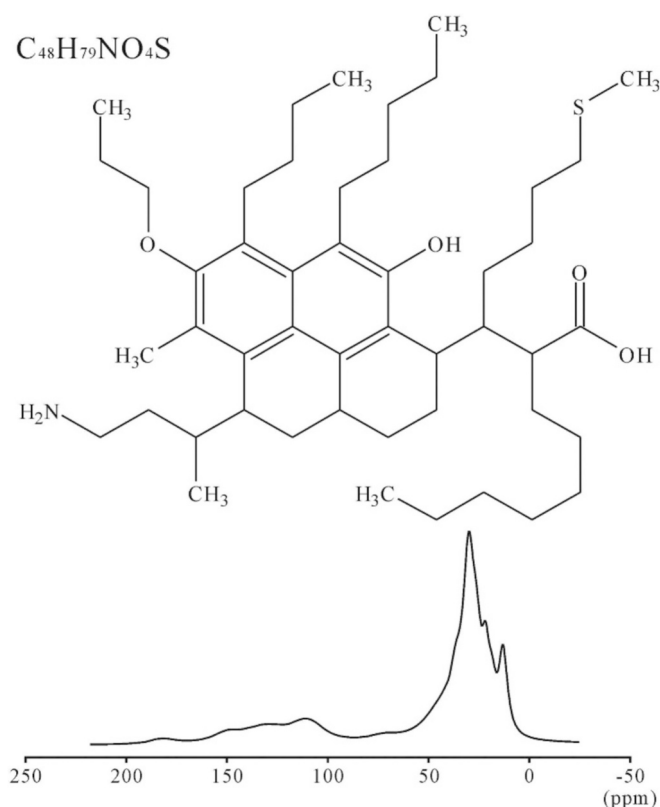


Fig. 6. The typical model for a 2D structure and the simulation ^{13}C NMR spectrum of petroleum resin [92] (Reused with permission).

alone, allowing for better control and preventing excessive breakdown of the oil molecules [94]. Also, the presence of a hydrogenation catalyst provides an abundant environment of hydrogen radicals. It saturates aromatic rings, particularly those with four or more rings, and removes heteroatoms through hydrodemetallization [95], hydrodesulfurization [32], etc. The number of rings in a molecule also influences the ease of heteroatom removal. Molecules with a higher number of rings present greater steric hindrance, making it more difficult to remove the heteroatoms [94]. Additionally, hydrogen radical acts as a radical scavenger to terminate polycondensation of aromatic ring cores resulting in a much lower yield of coke [96,97].

4. Catalyst in heavy oil hydrocracking

Catalysts are indispensable in the conversion and upgrading of heavy oils. It often consists of the hydrogenation of active metals doped on a carrier such as alumina, silica, titania, etc., or a mixture of them. The roles of support are not only to disperse HDY metal but also to promote an acidic site where cracking reactions are induced. Since heavy oil is a mixture of thousands of petroleum macromolecules, the upgrading reactions largely depend on the mass transfer of these molecules into the pore. Hence, pore size and support composition are the two most important factors determining process efficiency [98–101]. The hydrogenation-active metals, typically transition metals like molybdenum, nickel, or cobalt, promote the dissociation of H_2 molecules into H^* radicals [102]. These H^* act as a radical scavenger to stabilize the heavy hydrocarbon radical generated from cracking reaction, prohibit the core polycondensation, and promote essential reactions for the impurity removals of sulfur (hydrodesulfurization - HDS), nitrogen (hydrodenitrogenation - HDN), and metals (hydrodemetallization - HDM). For the effective conversion of heavy oils into valuable light products, a well-balanced combination of cracking and hydrogenation reactions is required. The general composition of a multi-functional catalyst used in heavy oil upgrading is shown in Fig. 8 [103]. In this section, the structural effects of active metal and support on heavy oil hydro-upgrading will be examined.

4.1. The structure of the catalytic active site

Catalysts play a crucial role in promoting hydrogenation, which is essential for increasing liquid hydrocarbon yield and suppressing coke formation. Platinum-group metals like platinum and palladium are renowned for their excellent hydrogenation capabilities and are widely used in various catalytic processes [104]. However, these noble metals are susceptible to sulfur poisoning [105], particularly in the presence of sulfur-rich heavy oil feedstocks. To address this limitation, transition

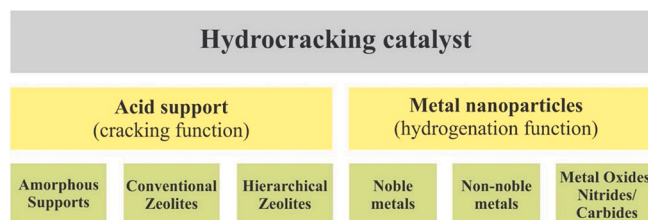


Fig. 8. The general composition of a heterogeneous catalyst for heavy oil hydrocracking [103] (Reused with permission).

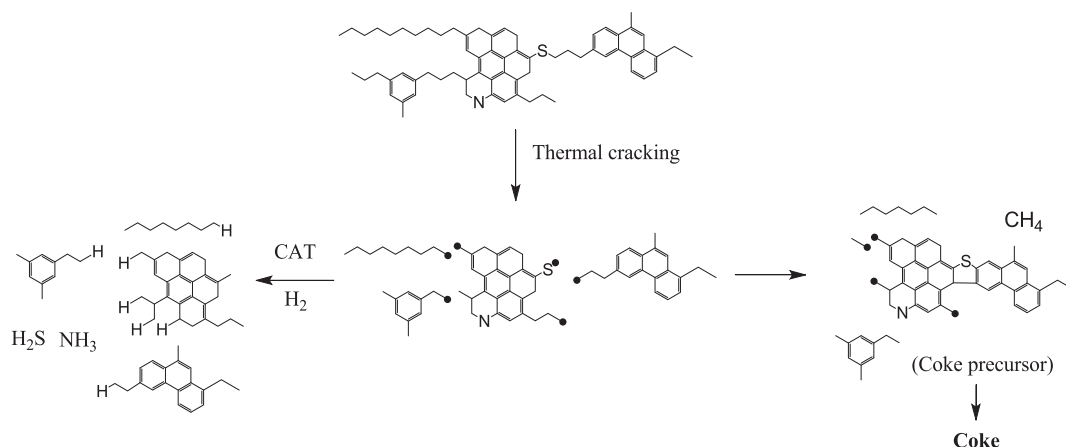


Fig. 7. General concept of heavy oil hydrocracking [93] (Reuse with permission).

metals such as molybdenum (Mo), nickel (Ni), cobalt (Co), and tungsten (W) have emerged as viable alternatives. Sulfides of Mo and W are commonly employed as primary catalysts, while Ni and Co are often used as promoters to enhance hydrogenation and hydrotreating activities, including hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodemetallization (HDM) [106–108].

Daage and Chianelli [102] proposed the Rim-Edge model to describe the structure and reactivity of molybdenum sulfide catalysts (Fig. 9 a). This model suggests that hydrogenation reactions primarily occur at the Rim sites, where the coordination geometry allows for the adsorption of reactants. The Basal planes, with their six-membered ring structure, are sterically hindered and less reactive. Iwata et al. [109] further investigated the hydrogenation activity of MoS₂ catalysts for heavy oil hydroprocessing. Their findings corroborated the importance of Rim sites, confirming that the number of active sites is directly related to the abundance of Rim sites in the catalyst structure. To enhance catalytic activity, it is crucial to prevent the aggregation and growth of MoS₂, thereby maximizing the number of exposed Rim sites.

The Rim-Edge model, while influential, has limitations in explaining the behavior of complex catalysts, especially those containing multiple metals [111]. Additionally, the model's focus on macroscopic properties may not fully account for atomic-level variations in catalyst structure, which can significantly impact catalytic performance [112]. A more recent model proposed by J.V. Lauritsen et al. [113] introduces the concept of Brim and CUS sites, visualized in Fig. 9b [110]. CUS sites, characterized by missing sulfur atoms at edges or corners, exhibit Lewis acid properties and attract reactants. In contrast, Brim sites, which do not require unsaturation, possess metallic characteristics and facilitate the formation of thiolate intermediates (R-S). These intermediates are highly reactive and readily undergo hydrogenation. During the heavy oil hydroprocessing, the hydrogenation and C–C, C–M (M represented the heteroelements of sulfur, oxygen, nitrogen, and metals) bond cleavage parallelly occurs over Brim and CUS sites.

