

Review

Beyond Waste: Future Sustainable Insights for Integrating Complex Feedstocks into the Global Energy Mix

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Abstract

The utilization of sustainable feedstocks offers significant opportunities for innovation in sustainable and efficient processing technologies, targeting a vacuum residue upgrade industry projected to be valued at around USD 26 billion in 2024. This review examines advances in catalytic strategies for upgrading waste-derived products (plastics, tires) and biomass, in addition to heavy oil feedstocks. Particular emphasis is placed on hydrogen addition pathways, specifically, residue hydroconversion facilitated by dispersed nanocatalysts and waste co-processing methodologies. Beyond nanoscale catalyst design and reaction performance, this work also addresses refinery-level sustainability impacts. The advanced catalytic conversion of heavy oil residue demonstrates superior conversion efficiency, significant coke suppression, and improved carbon utilization, while life cycle and illustrative techno-economic comparisons indicate greenhouse gas reductions and a net economic gain of approximately USD 2–3 per barrel relative to conventional refining under scenarios assuming decarbonized hydrogen production. Co-processing of plastics, tires, and biomass with heavy oil feedstocks is highlighted as a practical and effective approach. Together, these findings outline a rational catalytic pathway toward optimized refining systems. Within the framework of the circular carbon economy, these catalytic processes enable enhanced feedstock utilization, integration of low-carbon hydrogen, and coupling with carbon-capture technologies.

Keywords: sustainable feedstocks; heavy oil feedstocks; oil residues; biomass; plastics; hydroconversion; nanocatalysts; co-processing; life cycle assessment; circular carbon economy; emissions; environmental impacts



Academic Editors: Konstantinos Kalkanis, Constantinos S. Psomopoulos and Kiskira Kyriaki

Received: 2 December 2025

Revised: 4 January 2026

Accepted: 9 January 2026

Published: 14 January 2026

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1. Introduction

The chemical industry is critical for achieving sustainable development and a high quality of life for the global population. In 2022 alone, the production of primary chemicals—such as olefins, aromatics, methanol, and ammonia—accounted for approximately 935 million tons of CO₂ emissions [1]. Catalysis for sustainability represents a fundamental strategy in achieving industrial effectiveness, resource circularity, and environmental protection through ongoing advancements in catalyst design and process innovation. This involves the following [1,2]:

- Creating greener and more energy—efficient chemical reactions;
- Integrating renewable resources and waste as viable feedstocks;
- Minimizing harmful emissions, including nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter, and carbon oxides (CO₂, CO);

- Realizing closed-loop manufacturing schemes with minimal waste generation.

Within the scope of sustainability and circularity, there has been a growing focus on the processing of heavy oil- and waste-derived feedstocks. The concept of the circular carbon economy provides a framework for managing greenhouse gas emissions and optimizing carbon utilization across industrial systems directly supporting UN Sustainable Development Goals. The circular carbon economy emphasizes the four fundamental principles of reduce, reuse, recycle, and remove carbon and promotes the continuous flow of carbon through technological cycles as opposed to its release into the atmosphere.

Increasing attention is being devoted to advancing the processing of heavy feedstocks such as heavy crude oil, bitumen, refinery residues, and waste-based materials, including plastics, agricultural biomass, and industrial by-products. The industry is developing advanced catalytic and refining solutions to enhance feed flexibility and product consistency [3], effectively addressing the technical challenges associated with these materials, such as high viscosity, sulfur content, and complex molecular structures. Incorporating heavy oil and its by-products into the processing systems can substantially decrease the cost of fuel production. Techno-economic calculations, intended as an illustrative, scenario-based comparison, described in the Supplementary Materials (Part 1) and based on open-source data [4–7], demonstrate that even small increases in HOF conversion rates can yield proportional reductions in unit processing costs. For instance, a 5% increase in heavy fuel oil (HFO) conversion can result in an approximately proportional reduction in unit diesel production costs under fixed-capital conditions. However, the magnitude of cost savings depends strongly on plant scale, feedstock price, and downstream separation requirements. Similarly, agricultural waste and biomass residues present untapped potential for circular economy applications, which can be unlocked through the continued development and employment of efficient catalytic conversion technologies [8]. Furthermore, various other waste streams (mixed plastics, polluted water, etc.) possess significantly more complex compositions than the aforementioned feedstocks, necessitating sustainable treatment solutions.

Catalysis plays an important role in converting heavy feedstocks into higher-value products while reducing environmental impacts. Traditional thermal cracking and incineration methods have played a significant role in the industry. Catalytic processes now further enhance efficiency by offering improved selectivity, lower energy consumption, and increased product yields through methods such as hydroprocessing (e.g., hydrocracking and hydrodesulfurization (HDS)), cracking, and pyrolysis [9,10]. Catalysts assist the integration of renewable feedstocks, such as non-edible oils (e.g., palm kernel oil), into sustainable aviation fuel production via deoxygenation processes, hence reducing reliance on fossil fuels [11]. Catalytic methods for sustainable processing are especially pertinent, since they tackle the disposal of high-carbon-footprint materials and offer ecological benefits. By advancing catalysis for the effective transformation of heavy feedstocks (i.e., macromolecular resources), the chemical industry can facilitate the transition to sustainable, circular production systems. For sustainable catalysis, it is imperative to evaluate both catalyst efficacy (i.e., the catalytic process) and fabrication (i.e., catalyst manufacture).

This paper analyzes trends in catalytic techniques for sustainability, emphasizing hydrogen addition processes for heavy oil feedstocks (HOFs) as an ideal platform to incorporate sustainable feedstocks (plastics, biomass) as co-feeds into conventional refining systems. Additionally, the study evaluates probable gate-to-gate emissions from an advanced refinery utilizing advanced catalytic hydroconversion technology to transform heavy oil residue and compares these with a conventional refinery using the open-source Petroleum Refinery Life Cycle Inventory Model (PRELIM). In addition, we analyzed the contributions of oil and hydrogen production to emissions. A comparative cost analysis

was carried out to determine the benefits of emissions reduction and the associated costs. This work represents an initial effort to quantify climate impacts at the gate-to-gate level of a refinery utilizing integrated hydrogen addition technology for residue conversion.

The novelty of this review lies in its integrated, system-oriented perspective that links catalyst design and hydroconversion performance with refinery-level sustainability and illustrative economic implications. Building on prior PRELIM-based studies that establish crude quality and refinery configuration as the dominant drivers of emissions [12,13], and on techno-economic analyses that typically evaluate mitigation options in isolation [14,15], we use PRELIM and scenario-based economic tools comparatively to contextualize catalytic and process innovations within refinery-relevant deep-conversion pathways. In doing so, the review highlights hydroconversion as a distinct alternative to coking, particularly when coupled with low-carbon hydrogen and carbon capture, and situates these strategies within global refining and boundary-aware sustainability considerations [16,17]. Consequently, this review summarizes developments in catalytic methods for upgrading waste-derived feedstocks and heavy oil residues from a problem-oriented viewpoint, focusing on transferable principles that connect catalyst design, process performance, and refinery-level sustainability outcomes. In order to connect molecular-scale catalytic insights with process integration and life cycle considerations, a systematic methodological framework is used. This framework directs the conversation toward identifying important research gaps and avenues for the advancement of low-carbon and circular refining systems.

2. Methodological Framework and Scope of the Review

In order to synthesize recent developments in catalytic processing of complex, carbon-rich feedstocks—specifically, heavy oil residues, waste plastics, end-of-life tires, and biomass—within the framework of catalysis advancement and sustainability, this review employs a problem-driven and system-oriented methodology.

Catalyst synthesis, catalysis, process and feedstock chemistry, and system-level sustainability evaluations are all included in the reviewed literature. Priority was granted to studies that carry out the following:

- Discuss hydrogen addition processes;
- Present novel catalyst design and synthesis techniques applicable to heavy, heteroatom-rich, or waste-derived feedstocks;
- Offer information on product yields, emissions, depth of conversion, coke suppression, and scalability.

The review mainly covers emerging catalytic systems, including dispersed slurry-phase nanocatalysts, multifunctional and waste-derived catalytic formulations, and hybrid systems. Feedstocks are categorized based on their origin, ranging from oil-derived heavy residual feeds to polymer- and biomass-derived materials, thus combining feedstocks that are often treated separately in the literature within a single review.

Three interconnected levels are used to synthesize the evaluated studies (Figure 1):

- Catalyst level, which links reaction efficiency to catalyst synthesis technique, composition, structure, and functionality for a particular category of feed;
- Process level: assessing catalytic performance, product slates, operational and feed co-processing flexibility, and scalability;
- The sustainability and economic perspectives evaluate the effects of catalyst and process innovations on the environment and cost.

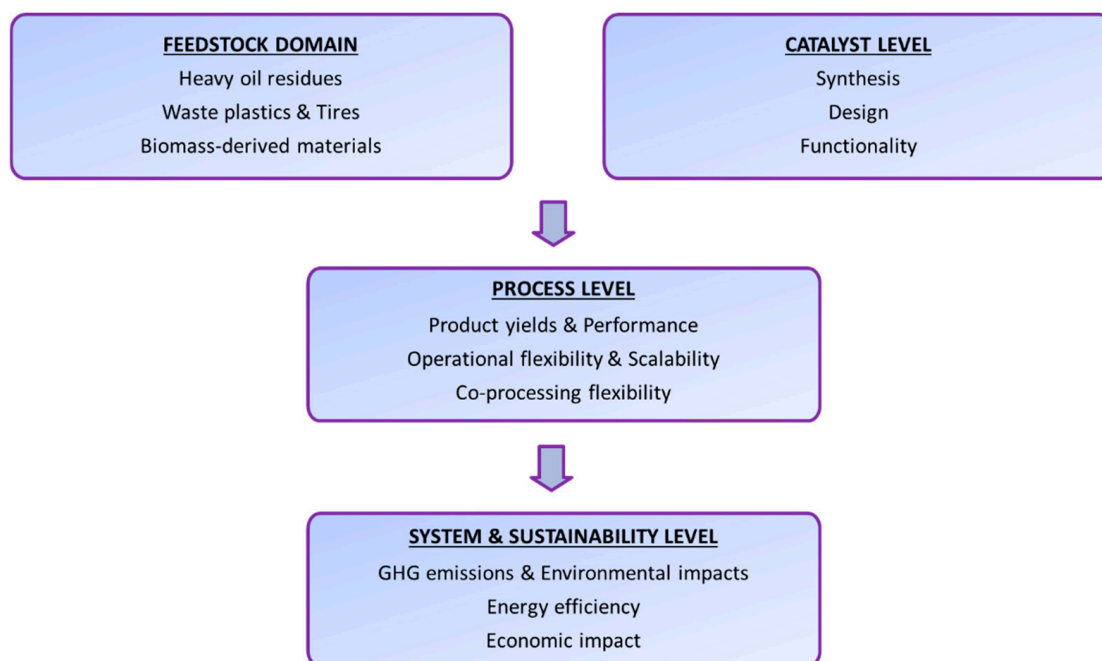


Figure 1. Methodological framework of the study.

Life cycle and economic considerations are incorporated as a comparative analytical tool rather than a full cradle-to-grave assessment, allowing consistent evaluation of relative changes in greenhouse gas emissions and operational economics across alternative pathways.

Scalable slurry-phase hydroprocessing using dispersed nanocatalysts, co-processing of macromolecular feeds, and system-level sustainability metrics within refinery-relevant contexts are rarely addressed in existing studies despite substantial research on catalytic upgrading of individual HOF and waste streams. In order to close this gap, this review synthesizes advanced catalysis with process performance and life cycle implications.

3. Feedstock Characteristics and Catalytic Challenges

The transformation of polymer-based, biomass-based, and oil-derived heavy feedstocks into valuable products relies on customized catalytic technologies, each specifically engineered to address the distinct physicochemical characteristics of the feedstocks. This section analyzes three primary categories of feedstocks: heavy oil residues, biomass, and waste polymers, emphasizing their problems and current catalytic processing methods.

3.1. Heavy Oil Feedstocks

Contemporary oil refining generates significant by-products, including atmospheric residue (AR) and vacuum residue (VR), which are the heaviest fractions following petroleum distillation. While global production statistics for AR and VR are not distinctly documented in the literature, the market for vacuum bottom residue in the Middle East and North Africa (MENA)—encompassing VR-derived products such as kerosene, vacuum gas oil (VGO), and bitumen—was valued at USD 25.95 billion in 2024 and is anticipated to reach USD 39.92 billion by 2034 [18]. The market for industrial refinery vacuum distillation units, which process these residues, is estimated at USD 1.2 billion in 2024 and is expected to grow to USD 2.5 billion by 2033, indicating the scale of residue processing and the demand for effective VR conversion technologies [19]. These feedstocks exhibit high viscosity and density (API gravity < 20°), elevated sulfur and nitrogen content (up to 6 wt% sulfur) and metals such as vanadium and nickel, and complex molecular structures (e.g., asphaltenes

and resins); advanced catalytic technologies can effectively manage these components to optimize conversion and minimize coke formation. Conventional catalytic methods for processing HOF include hydroprocessing (hydrocracking and hydrotreating) with bi-functional catalysts (e.g., NiMo/Al₂O₃ or CoMo/zeolite), where hierarchical porosity and metal sulfide phases are key for cracking and saturating macromolecular components and removing heteroatoms (S, N, metals) under high hydrogen pressure (80–270 bar) [20]. Fluid catalytic cracking (FCC) converts residues to gasoline and liquefied petroleum gas (LPG) using zeolites, with recent applications involving co-processing of pyrolysis oils from waste plastics or biomass [21]. Emerging technologies, such as slurry-phase nanocatalysts, in situ hydrogen donors, multifunctional catalytic systems, and plasma-assisted catalysis, are receiving increased attention.

3.2. Waste Tires and Plastics

Annually, about 1.5 billion tires are produced globally; this results in 17 million tons of end-of-life tires. About 3–4 billion are stockpiled worldwide, and that figure is expected to grow [22]. By 2030, this presents an expanding opportunity for innovative valorization technologies, with up to 1200 million end-of-life tires potentially available for sustainable processing [23,24], though the practical availability of that feed varies by region and is limited by transportation economics, regulatory frameworks, and collection infrastructure. The 2024 OECD Global Plastics Outlook [25] reported that global plastic production reached 435 million tons in 2020 and will rise to 736 million tons by 2040 without action. The current and anticipated percentage of recycled plastic in production is only 6%. By 2040 (compared to 2020 levels), mismanaged waste plastics would grow by 47% and leakage to the environment by 50%, endangering ecosystems. Waste tires and plastic can be a versatile and abundant feedstock for more sustainable manufacturing via chemical recycling, involving new catalytic routes to obtain high-value products. Key challenges include feedstock heterogeneity, impurities (such as chlorine), and catalyst fouling due to carbon deposition [21], which can be mitigated by integrated co-processing of polymer feed with HOF providing effective environment for hydrogen-rich conversion [26]. Zeolite-based catalysts, especially those with tailored acidity and pore architecture (e.g., ZSM-5, HY, and SAPO-11), have shown high activity in cracking long-chain hydrocarbons and enhancing product selectivity toward light olefins, aromatics, gasoline-range hydrocarbons [21], and even carbon nanotubes [27]. Catalytic pyrolysis and hydrocracking provide promising pathways for converting these waste streams into fuels, monomers, and other value-added chemicals [28]. Established industrially implemented catalytic processes for waste tire and plastic conversion are (i) catalytic pyrolysis or fast pyrolysis, yielding fuel-range hydrocarbons that can be co-fed together with the current refinery streams of the industrial FCC and hydroprocessing units [29], and (ii) gasification, partial oxidation of tires/plastics with steam/air, that produces syngas for methanol or Fischer–Tropsch fuels [30]. Emerging catalytic technologies such as tandem dehydrogenation and olefin cross metathesis [31] and photocatalytic depolymerization [32] are also promising routes to convert hydrocarbon plastics to value-added olefins and organic acids (e.g., polystyrene to benzoic acid), respectively.

3.3. Biomass-Derived Feedstocks

Biomass feedstocks range across agricultural residues, forestry by-products, and organic wastes with substantial regional variability.

According to recent estimates, as of 2023–2024, agricultural operations produce over 1.0 billion tons per year of agricultural waste worldwide, of which about 80% is organic and primarily lignocellulosic, consisting of crop residues such straw, husks, bagasse, and

stover [33]. Concurrently, the availability of biomass is greatly influenced by the wood-processing and forestry sectors; estimates for 2021–2022 show that forestry residues alone generate over 1.3 billion tons per year of lignocellulosic biomass annually worldwide, whereas the combined production of lignocellulosic biomass from agriculture, forestry, and industrial residues exceeds 180 billion tons per year; however, only about 8.2 billion tons per year are currently utilized for materials, fuels, or energy applications [34]. Land-use competition, food security concerns, seasonal fluctuations, and logistics all limit its availability for catalytic processing. Challenges for chemical processing include oxygen-rich composition, which might result in the formation of unwanted oxygenates during pyrolysis [35] and feedstock variability. Olive pits, wood chips, and food waste require tailored catalysts [21]. Catalytic pathways for processing biomass include (i) hydrodeoxygenation (HDO) that converts biomass-derived pyrolysis oil into hydrocarbons, for example, using NiMo sulfides or ZSM-5 zeolites [35]; (ii) catalytic pyrolysis with, for example, biochar-based catalysts [36]; and (iii) co-processing in FCC of pyrolysis oils from olive pits blended with FCC feedstock [21]. Co-processing biomass with HOF streams is highlighted in [37,38] as an effective route for deoxygenation relative to standalone biomass upgrading.

