

Review

Sustainable Aviation Fuel (SAF): A Mini-Review of Advances in Catalytic Pathways Using Lipid-Based Feedstocks and Plastic Waste

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Abstract

The fast growth of the aviation sector has intensified the need for sustainable alternatives to conventional fossil-based jet fuels. Sustainable aviation fuel (SAF) has emerged as one of the most promising strategies to reduce greenhouse gas emissions while remaining compatible with existing aviation infrastructure. Among the different feedstocks explored for SAF production, lipid-based resources such as vegetable oils, animal fats, and waste cooking oil have received considerable attention due to their high content of triglycerides and free fatty acids. Additionally, the increasing generation of plastic waste has stimulated interest in its catalytic valorization as an alternative carbon source for hydrocarbon fuel production. This mini-review summarizes recent advances in catalytic pathways for producing jet-fuel-range hydrocarbons (C_8 – C_{16}) from lipid-based feedstocks and polyolefins. Particular emphasis is given on hydroprocessing reactions, including deoxygenation, cracking, and isomerization, which are essential to adjust fuel properties and meet aviation specifications. In this context, bifunctional heterogeneous catalysts play a crucial role, particularly regarding the influence of the metal phase and catalyst support on catalytic activity and stability. Different support classes, including metal oxides, mesoporous silicas, and zeolites, are discussed. Carbon-based materials, especially carbon nanotubes (CNT), are also highlighted due to their outstanding chemical and textural properties.

Keywords: aviation fuel; hydroprocessing; lipid-feedstock upgrade; plastic waste valorization; bifunctional catalysts; carbon-based materials

1. Introduction

The transport sector plays a significant role in the global dynamics of modern societies, directly enabling the movement of people, goods, and services. Aviation, in particular, has undergone substantial market expansion over the past two decades, establishing itself as one of the most relevant economic activities worldwide. This growth has been accompanied by notable socioeconomic impacts, primarily driven by the rise in middle-class purchasing power and the reduction in airfares. In 2023, airlines around the world transported approximately 4.4 billion passengers and more than 61 million tons of cargo. These numbers are expected to grow significantly, with forecasts indicating that global air travel could reach close to 10 billion passengers by 2050 [1].

Despite the growth of aviation and the various benefits it brings to society, environmental concerns related to this activity require careful attention. While aviation facilitates



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global connectivity, it also contributes significantly to the emission of greenhouse gases (GHG) and other pollutants, primarily due to the combustion of petroleum-based aviation fuels [2]. Among the main emissions are carbon dioxide (CO₂), nitrogen oxides (NO_x), sulfates, particulate matter, and water vapor, the latter of which contributes to the formation of contrails [3]. Currently, aviation accounts for approximately 2.5% of total anthropogenic GHG worldwide. In 2023, global jet fuel consumption reached around 325 million m³, and projections indicate an average annual growth rate of about 3% in the next few years. If this trend continues, fuel demand could double by 2050. In this context, developing and implementing effective strategies to reduce the carbon footprint of aviation becomes increasingly critical [4].

The International Air Transport Association (IATA) has set a target to reduce CO₂ emissions by 50% in 2050, using 2005 levels as a baseline. Although advancements in aircraft design over recent decades—driven by developments in aviation engineering—have improved fuel efficiency, they are still not sufficient to fully decarbonize the sector [5,6]. In this context, sustainable aviation fuel (SAF), also known as bio-jet fuel, is one of the most promising alternatives to achieve the required CO₂ reduction target defined by IATA [5,7]. Biofuels represent a closed carbon cycle, as part of the CO₂ released into the atmosphere is neutralized by the CO₂ absorbed during the growth of the plants used to produce the fuel [8].

SAF can mainly be produced from biomass and waste, including feedstock rich in lipids, such as vegetable oils, animal fats, and waste cooking oil (WCO). These sources are particularly attractive for sustainable fuel production due to their high concentrations of triglycerides and free fatty acids, typically composed of carbon chains ranging from C₁₆ to C₂₂ [9]. Through catalytic processing, these long-chain molecules can be converted into hydrocarbons within the C₈ to C₁₆ range, which corresponds to the carbon distribution required for jet fuel. The use of lipid-based biomass thus represents a key strategy for achieving climate change mitigation targets by enabling the production of drop-in fuels compatible with existing aviation infrastructure [5,10,11].

In addition to lipid-based feedstocks, the limited availability of WCO and other biogenic resources poses a challenge for meeting the long-term demand for SAF at an industrial scale. In this context, the valorization of other feedstocks, particularly plastic residues, emerges as a complementary and strategic route for aviation fuel production. Plastic wastes are composed predominantly of carbon and hydrogen, exhibit high energy density, and are generated in large quantities worldwide, making them attractive alternative feedstocks for hydrocarbon fuel production [12,13]. Their catalytic conversion into jet-fuel-range hydrocarbons mainly addresses critical environmental issues associated with plastic waste accumulation and disposal [14]. Therefore, extending the scope of this work to include the catalytic upgrading of plastic residues aligns with the dual objective of producing C₈–C₁₆ hydrocarbons while promoting circular economy principles and environmentally responsible waste management.

From a process perspective, both lipid-based feedstock and plastic residues require catalytic upgrading to produce fuels that meet aviation specifications. Developing an efficient, low-cost, and effective catalytic system is a key focus for producing aviation fuel from renewable sources. Currently, lipid-derived sources cannot be used directly as drop-in fuels due to their high oxygen content, which lowers the high heating value (HHV) [15]. A higher HHV is desirable, as it improves fuel combustion efficiency. In addition, the high oxygen content leads to other drawbacks such as low chemical stability, high viscosity, strong acidity, and corrosiveness, which present challenges for storage and transportation [15–17]. To overcome these limitations, additional upgrading reactions, such as cracking and isomerization, are required to improve the physicochemical properties of

the fuel and adjust the carbon chain length to meet jet fuel specifications [18]. Similarly, plastic waste must undergo controlled catalytic conversion to adjust the hydrocarbon chain length, promote isomerization, and adjust fuel properties [19,20]. Although lipid-based feedstocks and plastic residues differ in structure, they share important similarities in their catalytic upgrading pathways. For triglycerides and fatty acids, conversion into jet-fuel-range hydrocarbons involves oxygen removal via hydrodeoxygenation, followed by C–C bond cleavage to adjust the carbon chain length. In contrast, plastics such as polyolefins are already oxygen-free; however, their conversion into C₈–C₁₆ hydrocarbons relies primarily on hydrogenolysis and hydrocracking, which also involve C–C bond cleavage. Despite these compositional differences, both systems depend on similar catalytic functionalities, particularly the balance between metal and acid sites, to achieve the desired product distribution.

Several catalysts have been investigated to improve selectivity toward hydrocarbons found in SAF, including transition metals (Ni, Co, Mo, and Fe) and noble metals (Pt, Pd, and Ru) supported on materials such as zeolites, oxides, mesoporous silicas, and carbon materials [9,21–25]. However, their low selectivity toward SAF-range fractions, high operational costs, and fast deactivation make their use less advantageous. Moreover, the high acidity of some of these materials can promote the overcracking of the substrate into small fractions, such as gasoline. On the other hand, the development of efficient bifunctional catalysts capable of balancing metal and acid functionalities has emerged as a key strategy to enhance catalytic performance and improve selectivity toward jet-fuel-range hydrocarbons. Given these limitations, carbon-based materials such as carbon nanotubes (CNT) have been proposed as alternative catalytic supports [26–30]. CNT offers a high surface area and excellent thermal and chemical stability, allowing good dispersion of active metal phases [31]. In addition, the ease of introducing oxygenated groups on its surface, enhancing CNT's acidity, makes these materials an interesting choice to use for cracking and isomerization reactions [32]. These features contribute to higher selectivity toward jet fuel-range hydrocarbons, improved resistance to deactivation, and the potential to reduce operational costs.