4.2. The structural and properties of support

Catalyst supports play a crucial role in determining the overall performance of a catalyst. They provide a physical framework for the active metal or metal oxide components, offering a large surface area that can accommodate numerous active sites. This increased surface area enhances catalytic activity generally. Additionally, the porous structure of the support facilitates mass transfer, allowing reactants and products to readily access the active sites. Therefore, the properties of the support, including acidity/basicity, surface area, and porosity, are critical factors influencing the performance of heterogeneous catalysts, alongside the chemical composition of the active phase.

Acidic sites on the catalyst promote cracking activity. Materials like alumina, crystalline zeolites, amorphous silica-alumina, and their mixtures, often exhibit a high acidity in both Lewis and Brønsted acid sites

and are commonly used as catalyst supports [114]. These materials, particularly zeolites with their well-defined microporous structure, offer high surface areas and strong acidity, leading to the optimizing yield of high octane gasoline components, i.e. selective cracking of complex crude oil molecules [115]. However, the overuse of acidity sites, especially Brønsted acid sites, in a catalyst led to an overcracking reaction, generated a high yield of low-valuable gas as well as triggered coke deposition [116,117].

It is crucial to emphasize that heavy oil upgrading involves the processing of complex petroleum macromolecular, especially asphaltene. Consequently, mass transfer plays a pivotal role in the efficiency of these processes. To enhance the diffusion of large asphaltene molecules, the development of porous-shaped supports or catalysts with macropores (>100 nm) is a promising approach. However, it is crucial to maintain a balance, as an excessive number of macropores can compromise the structural integrity of the catalyst particles [118]. Mesoporous alumina, with its interconnected or isolated network structure, offers an ideal support material. It combines the crystalline properties of alumina with a well-defined porous structure [119]. Catalysts with pore sizes ranging from 7 to 20 nm have demonstrated superior activity in hydrocracking applications compared to those with smaller pores (3–7 nm), as reported for Athabasca oil sand bitumen [120]. In particular, while microporous and mesoporous catalysts are effective for sulfur and nitrogen removal, microporous catalysts are particularly well-suited for hydrodemetallization (HDM) and hydrodeasphaltenization (HDAs) due to their ability to accommodate larger molecules [121]. M.S. Rana et al. [122] investigated the impact of alumina pore diameter on heavy oil hydrotreating (Fig. 10). The results

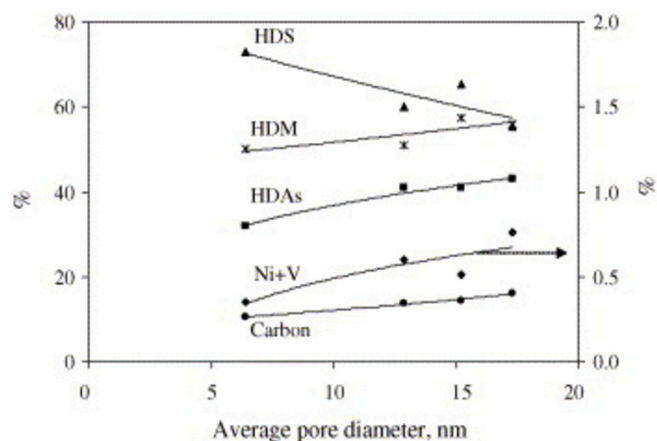


Fig. 10. The effect of average pore diameter on the HDM, HDS, and HDAs efficiencies in heavy oil hydroprocessing [121] (Reused with permission from Elsevier, Copyright© 2004).

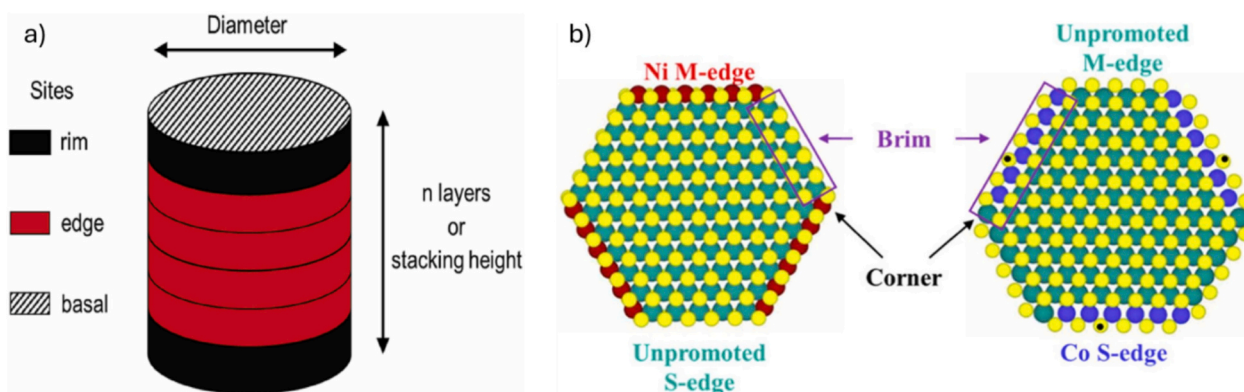


Fig. 9. The Rim-Edge (a) and Brim-CUS (b) model theories for the catalyst active site in heavy oil hydroprocessing [102,110] (Reused with permission).

indicated a positive correlation between pore size and HDM and HDAs efficiency, suggesting that larger pores facilitate the diffusion of heavy molecules to the active sites. Conversely, HDS efficiency was found to be more dependent on the dispersion of metal active sites rather than pore size.

In summary, the catalyst is the most important factor in heavy oil hydroprocessing. The selection of catalyst needs to be carefully made based on the properties of feedstock and, the goals of the process. The properties of active metal and support directly govern process efficiency. The detail for the development of hydroprocessing catalysts was systematically summarized by R. Prajapati et al. [123] and the most recent research on catalysts for heavy oil upgrading is shown in Table 2.

5. Catalyst deactivation in heavy oil upgrading

5.1. Catalyst deactivation by coke and metal depositions

The most common reason for catalyst decay in heavy oil upgrading is because of the formation and deposition of heavy carbonaceous material, so-called coke, over the catalytic active center. In the heavy oil system, asphaltene is often considered a solute since it is well-dispersed in the maltenes- a comprising of saturate, aromatic, and resin [81,85]. Before the existence of coke, the asphaltene content was found to increase at the beginning of upgrading [135,136]. It might be due to the polycondensation of resin which has been observed elsewhere [135,137,138]. Moreover, it has been reported that the consistent growing trends of the non-polar fractions such as naphtha and middle distillate during heavy oil hydrocracking regardless of the catalyst [139]. At the same time, the average alkyl chain lengths in asphaltene were decreased and aromaticity was increased [140,141]. The unflavored environment leads to an increase in the size of asphaltene agglomeration [142] and at a certain point, asphaltene breaks the compatibility state and then triggers the sedimentation. Research on the evolution of this sediment has pointed out that the solubility of this solid in toluene or tetrahydrofuran was decreased following the extended reaction time [143,144]. It indicates the transformation of coke from soft form which is asphaltene precipitate into the hard-coke as the reaction prolonged. The hypothesis for the chemical transformation of asphaltene molecular was proposed in Fig. 11 [145].

A mechanistic model for coke formation in heavy oil upgrading was proposed in 2007, focusing on the asphaltene structure as a “pedant-core building block” (Fig. 12) [146]. This model posits that asphaltenes consist of an aromatic core surrounded by various alkyl and aromatic side chains. During thermal upgrading, the side chains undergo cracking, leading to the generation of heavy radicals [147]. The converted asphaltene exhibits a high aromaticity and gradually becomes incompatible with the oil mixture. It leads to phase separation and subsequent polycondensation of the aromatic cores, ultimately forming coke. This mechanism is supported by observations made using pyrene as a model compound [148].

D.V. Pham et al. [149] studied the catalytic hydrocracking of heavy oil using feedstocks containing different amounts of asphaltene of 10.4–96.3 wt%. The content of asphaltene was found directly related to the stability of feedstock. During the slurry phase hydrocracking process, the unstable feedstock caused serious coke formation and limited the yield of desirable fractions such as VGO and middle distillate (MD), in agreement with the previous literature [150]. However, it was also found that the asphaltene content was not well correlated to the coke formation [151]. The quality of asphaltene is more critical for the controlling of coke. In particular, asphaltene having a higher aromaticity and degree of aromatic ring condensation resulted in a higher yield of coke [152–154].