Table 1 presents trends in catalysis for sustainability in the processing of certain feedstocks, as derived from recent reviews [1,39–41]. Contemporary catalysis trends prioritize green chemistry principles (atom economy, low-toxicity and cost-effective metals such as Fe and Ni over Pd and Pt, and renewable feedstocks), efficiency improvements (reduced activation energies in thermal processes, with a predominance of chemicals generated through catalysis), and waste valorization, redirecting food waste and plastics from landfills. Catalysis emphasizes heterogeneous catalysts (e.g., zeolites, metal oxides) for their recyclability and efficacy under extreme circumstances, in conjunction with biocatalysts for softer processes, thereby minimizing energy consumption, improving selectivity, and valorizing waste. Principal applications encompass cracking, hydrogenation, and depolymerization. Future catalysis will utilize computational tools, biomimicry, and the integration of renewable resources for metal-free, scalable systems. Challenges such as catalyst deactivation (e.g., coking) and scale-up will propel innovation in nanocatalysts and hybrid processes. The objective is to achieve net-zero emissions by 2050, with catalysis facilitating 95% circularity in chemicals. These developments align with the UN Sustainable Development Goals (e.g., 7: Affordable Energy, 12: Responsible Consumption) [2], have the potential to convert linear economies into circular ones, and will benefit from continued research, development, and supportive commercialization policies.

Current trends in catalysis, such as the adoption of green chemistry principles, heterogeneous catalysts, and emerging nanocatalytic systems, are paving the way for sustainable processing of these complex feedstocks. Among these advancements, slurry hydroconversion (hydrocracking) using dispersed nanocatalysts stands out as a promising technology [42–44]. This approach is particularly effective for processing heavy oil residues and vacuum residues, achieving almost total conversion even with feeds containing high metal and asphaltene content. Furthermore, its versatility extends to co-processing with waste tires, plastics, and biomass, enabling the integration of renewable and waste-derived streams into refinery operations, thus enhancing resource circularity and reducing reliance on fossil-based inputs. In the next section, we will examine in more detail this area of catalysis.

Table 1. Current and future trends in catalysis for processing heavy feedstocks [1,39–41].

Feedstock	Current Trends in Catalysis	Emerging/Future Trends in Catalysis
Heavy oil feedstocks (vacuum/atmospheric residues)	– Thermal catalytic cracking and hydroprocessing to upgrade viscous residues into lighter fuels/chemicals, reducing energy intensity and emissions. – Moving up the value chain via syngas routes: gasification of heavy fuel oils followed by catalytic synthesis of light hydrocarbons (e.g., GTL or related routes) as a viable pathway to decarbonize difficult streams. – Use of base metal catalysts (e.g., Ni, Co, Mo on supports like alumina) to replace precious metals, improving cost and toxicity profiles. – Hardening catalysts for harsh feeds: sulfur trapping (e.g., Mn oxides guided by sulfide stability/Ellingham), thermal/steam stability strategies such as La–aluminate-stabilized aluminas, and rare-earth/P-modified FCC zeolites to resist deactivation. – Integration with green engineering for lower-temperature operations, minimizing CO₂ from high-heat processes.	– Nanocatalysts and machine learning (ML) for predictive design, enabling low-temperature upgrading and CO₂ integration. – Focus on residue to chemicals with base metals, targeting zero-waste refineries. – Circular catalyst value chains for residue processing: recover precious/critical metals from spent catalysts/e-waste to manufacture next-gen hydrotreating/FCC catalysts, reducing primary mining impacts. – Electrocatalysis or photocatalysis hybrids to replace thermal processes, reducing energy use.
Polymer waste (plastics, waste tires)	– Shift from mechanical to chemical recycling/upcycling. Catalytic cracking/pyrolysis to fuels. Depolymerization and pyrolysis using zeolites or acid/base catalysts. – Enzyme catalysis for selective degradation under mild conditions, reducing microplastic pollution. – Heterogeneous catalysis (e.g., metal-free or nanocatalysts) for converting waste tires (rubber polymers) into syngas or carbon black. – Process intensification for mixed streams: mixed-plastic catalytic pyrolysis is progressing as a feedstock recycling route; quality upgrades (higher H/C, more diesel-range distillate) are reported when appropriate catalysts are used.	– Designing recyclable/earth-abundant catalysts (and reclaiming metals from waste streams) to make chemical recycling scalable and circular. – Metal-free catalysis to avoid toxicity, with computational design for selectivity. – Bio-inspired catalysts (e.g., enzyme mimics) for ambient-temperature depolymerization, scaling to industrial recycling. – Integration with renewable energy (e.g., solar-driven pyrolysis) for plastic to fuel, addressing 12% of global waste plastics.

Table 1. Cont.

Feedstock	Current Trends in Catalysis	Emerging/Future Trends in Catalysis
Biomass	- Thermochemical conversion at scale via catalytic fast pyrolysis (CFP) and hydrothermal liquefaction (HTL). Heterogeneous catalysis (e.g., zeolites, metal oxides) for biofuel production via HDO or fast pyrolysis, co-producing chemicals. - Bio-inspired/enzyme catalysts for selective conversion of lignocellulose to platform chemicals (e.g., succinic acid, bioethanol). - Integration with waste streams for circularity, reducing fossil dependency.	Computational catalysis (e.g., AI for ligand design) for selective deoxygenation, producing drop-in biofuels at scale.
		Multifunctional/bifunctional solids for cascades: new heterogeneous catalysts that work in polar media <300 °C and couple acid–base–metal functions to control chain growth/condensation before final HDO.
		Hybrid bio/heterogeneous systems with renewables, targeting 10% sustainable aviation fuel (SAF) by 2030.
		Circular integration: co-processing with plastics residues for diversified products.

Current trends in catalysis, such as the adoption of green chemistry principles, heterogeneous catalysts, and emerging nanocatalytic systems, are paving the way for sustainable processing of these complex feedstocks. As summarized in Table 1, among these advancements, HOF hydroprocessing and nanocatalysts, for example, hydroconversion (slurry-phase hydrocracking) using dispersed nanocatalysts [42–44], stand out as promising technologies. This approach is particularly effective for processing heavy oil residues and vacuum residues, achieving almost total conversion even with feeds containing high metal and asphaltene content. Furthermore, its versatility extends to co-processing with waste tires, plastics, and biomass, enabling the integration of renewable and waste-derived streams into refinery operations, thus enhancing resource circularity and reducing reliance on fossil-based inputs. In the next section, we will examine in more detail this area of catalysis.

4. Evolution of Catalysts for Heavy Oil Feedstock Conversion

4.1. Conventional Catalysts

At present, diverse carbon-rich feedstocks—including refinery residues, waste tires, plastics, and biomass—represent both a growing opportunity and a technical frontier. Advancing catalytic technologies pursue the efficient conversion of these complex materials into lighter and higher-value products while addressing their inherent processing challenges. Technologies for HOF conversion have historically relied on two main parallel pathways: (i) carbon-rejection methods, which rely on C–C bond cleavage (e.g., thermal and catalytic cracking, visbreaking, delayed coking), and (ii) hydrogen addition processes, which involve C–H bond formation (e.g., hydrocracking, hydroconversion).

Fundamental objectives of HOF conversion are as follows [45]:

- Transforming heavy, low-value fractions into lighter, more valuable liquid products such as gasoline, diesel, and petrochemical feedstocks;
- H/C ratio enhancement: increasing the H/C ratio of the hydrocarbon molecules, which improves the fuel’s energy density and reduces the specific CO₂ emissions per unit of energy produced upon combustion;
- Coke inhibition: reducing the formation of carbonaceous deposits (coke), which can rapidly deactivate catalysts and foul reactor systems;

- Viscosity reduction: lowering the inherent high viscosity to facilitate easier flow, transportation, and subsequent processing;
- Impurity removal: efficiently eliminating heteroatoms (sulfur, nitrogen, oxygen) and heavy metals to produce cleaner fuels and reduce environmental hazards like air pollution and acid rain.

Generally, thermal cracking methods like visbreaking were applied to HOF to reduce its viscosity. While these methods offer simplicity, they lack selectivity and quality of products, yielding low-quality products and limited carbon utilization. In contrast, catalytic processes, such as FCC and various hydroprocessing technologies (hydrocracking, hydroconversion, and hydrotreating), represent a more advanced and efficient approach. By lowering activation barriers for targeted reactions, catalytic processes frequently enable improved product selectivity, producing larger volumes of distillate fractions and fewer undesirable by-products (like coke and fuel gas) in comparison to purely thermal pathways, as shown in hydroprocessing and catalytic pyrolysis systems. Thus, the dual pressures for sustainable energy solutions and improved resource efficiency are encouraging broader application of hydrogen addition processes alongside carbon-rejection technologies, which generate low-value carbonaceous products and more waste [44,46,47].

Decades of progress in the petrochemical industry have produced numerous solid-supported (heterogeneous) catalysts (e.g., Mo/Al₂O₃, NiMo/Al₂O₃, CoMo/zeolite) that selectively facilitate bond-breaking and bond-forming reactions in basic refining technologies. These catalysts, typically consisting of an active component (metal sulphide) dispersed on a high-surface-area support, enable the shrinking, growth, and rearrangement of carbon atoms in conventional refinery feed. Conventional heterogeneous catalysts can be further optimized for HOF applications, particularly given the rich composition of HOF in asphaltenes, metals, sulfur, and nitrogen, as well as its inherent high viscosity and density. Managing catalyst deactivation due to pore blockage (Figure 2) is an important consideration in processing HOF with solid-supported (heterogeneous) catalysts, often necessitating costly regeneration or operation under extreme hydrogen pressures (~200 atm) in hydrogen addition processes, both of which significantly influence process economics [48].

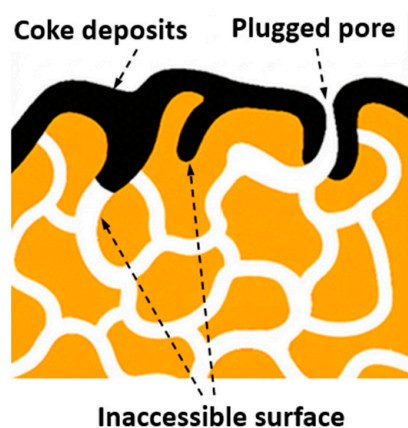


Figure 2. Scheme of pore blockage leading to deactivation of conventional catalyst during HOF processing.

4.2. The Shift to Dispersed Nanocatalysts

A paradigm shift in HOF processing has emerged with the development of unsupported (dispersed) nanocatalysts. These systems aim to maximize active site accessibility and mitigate diffusion limitations present in traditional supported systems, and they usually have the following characteristics:

- Composition: the active ingredients are sulfides of Mo, W, Ni, Co, and Fe. While Ni and Co are frequently utilized as promoters to increase hydrogenation and hydrotreating activities, sulfides of Mo and W are more frequently used as primary catalysts.
- Structure: metal sulfide particles that are nanoscale or ultra-sized, generated in situ or ex situ, and dispersed throughout the reaction mixture (Figure 3).
- Performance: superior activity, selectivity, and resistance to deactivation at low catalyst dosages (~0.05 wt%) and recyclability [42,43].

The HOF hydroprocessing technologies that are further addressed are shown in Table 2, which covers traditional supported catalysts, dispersed catalytic systems, and other advanced systems, emphasizing variations in feedstock flexibility, conversion efficiency, and operational problems in order to clearly separate the performance metrics of these technologies.

■ Mechanism of catalysis by dispersed nanocatalyst particles

Molybdenum disulfide (MoS_2) is the most studied and offered as a catalyst in this technology by commercial licensors [42,43] (Table 2). Dispersed nano- MoS_2 is used for HOF conversion in slurry-bed reactors, where the catalyst's dispersed nature effectively overcomes the diffusion limitations commonly encountered in traditional fixed-bed/ebullated bed reactor systems. The active phase of MoS_2 , predominantly the 2H phase, features a layered structure with distinct active sites as catalytic centers—the rim and edge positions on the MoS_2 layers, with rim sites demonstrating activity in both hydrogenation and HDS reactions, while edge sites are primarily involved in hydrogenation (Figure 3). The basal plane, in contrast, is generally considered unreactive [49,50].

Table 2. Overview of catalysts and processes for conversion of heavy oil feedstocks.

Type of Catalyst	Composition of Catalyst	Catalyst Synthesis Method	Process Parameters	Process Efficiency	Catalyst Advantages	Challenges
Supported hydroprocessing catalysts (e.g., $\text{NiMo}/\text{Al}_2\text{O}_3$, $\text{CoMo}/\text{Al}_2\text{O}_3$) [51]	Transition metal sulfides (Mo, W, Ni, Co), acidic carriers (alumina, silica, silica-alumina, zeolite, modified clays)	Oxide precursor synthesis, sulfidation, doping	Fixed-, moving-, ebullated, slurry-bed reactors. Pre-HDS, HDN, hydrodemetallization (HDM), hydrodeasphaltization (HAD) required. High H_2 pressure required (up to 20 MPa)	Conversion to lighter, more valuable products. High sulfur removal (viscosity reduction)	Versatile for HDS/HDN/HDM. Commercially available globally	Catalyst deactivation, operational limitations (overheating, pressure drop, mass transfer), limited catalyst life/performance
Unsupported (dispersed) Mo sulfide nanoparticles [43,49,50,52,53]	MoS_2 , nanosized particles, nanoslabs, rim/edge active sites, structure diversity depending on synthesis parameters	In situ (thermal decomposition, sulfidation) from precursors (oil-, water-soluble Mo salts) directly in HOF conversion reactor. In situ sulfidation by H_2S from feed	Hydroconversion: $P = 7 \text{ MPa}$, $T = 425\text{--}445^\circ\text{C}$, $\text{H}_2/\text{feed} = 1000\text{--}1500 \text{ nL/L}$, $\text{LHSV}^* = 0.4\text{--}1.5 \text{ h}^{-1}$, recycle mode. Slurry-phase hydrocracking: $T = 400\text{--}450^\circ\text{C}$, $P(\text{H}_2) = 15 \text{ MPa}$, recycle mode, purge 1–3 wt%	VR conversion per cycle—up to 70–93% wt; coke yield < 0.1% wt, high HDS, HDN, HDM activity (HDN > 90%)	High activity, effective hydrogenation, strong resistance to deactivation, coking inhibition, no diffusion limitation. Low catalyst dosage (~0.05 wt% Mo). Scavenging H_2S from feed. Recyclability	In situ synthesis leads to low control over catalyst morphology/particle size, additional units for emulsification/regeneration, catalyst recovery/reuse required
Dual-catalyst system: dispersed nano- MoS_2 plus cracking catalyst [43]	MoS_2 + cracking catalyst (H-Y zeolite/ $\text{SiO}_2\text{--Al}_2\text{O}_3$)	MoS_2 generated in situ from oil-soluble precursor; cracking catalyst added batch-wise (30–40 wt% of reactor hold-up)	$T = 430^\circ\text{C}$, $P(\text{H}_2) = 13 \text{ MPa}$, continuous catalyst replacement/regeneration	50% higher productivity vs. MoS_2 , low coke yield (<0.1% wt), stable activity over 200 h, sustained cracking activity, high HDN/HDS	Combines cracking and hydrogenation function, extends catalyst life, improves nitrogen removal	Rapid deactivation of cracking catalyst without MoS_2 , regeneration required
Dispersed Mo sulfide nanoparticles [54]	MoS_2	In situ from new oil-soluble precursor (cetyltrimethyl ammonium heptamolybdate)	$T = 410^\circ\text{C}$, $P(\text{H}_2) = 10 \text{ MPa}$, 1 h, Mo dosage = 2000 $\mu\text{g/g}$	Liquid yield: 96.4 wt%, coke: 0.19 wt%, gas: 3.4 wt%, HDM: 83.4 wt%, HDS: 59.2 wt%	High solubility in oil, small MoS_2 particles, high activity, low dosage	Complex synthesis, potential agglomeration, high H_2 pressure requirement for optimal performance

Table 2. Cont.