In this context, this mini-review summarizes recent advances in catalytic pathways for SAF production from lipid-based feedstocks and plastic waste, with particular emphasis on hydroprocessing reactions and the design of bifunctional heterogeneous catalysts, focusing on advances in the use and catalytic performance of carbon-based materials in the conversion of lipid feedstocks and polyolefins. This study provides a comparative analysis of both routes, highlighting common catalytic challenges and opportunities. It further emphasizes the role of carbon-based materials as catalyst supports and discusses how their properties influence catalytic performance across different reaction systems.

2. Sustainable Aviation Fuel: An Alternative Solution to the Energy Transition in Aviation

The aviation sector faces major challenges in reducing its CO₂ emissions. Air transport depends almost entirely on liquid hydrocarbon fuels because of their high energy content and storage stability. Unlike ground transport, the electrification of aviation is still far from being feasible for commercial aircraft [33]. As a result, aviation remains strongly dependent on fossil jet fuels, and its carbon footprint continues to grow with the increasing global demand for air travel [10,33,34].

In response to this challenge, international aviation governance bodies have established increasingly stringent environmental targets. The International Civil Aviation Organization (ICAO) has introduced the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA), a global program aiming to achieve carbon-neutral growth

from 2020 onwards [35]. The program encourages airlines to compensate for part of their CO₂ emissions and to increase the use of cleaner energy sources. In addition, IATA has endorsed an even more ambitious objective: a reduction in CO₂ emissions of 50% by 2050, compared to 2005 levels [4,35,36]. In this scenario, achieving any goal requires a systemic transformation of the aviation energy outlook.

Current projections by IATA indicate different contributions to decrease carbon emissions. The most promising one is the use of SAF, corresponding to 65% of the total emissions reduction. Moreover, new aircraft technologies are expected to contribute around 13%, operational and infrastructural improvements about 3%, and carbon offsets and captures approximately 19% (Figure 1) [33,37,38]. These numbers show that SAF is expected to provide the largest contribution to reducing aviation emissions, highlighting its central role in the sector's decarbonization strategy.

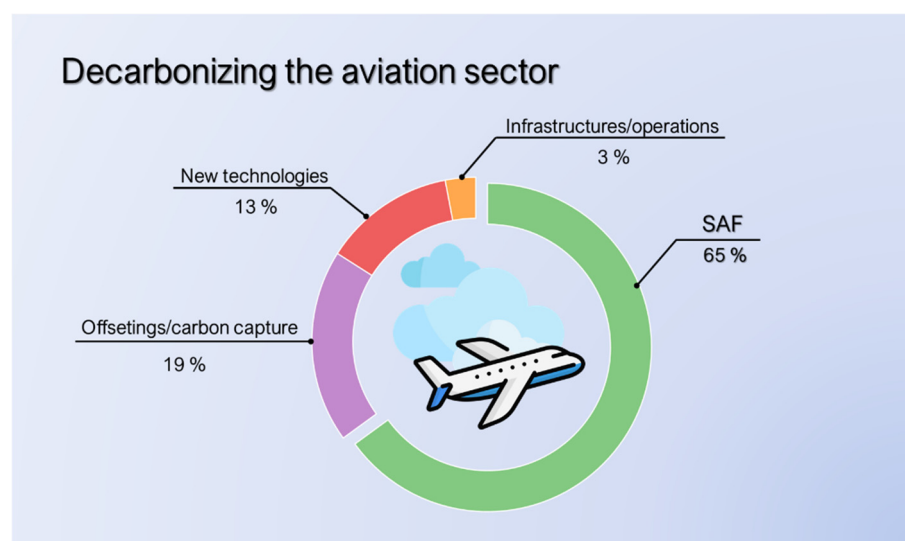


Figure 1. Contributions of the strategic possibilities to achieve the net-zero targets by 2050.

SAF has a hydrocarbon composition similar to fossil-based jet fuel, which leads to comparable exhaust emission profiles [38]. Currently, it is approved for use in blends of up to 50% with conventional jet fuel. However, there is still no technology commercially certified for producing 100% synthetic drop-in fuels (i.e., fuels that are fully compatible with existing aircraft engines and fuel distribution systems) [39].

SAF is composed of the same hydrocarbon range found in conventional jet fuel, typically from C₈ to C₁₆ [40]. Its composition is predominantly *n*-paraffins and iso-paraffins (65–75%), followed by aromatic compounds (10–25%), cycloalkanes (10–20%), and a small fraction of alkenes (<1%) [40]. It can be produced by a diverse number of renewable sources, such as oils and grease, waste cooking oil, algae oil, alcohols, urban waste, lignocellulosic biomass, and even CO₂ capture [41–43]. SAF can be considered sustainable as long as the feedstock does not compete with food crops or agricultural outputs, or it does not require additional resources such as water and land expansion. More broadly, SAF avoids environmental impacts such as deforestation, loss of soil productivity, and decline in biodiversity. Different from fossil fuels, which introduce new CO₂ into the atmosphere by releasing carbon, SAF operate within a closed carbon cycle: the CO₂ emitted during combustion is approximately equal to the amount previously absorbed by the biomass utilized as feedstock during its growth [33,36].

One important aspect of SAF is the set of physicochemical properties defined by the American Society for Testing and Materials (ASTM) standards. First, ASTM D7566—standard specification for aviation turbine fuel containing synthesized hydrocarbons—establishes the re-

quirements for synthetic aviation fuels produced from alternative and renewable feedstocks prior to blending [44]. Once the synthesized fuel is blended with conventional jet fuel within the approved limits, the final mixture must also comply with ASTM D1655—Standard Specification for Aviation Turbine Fuels—which defines the specifications for Jet A and Jet A-1 fuels currently approved for commercial aviation use [45]. These standards ensure that SAF blends meet the same performance and safety criteria as conventional petroleum-derived jet fuels. The key parameters are detailed in Table 1.

Table 1. Some parameters defined by the ASTM D7566 and D1655.

Parameter	Value
Density at 15 °C	0.775–0.84
Freezing Point (°C)	Max. −47
Flash Point (°C)	Min. 38
Viscosity at −20 °C (mm ² s ^{−1})	Max 8.0
HHV (MJ kg ^{−1})	42.8
Aromatic Content (vol. %)	8–25
Acid Number (mg _{KOH} g ^{−1} _{fuel})	0.1

To produce SAF that meets the specifications required for commercial aviation fuels, several technological pathways can be employed using a wide range of renewable feedstocks. These feedstocks are commonly classified into different generations according to their origin, sustainability profile, and impact on land use and food supply. Each generation is associated with specific conversion technologies and yields distinct fuel properties, making the selection of feedstock a critical factor in both the technical and environmental performance of jet fuel from non-petrochemical sources. Figure 2 illustrates the potential sources that can be used to obtain this biofuel. Each generation is also associated with a specific type of biofuel. For example, first-generation biomass is converted into first-generation biofuels, and this pattern continues across subsequent generations. First-generation feedstocks consist of edible crops rich in oils, sugars, and starches, such as vegetable oils, wheat, maize, and other agricultural products. Although the easy accessibility, these kinds of sources compete largely with the food supply. Second-generation feedstocks are obtained from non-edible lignocellulosic biomass, including agricultural residues, non-food crops, and municipal or industrial wastes. Because they originate from residues, these feedstocks offer the advantage of not competing with the food supply. However, their use is constrained by significant drawbacks, including fluctuations in feedstock quality and limited availability. Third-generation feedstocks are derived from macro- and microalgae, which represent emerging sources that do not compete with arable land or freshwater resources. Nevertheless, they require a high energy supply. Finally, fourth-generation feedstocks involve advanced pathways that include the use of unconventional biomass and the capture of atmospheric CO₂ through carbon capture technologies [15,41,46].