The addition of hydrogen and an HDY catalyst to heavy oil upgrading processes can significantly improve asphaltene stability [155,156]. This delayed the asphaltene phase separation and led to a substantial reduction in coke formation compared to thermal cracking [157]. The

size of the catalyst is also an important factor affecting the formation of coke. A submicron or micron in size could interfere with the formation and growth of coke. Meanwhile, the size which is bigger than asphaltene mesophase, in contrast, plays the role of a nucleation site for the agglomeration of asphaltene, hence resulting in a high coke yield during the upgrading process (Fig. 13) [158].

Using a different approach, X. Zhang and J. M. Shaw conducted a study on the impact of multiphase behavior on coke formation during low-temperature heavy oil hydroprocessing. The reactions were carried out using different mixtures of Athabasca vacuum bottoms (ABVB), decane, and hydrogen. During the upgrading, multiple phases including vapor (V), low-density liquid (L_1), and high-density liquid (L_2) were observed. The denser liquid phase was found to be associated with the coke formation [159]. It suggests that a mixture of heavy feedstock with a solvent can inhibit coke and enhance upgrading efficiency [160].

Heavy oil often contains significant amounts of various metals such as nickel, vanadium, and iron [95]. These heavy metals can accumulate on the surface of the catalyst used in the hydroprocessing of heavy oil. The presence of these deposited metals can inhibit the interaction between the reactants and the active sites on the catalyst, leading to serious deactivation of the catalyst. A study by Kohli et al. [137] investigated the loss in HDT catalyst activity, focusing on the effects of metal deposition from the asphaltenes and resins. The researchers used High-Resolution Transmission Electron Microscopy (HR-TEM) to analyze fresh, spent, and regenerated catalyst samples (Fig. 14). Before the reaction, the catalyst posed a clear multilayer of 3–4 layers structure of the active MoS_2 species, with an average length of 3.26 nm. However, it was difficult to observe the active species in the spent sample due to the extensive deposition of heavy metals and coke. In contrast, the regenerated catalyst exhibited two-layered slabs of the MoS_2 active species, with an average length of 2.81 nm. These changes in the catalyst structure, caused by the deposition of nickel (Ni) and vanadium (V), led to significant differences in the HDS activity of the catalysts, with the order being: regenerated < spent < fresh catalysts [161]. The presence of these heavy metals in the catalyst can also increase the olefin fraction through dehydrogenation, and lead to higher coke yields during heavy oil upgrading [162].

5.2. Catalyst deactivation by other heteroelements and sintering

Besides coke and metal deposition, nitrogen compounds present in heavy oil can also deactivate hydroprocessing catalysts [163]. These nitrogen compounds, primarily consisting of 5- and 6-membered heteroaromatic rings and anilines, often exhibit a high basicity [164]. This high basicity can hinder the HDS process by competitively adsorbing onto active catalyst sites, reducing their availability for sulfur removal [165,166]. A study by R. E. Roncolatto et al. [167] on spent FCC catalysts revealed that nitrogen compounds tend to accumulate on the external surface of the catalyst, while coke formation is more widespread. Removing nitrogen compounds through air combustion requires harsher conditions of a high temperature and a long resident time compared to coke, indicating a stronger bond between nitrogen compounds and the active sites.

The inhibition effect on catalyst performance has also been proven to depend on the structural properties of the sulfur compounds in the oil. A study by Kwak et al. [168] on the deactivation of $\text{CoMoS}/\text{Al}_2\text{O}_3$ catalysts revealed that in HDS of dibenzothiophene (DBT), the HYD pathway was more hindered by the presence of nitrogen compounds than the direct desulfurization (DDS) pathway. However, an opposite phenomenon was found in the HDS of 4-methyl dibenzothiophene (4-MDBT) or 4,6-dimethyl dibenzothiophene (4,6-DMDBT), where the direct desulfurization (DDS) pathway was more sensitive with nitrogen-containing compound than the HYD pathway. These differences are attributed to the varying degrees of steric hindrance to the C-S-C bond caused by the methyl groups connected to the ring structure. The removal of nitrogen from oil has been reviewed in detail by Prado et al. [169].

Table 2
Recent studies on catalysts for heavy oil hydroprocessing.

Heavy oil	Operating conditions	Catalyst	Conversion (wt%)	Results	Advantages and limitations of catalyst	Ref
Vacuum residue (9.8 wt% asphaltene)	130 bar H ₂ , 440 °C, 2 h	Mesoporous Fe ₂ O ₃	Vacuum residue conversion of 74.1–80.3 %.	The acidity and mesoporous structure of the catalyst directly govern vacuum residue conversion. The undesirable product yield of coke and gas was less in the presence of abundant hydrogenation active sites. As the Al/Si ratio increases, the number of Lewis acid sites rises while Brønsted acid sites decline. Catalysts with lower Al/Si ratios tend to have larger surface areas and higher mesoporous volumes, which can enhance active site accessibility and dispersion. The appropriate presence of hydrogenation and acid sites resulted in an effective upgrade.	Advantage: A catalyst based on iron oxide has a cost-effective advantage. Disadvantage: Iron oxide or iron sulfide is not a good hydrogenation catalyst leading to the formation of a large amount of gas and relatively high coke fractions.	[124]
Vacuum residue (10.7 wt% Conradson carbon residue)	430 °C, H ₂ / oil of 800 (v/v), 3 h.	MoS ₂ /Al ₂ O ₃ -SiO ₂ with different ratios of Al to Si	Vacuum residue conversion of over 75 %.		Advantage: Catalyst preparation was simple using common precursors of Al (NO ₃) ₃ ·9H ₂ O, (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O, sodium silicate and NH ₄ OH. Disadvantage: Feedstock conversion is quite low.	[125]
Maya heavy crude (33.6 wt% asphaltenes)	185 bar H ₂ , 425 °C, 1 h	Functionalized carbon nanofibers (CNF) coated with Ni-decorated MoS ₂ slabs	Asphaltene conversion of 73 %	Liquid yield ~60 wt%, coke yield 1.2 wt%, HDM and HDS >80 wt%	Advantage: catalysts with a high HDY activity result in excellent HDS and HDM with a low yield of coke. Limitation: The synthesis requires using large amounts of corrosive chemicals of nitric and sulfuric acids. Advantage: The catalyst showed promising activity with non-detectable coke formation.	[126]
Aguacate heavy crude (23.3 wt% asphaltenes)	70 bar H ₂ , 310–370 °C, 72 h.	Nano-nickel dispersed in PEG300	Residue conversion of 90.88 % at 370C, 72 h	Reaction rates were low at a temperature range of 310–330 °C. Hydrogen solubility was enhanced by the addition of PEG300. Hydrogen dissociation was found over the (111) lattice of the dispersed nickel nanoparticles.	Limitation: The operating temperature applied in this study is quite low leading to a very long reaction time to achieve an adequate conversion of residue. The catalyst synthesis requires expensive chemicals of nickel(II) acetate tetrahydrate and sodium borohydride.	[97]
Atmospheric residues (6.65–11.49 wt % asphaltenes)	Fixed bed reactors, 370 °C, 135 bar H ₂ .	NiMo/Al ₂ O ₃ (pore size 13–30 nm)	Asphaltene conversion of 70–90 %	Catalysts with a large pore size favors the removal of metals and asphaltene. The hydroprocessing efficiency showed a huge dependence on asphaltene and nitrogen contents in the feedstock. The loading of metal was proportional to HDA. The regenerated catalyst showed better HDAs than the fresh catalyst.	Advantage: Catalyst is a commercial type. Limitation: The deactivations by coke and metal deposit were found very severe.	[127]
Vacuum residue (33.0 wt% asphaltene)	190 bar H ₂ , 400–450 °C, 1 h	NiMo/Al ₂ O ₃	Asphaltene conversion of 50.0–80.3 %		Advantage: Catalyst is a commercial type. Limitation: Low catalyst activity and stability.	[128]
Heavy crude oil (35.2 wt% asphaltenes)	98 bar H ₂ , 372 °C, 1 h	4600 ppm of nano NiFe (25 % mol Ni)	Asphaltene conversion of 43.7 %	Liquid yield 50.5 wt%, HDN 36 wt %, HDS 35 wt%	Advantage: Catalyst activity was quite high even at a relatively low temperature. Limitation: Due to the small size of the catalyst, the recovery and recycling of this material is challenging.	[129]
Vacuum residue (23.1 wt% asphaltenes)	70 bar H ₂ , 400 °C, 4 h	1300 ppm unsupported nickel–tungsten sulfide (NiWS(x)) particles	Asphaltene conversion of 81.8 %	Liquid yield 71.6 wt%, HDS 86.5 wt%, coke yield 4 wt%	Advantage: Great upgrading efficiency with high sulfur removal and liquid yield. Limitation: The synthesis of the catalyst is difficult to scale up. The formation of undesirable coke was not well controlled.	[130]
Vacuum residue (23.1 wt% asphaltenes)	70 bar H ₂ , 400 °C, 4 h	Nanosheet-structured WS ₂	Asphaltene conversion of 75.3 %	Liquid yield 71.8 wt%, coke 9.1 wt%, HDM 96.5 wt%	Advantage: Catalyst activity was good with high HDAs, HDM, and liquid yield. Limitation: The formation of coke was very high which reduced the carbon utilization efficiency.	[131]
Vacuum residue (23.1 wt% asphaltenes)	70 bar H ₂ , 420 °C, 4 h	Cs-exchanged phosphotungstic acids (Cs _x H _{3-x} PW ₁₂ O ₄₀ , x = 1–3)	Asphaltene conversion of 78.3 %	Liquid yield 68.7 wt%, coke yield 9.2 wt%, HDS 60 wt%, HDM 95 wt%	Advantage: The catalyst exhibited a decent activity favoring a high liquid yield and a great HDM.	[132]
		NiMo/Al ₂ O ₃ -based catalyst	Asphaltene conversion of 76.2 %	Liquid yield 50.6 wt%, coke yield 15.5 wt%, HDS 63.1 wt%, HDM 98 wt%	Limitation: Low HDS and high yield of coke.	
Heavy oil (3.2 wt% asphaltenes)	Semi model: 110 bar H ₂ , 370 °C, 24 h	4000 ppm ultradispersed metallic nickel nanocatalyst	Asphaltene conversion of 43.7 %.	Residue conversion of 47 wt%, HDAs 50 wt%, HDS 20 wt%	Advantage: The catalyst showed a great dispersibility in heavy oil leading to a good upgrading performance. The spent catalyst had a similar size to the fresh	[133]