Type of Catalyst	Composition of Catalyst	Catalyst Synthesis Method	Process Parameters	Process Efficiency	Catalyst Advantages	Challenges
Dispersed Mo sulfide nanoparticles [55]	MoS ₂	In situ from trialkyl-methylammonium molybdate ILs	T = 430 °C, P(H ₂) = 12 MPa, 0.5–6.0 h, catalyst dosage = 600–1200 ppm	High performance: higher feed conversion (71.0 vs. 65.2 wt% for Mo-octoate), low coke yield (0.8 vs. 1.3 wt%)	Activity, compatibility with HOF, viable synthesis	Cost competitiveness vs. commercial precursors, optimization of alkyl chain length, scalability of synthesis
Dispersed Mo sulfide nanoparticles [56]	MoS ₂	In situ from oil-soluble Mo aryl-alkyl-dithiophosphates (Mo-Ar/Rs), Ar = benzyl, R = n-butyl	T = 430 °C, P(H ₂) = 70 atm, 1 h, 150 ppm Mo	Higher valuable product yields, lower coke and gas yields compared to Mo-R	Better oil solubility, lower MoS ₂ particle size, higher hydrogenation activity, improved selectivity	Performance varies with feedstock saturate content, precursor synthesis complexity
Dispersed Ni-Mo/V-Mo sulfide nanoparticles [57,58]	Ni ₃ S ₂ -MoS ₂ , V ₃ S ₄ -MoS ₂	In situ, sulfidation of oil-soluble precursors (Mo-naphthenate, Ni-octoate, V-acetylacetonate)	T = 450 °C, P(H ₂) = 16 MPa, 1 h, 300–600 ppm Mo, Ni(V)/(Ni(V) + Mo) = 0.2–0.4	Ni-Mo synergy: 72.1% conversion (vs. 64% for Mo). V-Mo additive effect: 69.6% conversion. Coke suppression: <0.2 wt%	Ni-Mo: reverse synergy (MoS ₂ on Ni ₃ S ₂). V-Mo: high HDS activity	Ni-Mo: limited H ₂ transfer in batch reactor. Ni-only: poor activity, high coke
Dispersed Co/Ni-TBC [6,59]	Co- or Ni-based calixarene	Coordination of metal nitrates with TBC [6] ligand	T = 420 °C, P(H ₂) = 8.5 MPa H ₂ , 1 h, 500 ppm catalyst	Naphtha yield: 12 wt.% (Co-TBC [6]), VGO conversion: 42.4% (with supported catalyst), negligible coke	Activity, coke suppression	Precursor cost, catalyst recovery difficulties
Dispersed Fe-Ni-S nanoparticles [60]	Fe _{4.5} Ni _{4.5} S ₈ mixed crystal sulfides	In situ, synthesis from oil-soluble Fe, Ni precursors	T = 440 °C, 1 h, P(H ₂) = 8 MPa, catalyst dosage = 500–1000 µg/g, sulfur powder added **	Lignite conversion: 97.1 wt%, liquid yield: 92.2 wt%, coke yield: 1.3 wt% (at 1000 µg/g catalyst dosage)	High activity, narrow particle size distribution, cost-effective renewable ligand for precursor synthesis	Control over bimetallic phase formation, scalability of precursor synthesis
MoS ₂ nanoparticles [61]	MoS ₂	Ex situ: precipitation from solution with ammonium molybdate and thioacetamide	1000 ppm Mo, P(H ₂) = 65 bar, T = 400 °C, 4 h, 1000 rpm	Liquid yield (70% selectivity), deep desulfurization, low aromaticity, high ring opening/depolymerization, high isomerization	High efficiency, mild hydroprocessing conditions, low-cost synthesis, no dependency on feed-derived H ₂ S for sulfidation	Effective distribution in feed, recyclability, scalability
Mo-containing composite nanocatalyst [62]	MoO ₂ , MoS ₂ , stabilized by low-density polyethylene (LDPE); 22.7 wt% Mo	Ex situ: from (NH ₄) ₆ Mo ₇ O ₂₄ in vacuum oil-LDPE medium, sulfided by dimethyl disulfide at 350 °C under argon	T = 445 °C, P(H ₂) = 70 atm, H ₂ /feed = 1000 nL/L, LHSV = 2.0 h ^{−1} , 0.05 wt% Mo	Feed conversion—50.4–51.8 wt, coke yield—0.2–0.5 wt	High stability, Mo content (22 wt%), low coke yield	Incomplete sulfidation, dispersing method is critical, complex synthesis, requires synthesis/regeneration units
Dispersed MoS ₂ nano-, ultrafine catalyst stabilized in vacuum residue [63]	MoS ₂ , stabilized in vacuum residue, 6–10 wt% Mo	Ex situ: from (NH ₄) ₆ Mo ₇ O ₂₄ and elemental sulfur/thiocarbamide in VR, thermal treatment at 350 °C under H ₂	T = 425 °C, P(H ₂) = 70 atm, H ₂ /feed = 1500 nL/L, LHSV = 0.4–1.4 h ^{−1} , 0.05 wt% Mo	Feed conversion—28.0–70.0 wt%, coke yield—0.1–3.4 wt%	High activity, costly precursor, high Mo content (6–10 wt%), no solid carrier, no in situ sulfidation needed, high activity; tunable morphology	Moderate synthesis complexity, polydispersity, requires synthesis/regeneration units
NiFe nanocatalysts [64]	NiFe (1:0.33, 1:1, 1:3)	Modified inverse microemulsion method	T = 372 °C, P(H ₂) = 9.8 MPa, 1 h	API increase from 13.1 to 18.3. Asphaltene conversion: 37.2–43.7%. Sulfur removal: 6.0 to 3.9 wt%. Nitrogen removal: 4687 to 2999 ppm. Viscosity reduced from 9691 to 798 cP	High activity at low loading, mild reaction conditions, abundant, low-cost metals (Ni/Fe), compatibility with feedstock, low particle sizes	Potential deactivation due to sulfur, requires surfactants, complex synthesis, scalability, regeneration

Table 2. Cont.

Type of Catalyst	Composition of Catalyst	Catalyst Synthesis Method	Process Parameters	Process Efficiency	Catalyst Advantages	Challenges
Ni nanoparticles dispersed on biochar [65]	Ni nanoparticles on biochar	Ex situ, impregnation of coffee grounds with $\text{Ni}(\text{NO}_3)_2$, calcination in H_2 atmosphere at 550°C for 2 h	$T = 180^\circ\text{C}$, 8 h, N_2 atmosphere; oil shale pyrolysis: $35\text{--}900^\circ\text{C}$	60.35% viscosity reduction, increased light fractions ($\text{C}_2\text{--C}_4$, saturates), reduced S/N heteroatoms, lowered pyrolysis onset T by 10°C and peak decomposition T by 8°C	Low cost, high dispersibility of Ni, sustainable (waste-derived biochar), mesoporous structure	Potential deactivation, scalability of synthesis, residual oil on catalyst post-reaction
Disposable red mud catalyst [66]	Mainly Fe_2O_3 , Al_2O_3 , TiO_2 , with SiO_2 , CaO , Na_2O	Calcined at 550°C for 2 h; in situ activation into pyrrhotite ($\text{Fe}_{(x-1)}\text{S}_x$)	$T = 470\text{--}500^\circ\text{C}$, $\text{P}(\text{H}_2) = 150$ bar, 1.2–3.0 g of red mud (4–10 wt.%), 2–4 h	VR conversion: 64–66 wt.%; coke yield reduced (1.13–2.40 wt.%); increased VGO yield; less gas and coke compared to thermal cracking	Low-cost waste-derived catalyst, coke suppression, improved selectivity, no need for sulfidation	Lower conversion than thermal cracking; limited control over selectivity; catalyst deactivation at high T; not reusable (disposable)
Dispersed magnetic nanohybrids [67,68]	Nano- Fe_3O_4 , Fe_3O_4 -MWCNT, Fe_3O_4 -NiO nanohybrids	Ex situ, co-precipitation from Fe chlorides, commercial hydroxy-MWCNT	Microwave-assisted catalytic upgrading: catalyst—0.01–1.0 wt.%, microwave power—400–1200 W, duration—8–12 min	Viscosity reduction (~12%), API increase (5.6%), sulfur reduction (16.6%)	Ease of catalyst recovery due to magnetic nature, low residence time, high efficiency	Ensuring uniform heating, high catalyst concentration and costs of catalyst regeneration, scalability

* LHSV: liquid hourly space velocity; ** feed: mixture of Anhui lignite coal and Merry atmospheric residue (4:6 by weight).

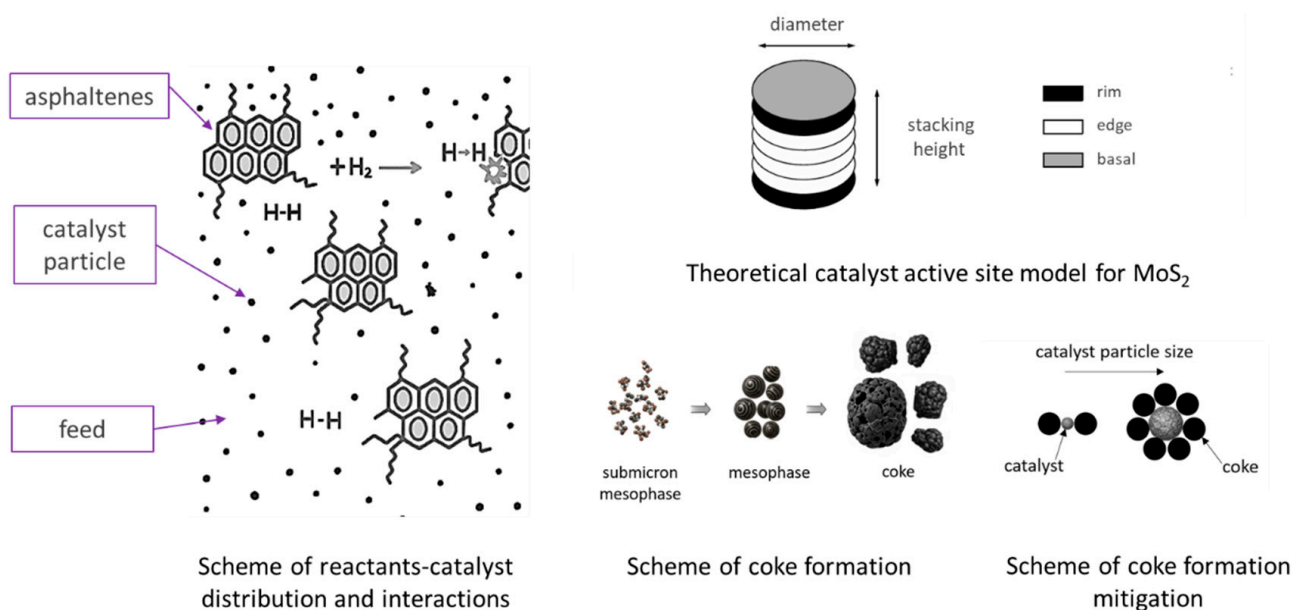


Figure 3. Mechanism of catalysis by dispersed nanocatalyst particles during hydroconversion.

The synthesis of these dispersed nano- MoS_2 catalysts typically occurs in situ within a hydroconversion (slurry-phase hydrocracking) reactor. This process involves introducing a molybdenum precursor, such as oil-soluble molybdenum naphthenate or reverse emulsions of ammonium molybdate, directly into the feeds. Under the elevated temperatures and reducing conditions within the reactor, these precursors undergo thermal decomposition and sulfidation. The sulfiding agent, hydrogen sulfide (H_2S), is often conveniently generated from the sulfur compounds naturally present in the heavy oil feedstock itself. This in situ formation yields nanosized MoS_2 particles. For other metals, precursor conditions required for active catalyst phase formation may differ. Figure 4 shows differences between process schemes with oil- and water-soluble precursors. In the case of in situ-generated nano- MoS_2 particles derived from both oil- and water-soluble precursors, the residual heavy fraction

that contains all of the catalyst that is still active is recycled back to the reactor (Figure 4a,b). To avoid the metal (V, Ni, etc.) buildup in the system, a small part of the residue is purged (1 to 3 wt%). With the purge stream, a limited amount of dispersed nano-MoS₂ is also removed. The purge can be further treated to recover Mo [69].

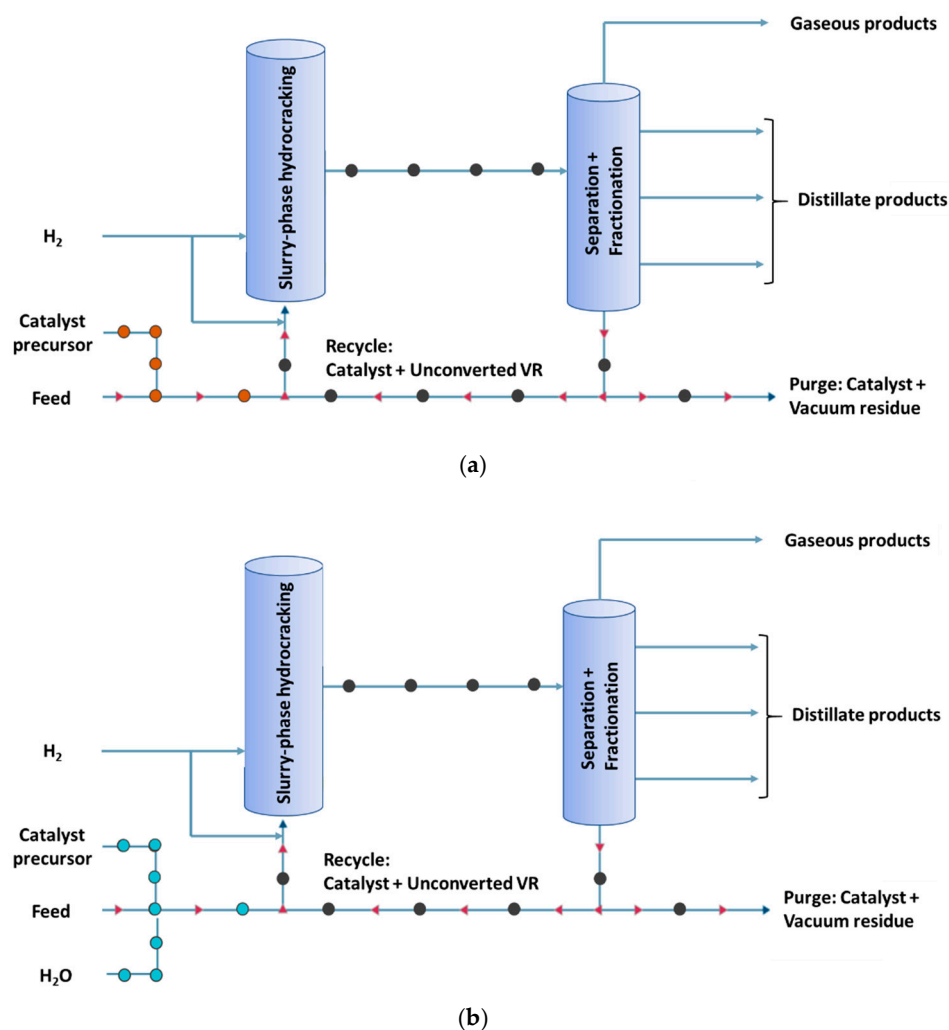


Figure 4. Simplified process scheme for heavy residue slurry-phase hydrocracking and hydro-conversion technology. Catalyst—dispersed nano-MoS₂, formed in situ from oil-soluble (a) and water-soluble precursor (b). Brown (a) and blue (b) circles indicate oil-soluble and water-soluble catalyst precursors, respectively; dark gray circles represent dispersed catalyst particles, and red triangles show the direction of residue flow.

The catalysis mechanism in the case of dispersed nanocatalysts includes generating hydrogen radicals (H^{*}s) from H₂ dissociation on active sites of dispersed metal sulfide nanoparticles. The fundamental reactions include the scission of carbon–carbon (C–C), carbon–sulfur (C–S), and carbon–nitrogen (C–N) bonds within the heavy, high-molecular-weight oil components, followed by the crucial hydrogenation of the resulting radical fragments. This dual functionality is critical not only for upgrading the oil but also for suppressing undesirable polycondensation and polymerization reactions that lead to coke formation.

Coke originates mainly from asphaltene aromatic core polycondensation after alkyl side-chain cleavage [48]. Coke formation, a major catalyst deactivation pathway, is mitigated through hydrogenation and radical scavenging, meaning hydrogen radicals from nanocatalysts saturate aromatic cores in asphaltenes, reducing polycondensation into coke.

The small particle size ensures close contact with large asphaltene molecules, minimizing diffusion limitations and increasing exposure of high-activity sites. Submicron- or micron-sized catalyst particles inhibit coke growth by physically interfering with asphaltene agglomeration. Larger particles, however, act as nucleation sites for coke deposition (Figure 3). A balance of hydrogenation and mild cracking activity is essential to maximize liquid yield while suppressing coke formation [42,48,49]. Typical operating conditions for these processes are severe, often involving temperatures ranging from 410 °C to 450 °C and high hydrogen pressures such as 6.0 to 20 MPa. The primary feedstocks are vacuum residue (VR) and various heavy crude oils characterized by high sulfur content and other impurities [43,70,71].

- Dispersed nanocatalysts from oil-soluble precursors

The most developed and consistently effective approach for deep bottom-of-the-barrel conversion of vacuum residue, according to the reviewed literature, is the use of dispersed MoS₂ nanocatalysts produced in situ from oil-soluble precursors. Independent studies consistently indicate that nano-MoS₂, acting as a hydrogenation and radical-stabilization catalyst, suppresses asphaltene polycondensation, transforms contaminating metals (Ni/V) into sulfides, and allows for remarkably low coke yields (<0.1%) under severe conditions [43,72,73].

At the performance level, MoS₂-based slurry systems exhibit a clear and reproducible advantage. Figure 4a presents a general scheme of process using oil-soluble precursor to generate nano-MoS₂ in situ. This catalyst is fully recyclable [43,72]. Under severe operating conditions (425–435 °C, 15–16 MPa), coke outputs are below 0.1%, and reported HOF conversions exceed 97%. When MoS₂ is mixed with supported cracking catalysts, this performance is further improved. The synergistic effects increase hydrodenitrogenation (HDN) (>90%) and reduce deactivation by metal deposition, hence prolonging the lifespan of supported catalysts [43]. In comparative studies, nano-MoS₂ and NiMo sulfide systems repeatedly emerge as benchmark catalysts, outperforming single-metal sulfides (Ni, Fe, W, V) and most bimetallic formulations (e.g., Ni-Mo, Co-Mo, Fe-Mo) in terms of activity and resistance to poisoning [57,58,66,74,75].

Commercial-scale validation of a nano-MoS₂-based process demonstrates technical feasibility and scalability under industrial conditions [72], yet other assessments emphasize unresolved challenges associated with catalyst formation control. Oil-soluble precursors—such as Mo-, Ni-, and Co-naphthenates, octoates, dithiocarbamates, and dithiophosphates—are favored due to their simpler loading procedure (direct mixing with HOF) compared to water-soluble precursors. This ensures uniform catalyst distribution and in situ activation. However, their increased expense and the knowledge gaps regarding in situ precursor-to-metal sulfide transformation remain major barriers to large-scale deployment [50,51].

- Dispersed nanocatalysts from water-soluble precursors

Water-soluble precursors (e.g., ammonium heptamolybdate, thiomolybdates, phosphomolybdic acid) are relatively inexpensive, but they necessitate forming well-dispersed and stable aqueous emulsions in HOF [74]. Therefore, their practical application depends on reverse emulsion stability, which involves dispersing an aqueous precursor solution in a continuous phase of hydrocarbons (Figure 5). Upon heating, water evaporates, facilitating precursor decomposition, yielding the catalytically active solid phase. When applied to slurry-phase hydroprocessing, this approach enables in situ generation of dispersed nano-MoS₂ via emulsification of ammonium heptamolybdate followed by decomposition and sulfiding under reaction conditions (Figure 4b).