Each feedstock type requires a specific technological pathway to convert it into the desired SAF hydrocarbon range. Currently, five routes enclosing nine production technologies have been approved by ASTM, in independent or co-processing units. The different routes are summarized in Table 2. These pathways differ in terms of feedstock compatibility, conversion chemistry, fuel yield, and sustainability performance, and they define the allowable blending limits and final fuel specifications.

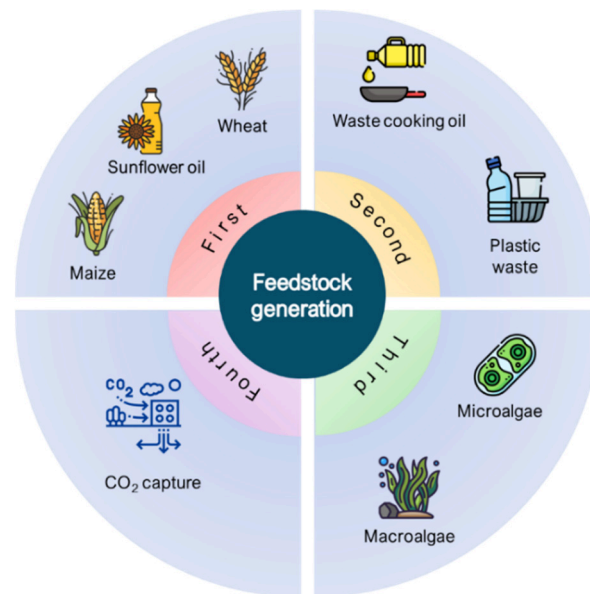


Figure 2. Types of feedstocks defined by generation.

Table 2. All technological routes to produce SAF are approved by the ASTM.

Route	ASTM	Technology	Possible Feedstocks	Blending Limits (%)
Oil-to-jet	D 7566	HEFA-SPK	Vegetable oils, animal fats, waste cooking oil	50
	D 7566	HC-HEFA-SPK	Algae	10
	D 7566	CHJ-SPK	Vegetable oils, animal fats, waste cooking oil	50
Gas-to-jet	D 7566	FT-SPK	Biomass, urban residues, natural gas, CO ₂ (associated with reverse water–gas shift; e-fuel production)	50
	D 7566	FT-SPK+A	Biomass, urban residues, natural gas, CO ₂ (associated with reverse water–gas shift; e-fuel production)	50
Alcohol-to-jet	D 7566	AtJ-SPK	Ethanol, isobutanol, and isobutene are produced from biomass or by converting the biochemical composition of gases	30
	D 7566	AtJ-SKA	Light alcohols are produced from biomass or by converting the biochemical composition of gases	50
Sugar-to-jet	D 7566	SIP-SPK	Sugar, starch, or lignocellulosic sugars	10
Co-processing	D 1655	Co-processing	Lipid sources, hydrocarbons from Fischer–Tropsch or hydroprocessed biomass	5–10

2.1. Oil-to-Jet

The oil-to-jet pathway encloses technologies that convert lipid-based feedstocks, such as vegetable oils, animal fats, waste cooking oil, and algae, into sustainable aviation fuel through hydroprocessing and related upgrading steps. In the hydroprocessed esters and fatty acids (HEFA)—synthetic paraffinic kerosene (SPK), lipid sources are hydrotreated into SAF. The resulting fuel can be blended with conventional jet fuel in concentrations of up to 50%. This process provides superior energy conversion efficiency among the

other pathways but is limited to oil feedstocks only [34]. A similar approach is used in the SPK from hydrocarbons obtained by HEFA (HC-HEFA-SPK), which applies the same hydrotreatment principle, but the feedstock target is mainly algae. As discussed above, algae have a high growth rate and do not compete with food. On the other hand, it can only be blended with petroleum-based aviation fuel up to 10% [40]. SPK from catalytic hydrothermolysis (CHJ-SPK) uses a hydrothermal process to convert oils and fats into hydrocarbons under high temperature and pressure, followed by upgrading through hydrotreatment. This pathway produces hydrocarbons with a molecular composition and chemical properties nearly identical to those found in petroleum-derived jet fuel, which ensures full compatibility with existing aviation fuel infrastructure. However, the process is limited by its high energy consumption due to the severe operating conditions required for hydrothermal conversion [47].

2.2. Gas-to-Jet

The gas-to-jet route is based on the conversion of biomass, wastes, captured CO₂, or other carbon-rich material into syngas (CO+H₂), which is subsequently transformed into SAF hydrocarbons via Fischer–Tropsch (FT) synthesis and downstream upgrading. The production of SPK by hydroprocessing of Fischer–Tropsch products (FT-SPK) converts the referred feedstocks, which are then catalytically upgraded into synthetic kerosene, approved for blending up to 50% [48]. Technologies based on atmospheric CO₂ capture coupled with reverse water–gas shift reactions are gaining increasing attention as a potential route for Fischer–Tropsch-based SAF production. However, they are not yet approved by ASTM (e-fuel production) [47]. In this case, CO₂ reacts with H₂ (produced from water electrolysis), producing CO and water. The CO produced is then hydrogenated, producing liquid fuels by Fischer–Tropsch synthesis [49]. Another variation in this route, known as SPK by Fischer–Tropsch with alkylation of light aromatics from non-petroleum sources (FT-SPK+A), incorporates an additional step to produce synthetic aromatics, improving compatibility with current aviation fuel systems [46]. Despite their ability to produce high-quality SPK, FT-SPK, and FT-SPK+A, they are limited by high capital costs, complex process configurations, energy-intensive conversion steps, and the need for blending with conventional jet fuel due to low aromatic content [47].

2.3. Alcohol-to-Jet

The alcohol-to-jet pathway (ATJ-SPK) involves the transformation of bio-derived alcohols, such as ethanol and isobutanol, produced from sugars or lignocellulosic biomass into SAF-range hydrocarbons through dehydration, oligomerization, and hydrotreatment processes. This route also includes the production of synthetic aromatic kerosene from ATJ (ATJ-SKA) to meet the minimum aromatic content required in aviation fuels [50]. Although the ATJ-SPK and ATJ-SKA pathways provide synthetic routes to produce paraffinic and aromatic hydrocarbons from bio-derived alcohols, their commercialization is limited by high production costs, restricted feedstock availability (mainly ethanol and isobutanol), energy-intensive conversion steps, and low overall fuel yield [51].

2.4. Sugar-to-Jet

The direct sugars-to-hydrocarbons pathway by synthesized iso-paraffins (SIP-SPK) employs engineered microorganisms to convert sugars into renewable iso-paraffinic hydrocarbons, which are subsequently upgraded to meet aviation specifications. These iso-paraffinic compounds exhibit higher energy density compared to ATJ-derived fuels, lower pollutant emissions, and combustion behavior similar to that of conventional jet fuel. Nevertheless, this pathway faces several limitations, including a product with high viscosity and poor combustion performance in turbine engines, depending on costly feedstocks,

high energy demand, and the lowest allowable blending ratio among ASTM-approved pathways, currently limited to 10% [52,53].