(continued on next page)

Table 2 (continued)

Heavy oil	Operating conditions	Catalyst	Conversion (wt%)	Results	Advantages and limitations of catalyst	Ref
Vacuum residue (6.82 wt% asphaltenes)	100 bar H ₂ , 410 °C, 1 h	2000 ppm of presulfided oil-soluble MoS ₂	Asphaltene conversion of ~100 %.	Liquid yield 83.4 wt%, coke yield 0.19 wt%, HDS 59.2 wt%, HDM 83.4 wt%	suggesting a highly recyclable catalyst. Limitation: The catalyst dosage was high, but the sulfur removal efficiency was low. Advantage: The catalyst showed a great activity toward liquid fraction. Coke yield was low. Limitation: The catalyst required a presulfurization process. The removal of metal and sulfur was relatively low.	[134]

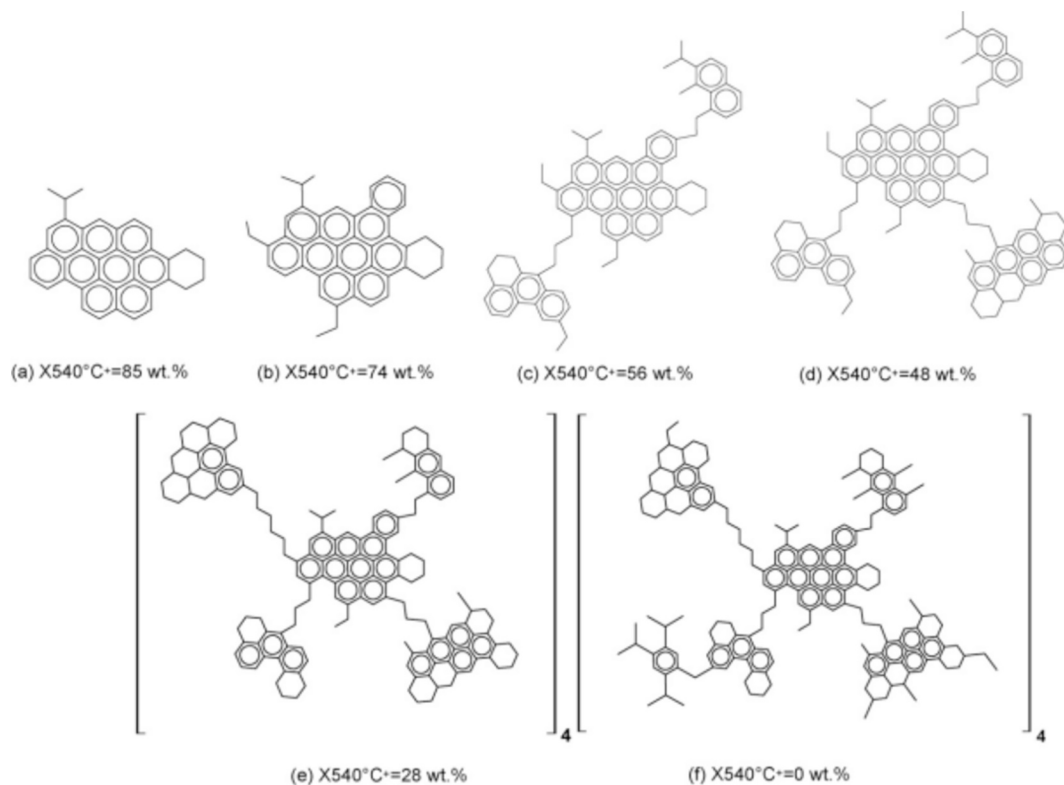


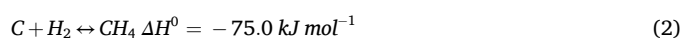
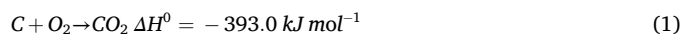
Fig. 11. The structure of asphaltene at different X540 °C residue conversions [145] (Reuse with permission from Elsevier. Copyright © 2008).

Heavy oil upgrading often involves multiple catalytic beds or reactors, with guard beds placed at the beginning to remove nitrogen and metal compounds that can poison the main HDS catalysts [170]. The arrangement of HDS and hydrocracking (HCK) catalyst beds depends on the desired product. HDS and HCK are typically located toward the end of the process to ensure high yields of clean liquid fuel. Fig. 15 illustrates a general scheme for heavy oil upgrading [95].

Catalyst deactivation in heavy oil hydroprocessing can be caused by various factors, including coke and metal deposition, nitrogen poisoning, and structural changes in the active metal species. While the temperature range for hydrodesulfurization (HDS) is typically 320–380 °C, hydrocracking requires higher temperatures (>400 °C) for complete conversion. However, high temperatures can also accelerate metal sintering, a process that permanently reduces catalyst activity [164,171]. Regeneration, often involving combustion to remove coke, can further exacerbate sintering and phase transformations at temperatures above 500 °C [137]. The next section will delve deeper into the challenges and strategies for regenerating spent HDS catalysts.

6. The regeneration of spent catalysts

The coke deposition onto the catalyst surface is the most common cause of catalyst decay in reactions involving hydrocarbons. In heavy oil upgrading, coking becomes much more serious due to the heavy of the feedstock [172,173]. Depending on the type of coke, different gasification techniques could be applied which are described in Eqs. (1)–(4). In heavy residue hydroprocessing, the coke naturally varies widely depending on feedstock properties and operating conditions. In general, coke generated from asphaltene-rich feed often has a much higher aromaticity and is difficult to dilute in any type of solvent. In contrast, coke formed by polycondensation of resin posed a lower average molecular weight with a higher aliphaticity and could be dissolved in solvents such as hexane, benzene, or tetrahydrofuran [174]. Hence, the feedstock composition influences the type of coke which requires different removal conditions for catalyst regeneration.