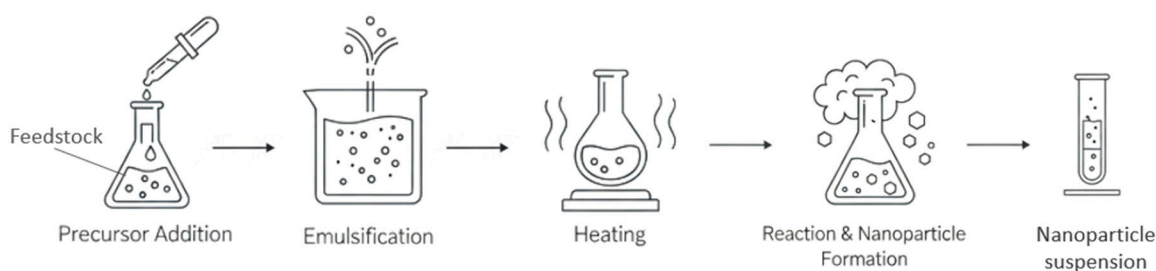


Figure 5. Scheme of nanocatalyst preparation from water-soluble precursor via reverse emulsion method.

The structure and morphology of nano-MoS₂ prepared in this manner may vary depending on the synthesis medium (feedstock), conditions, and sample preparation technique, from randomly distributed nanoslabs with 0.6–0.7 nm thickness and up to 50 nm length (Figure 6a) to spherical and rounded particles of 10–50 nm in diameter (Figure 6b) [42].

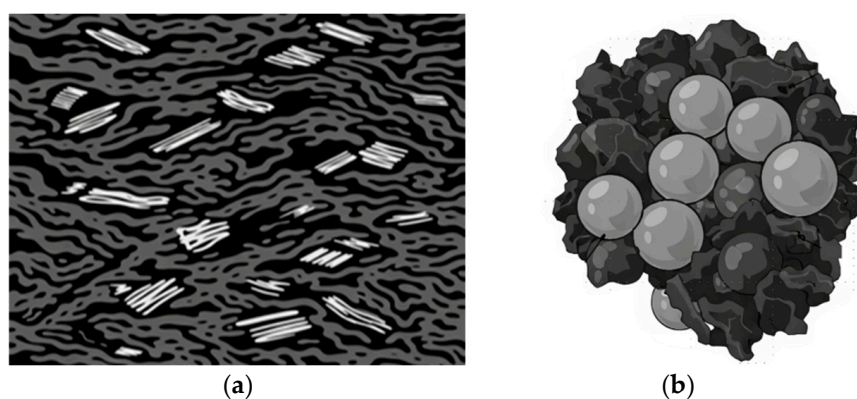


Figure 6. Visual models of MoS₂ particles (light gray, (a,b)) identified in hydroconversion products. The MoS₂ particles were synthesized in situ within the hydroconversion reactor.

From a performance standpoint, MoS₂ generated in situ in this manner demonstrates hydroconversion efficiencies that are competitive with or superior to established industrial benchmarks (76–93 wt% in recycle regime), while operating at significantly lower hydrogen pressures (~7 MPa versus 15–16 MPa for [43,72]) and low catalyst dosage (~0.05 wt%), suppressing coke to < 0.1 wt%, and leveraging feedstock sulfur for catalyst sulfiding [76,77]. In situ sulfiding simplifies catalyst activation. In addition, the catalyst stays active during the continuous operation and can be recycled with unconverted residue [76,77], as demonstrated in Figure 4a,b, while only a small part of it (1–3%) is unloaded as purge to avoid accumulating heavy metals introduced with HOF. The purge stream includes recycled residue and catalyst that can be regenerated and returned to the process as initial precursor [69]. All together, these attributes position water-soluble precursors as not merely economical alternatives to nano-MoS₂ derived from oil-soluble precursors but as enablers of lower-severity process windows. Beyond base activity, this in situ approach offers compositional flexibility not readily achievable with oil-soluble systems; water-soluble systems combine lower raw material costs with simpler regeneration, and recycling pathways via aqueous handling also offer compositional flexibility. Doping with Fe, Ni, Co, or Al allows the formation of polyfunctional dispersants with a specific structure (e.g., core-shell MoS₂/Al₂O₃) and enhanced performance under research conditions [78]. Such adaptability strengthens the case for water-soluble precursors in tailored catalyst design, although the added complexity of emulsion control remains a practical limitation.

Water-soluble systems combine cheaper raw materials with easier regeneration and recycling processes through aqueous handling when compared to oil-soluble precursors [69], making them especially appealing for applications involving slurry-phase hydrocracking that are cost-sensitive. A thorough comparison of the two precursor classes is provided in [79].

Taken together, recent studies indicate that dispersed nanocatalysts consistently deliver HOF conversion levels from 60% to 97%, with coke yields typically below 1 wt% and often below 0.1 wt%. Hydrogen consumption generally ranges between 1.5 and 2.5 wt% depending on feedstock quality, significantly improving liquid product yields compared to thermal upgrading.

From an industrial perspective, scalability of HOF hydroprocessing in the presence of dispersed nano-MoS₂ derived in situ from water-soluble precursors is evidenced by commercial licensors offering technologies [80]. While capital costs for such units are higher than thermal processes (e.g., pyrolysis, delayed coking, etc.), our analysis in Section 6 suggests their viability.

5. Advances in Catalysis by Dispersed Nanoparticles for HOF Processing

Recent innovations in dispersed nanocatalysts for HOF upgrading focus on three main directions:

- Enhancing catalytic performance through compositional modifications, tailored precursor design, and shifting from in situ generation toward ex situ-prepared, ready-to-use catalysts;
- Reducing costs and improving sustainability by partially or fully replacing expensive transition metals (e.g., Mo) with earth-abundant metals, waste-derived components, or renewable materials;
- Expanding feedstock flexibility by co-processing HOF with other macromolecular materials such as waste plastics, tires, and biomass.

These strategies collectively aim not only to improve efficiency but also to align catalytic upgrading with circular economy principles.

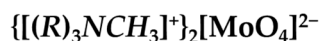
5.1. Novel Precursors and Synthesis Methods

A unifying understanding across recent developments in oil-soluble precursor chemistry is that molecular-level control over precursor solubility, breakdown, and in situ sulfide nanostructure formation governs catalytic efficiency in slurry-phase HOF hydrocracking more so than metal identity alone. While there are clear limitations, like synthesis complexity, hydrogen demand, and scalability, rational precursor design consistently results in smaller MoS₂ slabs, lower stacking, increased feedstock compatibility, and suppressed coke formation across a variety of systems.

Early demonstrations with a new oil-soluble precursor—cetyltrimethyl ammonium heptamolybdate (CTATTM)—illustrate that improved performance is achieved through tailored surfactant–metal assemblies, which generated well-dispersed MoS₂ nanoparticles, delivering high liquid yields and minimal coke in HOF hydrocracking [54]. Compared with conventional molybdenum salts, CTATTM generates ultra-thin (1–2 layer), short MoS₂ slabs in situ, delivering near-complete asphaltene conversion, low coke yields (<0.2 wt%), and high liquid recovery (96.43 wt%) at relatively mild temperatures ($T = 410\text{ }^{\circ}\text{C}$, $P(\text{H}_2) = 10\text{ MPa}$, catalyst dosage $2000\text{ }\mu\text{g/g}$). While the results are encouraging, reliance on high H₂ pressure and structurally elaborate quaternary ammonium precursors underscores the need for further optimization.

This approach is further improved by ionic liquid (IL)-based molybdate precursors, which integrate metal delivery with improved asphaltene solvation [81]. Trialkylmethylam-

monium molybdates with the composition illustrated in Figure 7 consistently outperform the reference oil-soluble Mo precursor (Mo-octoate), producing in situ-generated dispersed MoS₂ slabs with reduced lateral dimensions and stacking (Table 3), which correlates with higher HOF conversion and lower coke yields [55] (Table 2). Notably, the trihexylmethylammonium system achieves superior hydrogenation–cracking balance relative to Mo-octoate, underscoring that organic cation design can modulate active-site accessibility. With IL-based precursors, the synthesis method and catalytic procedure are more complicated than with CTATM. They may be suitable for more diverse refinery streams, nevertheless, as they provide better tunability and wider feedstock compatibility.



R = butyl (C₄H₉), hexyl (C₆H₁₃), or octyl (C₈H₁₇)

Figure 7. Structure of trialkylmethylammonium molybdate ILs.

Table 3. Comparison of MoS₂ synthesized from trihexylmethylammonium molybdate ([N₆₆₆₁]₂MoO₄) and commercial Mo-isooctoate. Data from [55].

Parameter	[N ₆₆₆₁] ₂ MoO ₄	Mo-Isooctoate
Slab length (nm)	~4	~5–6
Layer number	1–2	2–3
Contents of Mo (at.%)	89.5	87.6

Molecularly tailored dithiophosphate precursors exhibit a complementary design strategy. In comparison to solely alkylated counterparts, the addition of aromatic moieties to Mo aryl-alkyl-dithiophosphates (Mo-Ar/R) improves structural affinity with both aromatic and aliphatic fractions of HOF, leading to better dispersion and more selective HOF conversion [56]. Mo-Ar/R combines both benzyl (aromatic) and n-butyl (alkyl) groups, increasing its structural resemblance to diverse HOF components. In contrast, standard Mo dialkyl dithiophosphate (Mo-R) precursors contain only alkyl groups. Mo-Ar/R precursors consistently reduce coke and gas generation under moderate HOF hydrocracking conditions (T = 430 °C, P = 7 MPa) (Table 2) and produce smaller, less stacked MoS₂ domains than Mo-R systems (Table 4). This comparative advantage emphasizes feedstock–precursor matching as a crucial parameter in the design of dispersed catalysts. The paper emphasizes how HOF catalytic upgrading technologies may be advanced through rational precursor design, directly leading to sustainability improvements.

Table 4. Comparison of Mo-Ar/R vs. Mo-R catalysts (Ar = benzyl, R = n-butyl) in HOF hydrocracking. Data from [56].

Parameter	Mo-Ar/R	Mo-R
MoS ₂ morphology	Slab length < 7 nm (57.2%), stacking 1–3 layers (82.1%)	Slab length < 7 nm (53.8%), stacking 1–3 layers (77.4%)
H ₂ consumption	0.95–1.34 wt%	0.87–1.13 wt%

Beyond single-metal systems, bimetallic dispersed catalysts introduce synergistic effects that cannot be replicated through physical mixing of monometallic phases [58,60]. In Ni-Mo systems, derived from Mo-naphthenate and Ni-octoate, MoS₂ formed small, weakly stacked slabs (~6 nm), while Ni produced larger Ni₃S₂ crystallites (5–30 nm), resulting in a catalyst that was represented by Ni₃S₂ particles decorated with MoS₂ slabs. This Ni-Mo catalyst enhanced HDS and overall conversion, while simultaneously mitigating

coke formation, under severe HOF hydroprocessing conditions ($T = 450\text{ }^{\circ}\text{C}$, $P = 16\text{ MPa}$, catalyst dosage = 300–600 ppm) (Table 2) [57,58]. Dispersed nano-V-Mo systems obtained from Mo-naphthenate and V-acetylacetonate, on the other hand, showed only an additive effect and no phase interaction, highlighting the fact that synergy is very structure-specific rather than universal across bimetallic combinations. The study emphasizes the potential of dispersed mixed-metal catalysts for residue upgrading, with Ni-Mo showing the greatest promise because of its synergistic properties.

The synthesis of catalyst precursors increasingly incorporates bio-derived precursors and renewable ligands to address sustainability concerns. Fe-Ni sulfide catalysts, synthesized in situ from oil-soluble precursors, derived from *Jatropha* oil, demonstrate competitive activity in coal-oil co-processing at reduced hydrogen pressures ($P(\text{H}_2) = 8\text{ MPa}$) (Table 2) [60]. *Jatropha* oil, a vegetable oil produced from the seeds of the *Jatropha curcas* plant, a drought-resistant shrub native to Central America and Mexico, was used as a renewable ligand in precursor synthesis. While the oil is toxic and not suitable for human consumption, it can be used for industrial purposes. The performance of the *Jatropha* oil-derived $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ was better than that of Fe-Ni-octoate and Fe-Ni-oleate. The $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ mixed-crystal sulfides exhibited superior catalytic performance, achieving 97.1% lignite conversion and 92.2% liquid yield with low coke formation (1.3 wt%), illustrating how ligand selection can simultaneously influence catalyst performance and environmental footprint. However, compared to Mo-based systems, the comparatively larger particle sizes ($\sim 249\text{ nm}$) indicate intrinsic activity constraints that must be weighed against sustainability improvements.

Innovative organic scaffolds such as calixarene-based complexes [59] also provide stable and molecularly dispersed catalysts by enabling molecular-level metal isolation prior to thermal decomposition of precursors [59]. Co- and Ni-calixarene precursors generated sulfide nanoparticles in situ, enhancing HOF hydrogenation and reducing coke formation ($<0.1\text{ wt.}\%$) at low catalyst dosages (Table 2). Importantly, their strongest performance emerges when combined with conventional supported catalysts (e.g., W-Ni/ $\text{Al}_2\text{O}_3\text{-SiO}_2$) (Table 5), indicating that hybrid catalytic architectures may offer a pragmatic route to maximizing efficiency while minimizing metal consumption. Sustainability benefits include efficient HOF upgrading with minimal coke. Challenges remain with precursor cost and scalability, yet the potential for eco-friendly synthesis is notable.

Table 5. Performance of Co/Ni-TBC [6] catalysts for HOF hydrocracking (TBC [6] = *p*-tert-butylcalix [6] arene). Data from [59].

System	Catalyst	Conversion (wt.%)	Naphtha Yield (wt.%)	Middle Distillates Yield (wt.%)	Total Liquid Yield (wt.%)
Thermal cracking	None	34.3	10.7	19.2	29.9
Standalone dispersed	Ni-TBC [6]	32.4	11.7	16.7	28.4
	Co-TBC [6]	33.0	12.0	16.8	28.8
	Mixed Ni + Co-TBC [6]	35.0	12.1	19.6	32.0
Dual-catalytic system	Supported (W-Ni/ $\text{Al}_2\text{O}_3\text{-SiO}_2$)	39.0	10.7	22.3	33.0
	Supported + Ni-TBC [6]	41.3	11.7	23.6	35.3
	Supported + Co-TBC [6]	42.4	12.0	24.4	36.4

Collectively, these studies demonstrate that sustainable HOF conversion is unlikely to be achieved through a single “universal” catalyst formulation. Instead, performance gains

arise from the rational integration of precursor chemistry, nanoscale dispersion, feedstock compatibility, and process severity. Future progress will depend on balancing catalytic precision with synthetic simplicity, hydrogen efficiency, and cost, positioning molecularly engineered dispersed catalysts as adaptable—rather than monolithic—solutions for HOF upgrading.

5.2. Ex Situ vs. In Situ Nanocatalysts

A critical distinction in nanocatalyst development lies between in situ generation (catalyst formed from precursors under catalytic reaction conditions) and ex situ preparation (pre-synthesized, pre-sulfided catalysts introduced into feed) [82]. The synthesis routes and systems we discussed above refer to in situ generation. The ex situ methods produce catalysts that are prepared and sulfided in external reactors and then mixed with HOF at the required dosage before being fed to the hydrocracking reactor. Figure 8 shows the basic distinction between these two approaches. The core principles lying behind ex situ catalysts are as follows:

- Precision engineering of catalyst properties (size, morphology, sulfidation level) before introducing them into the reactor;
- Decoupling synthesis from reaction conditions, allowing independent optimization of catalyst formation and hydroconversion;
- Eliminating reliance on feedstock sulfur, which is crucial for in situ sulfidation but problematic for low-sulfur residues.

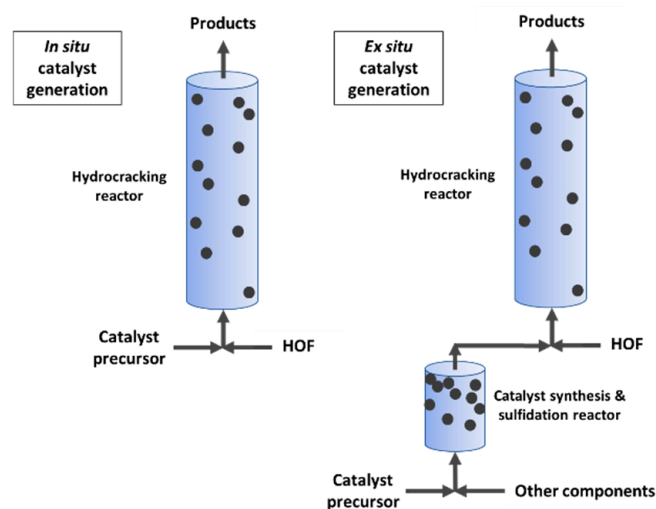


Figure 8. Schematic comparison of in situ and ex situ generation methods for dispersed hydrocracking catalyst.

Ex situ-engineered nano-MoS₂ systems illustrate the benefits of controlled catalyst formation. Pre-synthesized MoS₂ nanoparticles (<100 nm) introduced into vacuum residue exhibited high liquid yields (70%), deep desulfurization (reducing sulfur content from 6.97 wt% to 2.91 wt%), and minimal coke (<0.1 wt%) at relatively mild conditions (400 °C, 65 bar H₂), demonstrating that well-defined sulfide phases can rival or outperform in situ-catalysts without relying on feed-derived sulfur [61]. Notably, these gains were achieved using aqueous-phase synthesis and inexpensive precursors (ammonium molybdate and thioacetamide) (Table 2), underscoring that enhanced catalytic performance does not necessarily require complex supports or promoters.