2.5. Co-Processing

Finally, co-processing technologies allow renewable feedstocks such as lipid sources and treated biomass to be processed together with petroleum streams in existing refinery units, resulting in partially renewable jet fuel with blending limits ranging from 5 to 10%. This pathway enables the production of lower-carbon-intensity fuels, leverages existing petroleum refinery infrastructure, and offers flexibility to process a wide range of biogenic feedstocks. Yet, co-processing requires efficient oxygen removal and is associated with operational challenges related to feedstock variability, blend ratios, and product property fluctuations, which can impact process stability and fuel quality [47,54].

Among all ASTM-approved pathways, the HEFA route currently stands out as the most commercially mature and widely deployed option for SAF production [43]. Unlike other pathways that are still limited by low technology readiness levels, high capital costs, or strict feedstock constraints, the HEFA process benefits from existing refinery infrastructure, scalable feedstock supply chains, and proven compatibility with aviation fuel specifications [55]. As a result, HEFA-derived fuels account for the majority of global SAF production and are projected to remain the dominant pathway in the short-to-medium term.

Given its industrial relevance and strategic role in aviation decarbonization, the hydroprocessing of lipid-based feedstocks to produce SAF-range hydrocarbons has gained significant attention from both the scientific community and the aviation fuel industry. A wide range of renewable lipids can be used as feedstocks, particularly waste cooking oil classified as a second-generation resource. However, several challenges remain to ensure their suitability for aviation use, including the need to meet strict physicochemical requirements, reduce production costs, and improve overall process efficiency.

Moreover, the HEFA pathway has emerged as the most strategically relevant route for short-term implementation of SAF, as it is currently the only production technology operating on a commercial scale. Its implementation has been supported by regulatory policies and market incentives favoring drop-in fuels compatible with existing aircraft engines and fuel distribution infrastructure. As airlines and fuel suppliers move toward established decarbonization targets, understanding the HEFA process becomes essential to assessing its technical maturity, economic viability, and potential for large-scale commercialization. The next section provides a detailed analysis of this pathway, including conversion mechanisms and upgrading strategies required to meet aviation fuel specifications.

3. Hydroprocessing of Lipid-Based Sources

As discussed in the previous section, lipid-based feedstocks can be hydroprocessed through different technological oil-to-jet routes for the production of SAF. A fundamental aspect in understanding the conversion of these materials into liquid hydrocarbons is their chemical composition. Most lipid feedstocks, such as vegetable oils, animal fats, and waste cooking oil (WCO), are predominantly composed of triacylglycerols, classified as simple or neutral lipids, in which a glycerol backbone is esterified with three fatty acid chains (Figure 3). Free fatty acids are also present, especially in thermally degraded or previously processed sources [56].

The carbon chain presented in these lipid structures typically ranges from 14 to 22 carbon atoms [9]. Filho et al. [57] investigated the fatty acid composition of soybean oil, palm oil, and WCO. The results demonstrated that soybean oil and WCO are predominantly composed of C₁₈ fatty acids, mainly linoleic and oleic acids, whereas palm oil is rich in C₁₆ fatty acids, primarily palmitic acid. Minor fractions of other fatty acids ranging from C₁₂ to

C₂₄ were also identified. This carbon chain distribution closely matches the hydrocarbon range required for jet fuel production, reinforcing the suitability of lipid-based feedstocks as promising precursors for the generation of liquid transportation fuels.

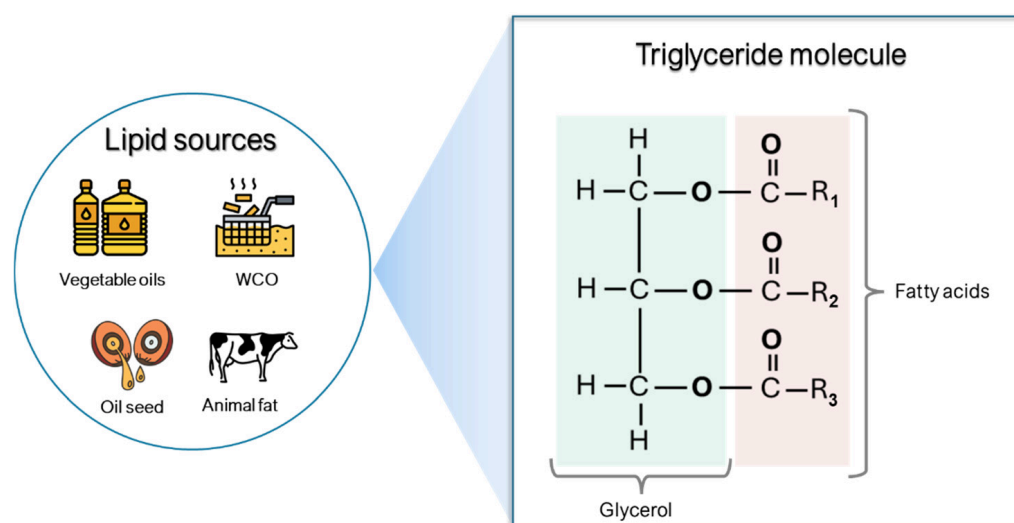


Figure 3. Structure of the triglyceride molecules present in lipid sources.

The use of oils and fats for biodiesel production via transesterification reactions has been extensively studied over the past decade [58,59]. However, the transesterification route leads to the formation of oxygenated esters (fatty acid alkyl esters), decreasing some physicochemical properties required for fuels. In this scenario, hydrotreated vegetable oil processes have gained significant attention for the production of green diesel, as the removal of oxygen from triglycerides and free fatty acids results in hydrocarbons with superior fuel properties [60]. This hydroprocessing approach can also be targeted at the aviation fuel range, in which case the process is referred to as HEFA, enabling the production of sustainable SAF compliant with ASTM specifications.

Hydrotreating lipid-based sources plays an important role in the final quality parameters of SAF. The removal of heteroatoms—mainly oxygen—enhances the chemical stability, decreases the viscosity, the acidity, and the corrosiveness [15,18]. Another critical property is the HHV, which is directly associated with the degree of deoxygenation. Since oxygenated compounds exhibit lower energy density, their conversion into fully deoxygenated hydrocarbons significantly increases the HHV, resulting in a fuel with greater combustion efficiency and improved overall energy performance [61].

Since oils and fats cannot be directly used as fuels, these feedstocks must undergo the HEFA processing stages to meet the fuel quality and commercialization parameters previously described (Table 1). This SAF production route comprises several steps, as illustrated in Figure 4. Initially, lipid feedstock is pretreated to remove any impurities (e.g., solids, phospholipids, sulfur, water). After that, the pretreated oil is subjected to hydrotreatment for the removal of heteroatoms, mainly oxygen. Deoxygenation reactions occur in the presence of hydrogen and catalysts, producing deoxygenated compounds that are subsequently directed to the cracking and isomerization stages, where hydrogen and catalysts are also employed [18].

The cracking step is essential to adjust the liquid hydrocarbon fraction within the carbon number range required for jet fuel, since the sole deoxygenation of triglycerides typically yields products within the diesel range (C₁₅–C₂₂). Isomerization reactions, in turn, are required to introduce branching into the hydrocarbon chains, thereby improving the freezing point and cold-flow properties of the renewable aviation fuel [11].