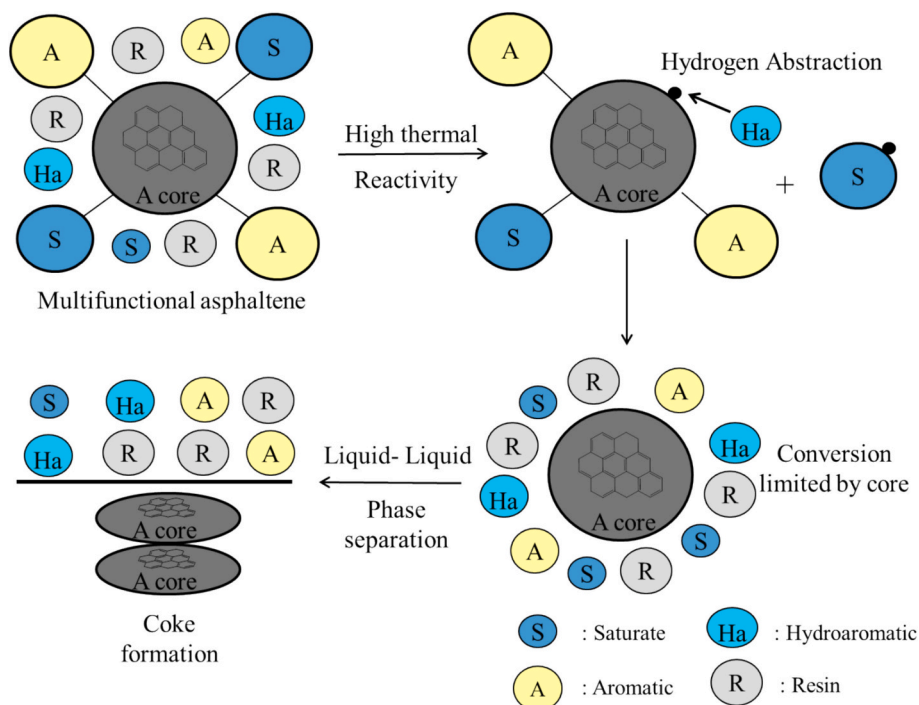


Fig. 12. The physicochemical transformation of asphaltene in heavy oil upgrading [146] (Reuse with permission).

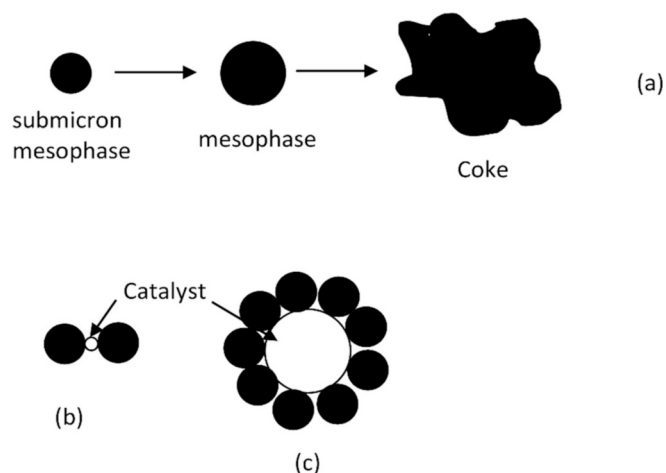
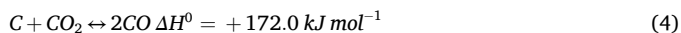
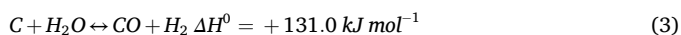


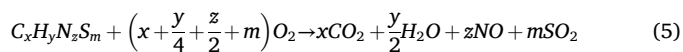
Fig. 13. The growth of coke (a), a submicron or micron size of catalyst prohibiting coke formation; and large catalyst particles promoting coke growth (c) [158].



6.1. The regeneration of spent catalyst using the combustion method

Among the above-mentioned methods for coke removal, the combustion pathway using oxygen or air is the most frequently used [175,176]. The basic nature of this reaction is highly exothermic with a fast reaction rate. To minimize safety risks, a diluted air mixture is used as the oxidizing agent in the early stages of regeneration. Once the most reactive coke has been removed, pure air can be introduced to complete the process. Nevertheless, rigorous temperature control is essential to ensure safe operation [177]. Depending on the type of coke, the removal temperature range is from 250 °C to 500 °C [178]. Besides, the spent

catalyst often contains 1.5–2 wt% of hydrogen (the hydrocarbon trapped in the catalyst pore [179]), 4.4–7 wt% of sulfur and approximately 0.5 wt% of nitrogen [180]. The general combustion of coke involved other heteroelements is shown in Eq. (5).



Notably, CO₂ is always a major product in the outlet gas generated after oxidative regeneration, even when oxygen is scarce. This can be explained by the well-established mechanism of hydrocarbon autoxidation, involving the chemisorption of oxygen and the subsequent formation of surface intermediates such as peroxy radicals and hydrogen peroxides [181,182]. The mechanism of oxygenated complex formation during autoxidation of coke is shown in Fig. 16. At the beginning of the regeneration process with a low temperature, the weight of the spent catalyst was found to be increased due to the chemisorption of O₂ and the formation of surface complexes. However, these complexes quickly decomposed when the operating temperature reached the critical point and triggered the combustion [182].

K. Matsushita et al. [183] conducted a study on temperature-programmed oxidation (TPO) of coke with different ages of spent catalyst. The TPO profile exhibited two distinct CO₂ desorption peaks centered around 573 K and 700 K, corresponding to the removal of soft and hard coke, respectively. Soft coke, composed of reversibly adsorbed precursors like aromatics and asphaltenes from the feedstock, can be removed at lower temperatures [184]. In contrast, hard coke, which is strongly bound to the catalyst, requires higher temperatures for the removal [185]. Importantly, the transformation of soft to hard types was observed with the time on stream. It indicates that the formation of coke is due to the polycondensation of asphaltene aromatic core and occurs when asphaltenes are exposed to a severity condition for a long period [64,186].

The effectiveness of this method is varied. K. Kohli et al. studied [187] the regeneration of NiMo/Al₂O₃ spent catalyst obtained from HDS of heavy oil. The regenerated process involved an air-calcination at 550 °C followed by reactivation in the CS₂-saturated H₂ flow at 400 °C. As a result, catalyst activity was fully gained. In another work reported by A. Pimerzin et al. [188], only 72 % of HDS activity was recovered