Composite systems have further advanced the concept of ex situ catalysts by simultaneously addressing nanoparticle stabilization and feed compatibility [62]. In this context, Mo-rich composite nanocatalyst (Figure 9a), synthesized via the technique reported in [62],

with MoS_2 , MoO_2 , and oxysulfides, stabilized in a LDPE-matrix, illustrates how polymer matrix can simultaneously address dispersion nanocatalyst stability and improved hydro-conversion performance. It achieves up to 57.8 wt% VR conversion while reducing coke formation to 0.5 wt% (vs. 4.2 wt% of coke in the reference experiment) (Table 2). The resulting composite catalyst showed bimodal particle distribution (5–10 nm and 50–500 nm). Notably, dispersion methodology emerged as a key performance determinant, with enhanced activity achieved via sonication. The hybrid approach—combining ex situ and in situ catalysts—yielded a more balanced performance profile (conversion, 51.8%; coke, 0.2 wt%). The use of polyethylene as a nanoparticle stabilizer in that case may serve for repurposing plastic waste. However, challenges remain in optimizing synthesis, especially regarding particle size and polydispersity, dispersion methods (e.g., sonication energy costs), and scaling the synthesis.



Figure 9. Ex situ catalysts: (a) Mo sulfide ex situ LDPE-stabilized catalyst, (b) Mo sulfide ex situ VR-stabilized catalyst.

Heavy feedstocks also may serve as a stabilizing medium, allowing the preparation of catalyst-rich concentrates via reverse emulsion techniques. The study [63] demonstrates that ex situ, synthesized, dispersed MoS_2 catalysts (dispersions), obtained from ammonium paramolybdate and elemental sulfur or thiocarbamide, can be effectively stabilized in vacuum residue at high Mo loadings (6–10 wt%) with particle sizes ranging from 50 to 300 nm (Figure 9b). Compared with alternative morphologies, these MoS_2 -based catalysts demonstrated superior hydrogenation and HDS activity, achieving 55–70% conversion with low coke formation (0.2–0.9 wt%) (Table 2). The structural diversity of the synthesized catalysts (e.g., single-layer slabs, solid spheres, and hollow spheres) correlated with their reaction performance and selectivity. The study [63] highlighted the role of particle morphology and sulfidation efficiency in catalytic activity, with ex situ-prepared single-layered MoS_2 catalyst providing more accessible active sites for hydrogenation and cracking reactions.

Notably, the described ex situ Mo-sulfide-based catalysts are carrier-free and synthesized directly in the hydrocarbon/polymer environment using low-cost precursors. The PE- and VR-stabilized ex situ nano- and ultrafine catalysts achieve stable dispersion in HOF and offer improved handling and process flexibility. Their ability to process sulfur-lean feedstocks and tolerate high asphaltene content makes them particularly suited for decentralized and sustainable upgrading schemes involving residues, bitumen, or waste plastics.

Beyond Mo-based systems, ex situ NiFe nanocatalysts prepared via inverse microemulsion demonstrated effective viscosity reduction and asphaltene conversion under relatively mild conditions [64]. The resulting NiFe catalysts were semi-solid gels (concentrate of nanoparticles + surfactant residues) containing 10–30 wt% Ni+Fe in the organic phase. Unlike conventional thermal cracking, the finely dispersed (1–20 nm) spherical NiFe nanoparticles, dominated by active FeS phases, enabled substantial upgrading efficiency at low metal loadings (<0.5 wt%) (Table 2). Under HOF hydrocracking conditions (372 °C, 9.8 MPa H_2 , 1 h), these catalysts markedly outperformed non-catalytic processes, increasing API

gravity (13.1 to 18.3), reducing viscosity (9691 to 798 cP), and achieving 37–44% asphaltene conversion, alongside moderate heteroatom removal (Table 6). Compared with Mo-based analogues, the use of earth-abundant Ni and Fe offers clear economic and sustainability advantages while maintaining competitive upgrading performance. Nonetheless, issues related to nanoparticle agglomeration and sulfur-induced deactivation remain limiting factors, indicating that further optimization is required to ensure long-term stability and industrial viability.

Table 6. Comparison of NiFe nanocatalysts vs. reference systems in heavy crude oil hydrocracking. Data from [64].

Parameter	Feedstock	No Catalyst	NiFe Catalyst		
Catalyst composition	-	-	NiFe (1:0.33)	NiFe (1:1)	NiFe (1:3)
Active phase	-	-	FeS/Ni(OH) ₂	FeS/Ni	FeS/Ni
API gravity, °	13.1	14.0	17.0	18.0	18.3
Viscosity, cP	9691	3092	1050	869	798
Asphaltene conversion, %wt	32.5	13.8	37.2	37.0	43.7
Sulfur, wt%	6.0	5.0	4.4	4.0	3.9
Nitrogen, ppm	4687	4280	3188	3060	2999

Similarly, biochar-supported, ex situ-prepared Ni-catalysts derived from waste coffee grounds [65] demonstrate how low-cost biomass carriers can rival conventional supports in unconventional oil upgrading. Compared with oxide-based catalysts, the Ni/biochar system combined high Ni dispersion (7.9 nm) with a mesoporous, high-surface-area carrier (113.9 m² g^{−1}), translating into measurable performance gains in both HOF upgrading and oil shale pyrolysis. Under mild, non-hydrogenative conditions, the catalyst achieved higher viscosity reduction (60.4%, 21.5% higher than non-catalytic treatment), deep sulfur removal (0.2 wt%), and enhanced light-fraction formation, indicating effective catalytic cracking rather than mere thermal effects (Table 2). In oil shale pyrolysis, the observed downward shifts in kerogen decomposition temperatures (8–10 °C) further confirm reduced energy demand and improved catalytic efficiency relative to conventional systems. Notably, these improvements were obtained at low catalyst loadings (0.25–1 wt%), underscoring the functional advantage of the biochar support over synthetic carriers such as Al₂O₃. While the study primarily addresses thermal and catalytic cracking rather than true hydroprocessing, it provides a compelling proof of concept for sustainable, biomass-derived catalyst supports in HOF upgrading.

Industrial by-products such as red mud (RM) have emerged as ex situ catalyst precursors for vacuum residue hydrocracking, offering both functional and sustainability advantages (Table 2). RM, an industrial by-product from alumina production, is composed primarily of Fe₂O₃, Al₂O₃, and minor oxides. The study [66] demonstrates that RM undergoes in situ sulfidation to form pyrrhotite (Fe_(X−1)S_X), an active hydrocracking phase, eliminating the need conventional catalyst pre-sulfidation. Compared with non-catalytic operation, RM significantly suppresses coke formation, indicating improved hydrogen utilization and enhanced reactor operability (Table 7). While overall conversion remains dominated by thermal pathways, RM selectively moderates cracking severity, shifting product distribution toward VGO rather than light gases or coke. The increased unreactive fraction relative to the reference case confirms suppression of deep cracking in favor of partial upgrading. Collectively, these results position RM not as a high-activity catalyst but as an effective process modifier that improves selectivity and stability, reinforcing the

potential of waste-derived materials to deliver incremental yet meaningful performance gains in HOF upgrading.

Table 7. Results of HOF upgrading without catalyst and with RM catalyst. Adapted from [66].

Parameter	No Catalyst	RM Catalyst	Effect of Catalyst
Yield of products (wt%):			
Coke	14.07	1.13	↓ 92% reduction
Gas	14.65	9.93	↓ 32% reduction
Naphtha	5.52	4.30	Slight decrease
Diesel	27.00	27.28	Minimal change
VGO	11.45	21.53	↑ 88% increase
Unreacted feed	27.31	35.83	↑ 31% increase
Conversion	72.69	64.17	↓ 8.5% reduction

Thus, ex situ synthesis broadens the methodological framework for sustainable HOF upgrading by enabling waste valorization, greater process flexibility, and the rational design of catalysts suited to sulfur-lean or unconventional feedstocks. Recent advances emphasize synergistic rather than purely material-specific effects, as demonstrated by the microwave-assisted catalytic upgrading strategy proposed in [68]. This study using magnetic nanohybrids and microwave radiation showed the potential combined positive effect of superparamagnetic iron oxide (Fe_3O_4) nanoparticles, which have excellent magnetic properties, and their nanohybrid with multiwalled carbon nanotubes (MWCNT) and nickel oxide (NiO) nanoparticles. Among the tested systems, Fe_3O_4 -MWCNT nanohybrids showed superior upgrading efficiency relative to Fe_3O_4 -NiO nanohybrid and Fe_3O_4 nanoparticles as reflected in greater viscosity reduction and API improvement under identical electromagnetic conditions (Table 2). The integration of microwave-assisted catalytic upgrading offers a greener alternative to conventional thermal methods, leveraging nanoparticle-enhanced cracking and electromagnetic heating for sustainable HOF upgrading.

Likewise, the application of high-entropy alloy (HEA) nanocatalysts demonstrates potential: while primarily tested in wastewater treatment, their defect-rich structures and durability provide a transferable design paradigm for multifunctional catalytic systems. High-entropy alloy-based catalysts offer a durable and scalable solution for wastewater treatment—targeting organic pollutants, heavy metals, and non-biodegradable organics—and for green chemical processes. The nanodendritic PtRhCoNiMn catalyst reported in [83] outperformed Pt black and other noble metal catalysts in aqueous hydrogenation of 4-nitrophenol and Cr(VI), with sustained performance over multiple cycles. Toxic pollutants were converted into less harmful forms. Such performance is attributed not merely to composition but to the unique defect density and electronic heterogeneity due to HEAs' dendrite-like morphology, nanodimensions, and composition, which promote efficient active-site utilization. The high reusability (>96% activity retention after seven cycles) underscores their potential for scalable deployment, addressing both economic and sustainability constraints. Overall, this study positions HEAs as a robust catalytic platform whose structural and compositional features are directly relevant to applications connected with converting high-molecular organic and metal-containing components in HOF.

In conclusion, recent advances in dispersed nanocatalysts for HOF conversion indicate a clear transition from conventional, single-function systems toward multifunctional, waste-derived, and feed-adaptive catalysts. The convergence of rational molecular design, ex situ synthesis strategies, and the integration of renewable or waste-derived materials

underscores the considerable potential of these catalysts to advance sustainable HOF upgrading and related conversion processes. Furthermore, emerging multifunctional systems, such as magnetic nanohybrids and high-entropy alloy nanocatalysts, which already demonstrate promise in cross-sectoral applications, may also prove effective as standalone dispersed catalysts or as complementary components in dual-catalytic systems. From a sustainability perspective, advanced dispersed catalysts demonstrate a promising balance of high activity and selectivity, resulting in better product slate and quality by increasing yields of valuable light and middle distillates, while simultaneously eliminating low-quality fuel like coke—a significant source of CO₂ emissions. Also, operating at milder conditions translates directly to reduced energy consumption, which is the primary driver of CO₂ emissions in refineries, as detailed in Section 6.

6. System-Level Climate Impacts and Life Cycle Perspectives

Having explored the chemical mechanisms and catalyst design for HOF conversion, it is essential to evaluate how these micro-level innovations impact the macro-level sustainability of a refinery. To this end, we employ LCA as a methodological tool used to quantify environmental impacts across the productive supply chain of a product or service. According to ISO 14044 [84], environmental impacts of a product are caused by both the use of renewable and non-renewable natural resources and the emissions or waste released to the environment, which affect ecosystems, resources, and human health. LCAs have been implemented in the conventional oil and gas sector, since they provide a systems-level perspective by quantifying energy use and environmental impacts from crude extraction through refining and, ultimately, to the combustion of final products. This approach has become increasingly important, as policy instruments (e.g., low-carbon fuel standards) and investment decisions rely on robust carbon intensity benchmarks [85]. In the previous sections, new catalytic hydrogen addition technologies for the deep processing of carbon-containing residues, in particular heavy oil residues, were described. This section estimates the potential environmental releases from the advanced oil refinery with the implemented hydrogen addition technology for deep processing of heavy oil residue (such as hydroconversion (slurry-phase hydrocracking)), described in the previous sections, and compares it with potential emissions from conventional oil refinery.

The open-source Petroleum Refinery Life Cycle Inventory Model (PRELIM, version 1.6, 2022) was applied with a gate-to-gate refinery boundary for estimating energy use and environmental releases from petroleum refining [12,86]. PRELIM standard outputs focus on refinery operations and do not include upstream crude extraction and transport. The system boundary includes refining energy demand (electricity, steam), hydrogen supply, the refinery itself (including conventional process units), and refinery gas management. Allocation of energy use and emissions to products follows an energy-based allocation consistent with PRELIM settings. The modeled configuration represents a deep-conversion coking refinery with a residue hydroconversion refinery. Electricity and steam pathways were selected based on PRELIM default global average energy mixes and on-site natural gas-fired utilities.

The model enables life cycle assessments (LCAs) for refinery products based on subprocess flows and environmental impact potentials per barrel of crude oil in accordance with ISO 14044 [84]. Table 8 describes the main environmental impact categories. The resulting numbers on environmental impacts provided by PRELIM represent potentials, not observed impacts, and depend on system boundary, allocation, and regional background conditions. Figure 10 shows the refinery configuration used in this study, which aligns with the configuration modeled in PRELIM [86]. A more detailed schematic of the vacuum residue hydroconversion process is provided in Figure 4b.

conversion refinery with a residue hydroconversion unit—a technology not commonly represented in prior PRELIM studies. Thus, this study demonstrates the influence of novel residue conversion technology. The results show the impact of residue conversion technologies on emissions and their interaction with upstream emissions, particularly, from hydrogen production. We compare gray, blue, and green hydrogen scenarios to show how decarbonizing hydrogen supply reshapes the competitiveness of advanced hydroconversion—a nuanced analysis not fully explored in earlier emission analysis models for petroleum refining.

The crude refining scenarios examined were as follows:

- Scenario A: conventional refinery scheme with a delayed coking unit for processing heavy residue boiling above 525 °C (VR);
- Scenario B: advanced refinery scheme with a residue hydroconversion unit for processing VR.

A refining capacity of 100,000 bbl/d was assumed. The crude type selected from the PRELIM library is described in Table 9. To simulate the VR processing scenarios of interest, a heavy crude was chosen whose composition closely matches the feedstock in the referenced hydroconversion studies [42,49,53,63,77,87,88]. The VR processing parameters were adjusted to replicate the hydroconversion material balance [87,88] (Table 10). All other input data for both scenarios were drawn from the PRELIM model's default inventory, which incorporates global average industry data for refinery main processes and subprocesses. The initial and raw data and results of calculations are presented in Supplementary Materials, Part 2. As an upgrading process for raw product streams, PRELIM uses hydrotreatment.

Table 9. Properties of the crude oil and its >525 °C fraction (vacuum residue) used as inputs to the PRELIM model.

Property	Whole Crude	>525 °C Fraction (Vacuum Residue)
Sulfur content, wt %	2.0	4.7
Nitrogen content, ppm	1050	3985
API gravity, ° API	31.7	6.7
Density, kg/m ³	863	1020
Hydrogen content, wt %	12.8	10.8
Microcarbon content, wt %	3.8	18.0

Table 10. Material balance of the hydroconversion process (catalyst concentration—0.05% wt Mo, P = 7.0–10.0 MPa, T = 445 °C, H₂: feed = 1000 nL/L, LHSV = 1 h^{−1}). Data from [87,88].

Stream	% wt.
Input:	
VR (vacuum residue)	66.0
Recycle stream (containing recycled catalyst)	29.5
H ₂ consumption	2.4
Water	2.0
Catalyst precursor (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.1
Total input	100.0

Table 10. *Cont.*

Stream	% wt.
Output:	
Raw gaseous products (C ₁ –C ₄ , H ₂ S, NH ₃)	3.8
Distillates, total	89.7
IBP–180 °C	14.5
180–350 °C	36.7
350–525 °C	38.5
Residue (>525 °C), including nanocatalyst *	6.5
Total output	100.0

* An output stream of residue >525 °C, including spent catalyst, in an industrial scenario is sent to an existing coking unit, resulting primarily in a standard coking product slate. The emission estimation does not consider this subprocess.

Table 11 summarizes the PRELIM outputs, including yields of the main refinery products, energy requirements, and potential environmental impact categories. Contribution of energy and process streams to environmental impact categories for scenario B is demonstrated in Figure 11.

Table 11. Comparative results calculated using the PRELIM model.

Parameter	Scenario A	Scenario B
Refinery product yields (wt%):		
Gasoline	26.0	26.9
Naphtha	4.7	5.2
Jet fuel	12.1	12.3
Ultra-low-sulfur diesel	31.1	31.8
Refinery fuel gas	4.7	5.6
Fuel oils	10.8	11.5
Coke	4.0	0
Sulphur	0.9	1.1
Asphalt	2.2	2.2
Lubricants	0.5	0.5
BTX (benzene, toluene, xylenes)	1.9	2.0
VGO (vacuum gas oil)	1.1	0.9
LCA results:		
Total energy consumption (MJ/bbl crude), including:	549.2	581.5
Hydrogen production via SMR	59.1 (10.8%)	76.0 (13.1%)
Heat (from natural gas)	341.8 (62.2%)	349.0 (60.0%)
Steam (from natural gas)	28.5 (5.2%)	26.6 (4.6%)
Electricity	23.2 (4.2%)	25.9 (4.5%)
Other sources	96.6 (17.6%)	104.0 (17.9%)

Table 11. Cont.