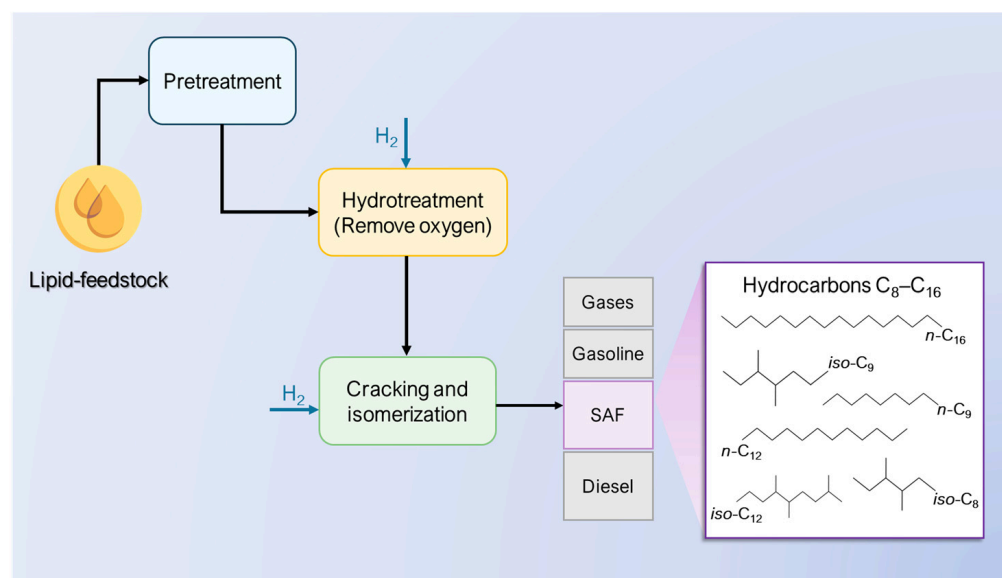


Figure 4. Simplified schematic of the HEFA route to the conversion of lipid feedstock into liquid fuels, focusing on SAF products.

A typical HEFA process results in a mixture of liquid hydrocarbons ranging from the gasoline to the diesel fractions, as well as gas products (C_1 – C_4 compounds). Ideally, the process should maximize the production of hydrocarbons within the C_8 – C_{16} range. Therefore, careful control of the cracking reactions is essential to prevent excessive chain scission, which would otherwise increase the formation of lighter hydrocarbons (gasoline and gases) and reduce overall liquid yield. Thus, the balance between deoxygenation, cracking, and isomerization reactions must be optimized to achieve the desired fuel properties while maintaining high conversion efficiency.

3.1. Deoxygenation

Deoxygenation reactions are a well-established reaction in petrochemical refineries, which are used to remove the oxygen content in petroleum derivatives [62]. Overall, lipid sources have 40% of oxygen content, which makes the removal a great challenge to turn oil into a drop-in fuel [18].

In this context, different reaction pathways have been reported in the literature for the deoxygenation of lipid-based compounds: hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO_2) [63]. The reaction mechanisms of these routes are illustrated in Figure 5 [64]. Considering stearic acid (a fatty acid molecule used as a model compound for lipidic biomass), the three reaction routes lead to oxygen removal through distinct chemical transformations. Stearic acid can first be deoxygenated via the DCO_2 route, producing *n*-heptadecane and CO_2 , or through the HDO pathway. In the HDO route, the fatty acid is hydrogenated, releasing the first oxygen atom in the form of water. Subsequently, the corresponding aldehyde (octadecanal) can either lose its oxygen atom via the DCO route—resulting in *n*-heptadecane and CO—or continue undergoing HDO reactions. Another oxygen atom is then removed as water, forming the corresponding alcohol (octadecanol), which is further hydrogenated to produce the *n*-alkane (*n*-octadecane). Overall, each molecule of fatty acid requires three moles of hydrogen, producing the corresponding alkane and two moles of water through the HDO route [65]. In contrast, the DCO and DCO_2 pathways release GHG and result in a reduction in one carbon atom in the hydrocarbon chain [11].

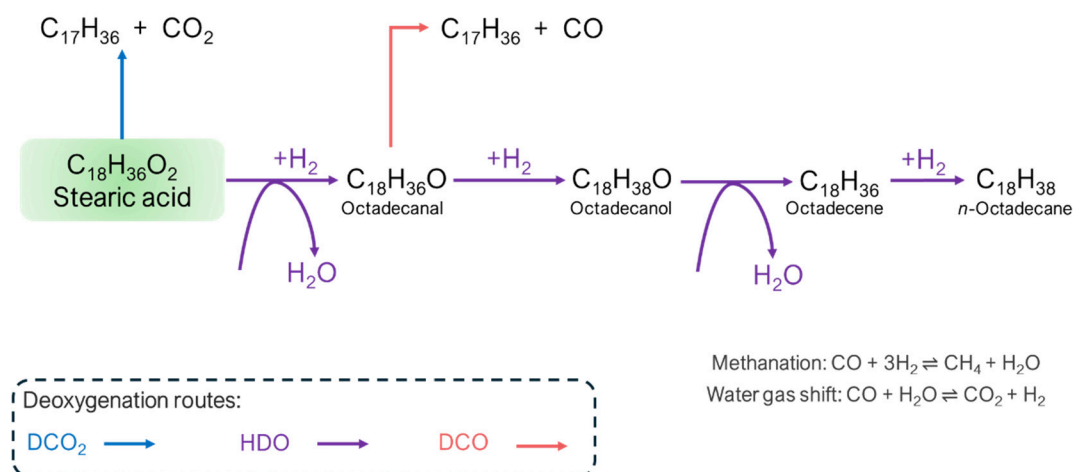


Figure 5. Possible deoxygenation pathways of stearic acid.

Side reactions may occur in which the CO and CO₂ produced via the DCO/DCO₂ routes participate in reversible reactions with H₂, leading to the formation of additional CH₄ and water through methanation and water–gas shift reactions [66].

These reactions usually occur simultaneously during hydrotreatment, and their predominance depends on the catalyst type, reaction temperature, hydrogen pressure, and feedstock composition [67,68]. Nevertheless, the HDO route stands out from DCO and DCO₂ because it does not generate CO or CO₂, representing a more environmentally benign pathway by minimizing GHG emissions [62].

Catalysts play a crucial role in deoxygenation reactions. In general, supported mono- or bimetallic catalysts are widely employed, with transition metals such as Ni, Co, Mo, Fe, and W being the most common [69–71]. Noble metals like Pt and Pd also exhibit excellent catalytic performance but are often avoided due to their high cost [25,72]. The metal must be well dispersed on the support and highly reduced to enhance the hydrogen dissociation on the metal phase. In bimetallic catalysts, electron transfer between the two metals can improve the reducibility of the active phase and promote hydrogen activation. Therefore, promoters such as Ni and Co are often incorporated together with Mo (in its oxide or sulfide form) or W to enhance the catalytic activity [61].

In addition to the metal phase, the selection of appropriate support is essential. One of the most important properties of a support for lipid deoxygenation reactions is its mesoporous nature, which facilitates the diffusion of large molecules such as triglycerides and fatty acids, minimizing external mass-transfer limitations. Accordingly, metal oxides (Al₂O₃, SiO₂, TiO₂, and ZrO₂) and mesoporous silicas (SBA-15, MCM-41, and MCM-48) are commonly used as supports in the deoxygenation of lipid feedstocks [9,11,24].