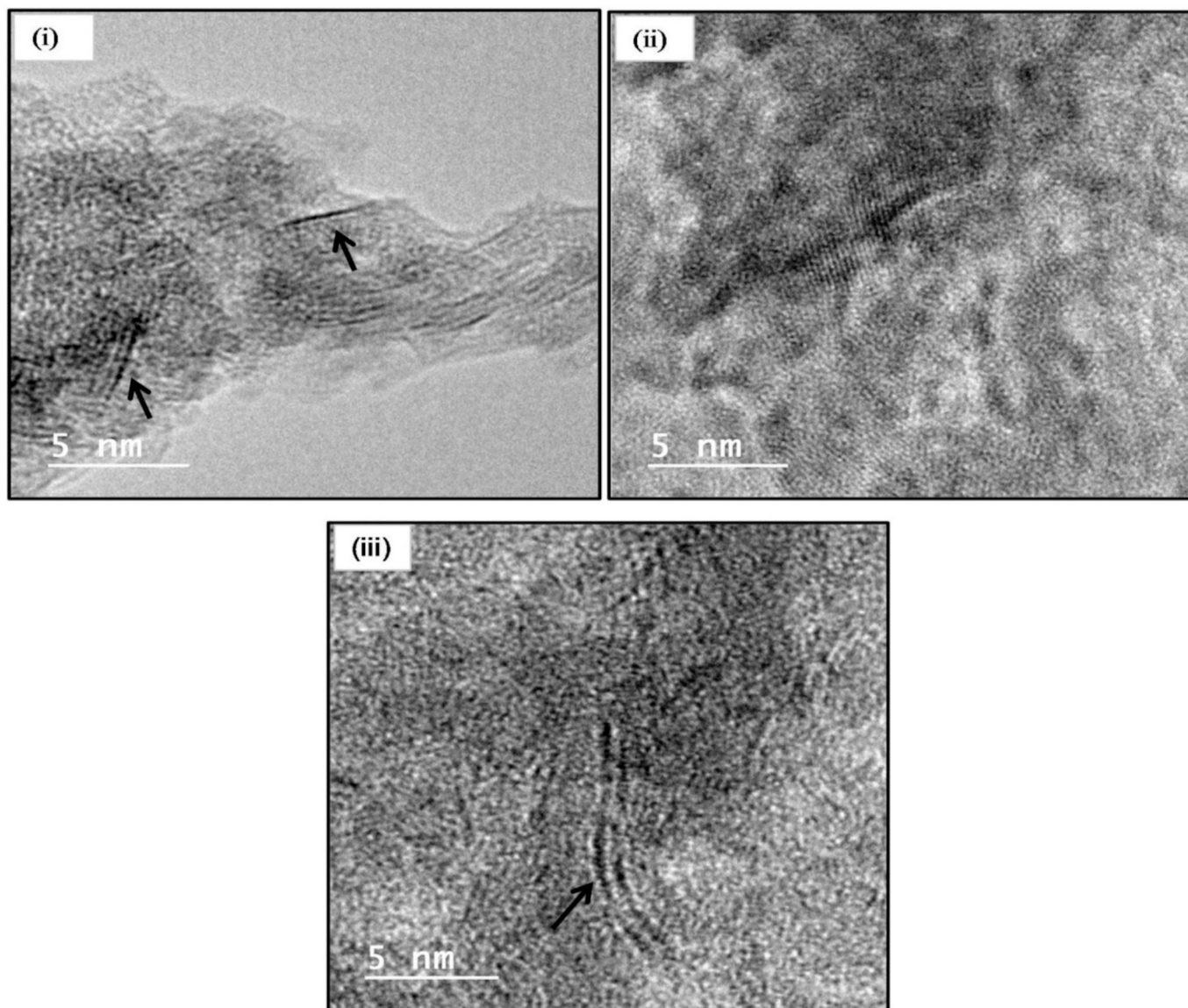


Fig. 14. The HR-TEM analysis for catalysts (i) before reaction (ii) after reaction, and (iii) after regeneration [137] (Reused with permission).

after the air-regeneration method was applied to the spent of CoMo/Al₂O₃. The main difference between these two studies is the age of the catalyst. K. Kohli et al. [187] recovered and regenerated the HDS catalyst after 6 h of reaction time. Meanwhile, in the study conducted by A. Pimerzin et al. [188], a two-year spent catalyst was employed. As time goes by, the polycondensation of the aromatic core forms a hard-coke type which is heavy and has a low H/C ratio [135] challenging the regeneration process. A T. Aguayo et al. [189] have found that the oxidation rate of coke was strongly influenced by the nature of coke. The activation energy for a low H/C ratio coke was found to be much higher than hydrogen-rich coke [190]. It suggests that the effectiveness of catalyst regeneration largely depends on the morphology of coke.

6.2. Catalyst regeneration using gasification agents

Despite a huge advantage coming from the ease of operation and highly available oxidation reagent in the combustion method, the biggest disadvantage is the highly exothermic nature of the main reaction. As a consequence, the catalyst regeneration is easily overheated causing metal sintering and permanent degradation [191,192]. Another uncommon method uses hydrogen reductant [189,193]. The advantage

of it, as presented in Eq. (2), is a much lower exothermic reaction giving a better control of regeneration in comparison to the combustion method.

George et al. [194] reported that the use of pure hydrogen at 773 K did not lead to significant coke removal from a spent NiMo/Al₂O₃ catalyst. The thermodynamic unflavored of the methanation reaction (Eq. (2)) at such temperatures suggests that the type of coke present, rather than the regeneration conditions, was the primary obstacle to coke removal. In a study by S.J. Jong et al. [195], it was observed that Brønsted acid sites in H-ZSM-5 zeolite play a significant role in H₂ regeneration. Using xenon adsorption and ¹³C CP-MAS NMR spectroscopy, they found that coke located near these acid sites was preferentially removed during the regeneration process.

The major disadvantages of the coke hydrogenation method are the low effectiveness when operating at moderate operating temperature [196] and the difficulty of removing the hard coke having a low H/C ratio [197,198]. The hydrogen reactivation was only successful for the H/C ratio of coke greater than 1.0. Silva et al. [199] demonstrated that hydrogen treatment was limited to removing soft coke from spent NiMo/Al₂O₃ catalysts. Hard coke deposits were highly inert and required a higher operating temperature (>500 °C) and pressure (>15 MPa) to be

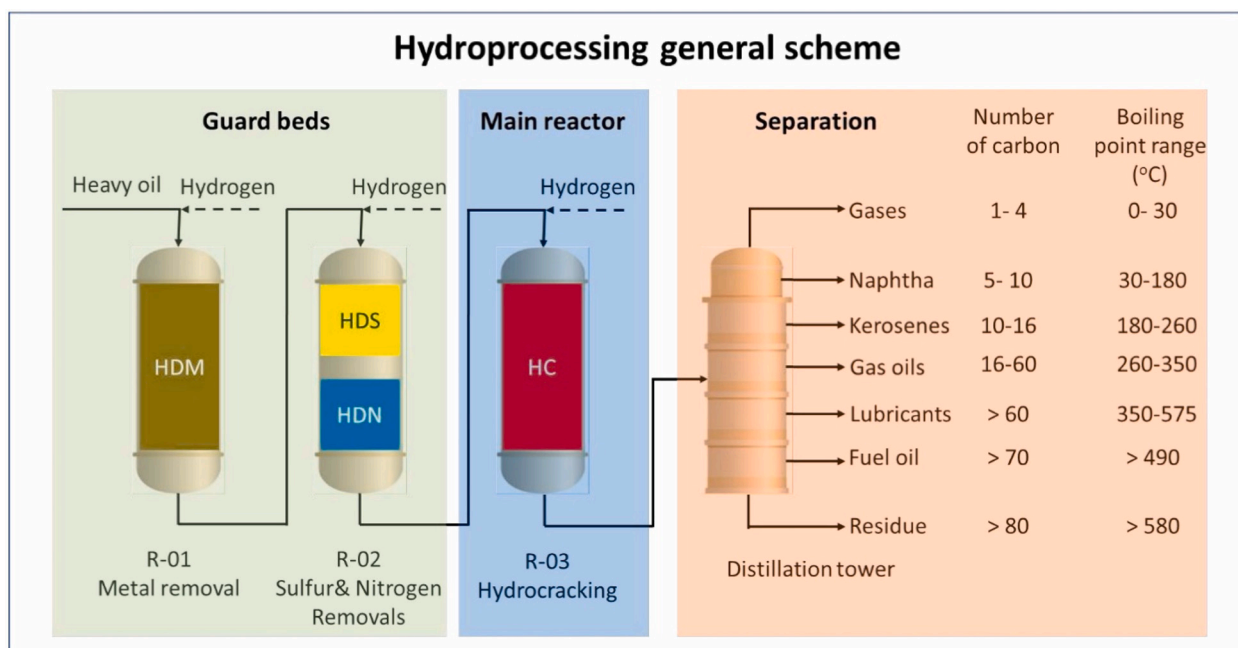


Fig. 15. Heavy oil hydroprocessing general scheme [95] (Reused with permission).

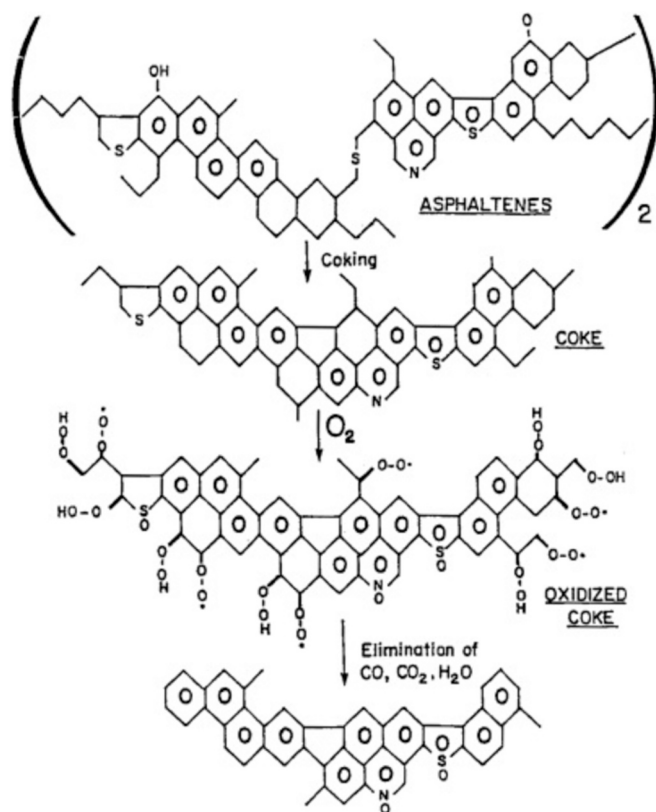


Fig. 16. Mechanism of oxygenated complex formation during autoxidation of coke [177] (Reused with permission).

partially removed [200]. Moreover, hydrogen is a costly reactant, and the production of methane is also a greenhouse gas and is being restricted by government policies. Hence, the application of this technology is still on the laboratory scale.