Parameter	Scenario A	Scenario B
Environmental impact categories:		
Global warming potential (GWP) (kg CO ₂ eq/bbl crude)	40.4	43.5
Acidification (kg SO ₂ eq/bbl crude)	3.1×10^{-2}	3.2×10^{-2}
Particulate matter formation (kg PM _{2.5} eq/bbl crude)	4.2×10^{-3}	4.4×10^{-3}
Eutrophication (kg Neq/bbl crude)	1.6×10^{-3}	1.6×10^{-3}
Ozone depletion (kg CFC-11eq/bbl crude)	1.2×10^{-7}	1.2×10^{-7}
Smog (kg O ₃ eq/bbl crude)	0.7	0.8
Human health, cancer (CTUcancer/bbl crude)	3.4×10^{-9}	3.5×10^{-9}
Human health, non-cancer (CTUoncancer/bbl crude)	2.7×10^{-7}	2.7×10^{-7}
Ecotoxicity (CTUeco/bbl crude)	1.0	1.0

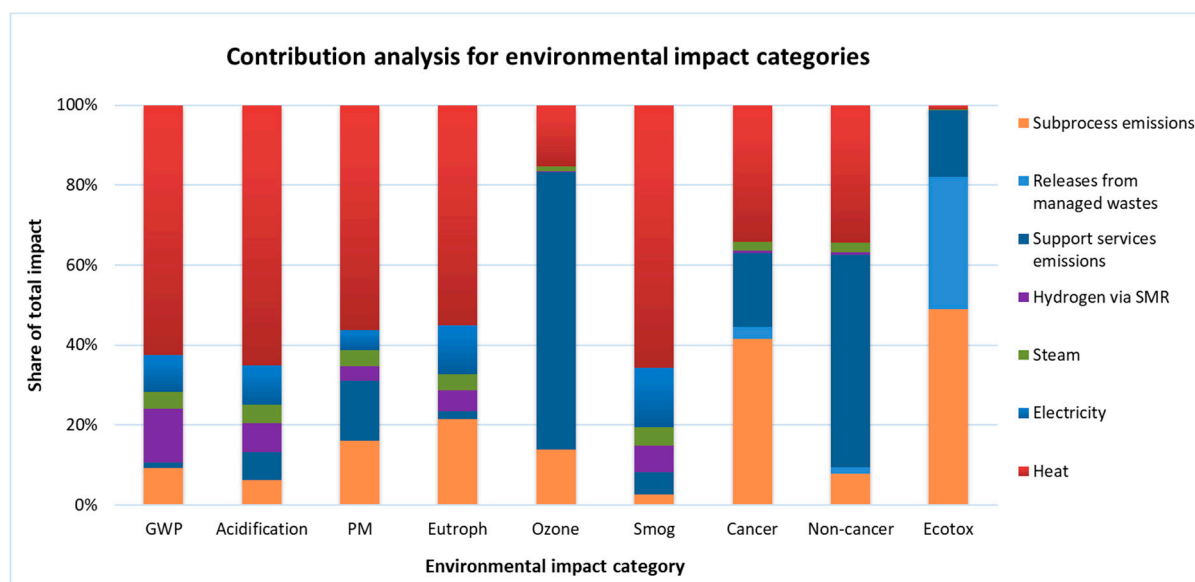


Figure 11. Life cycle environmental impact contributions from different sources in crude oil refining via scenario B.

Table 11 shows that scenario B exhibits slightly higher overall conversion to liquid fuels, however, this gain is partly offset by increased production of fuel gas and heavy ends, which have lower market value and less favorable environmental performance. Notably, Scenario B eliminates coke formation (4.0 wt% in Scenario A). Total energy consumption increases from 549.2 MJ/bbl (Scenario A) to 581.5 MJ/bbl (Scenario B), indicating a 6% rise. A significant driver is the higher hydrogen demand in Scenario B (76.0 MJ/bbl vs. 59.1 MJ/bbl in Scenario A). According to Figure 11, which shows the contribution of different energy and process streams to emission categories, the largest contribution to greenhouse gas emissions is due to heating provided by natural gas. Both hydrogen production and heating refinery streams are dependent on natural gas, which is a carbon-intensive source. In total energy consumption for the crude refining scenarios A and B, natural gas remains the main energy source (60% and higher) (Table 11). The global warming potential for scenario B increases from 40.4 (for scenario A) to 43.5 kg CO₂eq/bbl, reflecting higher hydrogen use. Other categories—acidification, particulate matter formation, and photochemical smog—also increase slightly, while eutrophication, ozone depletion, and ecotoxicity remain unchanged. Both cancer and non-cancer toxicities remain nearly identical between scenarios. These

increments are modest in magnitude but consistent across categories, suggesting that Scenario B's additional processing intensity raises environmental burdens.

While PRELIM standard outputs focus on refinery operations, this study expands the boundary to include upstream emissions for comparative purposes. To see the full picture, we also included in analysis emissions associated with crude oil recovery and production of the catalyst precursor, ammonium paramolybdate (APM, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), for the VR hydroconversion unit of Scenario B:

- For crudes with an API gravity around 31.5 °API, greenhouse gas emissions for the recovery stage range from 20 to 61.5 kg CO₂-eq/bbl [89]. Based on the specific crude's API (31.7 °API; Table 9), upstream (recovery/production only) greenhouse gas emissions were assumed to be 41 kg CO₂-eq/bbl;
- Ammonium paramolybdate (APM) production involves mining and roasting molybdenite (MoS₂) to molybdenum trioxide (MoO₃), followed by leaching and crystallization. Drawing on recent life cycle inventories [90,91], the cradle-to-gate emission factor for APM is 12.1 kg CO₂-eq/kg APM. At a refinery throughput of 100,000 bbl/d, this adds 0.76 kg CO₂-eq/bbl crude.

The comparative LCA between the conventional refining (Scenario A) and the advanced refining (Scenario B) highlights the trade-offs of implementing residue hydrogen addition technologies. Scenario B improves product slate quality by increasing yields of valuable light and middle distillates, while simultaneously eliminating coke formation—a key advantage, since coke combustion represents a significant source of CO₂ emissions in conventional refining and its further use. Importantly, coke combustion in Scenario A contributes an additional 15.3 kg CO₂eq/bbl crude if considered (Table 12), significantly worsening its climate footprint. When this factor is included, the total GHG emissions, including crude production emissions, for Scenario A reach 96.7 kg CO₂eq/bbl, which is 12% higher than total GHG emissions for Scenario B, showing that the advanced pathway can outperform conventional delayed coking when additional system impacts are considered.

Table 12. Greenhouse gas emissions for H₂ production pathways, their effect on Scenario B totals and comparative cost estimation results (Supplementary Materials, Part 3).

Source of Emissions	Scenario A		Scenario B	
	Gray H ₂ (SMR Without CO ₂ Capture)	Gray H ₂ (SMR Without CO ₂ Capture)	Blue H ₂ (SMR with CO ₂ Capture)	Green H ₂ (Electrolysis)
H ₂ production *, g CO ₂ eq/MJ	91.0	91.0	20.4	7.7
Crude oil refining, kg CO ₂ eq/bbl crude (via PRELIM; H ₂ production emissions are taken into account)	40.4	43.5	38.9	38.1
Additional sources (not accounted for in PRELIM):				
Crude recovery, kg CO ₂ eq/bbl crude	41.0	41.0	41.0	41.0
Potential CO ₂ emissions from coke combustion, kg CO ₂ eq/bbl crude	15.3 **	-	-	-
Catalyst precursor production for VR hydroconversion unit, kg CO ₂ eq/bbl crude	-	0.76	0.76	0.76

Table 12. Cont.

Source of Emissions	Scenario A		Scenario B	
	Gray H ₂ (SMR Without CO ₂ Capture)	Gray H ₂ (SMR Without CO ₂ Capture)	Blue H ₂ (SMR with CO ₂ Capture)	Green H ₂ (Electrolysis)
Total greenhouse gas emissions, kg CO ₂ eq/bbl crude	96.7	85.3	80.7	79.9
Operating energy cost, USD/bbl	2.62	2.92	3.55	5.14
Net value (incl. energy and O&M/catalyst), USD/bbl	101.68	103.81	103.17	101.59
Marginal abatement costs, USD/tCO ₂ eq	-	−186	−93	+6

* Estimated using GREET model (well-to-gate analysis, assuming US mix energy grid, CO₂ to be captured in blue H₂ production—92.5% [92]). ** Elemental composition of coke (PRELIM): hydrogen, 3.5 wt%; sulfur, 5.4 wt%; nitrogen, 1.15 wt%. CO₂ yield was calculated assuming total conversion of carbon from coke.

Table 12 also explores the influence of different hydrogen production pathways on Scenario B outcomes, showing that the carbon intensity of hydrogen supply reshapes the comparative performance of the refinery. With gray hydrogen from steam methane reforming (SMR), Scenario B—from PRELIM results—initially appears less favorable due to its higher hydrogen demand. However, when blue hydrogen (SMR with carbon capture and storage) or green hydrogen (electrolysis) is considered, total GHG emissions for Scenario B decrease substantially to 80.7 and 79.9 kg CO₂eq/bbl, respectively. While gate-to-gate emissions show specific trends, the overall climate impact is heavily dependent on the upstream hydrogen source. As detailed in the sensitivity analysis (Table 12), the potential for emission reduction is contingent upon decarbonizing hydrogen production.

The results underline that the environmental value of advanced refining technologies is contingent on decarbonizing hydrogen production and energy generation. Without clean hydrogen and CO₂ capture, the gains in product yield and coke elimination risk being offset by increased refinery energy intensity. With clean hydrogen and energy, the advanced pathway becomes a clear improvement in sustainability over conventional residue upgrading.

Beyond the environmental indicators, the illustrative cost analysis clarifies the trade-offs between emissions abatement and economic performance across refinery configurations. This economic analysis is intended as illustrative, scenario-based comparison designed to evaluate relative trends between alternative refinery pathways. However, these analyses are not predictive, market-representative, or investment-grade assessments but are used to support insights into environmental performance and cost drivers under defined system boundaries.

Detailed calculation methodology and results based on on-line available price values for natural gas, electricity, hydrogen, and product prices [93–98] are presented in Supplementary Materials, Part 3. Under identical market conditions, Scenario B using gray hydrogen exhibits a total operating cost of 2.92 USD/barrel versus 2.62 USD/barrel for Scenario A, but its improved product yields raise the net value to USD 103.8 per barrel—an increase of +2.1 USD/barrel. Transitioning from gray to blue or green hydrogen raises operating energy costs (up to 5.1 USD/barrel) while reducing emissions from 85.3 to 79.9 kg CO₂ eq per barrel and lowering the marginal abatement cost from −186 to +6 USD/tCO₂eq. The hydroconversion pathway (Scenario B) provides measurable emission benefits. The advantage grows when carbon emission pricing or low-carbon hydrogen incentives are introduced. Economically, Scenario B with blue hydrogen remains competitive with conventional refining (net value per barrel remains USD 103.17 USD, above the USD 101.68 of

conventional refining), whereas green hydrogen currently incurs a small cost penalty (the overall net value remains nearly equal to Scenario A (difference < 0.1 USD/barrel)) that could be offset by carbon credits or policy support. While green hydrogen can substantially reduce life cycle emissions, its high current operating costs and infrastructure requirements present a significant economic barrier, likely limiting its near-term adoption for heavy feedstock upgrading.

The life cycle assessment presented thus far is based on a specific crude oil with an API gravity of 31.7°. To understand how crude quality influences the results, the PRELIM model was run for the conventional refinery scenario (Scenario A, with delayed coking) using two additional crude types: a heavier crude (23.3 °API) and a lighter crude (41.2 °API). The results are summarized in Table 13.

Table 13. Crude type sensitivity analysis for Scenario A calculated using the PRELIM model.

Parameter	Crude's °API		
	23.3	31.7	41.2
Refinery product yields (wt%):			
Gasoline	18.6	26.0	28.5
Naphtha	1.7	4.7	6.7
Jet fuel	12.4	12.1	11.6
Ultra-low-sulfur diesel	37.7	31.1	29.5
Refinery fuel gas	5.5	4.7	4.7
Fuel oil	13.4	10.8	10.1
Coke	4.7	4.0	3.4
Sulphur	0.3	0.9	0
Asphalt	1.9	2.2	1.3
Lubricants	0.7	0.5	0.5
BTX (benzene, toluene, xylenes)	0.7	1.9	0.5
VGO (vacuum gas oil)	1.3	1.1	0.8
LCA results:			
Total energy consumption (MJ/bbl crude), including:	560.2	549.2	549.4
Hydrogen production via SMR	141.8	59.1	34.6
Heat (from natural gas)	288.3	341.8	335.9
Steam (from natural gas)	26.8	28.5	39.3
Electricity	25.6	23.2	21.6
Other sources	77.5	96.6	117.7
Global warming potential (GWP) (kg CO ₂ eq/bbl crude)	46.0	40.4	37.9

Results for a heavier (23.3 °API) and a lighter (41.2 °API) crude confirm that while absolute yields and energy requirements vary, the order and direction of the results remain consistent. Heavier crudes exhibit lower yields of high-value products and higher GWP (46 kg CO₂ eq per barrel), whereas lighter crudes reduce GWP to ≈38 kg CO₂ eq per barrel. The trend demonstrates that hydroconversion would be even more advantageous for heavier feedstocks, where coking penalties and hydrogen intensity rise sharply. Hence, the qualitative conclusions of the comparative LCA are robust across crude qualities.

Unlike general refinery LCAs that focus on standard configurations, this study specifically isolates the impact of new residue conversion technology. By coupling the experimen-

tal and literature-derived process data with system-level analysis, we provide new insights into how high-conversion technologies influence emissions and interact with varying carbon intensities of hydrogen production routes (gray, blue, green). This offers a unique interpretation of how specific processing route choices drive refinery-wide decarbonization.

7. Co-Processing Heavy Oil Feedstocks with Alternative Feed

The integration of waste polymer- and biomass-derived feedstocks into refining systems is effectively realized through co-processing with heavy oil feedstocks via catalytic hydrogen addition processes. In slurry-phase hydrocracking processes catalyzed by dispersed nanocatalysts, HOFs perform a dual function: they act as stabilizers for catalyst nanoparticles—primarily due to the presence of polar resins and asphaltenes—and simultaneously participate as reactants undergoing transformations that lead to the formation of valuable products [42,99]. The stabilizing effect of heavy oil feedstocks on dispersed nanocatalysts depends strongly on resin and asphaltene content, which varies significantly across crude sources. Thus, HOF's dual function imparts impressive tolerance and hydrogenation efficiency to slurry-phase nanocatalyst-based hydrocracking systems, making them an appropriate platform for integrating other challenging macromolecular feedstocks. This concept of co-processing allows waste or renewable streams (such as biomass, plastics, waste tires) to be transformed in synergy with HOF, enabling optimized conversion and valorization of otherwise difficult-to-convert sustainable materials [37,38,76,100].

This section examines recent progress in catalytic strategies for co-processing HOF with selected alternative feedstocks, highlighting both advantages and implications for sustainability, and covers some emerging catalysis cases. Table 14 presents an overview of catalytic processes for converting alternative feedstocks.

7.1. Co-Processing Biomass with Heavy Oil Feedstocks

Biomass represents a renewable but structurally complex feedstock for co-processing with petroleum residues. While its macromolecular nature (cellulose, hemicellulose, lignin) poses challenges for solubility and reactivity, the hydrogen-rich environment and stabilizing properties of HOF, together with dispersed nanocatalysts, offer a promising medium for upgrading biomass into liquid fuels and chemicals.

Among industrially viable pathways for biomass processing, thermochemical routes such as catalytic pyrolysis and hydrothermal liquefaction/hydroprocessing are effective for large-scale implementation. These processes generate complex patterns of products, with crude oil-like mixtures enriched in aromatics, short-chain organic acids, sugars, and carbonyl-containing species, which require subsequent upgrading and deoxygenation to yield drop-in fuels.

Table 14. Overview of catalysts and processes for converting biomass and polymer waste.

Type of Catalyst	Composition of Catalyst	Catalyst Synthesis Method	Process Parameters	Feedstock	Performance	Catalyst Advantages	Challenges
Dispersed Mo sulfide nanoparticles [37]	MoS ₂	In situ: from water-soluble precursor	T = 425 °C, P(H ₂) = 7 MPa, 0.05 wt% Mo, 2–3 h	Pine/fir sawdust (up to 32 wt%) in vacuum residue	Distillate yield < 35–40 wt%, gas yields –16 wt%, coke < 5 wt%	High activity, increases liquid yield, costly precursor, enables direct conversion of raw biomass in HOF	Limited catalyst morphology control, emulsification step and catalyst regeneration required
Dispersed Mo sulfide nanoparticles [101]	MoS ₂	In situ: from water-soluble precursor	T = 420–460 °C, P(H ₂) = 5–8 MPa, 0.05 wt% Mo	Lake Baikal algae (10–50 wt%) + heavy oil residue	Distillate yield < 40.7 wt%, reduced H/C ratio in residue. Fuel yield dependent on algae content	Effective for high-oxygen biomass, utilizes feed sulfur	High gas yields, variable product quality with biomass content
Unsupported NiMoS [102]	NiMo sulfide	Hydrothermal synthesis (200 °C, 12 h), from thiourea, Ni (II) nitrate, ammonium molybdate (Ni:Mo = 1:2 molar)	T = 400 °C, P(H ₂) = 75 bar, 6 h, hexadecane solvent, lignin–oil—1:1	Kraft lignin + pyrolysis oil (from pine sawdust)/4-propylguaiaicol	Char suppression (3.7 wt% vs. 14.7 wt% for reference); bio-oil yield, 56.4 wt%; functional group synergy (–OH, –OCH ₃ , –C ₃ H ₇)	High HDO activity, mesoporous structure, synergistic intermediates stabilization	Catalyst deactivation, oligomerization, high catalyst loading
Dawson POM-based PTC (phase transfer catalysts (PTC)), polyoxometalates (POMs) [103]	TBA ₆ -P ₂ W ₁₇ -SO ₃ H (TBA = tetrabutyl ammonium, P ₂ W ₁₇ = Dawson polyoxometalate, –SO ₃ H = sulfonic acid group)	Modification of POM cluster with sulfonic acids via oxidation of (3-mercaptopropyl)tri-methoxysilane	Esterification of oleic acid with methanol (70 °C, 20 min); fructose dehydration to 5-Hydroxymethylfurfural (5-HMF) (100 °C, 2 h)	Variety of acids and alcohols, carbohydrates, oleic acid, methanol, fructose	Yield and selectivity for oleic acid and methanol—98.7 and 99.0%, for fructose—5-HMF yield—99.0%	Superacidity (H ₀ < –11.4), self-separating emulsion, recyclability, high substrate compatibility	Limited efficiency for polysaccharides, requires solvent optimization
Al ₂ O ₃ nanoparticles [104]	Al ₂ O ₃	Co-precipitation, <i>Phyllanthus emblica</i> seed extract as reducing and capping agent	Pyrolysis: catalyst dose 0.6 g, T = 450 °C, time = 20 min, N ₂ medium	Melia azedarach fruit biomass	Bio-oil yield, 64.8 wt%, biochar yield, 29.2 wt%; biogas yield, 6 wt%; bio-oil with improved physicochemical properties	Sustainable synthesis, high bio-oil yield, recyclable catalyst	Potential coke formation, process optimization required
Dispersed Mo sulfide nanoparticles [100]	MoS ₂	In situ: from water-soluble precursor	P(H ₂) = 7 MPa, T = 450 °C, 0.05 wt% Mo, 2 h	VR (66.5 wt%) mixture with tire rubber and/or PE (1:1)	Yields of liquid products and solid residues of 40.9–47.1 and 23.1–30.2	High activity, low Mo loading, activation by native sulfur	Limited control over nanoparticle size, emulsification stage
NiMo/γ-Al ₂ O ₃ [26]	Ni-Mo on γ-alumina support	Impregnation of Al ₂ O ₃ with Ni/Mo salts, calcination, sulfidation	P(H ₂) = 8.2 MPa; T = 430 °C; catalyst, 1–5 wt%; 1 h batch	LDPE/HDPE/PP/PS in light Arabian residue (3:2 oil–polymer)	PS: 97.4% conversion; HDPE: 86.9% conversion; LDPE: 84.4% conversion	High conversion, industrial maturity, handles mixed feeds	High catalyst load (1–5 wt%), potential deactivation
Zeolite ZSM-5 [26]	ZSM-5 (SiO ₂ / Al ₂ O ₃ = 30)	Hydrothermal synthesis	FCC at T = 450–500 °C	PE, PS in oil fractions	PE: 50–60 wt% gasoline, PS: >84% styrene recovery	Shape-selective cracking, high aromatics yield	Rapid deactivation
Waste plastic (LDPE, HDPE, PP) [105]	Polyethylene, polypropylene	Chopped and mixed with heavy feed	T = 420–450 °C, P(H ₂) = 6 MPa, 2 h	Heavy crude oil, VR	Increased middle distillate yield (up to 56 wt%), reduced coke formation (8.8–18.3 wt%), improved H/C ratio	Low-cost hydrogen donor, reduces hydrogen demand, environmental benefits (waste plastic utilization)	Requires pre-mixing, variability in plastic composition, coke formation at higher temps

Table 14. Cont.