Deoxygenation reactions typically require temperatures in the range of 300–420 °C for the hydrodeoxygenation of oils and somewhat lower temperatures (250–360 °C) when fatty acids or their derivatives are used as substrates [63]. Typical H₂ pressures range from 20 to 50 bar for oil feedstocks and from 10 to 40 bar for fatty acids [61]. Although this process is widely applied in industry, the need for high hydrogen pressures to ensure efficient C–O bond cleavage is not advantageous in terms of cost and safety. Furthermore, coke formation during the reaction can lead to catalyst deactivation [73].

3.2. Cracking and Isomerization

Cracking and isomerization are the subsequent steps that complement the deoxygenation stage in the HEFA process. After deoxygenation, a large amount of aliphatic

hydrocarbons is produced. However, this paraffinic oil exhibits poor cold-flow properties, making it incompatible with aviation fuel specifications [66].

Cracking reactions can occur in the presence of only temperature (thermal cracking) or be enhanced by the presence of hydrogen (hydrocracking) [11]. These reactions increase the formation of lighter alkanes, improving the selectivity in the desired n -C₈-C₁₆ hydrocarbons. On the other hand, the isomerization reaction can process those normal alkanes into branched hydrocarbons (iso-alkanes). Increasing the ratio iso-alkanes/ n -alkanes (iso/ n) is extremely relevant in terms of fuel performance, mainly to the freezing and flash point [61,73,74]. One advantage is that both cracking and isomerization can occur simultaneously over bifunctional supported catalysts. Once deoxygenation reactions are catalyzed on the catalyst's metal sites, forming n -alkanes, cracking and isomerization reactions take place more commonly in the support's acid sites [74].

The classical reaction mechanism for cracking and isomerization takes place over bifunctional catalysts, which contain metallic sites that promote hydrogenation/dehydrogenation reactions and acid sites responsible for cracking and isomerization [75]. Initially, the n -alkane is dehydrogenated on the metallic sites, forming the corresponding n -alkene (Figure 6). The olefin then migrates to the Brønsted acid sites, where it becomes protonated to produce an alkylcarbenium ion [11,75]. This intermediate can also be formed by the direct protonation of the n -alkane, followed by dehydrogenation, but the formation of the alkylcarbenium ion is more favorable through olefin protonation. Once formed, the alkylcarbenium ion may undergo skeletal rearrangements to produce mono-, di-, or tri-branched carbenium ions. At this stage, cracking occurs via β -scission (C–C bond cleavage), generating branched alkylcarbenium ions (still adsorbed on acid sites) and smaller olefins [76]. The isomers then desorb from the acid sites and, together with the olefins produced during cracking, are subsequently hydrogenated on the metallic phase, producing the corresponding alkanes [76,77].

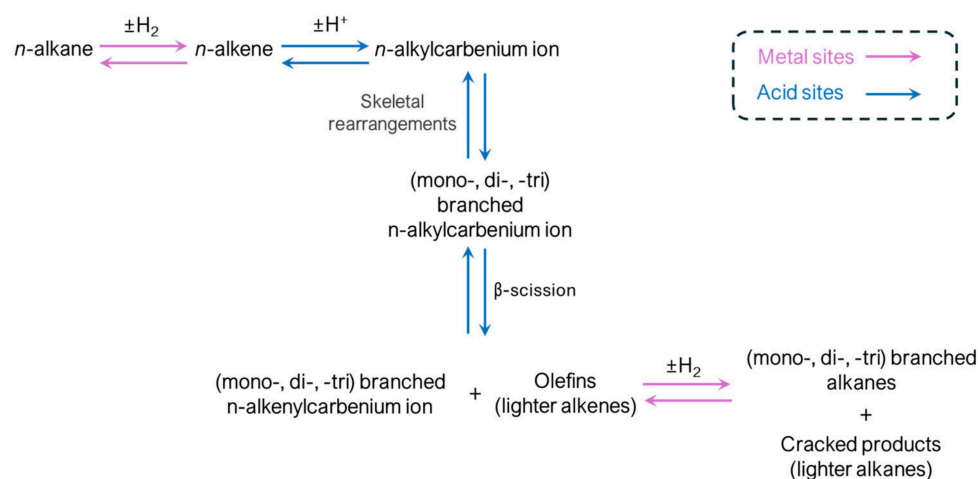


Figure 6. Isomerization and cracking pathways of an n -alkane.

Catalysts used in the cracking and isomerization of lipid feedstocks should exhibit moderate acidity in order to promote isomerization while avoiding excessive cracking. The literature reports several types of acid catalysts, including zeolites in their protonic form (H-ZSM-5, H-ZSM-22, H-Y, H- β , H-USY), alumina-modified mesoporous silicas (Al-MCM-41, Al-MCM-48), and silicoaluminophosphates [23,25,78–80].

The overall efficiency of the HEFA process strongly depends on the nature and balance of the catalytic functions involved. Since deoxygenation, cracking, and isomerization reactions occur through hydrogenation/dehydrogenation steps and are acid-catalyzed, the design of suitable heterogeneous catalysts is of great importance. As mentioned, bifunc-

tional catalysts combining metal and acid sites are used, in which the metal phase activates hydrogen and promotes deoxygenation, while the support provides the acidity necessary for skeletal rearrangement and cracking reactions. Thus, the balance between metal and acid functions is crucial for controlling the degree of isomerization and, consequently, the cold-flow properties of the final fuel. Moderate acidity is generally preferred to avoid excessive cracking. Moreover, temperature must be carefully controlled, since isomerization is favored at lower temperatures (200–300 °C), while deoxygenation typically requires higher temperatures (300–400 °C) [11]. In this context, extensive research has been devoted to the development of catalysts with optimized metal-acid balance, stability, and pore structure, combined with operational conditions. A more detailed understanding of the heterogeneous catalysts involved in the HEFA process is discussed in the following section.

4. Bifunctional Heterogeneous Catalysts

As previously discussed, the selection of an appropriate catalyst plays a crucial role in deoxygenation, cracking, and isomerization reactions. Although the HEFA process generally operates with distinct units for deoxygenation and for cracking/isomerization, numerous studies in the literature have demonstrated the conversion of lipid feedstocks into liquid fuels through a single-step process. Therefore, the appropriate choice of the metal phase and the support is essential.

4.1. Metal Phase

Recent advances in the choice of the metal phase are mainly concentrated around the use of non-noble transition metals. Regarding the type of feedstock used in the HEFA process, many aspects must be taken into account, such as the removal of heteroatoms and hydrogenation reactions. The first critical part for lipid feedstocks is the removal of oxygen, which approaches the cleavage of C–O and C=O bonds. Metals with elevated oxophilicity, such as Fe and Mo, are excellent candidates to promote deoxygenation from triglycerides [24].

Conventional deoxygenation catalysts include Mo, mainly in its sulfide form (MoS₂). Promoters such as Co and Ni are commonly added to enhance the activity of MoS₂ by donating electrons to Mo and weakening the metal–sulfur bond [81]. This facilitates hydrogen dissociation on the metallic phase, thereby improving hydrogenation reactions. Despite their wide application, metal-sulfide catalysts require the continuous addition of sulfur-containing compounds to the feedstock to maintain high catalytic activity. This practice negatively affects both the process and the final product quality, particularly regarding sulfur content. Furthermore, the water generated as a by-product can significantly suppress the activity of sulfide catalysts [82].