The coke gasification using CO₂ or steam (Eqs. (3–4)) is getting more attention because of the lower greenhouse gas emission emitting to the

environment in comparison to other methods [201–203]. In the case of CO₂ gasification, the operating temperature requires at least 700 °C to obtain effective coke removal [204]. At this condition, the sintering of active metal is quite significant. The reaction of coke with steam occurs at a similar temperature range but the rate is 2–5 times faster than that of CO₂ [205,206]. However, steam could interact with support such as alumina leading to a permanently damage catalyst porous structure [207,208]. The advantages and limitations of each common coke removal process are reviewed in Table 3.

The Integrated Residual Cracking and Gasification (ICCG) process offers a stepwise approach to the value-added utilization of heavy oil and petroleum residues. As illustrated in Fig. 17, heavy oil is initially cracked into volatiles, with simultaneous coke formation. Subsequently, the coke is gasified with steam to produce syngas. This steam gasification process can also be used to regenerate spent catalysts. The hydrogen generated from this process can be recycled to hydrotreat the cracked oils. Finally, the regenerated catalyst particles can be recirculated to the reactor to provide the necessary heat for catalytic cracking [209].

6.3. Mitigation of catalyst sintering after thermal regeneration

Based on Table 3, the traditional methods suffer from active metal sintering due to overheating or a high operating temperature. To address this issue, researchers have explored using an additional leaching process. Albemarle introduced a commercial technology called REACT in 2003 to reactivate spent STARS catalysts. This process restores over 90 % of the fresh catalyst’s activity by redistributing metals and reconstructing the type II active phase. Details of the reactivation process are outlined in the patent application by Ginestra et al. [210] and Eijsbouts et al. [211]. These patents list a variety of chelating agents, including citric acid, tartaric acid, oxalic acid, malonic acid, butanediol, glycolic aldehyde, acetaldo, and various glycols, that can be employed in the reactivation process [212]. Numerous spent HPR catalysts have been successfully reactivated using this method, as confirmed by published data.

Even though the recovery in catalytic activity has been proven experimentally, the mechanism of this method was still not yet clear. Mazoyer et al. [213] investigated the impact of chelating agents, such as diammonium salt of ethylene diaminetetraacetic acid, on a calcined

Table 3
The advantages and limitations of common coke removal processes.

Removal agent	Reaction temperature (°C)	Removal rate	Advantages	Disadvantages
Oxygen/Air	400–600	$O_2 > H_2O > CO_2 > H_2$	Reactants are highly available. The removal rate is rapid, and the process is well-developed.	Catalyst is easy to be overheated leading to active metal sintering. The regenerated catalyst requires reactivation.
Hydrogen	> 800		The reaction is much less exothermic, giving better control of the process. The regenerated does not require reactivation.	Hydrogen is a costly reactant. The reaction rate is very low in comparison to other agents. A high operating temperature possibly leads to active metal sintering.
Carbon dioxide	700–950		No greenhouse gas emission is produced. CO_2 is a relatively cheap reactant and the removal rate is moderate.	Catalyst activity and stability are often decreased due to metal sintering.
Steam	700–950		Water is an abundant reactant. The product gas is a mixture of H_2 and CO so-called syngas and it has many applications in different chemical engineering processes.	At a high temperature, water can destroy the structure of alumina support.

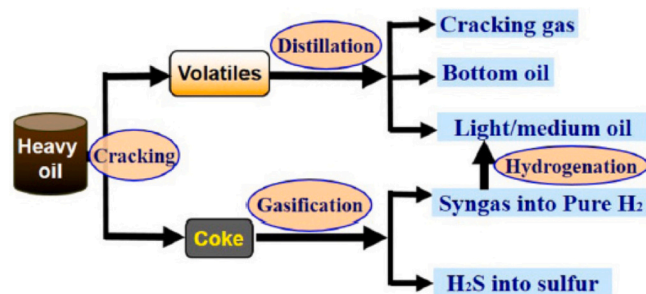


Fig. 17. Reaction flow of heavy oil during integrated cracking and coke gasification process [209] (Reused with permission).

CoMo/Al₂O₃ catalyst. The study revealed that the chelating agent effectively dissolved the undesirable CoMoO₄ crystalline phase, leading to a more dispersed distribution of Co²⁺ cations on the catalyst surface. This, in turn, facilitated the formation of the active Co-Mo-S phase. However, the chelating agent was unable to solubilize Co²⁺ from the stable CoAl₂O₃ spinel structure. In a similar study, Costa et al. [214] explored the role of glycol-based additives in enhancing the activity of CoMo and CoMoP catalysts. For catalysts with a P/Mo molar ratio below 0.4, the addition of the additive resulted in the formation of Anderson heteropolyanions like AlMo₆O₂₄⁹⁻ and AlMo₆O₄₀⁷⁻. This redissolution phenomenon, however, was limited by the low solubility of these heteropolyanions. In the case of CoMoP catalysts with a P/Mo ratio

exceeding 0.4, the formation of PCoMo₁₁O₄₀⁷⁻ was observed. In both cases, the chelating agents played a crucial role in the redissolution of the inactive form of active metal and the redispersion of active components, leading to enhanced catalytic performance.

6.4. Recent advantages in hydroprocessing catalyst regeneration

CO₂ gasification is an energy-intensive process due to its highly endothermic nature. To achieve an auto-thermal process, oxygen can be added to the CO₂-rich atmosphere [215,216]. The combustion of coke with oxygen provides the necessary energy for CO₂ gasification [217]. Alenazey et al. [215] proposed integrating air combustion and CO₂ gasification to minimize energy consumption, reduce greenhouse gas emissions, and mitigate catalyst sintering. This one-stage FCC regeneration process, illustrated in Fig. 18 [218], involves mixing oxygen from an air separation unit with CO₂ to regenerate the spent catalyst. A significant amount of CO is produced, and the excess unreacted CO₂ is recycled within the system [219,220].

In a similar approach, Zhang et al. [221] demonstrated that the addition of 3 % O₂ to steam significantly reduced regeneration time. They found that coke could be removed from the catalyst at temperatures below 800 °C in just 10 min, compared to 30 min with pure steam. This reduction in regeneration time was attributed to a decrease in activation energy from 115 to 45 kJ/mol. Coupling steam gasification with oxygen combustion also is used to optimize the heat balance in various processes. Gorma et al. [222] proposed a step-out improvement to the Fluid Catalytic Cracking (FCC) process, where the heat balance was optimized by combining steam gasification and oxygen combustion. This integrated approach allowed for the efficient removal of large quantities of coke from the catalyst.

Besides, the addition of certain metal dopants has been demonstrated as an effective method to increase the coke removal rate during catalyst regeneration. Metals such as Mn [223], La [224], alkali/alkaline earth elements [216,225], and V [202,226] have all been found to improve the adsorption of regeneration agents and facilitate the coke removal reactions.