Type of Catalyst	Composition of Catalyst	Catalyst Synthesis Method	Process Parameters	Feedstock	Performance	Catalyst Advantages	Challenges
Waste plastic [106]	Waste plastic (packaging materials)	No synthesis required (direct use of waste plastic)	T = 390–470 °C, P(H ₂) = 40–100 kg/cm ² , 30–120 min	Heavy crude oil, VR	Conversions: HDM, 95–98%; hydrocracking, 70–84%; middle distillates, 47–56 wt%; coke yield, 8.82–18.27 wt% (vs. 9.84–35.12 wt% for reference); improved H/C ratio and product density/viscosity	Costly material, no pretreatment needed, effective for high-asphaltene feeds, reduces coke formation, enhances H/C ratio	Requires high temperature/pressure, potential variability in waste plastic composition
Zinc and MoS ₂ [107]	Zn metal pellets and unsupported MoS ₂	Commercially provided	Hydrothermal liquefaction: T = 360–410 °C, subcritical water, in situ H ₂ generation from Zn-H ₂ O reaction	Scrap tires	Mitigated O, N, S content, inhibited polyaromatic formation cracking of heavier compounds into lighter ones, preserved oil yield	Synergistic effect: Zn aids hydrogenation, MoS ₂ maintains catalytic stability, ZnO promotes HDO, HDS, HDN	Reaction between ZnO and H ₂ S; MoS ₂ may increase N-containing compounds
Spent FCC catalyst (FAU-type) [108]	Y-type zeolite with Al ₂ O ₃ impurities (from FCC)	Spent catalyst calcined at 550 °C to remove coke	Catalytic pyrolysis under induction heating (T = 650 °C, 10 min, N ₂)	HDPE, LDPE, PP	Moderate gas yield (62.4–75.2 wt%), liquid yield < 35.9 wt%, rich in alkenes (C ₉ –C ₄₀)	Lower coke yield (1.32–1.70 wt%), mesoporous structure (147.5 m ² /g)	Weak Brønsted acidity (132.5 µmol/g), limited aromatization capability
Coal fly ash (CFA) [109]	Amorphous aluminosilicate, quartz, mullite, hematite, magnetite	Used as is, no synthesis required	Pyrolysis: T = 723 K; liquid-phase contact mode; feed to catalyst, 2:1	Polymers, mainly PE	Oil yield, 36.2 wt %; reduced wax formation; increased light hydrocarbons (28%)	Null cost, no pre-treatment required, waste utilization	Lower selectivity for light hydrocarbons compared to HX/CFA
HX/CFA (acid zeolite) [109]	HX zeolite (acidified NaX/CFA)	Ion exchange of NaX/CFA with NH ₄ Cl, calcination at 400 °C for 4 h under inert atmosphere	Pyrolysis: T = 723 K; liquid-phase contact mode; feed to catalyst, 2:1	Polymers, mainly PE	Highest oil yield (44 wt %), 70% gasoline-range hydrocarbons (C ₆ –C ₉), lowest degradation energy	Strong acidity, high selectivity for light hydrocarbons, reduced energy needs	Higher char yield, complex synthesis process
Core-shell MCM-22/ZSM-5 [110]	MCM-22 core, ZSM-5 shell, Si/Al ratios varied (20–120)	Hydrothermal synthesis for MCM-22 core, steam-assisted crystallization for ZSM-5 shell, modification	Catalytic cracking of polyethylene at T = 550 °C, fixed-bed reactor	LDPE	Liquid yield, 23.4%; BTEX selectivity, 79.8%; p-xylene proportion, 49.2% in xylenes	Enhanced shape selectivity, hierarchical porosity, reduced coke formation (2.5% yield)	Complex synthesis; sensitivity to Si/Al ratio in shell layer
Magnetic metal-modified HY zeolite (Fe, Co, Ni) [111]	Fe ₂ O ₃ , Co ₂ O ₃ , Ni ₂ O ₃ on HY zeolite (Si/Al = 12)	Incipient wetness impregnation of metal nitrates, calcination at 700 °C, optional H ₂ reduction	Pyrolysis: T = 550 °C, P-atmospheric, N ₂ flow = 60 mL/min, feed–catalyst ratio = 3:2	LDPE	Oil yield, 74.3 wt%; iso-alkane selectivity, 51.6–54.9%; SAF selectivity, 84.3%	Magnetic recovery, no external H ₂ required, tunable acidity, costly material	Catalyst deactivation, regeneration required
Fe-based catalyst [27]	(Mn + Fe)/MgO	One-step impregnation	Catalytic pyrolysis (two-stage reactor: pyrolysis at T = 450–550 °C, catalytic reforming at 600–800 °C)	PP	Carbon nanotubes yield, 235 mg/g; selectivity 92.6%	Uniform distribution of α-(Fe _{1-x} Mn _x) ₂ O ₃ , enhanced carbon solubility	Optimal Mn/Fe ratio required to balance yield and purity

An integrated strategy for upgrading biomass-derived liquids through slurry-phase co-hydroprocessing of pine sawdust pyrolysis oil with Kraft pine lignin using dispersed NiMoS catalysts is presented in [102]. Rather than treating pyrolysis oil or lignin independently, the study demonstrates that co-processing enables synergistic stabilization of reactive intermediates, allowing efficient HDO under comparatively mild conditions (400 °C, 75 bar H₂). In contrast to conventional fixed-bed approaches, the slurry-phase system, including commercial Kraft lignin, pyrolysis oil, and a paraffinic solvent over an unsupported NiMoS promotes contact between catalyst and oxygen-rich feeds, resulting in substantially reduced char formation and enhanced bio-oil yields (Table 14). The NiMoS unsupported catalyst, synthesized hydrothermally, exhibited a mesoporous structure with a surface area of 49.3 m²/g, an average MoS₂ slab length of 6.34 nm, and a stacking number of 3.6. Comparative analysis (Table 15) highlights the key role of co-feeds in suppressing lignin-derived repolymerization. While Kraft lignin alone produced limited bio-oil (26.9 wt%) with significant char formation, co-processing with pyrolysis oil completely eliminated char and increased bio-oil yield to 42.8 wt%, with cycloalkanes as the dominant products.

Table 15. Summary table of key bio-oil compositions and yields. Data from [102].

Feedstock	Conditions	Bio-Oil Yield (wt%)	Main Components (wt%)	Char Yield (wt%)
Kraft lignin (KL)	400 °C, 6 h, NiMoS	26.9	Cycloalkanes (21.6%), alkylbenzenes (3.2%)	14.7
Kraft lignin + Pyrolysis oil (PO)	KL:PO = 1:1, 400 °C, 6 h, NiMoS	42.8	Cycloalkanes (>30%), alkylbenzenes	0
Kraft lignin + 4-Propylguaiaicol (PG)	KL:PG = 1:1, 400 °C, 6 h, NiMoS	56.4	Cycloalkanes (35%), alkylbenzenes (10.5%)	3.7
Kraft lignin	400 °C, 6 h	17.9	Phenolics, oxygenates	54.8

Model compound experiments further clarify mechanistic effects: 4-propylguaiaicol effectively stabilized lignin fragments, reducing char to 3.7 wt%, yet the full pyrolysis oil outperformed individual models, indicating synergistic interactions among its diverse functional groups. This comparison underscores that whole pyrolysis oil provides broader radical-quenching and hydrogen transfer pathways than single-compound surrogates.

The results collectively demonstrate the effectiveness of dispersed NiMoS catalysts for integrated lignin and pyrolysis oil upgrading, particularly in suppressing char and promoting hydrocarbon formation. However, the approach also reveals limitations: extended reaction times lead to oligomerization, and reliance on pyrolysis oil as a co-feed implies prior thermal preprocessing, which constrains claims of fully direct biomass conversion. Despite these challenges, the study provides strong evidence that dispersed sulfide catalysts offer a promising route for intensifying biomass co-processing within biorefinery-relevant solvent systems.

Many studies focus on pyrolysis oils as candidates for co-processing with petroleum-derived feedstocks via a hydroprocessing method [112,113], whereas fewer investigations have addressed the direct co-feeding of raw biomass with HOF under slurry-phase hydroconversion [37,38]. Comparative analysis of these approaches indicates that direct co-processing offers greater integration of biomass conversion and residue upgrading, primarily due to the in situ formation of highly dispersed MoS₂ nanoparticles that promote synergistic reactions under relatively mild conditions.

Studies [37,38] demonstrate that co-processing lignocellulosic (pine and fir sawdust) and algal biomass with vacuum residue using in situ-generated nano-MoS₂ enables higher distillate yields and improved product quality compared with pyrolysis-derived biofuels. Under comparable operating conditions (≈ 425 °C, 7 MPa H₂), sawdust co-feeding achieved 35–40 wt% distillate yields with substantially reduced oxygen and sulfur contents (Table 14), highlighting the superior deoxygenation efficiency of slurry-phase hydroconversion. Increasing biomass content in a mixture with VR up to 32 wt% enhanced overall conversion while suppressing coke formation, underscoring a synergistic interaction between biomass-derived oxygenates and vacuum residue polyaromatics [37]. This behavior contrasts with conventional pyrolysis routes, which require higher temperatures (425 °C vs. >500 °C) and often yield oxygen-rich liquids. The mechanism involved decarboxylation and hydrogenation with cellulose and lignin from sawdust co-feed contributing significantly to light fractions. The process underscores the dual benefit of dispersed nanosized catalysts in hydroconversion: enhancing reaction efficiency while promoting sustainable biomass utilization.

A similar synergistic trend was observed during co-processing of algal biomass (Lake Baikal eutrophication waste) with vacuum residue [101], where in situ-generated MoS₂ nanoparticles (5–150 nm) enabled effective hydrogenation and deoxygenation at low catalyst loadings (0.05 wt% Mo) (Table 14). Compared with lignocellulosic feedstocks, algal biomass at 10–50 wt% mixed with vacuum residue contributed more readily to middle distillate formation, reflecting differences in biochemical composition and reactivity. Algal components contributed to lighter fractions, while nano-MoS₂ facilitated hydrogenation and deoxygenation. This dual waste valorization strategy addresses two critical environmental challenges simultaneously—mitigating harmful algal blooms caused by eutrophication and upgrading heavy petroleum residues. Overall, these studies collectively indicate that dispersed nano-MoS₂ systems outperform conventional biomass pre-conversion strategies by simultaneously reducing hydrogen demand, enhancing distillate selectivity, and enabling dual waste valorization, thereby offering a more integrated and sustainable pathway for bio-petroleum co-processing.

Thus, the last two papers highlight how one catalytic approach (hydroconversion in the presence of a dispersed nanocatalyst) can be adapted for different biomass types while maintaining benefits of waste valorization. Overall, co-processing biomass with HOF demonstrates clear synergistic benefits: hydrogen transfer from petroleum residues stabilizes biomass intermediates, dispersed nanocatalysts improve liquid yields, and operational severities are reduced compared to stand-alone biomass conversion. Nonetheless, challenges remain in catalyst design, feedstock compatibility, and process optimization to balance high conversion with minimized formation of solids.

Analysis of broader trends in biomass integration in catalytic processes highlights hybrid catalyst designs that deliberately bridge homogeneous and heterogeneous regimes. In this context, study [103] introduces a self-separating catalyst combining the advantages of phase transfer catalysts (PTCs) and POMs—TBA₆-P₂W₁₇-SO₃H (TBA = tetrabutyl ammonium)—as a sustainable solution for biomass conversion (Table 14). PTC combines the advantages of both homogeneous and heterogeneous catalytic processes, such as high activity, mild reaction conditions, fast reaction rates, good accessibility to the active sites, and excellent recovery and recycling features, while POMs are a class of discrete anionic metal (V, Mo, W, etc.) oxides with high acidic properties and high thermal stability. TBA₆-P₂W₁₇-SO₃H with particle sizes of 30 to 50 nm strategically addresses a recurring limitation in biomass catalysis—balancing high activity under mild conditions with catalyst recoverability—by exploiting emulsion formation during reaction and spontaneous phase separation afterward. Compared with conventional mineral acids and unmodified

POMs, the catalyst demonstrates exceptional performance across multiple biomass-derived substrates, achieving near-quantitative conversions in fatty acid esterification and fructose dehydration under relatively mild conditions. The reported >98% conversion in oleic acid esterification and 99% yield in fructose-to-5-HMF conversion surpass those of H₂SO₄-based systems while mitigating corrosion and separation issues (Table 16). This comparative advantage underscores the effectiveness of combining PTC accessibility with POM acidity rather than relying on either approach alone.

Table 16. Feedstock processing capabilities of TBA₆-P₂W₁₇-SO₃H catalyst. Data from [103].

Feedstock	Specific Feedstock	Reaction Type	Conditions	Product	Yield (%)	Time
Free fatty Acids	Oleic acid	Esterification with ethanol	70 °C, ethanol	Ethyl oleate	99.2	30 min
	Propionic/butyric/valeric acids	Esterification with methanol	70 °C	Methyl esters	97.1–97.6	20–25 min
Long-chain acids	Lauric acid	Esterification with benzyl alcohol	70 °C	Benzyl laurate	96.6	120 min
	Caproic acid	Esterification with benzyl alcohol	70 °C	Benzyl hexanoate	97.6	120 min
Carbohydrates	Fructose	Dehydration to 5-HMF	100 °C, 1,4-dioxane	5-Hydroxymethylfurfural	99.0	2 h
	Glucose	Dehydration to 5-HMF	100 °C, 1,4-dioxane	5-HMF	57.9	2 h

The catalyst forms an emulsion during the reaction, enhancing substrate–catalyst interaction, and self-separates post-reaction for easy recovery and reuse without loss of activity. It shows broad substrate compatibility, making it highly efficient and sustainable for biodiesel production and other acid-catalyzed reactions. However, its limited efficacy for glucose and polysaccharide-derived substrates reveals an intrinsic limitation when applied to more recalcitrant biomass fractions and underscores the need for further structural tuning—rather than simple acidity enhancement—to broaden applicability. Additionally, potential leaching and long-term stability under repeated cycling remain open questions, indicating that while the catalyst represents a strong proof of concept, its scalability and durability warrant further critical evaluation.

In contrast, study [104] adopts a heterogeneous, thermochemical route, employing bio-synthesized Al₂O₃ nanoparticles as catalysts for pyrolysis of *Melia azedarach* fruit biomass. Al₂O₃ nanoparticles are derived via co-precipitation using AlCl₃ as a precursor and *Phyllanthus emblica* seed extract as a reducing and capping agent (Table 14). Al₂O₃ synthesized via the multistep technique exhibited high purity (26.71% Al, 38.58% O) and a spherical morphology with an average size of 5.7 nm. While the reported improvements in bio-oil yield (64.8% versus 43.24% via non-catalytic pyrolysis) and fuel quality relative to non-catalytic pyrolysis demonstrate the effectiveness of nanoscale oxides in promoting deoxygenation and cracking reactions [104], the principal contribution lies less in catalytic novelty than in process intensification and sustainability. The catalyst was recyclable—five cycles with minimal activity loss (<5% yield drop)—and ensured efficient biomass conversion with minimal side reactions. The use of plant-derived reagents for catalyst synthesis and the moderate catalyst consumption enhance environmental compatibility

and cost-efficiency, though challenges include optimizing catalyst regeneration and scaling production. In the context of hydroconversion, these bio-derived nanoparticles could be dispersed in slurry phases to enhance cracking of biomass co-feeds, synergizing with MoS₂ nanocatalysts for better HDO and reduced external H₂ needs, ultimately lowering system-level CO₂ emissions through integrated waste valorization.