One of the main drawbacks of using Mo-based catalysts lies in their difficult reduction behavior. Oxides such as MoO₂ and MoO₃ are formed when a reducing temperature between 500 and 600 °C is applied [26]. However, Mo-oxides are not stable because they are prone to oxidation, which lowers their activity over time [83]. Other alternatives are reported by many authors to improve the stability of Mo species, producing carbide (Mo₂C) or phosphide (MoP), but require elevated temperature under hydrogen to produce them [84]. Nevertheless, many studies have demonstrated the high activity of MoO₂ species alone and doped with Co or Ni to convert fatty acids and waste cooking oil, demonstrating the potential to explore oxide species [26,85–87].

Supported Co and Ni catalysts are also frequently employed as active phases. Hydrogen molecules dissociate well on Ni metallic particles, making these catalysts highly efficient for hydrogenation reactions [88]. However, this strong hydrogenation capability can also promote coke formation, leading to carbon deposition on the active sites and a

consequent decrease in catalytic activity [89]. In addition, Ni-based catalysts generally exhibit moderate selectivity toward cracking reactions, producing hydrocarbons mainly in the C₁₀–C₁₇ range from lipid feedstocks [89,90]. In contrast, Co-based catalysts show excellent selectivity for deoxygenation and hydrogenolysis reactions, and several studies have reported a higher formation of isomerized products during the conversion of lipids into liquid hydrocarbons [61,90,91]. On the other hand, Co is somewhat more difficult to reduce compared to Ni and tends to form metallic aggregates on the catalyst surface, which decreases metal dispersion and increases the particle size of the metallic phase [92].

Noble metals such as Pt, Pd, and Ir are also highly efficient for hydrogenation reactions. However, besides their high economic cost, these metals tend to exhibit higher selectivity toward the DCO and DCO₂ pathways [25,72,93].

4.2. Supports

The selection of appropriate support for the reactions involved in the HEFA process is crucial to ensure good metal dispersion, as well as thermal and mechanical stability. Moreover, mesoporous materials are particularly suitable for facilitating the cracking of triglycerides into *n*-alkanes and iso-alkanes within the catalyst pores. The literature on the catalytic upgrading of lipid feedstocks reports a wide range of support materials, including metal oxides, mesoporous silicas, zeolites, and carbon-based materials.

Metal oxides such as SiO₂ and γ -Al₂O₃ are commonly employed in the petrochemical industry as catalyst supports in hydrotreating units, with Co–MoS/Al₂O₃ being the most widely used system. In addition to their high mechanical and thermal resistance, these materials exhibit large specific surface areas (200–500 m² g_{cat}^{−1}) and predominantly mesoporous structures [21,94]. However, alumina is known to be metastable in the presence of water vapor and highly susceptible to structural degradation, undergoing partial transformation into hydrated boehmite [95].

Silica-based mesoporous materials such as SBA-15, MCM-41, and MCM-48 have gained significant attention because they combine moderate acidity, high specific surface area, and large pore diameters [96,97]. These materials present several benefits over conventional alumina supports, including higher surface areas (typically 600–1000 m² g_{cat}^{−1}) [9,98]. Their mesoporous frameworks enable a more effective dispersion of active sites both within the pores and on the external surface of the support. However, the application of such materials in catalytic HDO reactions remains challenging, as they tend to be structurally unstable under severe hydrothermal conditions. Prolonged exposure to steam can lead to a gradual loss of surface area and eventual collapse of the internal pore structure due to partial steam pressure effects [93].

Zeolites are generally microporous crystalline solid acid materials that facilitate the selective conversion of desired hydrocarbon products (isomers, aromatics, cyclic and aliphatic compounds). They are composed of corner-sharing TO₄ tetrahedra, where T typically represents Si and Al in their conventional form, giving rise to aluminosilicate structures. In these frameworks, adjacent SiO₄ and AlO₄[−] tetrahedra are interconnected through shared oxygen atoms [99]. Their tunable acid–base properties also make these materials highly attractive. In fact, the incorporation of AlO₄[−] tetrahedra into the zeolite framework introduces a negative charge, which is compensated by protons (H⁺), giving rise to Brønsted acid sites (BAS). Moreover, aluminosilicates can also act as Lewis acids in reactions like Friedel–Crafts alkylation, due to the formation of extra-framework Al³⁺ species through dealumination [100]. A modernite framework inverted (MFI) zeolite structure is represented in Figure 7.

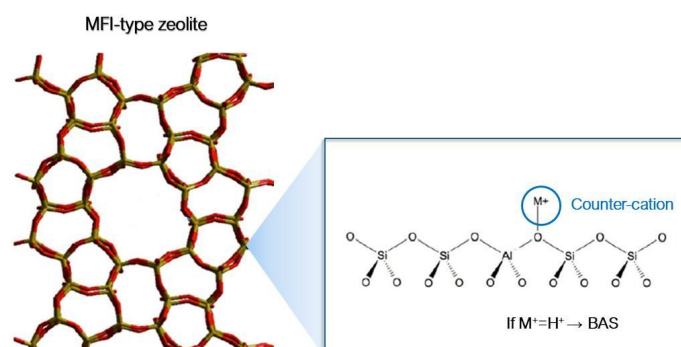


Figure 7. Representation of an MFI-type zeolite with 10-membered rings with silicoaluminates structured.

Among the zeolites employed in the catalytic conversion of lipid-based feedstocks, the most commonly used are ZSM-5, ZSM-22, zeolite Y, zeolite β , and USY [96,99,101–103]. Despite their widespread use, zeolite-based catalysts present certain drawbacks associated with their strong acidity, which often leads to excessive cracking and reduced selectivity toward the desired products [23,80,95,99]. Furthermore, because both the reactants and products are typically long-chain molecules, zeolites may suffer from diffusion and mass transfer limitations within their microporous frameworks [61]. To address these issues, various strategies have been proposed to introduce mesoporosity into zeolite structures, such as dealumination and desilication treatments, which generate hierarchical frameworks combining micro- and mesopores [101,103–105]. These structural modifications can enhance molecular accessibility and mitigate diffusional constraints. However, highly acidic zeolite-based supports remain susceptible to rapid deactivation due to the deposition of carbonaceous species on active sites, ultimately diminishing catalytic performance during deoxygenation reactions [95,99].

Finally, carbon-based materials are excellent supports, with the possibility to modify their chemical surface to suit specific properties, such as acidity and porosity. The capacity of carbon atoms to participate in covalent bonds with other carbon atoms in different hybridization states (sp , sp^2 , sp^3) or with nonmetallic elements enables them to form a wide range of structures, from small molecules to long chains [106]. Furthermore, carbon-based materials have high potential for recyclability and reusability, elevated chemical stability in acidic or basic media, low corrosion capability, and high thermal stability [107]. Their surface is composed of a variety of organic functional groups, anchoring different heteroatoms, which contribute to the acid-base character and textural properties [107,108].

For hydroprocessing reactions to convert oils into SAF, some studies have reported using carbon-based catalysts, often using commercial systems such as Pd/AC and Ru/C. Other works have investigated the use of activated carbon (AC), CNT, and carbon nanofibers (CNF) to assess their catalytic performance in the conversion of model compounds, vegetable oils, and WCO [26,29,109,110]. Since the textural properties are a key parameter for the choice of the supports, the use of AC with extended microporosity is less suitable, especially if it is applied to a complex feedstock such as WCO. In contrast, CNT and CNF offer more favorable mesoporous characteristics that facilitate mass transport and improve the dispersion of active species.