Recently, plasma-based regeneration has emerged as an alternative to traditional high-temperature oxidative methods for catalyst rejuvenation. The key advantage of plasma regeneration is that it can operate at significantly lower temperatures. For instance, H. Srouf et al. [227] studied the plasma-based regeneration of CoMoP/Al₂O₃ catalysts. Their results showed that the sulfur and coke deposits were eliminated at just

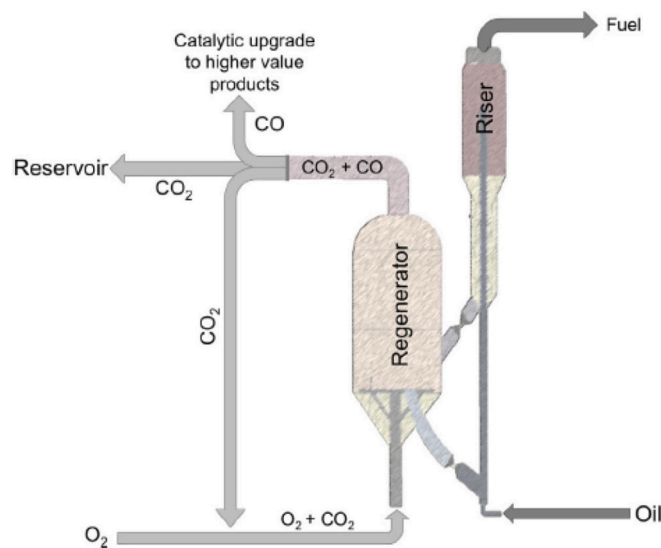


Fig. 18. One-stage FCC regeneration system under a rich CO₂ atmosphere [218] (Reused with permission).

250 °C, compared to the 400 °C required in the conventional regeneration approach. However, despite the promising results in removing the undesirable deposits, the plasma treatment led to the formation of a refractory CoMoO₄ phase, even at temperatures as low as 200 °C. This implies that localized “hot spots” were created during the plasma exposure, which prohibited the full restoration of the catalytic activity. A detail on the application potential of plasma for the regeneration of catalysts can be found in a review written by D H. Lee [228].

7. Mitigation of catalyst deactivation in heavy oil hydroprocessing

Coke formation is a major challenge in heavy oil hydroprocessing. This carbonaceous deposit not only deactivates the catalyst by blocking active sites but also leads to reactor fouling, reducing process efficiency [170,229]. The accumulation of coke diminishes product yield as feedstock is consumed without being converted to valuable products [230]. Moreover, coke formation can have environmental implications due to the possibility of the generation of greenhouse gases in the regeneration of catalysts. Hence, effective coke mitigation strategies are crucial for ensuring the economic viability, operational efficiency, and environmental sustainability of heavy oil upgrading processes.

In heavy residue processing, the formation of coke includes physical and chemical transformations of asphaltene [64]. The hydroprocessing requires an adequate combination of hydrogenation and cracking reaction to avoid incompatible asphaltene as well as polycondensation of aromatic core [231,232]. Particularly, hydroprocessing is often conducted at a high temperature to increase productivity. However, the cracking reaction is also promoted and becomes dominant at this condition leading to rapid catalyst decay by coke. The use of high hydrogen pressure was proven as an effective method [7,157,233]. However, it only works up to a certain level [155] and also requires a complicated reactor design.

The enhancement of hydrogenation could also be done by using a good catalyst. Current research on catalyst development is primarily focused on maximizing the utilization of active metal species in hydrogenation reactions. A common approach is to persulfide the metals to obtain highly active metal sulfide nanocrystals [106,134,234–237]. Another interesting avenue is to exploit the potential hydrogenation

activity of metal impurities present in asphaltenes. Recently, Lee et al. [238] reported a successful strategy to convert the vanadyl porphyrins in asphaltenes into hydrogenation active V₂S₃ form during asphaltene hydrocracking when tetralin was used as a solvent. This conversion resulted in significantly improved hydrogen uptake and asphaltene conversion, while also suppressing coke formation. The employment of external hydrogen donors has been explored as an effective method to enhance upgrading efficiency [239–243]. However, this method faces some practical limitations. It often requires large amounts of expensive hydrogen donors, and the recovery of them from the product can be challenging.

Another strategy is to delay the sedimentation of asphaltene by improving its stability during hydroprocessing. One technique is the addition of artificial asphaltene dispersants. These dispersants can change the colloidal stability of asphaltene in the feedstock. During heavy oil upgrading, the conversion of asphaltene into valuable fraction was found to be more efficient with a much lower yield of coke [141]. Another solution is the addition of aromatic diluents to the feedstock, which helps increase the asphaltenes compatibility during the reaction [244–246]. In a similar attempt, partial refluxing of products, such as the VGO fraction, has also been proven to be a good solution for controlling sediment formation [247]. Furthermore, the use of additives that disturb the aromatic core polycondensation has been verified to be another effective approach [248–250]. The ideal conversion of heavy oil with high effectiveness in the removal of heteroelements metals, sulfur, oxygen, and nitrogen as well as minimizing coke formation is shown in Fig. 19 [95].

8. Conclusions

Catalyst deactivation and regeneration are crucial factors in the efficiency and sustainability of heavy oil hydroprocessing. This review provides a comprehensive exploration of the key influences on catalyst deactivation, including coke formation, metal poisoning, and sulfur poisoning. It delves into the underlying mechanisms and their detrimental effects on catalyst performance and reactor operations. This review discusses various regeneration techniques, such as combustion and gasification using carbon dioxide, hydrogen, and steam. It evaluates the effectiveness of these methods in removing coke and restoring catalyst

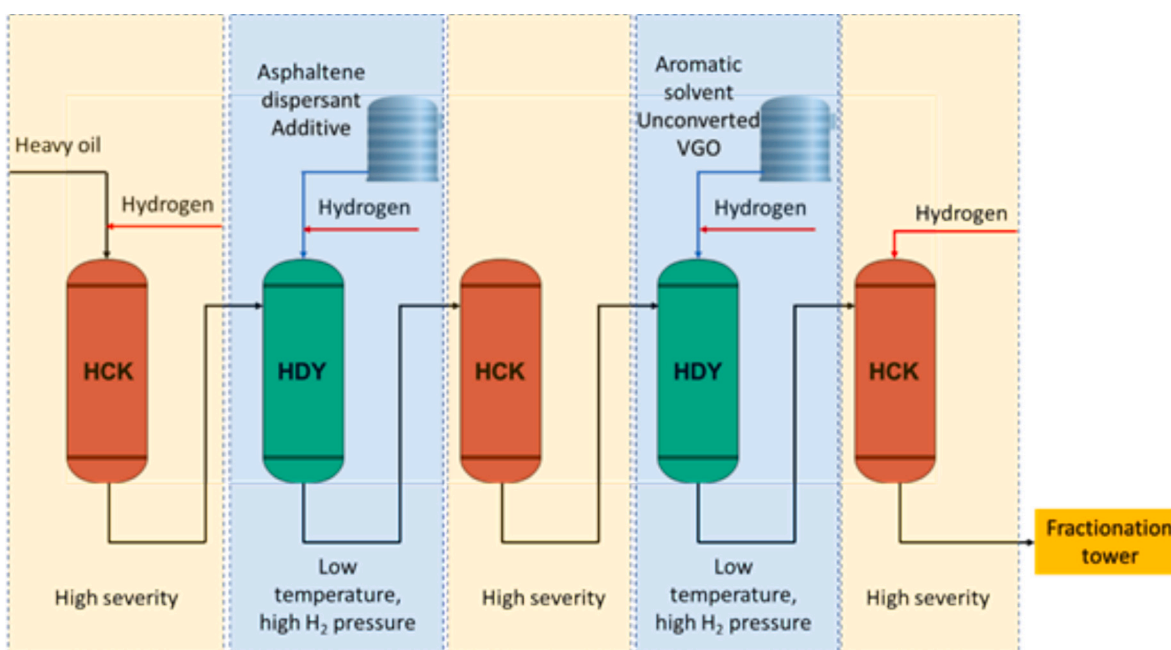


Fig. 19. The ideal heavy oil upgrading system with high heteroelements removal efficiencies and minimization of coke formation. [95] (Reuse with permission).

activity. Additionally, the review explores strategies to mitigate coke formation, including feedstock pretreatment, the addition of coke-delayed agents, and the development of more robust catalysts. By understanding these critical aspects, refineries can optimize their operations, enhance product yields, and minimize environmental impact. This review offers valuable insights for researchers and engineers seeking to advance the field of heavy oil hydroprocessing.

CRedit authorship contribution statement

Puong T.H. Pham: Writing – original draft, Data curation. **Cham Q. Pham:** Investigation, Data curation. **Thi-Tam Dam:** Data curation. **Quang-Anh Nguyen:** Formal analysis, Data curation. **Tung M. Nguyen:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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