Taken together, these studies illustrate two divergent but complementary trajectories in biomass catalytic conversion: molecularly engineered hybrid catalysts that maximize efficiency under mild conditions and robust inorganic nanocatalysts that enhance thermochemical conversion at scale. Future progress will likely depend on integrating the phase behavior control and selectivity of hybrid systems with the durability and throughput advantages of oxide-based catalysts rather than optimizing either paradigm in isolation.

7.2. Co-Processing Polymer-Derived Feed with Heavy Oil Feedstocks

Waste plastics and tires represent hydrogen-rich co-feeds whose role in slurry-phase hydroconversion extends beyond simple conversion. When introduced into slurry-phase hydroconversion, they act not only as reactants but also as hydrogen donors, mitigating coke formation and improving the cracking efficiency of heavy residues. This dual role positions polymer waste as a valuable co-feed in integrated upgrading strategies. This co-processing not only mitigates plastic waste accumulation but also reduces coke formation and external hydrogen requirements, enhancing process efficiency and sustainability.

Early works [105,106] demonstrated that polyolefin waste (LDPE, HDPE, PP) can effectively serve as a hydrogen-donating catalyst for HOF upgrading (Table 14). Compared with conventional catalytic hydrocracking, these systems operate under moderate conditions (T = 420–450 °C, P (H₂) = 6 MPa) while achieving comparable middle distillate yields (up to 56 wt%) and significantly lower coke formation. In [106], this approach was expanded to packaging materials as the plastic waste. The critical distinction is not yield maximization alone but the reconfiguration of hydrogen supply: polymer-derived hydrogen directly participates in cracking reactions, eliminating the need for additional solvents or catalysts. However, while high HDM and hydrocracking conversions (95–98% and 70–84%) were reported [106], these benefits are contingent on controlled plastic-to-feed ratios and relatively high reaction severity, indicating that hydrogen donation alone cannot fully compensate for limited intrinsic catalyst activity. The process aligns with circular economy principles by integrating polymer-derived materials into fuel production and redefines plastics from being problematic waste to functional reactants, reducing external hydrogen demand by leveraging the hydrogen-donating properties of the polymer.

Complementary strategies have explored in situ hydrogen generation rather than direct hydrogen donation. Study [107] illustrates a new approach of Zn-assisted catalysis by dispersed MoS₂ in hydrothermal liquefaction of waste tires without external H₂ supply. Under subcritical water conditions (360–410 °C, 10–18 MPa), Zn reacts with water to generate in situ H₂ (0.32 MPa) and ZnO, while the commercial 2H-MoS₂ catalyst facilitates hydroprocessing reactions. Compared with polymer co-feeding, Zn-mediated water treatment generates hydrogen internally but at insufficient partial pressures (0.32 MPa) to enable deep heteroatom removal. The process yielded 39–50 wt% of aromatic-rich liquid oil (Table 14). While synergistic Zn-MoS₂ effects improved heavier fractions' cracking and reduced aromatic condensation, nitrogen enrichment and incomplete desulfurization highlight the limitations of low-pressure in situ hydrogen. This comparison underscores a key disadvantage: hydrogen self-sufficiency can reduce external inputs but may constrain upgrading depth unless hydrogen availability is adequately enhanced.

Direct comparisons of polymer types further reveal that co-processing outcomes are influenced by polymer chemistry rather than polymer presence alone. Hydroconversion of

vacuum residue with HDPE over dispersed nano-MoS₂ catalyst consistently outperforms tire rubber in residue reduction and liquid yield as discussed in [26] and reported in [100] (Table 14). Co-feeding the hydroconversion unit (at T = 450 °C, P = 7 MPa) with polymer waste (tire rubber and HDPE) resulted in liquid yield reduction (to 40.9% compared with VR) (Table 17). HDPE addition maintains a moderate liquid yield (47.1 wt%), indicating better conversion efficiency than rubber. Linear polyolefins facilitate hydrogen transfer and cracking, whereas rubber-derived feeds promote cross-linking and residue formation. Notably, blending HDPE with rubber mitigates the negative impact of rubber, suggesting synergistic effects in mixed streams. When benchmarked against conventional supported catalysts (NiMo/ γ -Al₂O₃, ZSM-5), dispersed nano-MoS₂ in slurry systems exhibits superior residue suppression (Table 14), highlighting the importance of catalyst–feed compatibility rather than catalyst acidity alone. Thus, investigations revealed that the type of polymer strongly affects conversion efficiency, and mixed polymer streams require careful feed management or catalyst advancements.

Table 17. Results of hydroconversion of vacuum residue with polymer waste (HDPE and tire rubber) in the presence of dispersed nano-MoS₂. Adapted from [100].

Feedstock Composition	100% VR	33.5% Rubber + 66.5% VR	33.5% HDPE + 66.5% VR	16.75% HDPE + 16.75% Rubber + 66.5% VR
Products (wt %):				
Gas	24.3	24.9	29.8	35.8
Liquid hydrocarbons	48.2	44.9	47.1	40.9
Unconverted residue	27.5	30.2	23.1	23.3
Toluene insolubles	18.87	27.63	21.3	22.5

Beyond hydroconversion, recent studies expand polymer valorization toward broader catalytic systems and advanced heating technologies. Waste-derived catalysts, such as spent FCC catalysts [54] or coal fly ash (CFA)-derived zeolites [109], demonstrate that catalyst circularity complements feedstock circularity. Compared with virgin zeolites, these materials often achieve peak selectivity at lower coke formation (Table 14), reduced energy demand, or improved sustainability metrics. Induction-heated pyrolysis of plastics (HDPE, LDPE, PP) using spent FCC catalysts enabled complete conversion in 10 min at 650 °C, reducing energy consumption by 85% compared to conventional resistive heating. Challenges, like catalyst deactivation and wax formation in thermal pyrolysis, remain [54].

The increasing generation of CFA from coal-fired power plants presents significant environmental challenges. Currently under interest is its application in catalysis and manufacturing catalysts [114]. FA is a fine, powdery by-product generated during the combustion of pulverized coal in thermal power plants. It is primarily composed of SiO₂, Al₂O₃, Fe₂O₃ (up to 70–90% combined), and CaO, MgO, unburned carbon, and trace metals (e.g., Ti, K, Na, heavy metals). Due to its chemical composition and porous structure with low density (~0.5–1.0 g/cm³), it serves as a promising catalyst or catalyst support. The study [109] explores low-cost, waste-derived catalysts—CFA and zeolites synthesized from CFA (NaX/CFA and HX/CFA)—for the pyrolysis of plastic film residues (Table 14). The novel use of CFA as both a direct catalyst and a precursor for zeolite synthesis reduces reliance on expensive conventional catalysts while repurposing hazardous waste. The acidified HX/CFA zeolite exhibited exceptional performance, lowering the process temperature and energy demand, while producing high yields of gasoline-range hydrocarbons (Table 8). Both approaches [54,109] demonstrate how waste-derived catalysts can drive

sustainable catalytic processes by balancing economic viability, energy efficiency, and environmental benefits.

Advanced zeolite architectures and multifunctional catalysts illustrate how selectivity can be deliberately engineered. Core-shell MCM-22/ZSM-5 systems for the catalytic cracking of low-density polyethylene (LDPE) enhance aromatics selectivity and coke resistance relative to conventional ZSM-5 [110], while magnetic Fe₂O₃/HY catalysts enable single-step waste LDPE pyrolysis producing sustainable aviation fuel without external hydrogen or high-pressure hydroisomerization [111] (Table 14). However, for core-shell MCM-22/ZSM-5, challenges, such as coke deposition and structural degradation during regeneration, require further optimization for long-term industrial application. The magnetic properties of Fe₂O₃/HY catalysts facilitate recycling, while coke deposition is remedied through oxidative regeneration, maintaining performance over six cycles, converting non-recyclable plastics into drop-in jet fuel components under mild conditions, offering a scalable route to decarbonize aviation. These approaches contrast with hydroconversion by prioritizing product specificity and operational simplicity over maximal hydrogen utilization. Similarly, Mn-promoted metal catalysts redirect polymer carbon toward high-value nanomaterials (carbon nanotubes (CNTs)) [27], emphasizing that polymer waste need not be confined to fuel pathways alone. These catalysts, particularly those based on Fe, Co, and Ni, enhance metal dispersion, carbon solubility, and thermal stability, with optimized Mn doping (e.g., 5 wt.%) improving CNT yield and selectivity while minimizing amorphous carbon formation. The incorporation of Mn as a promoter improves metal-support interactions and thermal stability, making the process more efficient. Collectively, these studies indicate that co-processing polymers with heavy oil feedstocks is most effective when polymer chemistry, catalyst design, and hydrogen management are aligned. Polyolefin-rich streams combined with nanoscale sulfide catalysts consistently deliver improved hydrogen balance and coke suppression, whereas elastomer-rich feeds require either dilution or tailored catalysts to avoid residue accumulation. While co-processing can reduce external hydrogen demand, upgrading depth remains sensitive to reaction severity and target product slate. Thus, processing of polymer-derived feedstocks is optimized through co-processing with HOF, which offers multiple benefits, including an improved hydrogen balance, coke suppression, and the valorization of mixed waste streams. Figure 12 illustrates general flow diagram for integration of biomass or polymer waste streams into HOF hydroconversion. This co-processing strategy illustrates a pathway toward process optimization, waste valorization, and reduced carbon intensity in petroleum refining. Although co-processing can reduce external hydrogen demand in some configurations, HOF upgrading often remains hydrogen-intensive depending on severity and target product slate. Efficiency of conversion is strongly dictated by the choice of polymer-derived waste and catalyst system, with polyolefin-rich streams and nanosized sulfide catalysts showing particular promise.

Beyond hydroconversion, emerging catalytic technologies—such as waste-derived zeolites, magnetic hybrids, and promoted nanocatalysts—demonstrate potential for integrating waste plastics into broader sustainable value chains. These systems enhance selectivity, catalyst recyclability, and operation under milder conditions. Furthermore, advances in polymer valorization have expanded the suite of available catalytic pathways to include zeolite-based cracking, induction-heated pyrolysis, and the use of waste-derived catalysts. These methods complement hydroconversion by diversifying the product spectrum toward aromatics, jet fuels, and carbon nanomaterials, thereby embedding circular economy principles into catalyst and feedstock design. Realizing the full sustainability potential for the technologies under discussion requires deeper mechanistic understanding,

optimized catalyst formulations, and rigorous techno-economic assessments to ensure scalability, efficiency, and system-level environmental benefits.

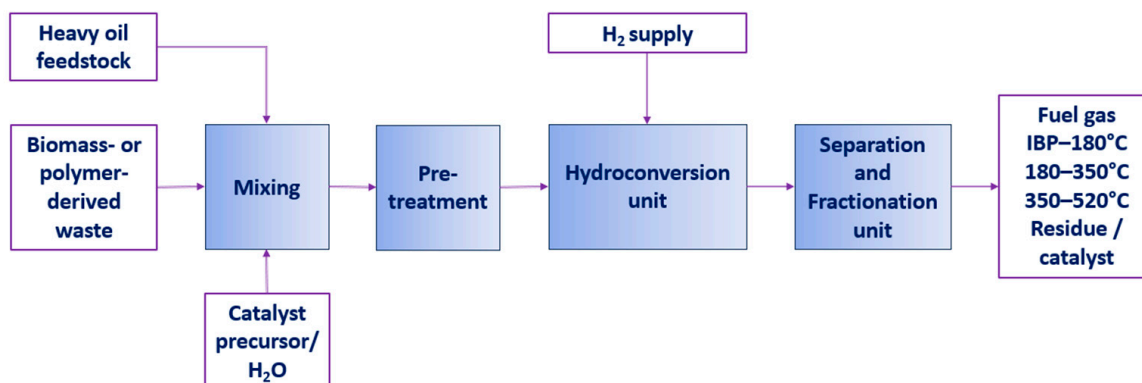


Figure 12. Scheme of the co-processing strategy, illustrating the integration of biomass and polymer waste streams into HOF hydroconversion.

8. Conclusions

Catalytic hydroconversion and co-processing of complex feedstocks (heavy oil residues, plastics, tires, and biomass) directly supports oil downstream refining strategies from a system-level perspective, aligns process optimization with the principles of the circular carbon economy, and provides a technically viable pathway to convert low-value, carbon-rich materials into higher-value distillates, while suppressing coke formation and improving hydrogen utilization relative to conventional residue upgrading routes.

Advances in dispersed and multifunctional nanocatalysts enable higher conversion efficiency, greater feedstock flexibility, and operation under milder conditions, translating into improved product slates and reduced energy intensity—key levers for lowering refinery-level greenhouse gas emissions.

System-level analysis of the hydroconversion-based refining scheme reveals that process-level improvements alone are insufficient to guarantee sustainability gains. Hydrogen demand and sourcing emerge as dominant drivers of both economic and environmental performance, often outweighing incremental gains achieved through yield optimization.

Illustrative life cycle and techno-economic assessments indicate that advanced catalytic upgrading of heavy oil residues can achieve net operating benefits on the order of USD ~2–3 per barrel under current conditions, while reducing system-wide greenhouse gas emissions by up to ~10–15%, depending on hydrogen supply pathways. However, it is important to note that market feedback effects and infrastructure constraints may limit the realizable benefits of yield-driven optimization in practice. Without consideration of product demand elasticity, capital investment requirements, and hydrogen logistics, theoretical gains may not translate into practical advantages. From a circular carbon economy perspective, integrating waste- and bio-derived feedstocks into refinery upgrading schemes enhances carbon reuse and recycling, particularly when coupled with low-carbon hydrogen and carbon capture technologies. Future research and deployment efforts should prioritize closer coupling of catalyst design with refinery-wide process modeling and validation, systematic evaluation of low-carbon hydrogen integration, and unified assessments that link laboratory-scale performance with industrial, economic, and environmental realities.

Notably, our analysis focuses on operating expenditures and does not account for the significant capital expenditures required for retrofitting refineries, implementing carbon capture facilities, or building electrolyzers for green hydrogen production. From an operational perspective, the results indicate that refiners with high residue conversion capacity can reduce both emissions intensity and improve economics, provided that carbon

capture and hydrogen sourcing are optimized. Due to the exclusion of capital expenditure and existing infrastructure constraints, future work should address these investment barriers (capital expenditures, hydrogen logistics, dynamic market feedbacks). Policy instruments, such as carbon pricing and incentives for low-carbon hydrogen, are essential to bridge the cost gap for advanced scenarios, transitioning them from theoretically viable to economically competitive.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en19020413/s1>, Table S1: Mass balance of hydroconversion process with recycle; Table S2: Characteristics of hydroconversion products; Table S3: Emission factors (gCO₂e/MJ) used in PRELIM model; Table S4: Properties for crude assay used in PRELIM model; Table S5: Results for coking-refinery, “gray” H₂ (via PRELIM); Table S6: Results for hydroconversion-refinery, “gray” H₂ (via PRELIM); Table S7: Results for hydroconversion-refinery, “blue” H₂; Table S8: Results for hydroconversion-refinery, “green” H₂; Table S9: Process input intensities per barrel of crude; Table S10: Energy cost breakdown; Table S11: Netback analysis; Table S12: Emissions and abatement economics; Table S13: Consolidated cost and value overview. References [4–7,12,86,93–98] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, M.K. and A.M.; methodology, M.K., A.M. and M.B.; software, M.K.; validation, M.K.; resources, M.K., A.M. and M.O.; writing—original draft preparation, M.K., A.M. and M.O.; writing—review and editing, A.M., M.B. and A.A.-Q.; visualization, M.K.; supervision, A.M., M.O. and A.A.-Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: This manuscript serves as an analytical review, utilizing the literature for analysis and producing new assessment data. The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Authors Malkan Kadiyeva, Anton Manakhov and Maxim Orlov are employed by the company Aramco Innovations LLC. Authors Mustafa Babiker and Abdulaziz Al-Qasim are employed by the company Saudi Aramco. All authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

AR	atmospheric residue
API	American Petroleum Institute
bb1	barrel
bb1/d	barrels per day
BTEX	benzene, toluene, ethylbenzene, xylenes
BTX	benzene, toluene, xylenes
CCS	carbon capture and storage
CFA	coal fly ash
CFP	catalytic fast pyrolysis
CO ₂ -eq	carbon dioxide equivalent
CNR	catalytic naphtha reformer
CNT	carbon nanotube
CTAB	cetyltrimethyl ammonium bromide
CTU	comparative toxic unit
CTUcancer	comparative toxic unit for humans (cancer)
CTUeco	comparative toxic unit for ecosystems
CTUoncancer	comparative toxic unit for humans (non-cancer)

EST	Eni Slurry Technology
FCC	fluid catalytic cracking
GHGs	greenhouse gases
GO	gas oil
GREET	Greenhouse gases, Regulated Emissions, and Energy use in Technologies
GTL	gas to liquid
GWP	global warming potential
HAD	hydrodeasphaltenization
HDM	hydrodemetallization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HDPE	high-density polyethylene
HFO	heavy fuel oil
HOF	heavy oil feedstock
HTL	hydrothermal liquefaction
HY	faujasite zeolite (Y zeolite)
IBP	initial boiling point
ILs	ionic liquids
ISO	International Organization for Standardization
LCA	life cycle assessment
LCIA	life cycle impact assessment
LDPE	low-density polyethylene
LHSV	liquid hourly space velocity
LPG	liquefied petroleum gas
MENA	Middle East and North Africa
ML	machine learning
PM2.5	particulate matter (2.5 µm or smaller)
POM	polyoxometalate
PP	polypropylene
ppm	parts per million
PRELIM	Petroleum Refinery Life Cycle Inventory Model
PS	polystyrene
PTC	phase transfer catalyst
R&D	research and development
SAF	sustainable aviation fuel
SAPO-11	silicoaluminophosphate-11
SMR	steam methane reforming
TBA	tetrabutyl ammonium
ULSD	ultra-low-sulfur diesel
UN SDGs	United Nations Sustainable Development Goals
VGO	vacuum gas oil
VR	vacuum residue
wt%	weight percent
ZSM-5	Zeolite Socony Mobil-5

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