Given their unique structure, high purity, and superior mechanical and chemical stability, CNTs have emerged as a promising support. The discovery of multi-walled carbon nanotubes (MWCNT) dates to 1991, when Sumio Iijima identified them in carbon soot generated via the arc-discharge technique. CNT are based on a hexagonal lattice of sp^2 carbon atoms, such as graphene. Single-walled carbon nanotubes (SWCNT) have diameters of around 0.4–2 nm and are several micrometers long, with an empty internal space, while

MWCNT consists of concentric cylinders with an interlayer spacing of 3.4 Å and a diameter typically on the order of 10–20 nm [106,111,112].

Their electrical and mechanical stability, high surface area, and pore volume make CNT an outstanding material in catalytic applications. Those last textural properties ease the metal dispersion as well as the diffusion of reagents and products into the CNT's surface, due to the absence of micropores [111]. Additionally, CNTs have elevated thermal stability, and when combined with their other advantageous features, this class of materials becomes particularly suitable for hydroprocessing reactions of lipid feedstocks [106,107].

Heteroatom groups, such as oxygen, can be incorporated on the CNT surface, aiming to enhance their catalytic activity. This chemical change can enhance their dispersibility in different solvents, water, and increase the acid character by the introduction of oxygenated groups such as carboxylic acids, carboxylic anhydrides, and lactones [113–115]. In this context, these attributes position CNT as exceptional catalyst supports for the hydroprocessing of lipid feedstocks.

5. Catalytic Upgrading of Lipid-Based Feedstocks

Given the reactions involved in the conversion of lipid-based feedstocks and the catalysts required to produce hydrocarbons in the C₈–C₁₆ range, this section reviews the state of the art in the catalytic upgrading of fatty acids, vegetable oils, and WCO. Understanding each feedstock individually, starting from model compounds and progressing to more complex systems, is essential for selecting appropriate reaction conditions and catalyst formulations.

5.1. Catalytic Conversion of Fatty Acids

Fatty acids are carboxylic acids that constitute triglyceride molecules. Hence, they are often employed as model compounds to represent the behavior of vegetable oils in catalytic upgrading studies. Fatty acids can be classified as saturated or unsaturated. Saturated fatty acids have fully hydrogenated chains and typically remain solid at room temperature, while unsaturated fatty acids contain one or more double bonds, which lowers their melting point and generally makes them liquid under ambient conditions [116]. The short-name nomenclature for fatty acids is typically expressed as the number of carbon atoms in the chain followed by the number of double bonds. For instance, oleic acid contains 18 carbon atoms and one double bond, located between carbon 9 and 10, and is therefore designated as C18:1. In contrast, palmitic acid has a 16-carbon fully saturated chain and is represented as C16:0 [57].

Due to their well-defined molecular structures, fatty acids allow for a clearer interpretation of deoxygenation pathways (HDO, DCO, and DCO₂), cracking and isomerization, and help isolate intrinsic catalytic effects without the complexity introduced by multicomponent systems such as real lipid sources.

Studies using monometallic catalysts supported on zeolites were among the first reported in this field. Table 3 summarizes the latest achievements showing the catalytic systems and their performance in terms of substrate conversion (X), yield (Y), and selectivity (S) of the main products. Shi et al. [85] evaluated the bifunctional Mo/H-ZSM-22 catalyst for the conversion of palmitic acid into branched C₁₅ and C₁₆ (entry 1, Table 3). According to the authors, the Mo⁴⁺/Mo⁶⁺ ratio in Mo/ZSM-22 strongly affects HDO/HDC selectivity during palmitic acid upgrading. Mo⁶⁺ species (MoO₃) promote the DCO pathway, whereas Mo⁴⁺ (MoO₂) favors HDO, demonstrating that Mo oxides themselves possess catalytic activity for these reactions. Despite promising results, after two consecutive reaction cycles, coke deposition on Brønsted acid sites reduced the isomer selectivity and increased the formation of linear alkanes.

Table 3. Results of catalytic conversion of fatty acids.

Entry	Feedstock	Catalyst	Experimental Set Up	Reaction Conditions	Catalyst:Fatty Acid	Solvent	Performance (%)	Ref.
1	Palmitic acid	Mo/H-ZSM-22	Batch	260 °C, 40 bar ^a , 4 h	1:5	<i>n</i> -decane	X = 100 S _{n-C14-C16} = 40.3 S _{iso-C15-C16} = 59.7	[85]
2	Palmitic acid	Co/H-ZSM-22	Batch	260 °C, 20 bar ^a , 4 h	1:5	<i>n</i> -decane	X = 99 S _{n-C14-C16} = 26.6 S _{iso-C15-C16} = 73.4	[91]
3	Palmitic acid	Ni/H-ZSM-22	Batch	260 °C, 40 bar ^a , 4 h	1:5	<i>n</i> -decane	X = 99.2 S _{C16} = 79.6	[23]
4	Oleic acid	Ni/ZSM-22-mesoSiO ₂	Fixed bed	320 °C, 40 bar ^a , WHSV ^c of 10 s ^{−1}	1:12.5	Cyclohexane	X = 100 S _{C8-C16} = 54.8 ^b	[117]
5	Oleic acid	Pt/ZSM-5-nanosheets	Batch	320 °C, 18 bar ^d , 5 h	1:10	Solvent free	X = 97.4 Y _{C8-C17} = 83.8	[118]
6	Oleic acid	Sn-Fe-Cu/SiO ₂ -Al ₂ O ₃	Batch	320 °C, 21 bar ^a , 8 h,	1:20	Solvent free	X = 100 Y _{C8-C16} = 71.7	[24]
7	Palmitic acid	Pt/C	Batch	350 °C, 1 h, pressure not determined	1:2	Formic acid	X = 30 Y _{n-C16-C15} = 5.2	[72]
8	Oleic acid	Pt/C	Batch	330 °C, autogenous pressure, 1.5 h	1:10	Water	X = 80 Y _{nC13-C17} = 9.5	[119]
9	Stearic acid	Fe-Ni/C	Batch	330 °C, 1 bar of N ₂ , 3 h	1:3	Solvent-free	X = 99.9 S _{n-C17} = 76.8	[69]
10	Palmitic acid	Co-Mo/CNT	Batch	200 °C, 40 bar ^a , 4 h	1:5	<i>n</i> -decane	X = 100 S _{n-C15-C16} = 58.6	[28]
11	Palmitic acid	Ni/CNT	Batch	240 °C, 20 bar ^a , 4 h	1:2	<i>n</i> -decane	X = 97.2 Y _{n-C16-C15} = 92.1	[27]
12	Palmitic acid	Co-Mo/CNT _{ox}	Batch	350 °C, 30 bar ^a , 6 h	1:10	<i>n</i> -decane	X = 100 Y _{n-C16} = 90.9	[120]
13	Palmitic acid	Co-Mo/CNT-HZSM-5	Batch	325 °C, 20 bar ^a , 3 h	1:5	<i>n</i> -decane	X = 100 S _{n-C8-C16} = 12.4 S _{iso-C8-C16} = 21.2	[121]

^a Initial H₂ pressure at room temperature; ^b Including *n*- and iso-alkanes; ^c Weight hourly space velocity; ^d Initial CO₂ pressure at room temperature.

Cao et al. [91] investigated Co/H-ZSM-22 for palmitic acid conversion at 260 °C, 20 bar of initial H₂ for 4 h, reporting a total of 73.4% iso-C₁₅ and iso-C₁₆, attributed to the zeolite's Brønsted acid sites (entry 2, Table 3). Additionally, C₁₆ was the main product, indicating that Co favored the HDO route. Ni/H-ZSM-22 was evaluated by Li et al. [23] under similar conditions (260 °C, 40 bar of initial H₂, 4 h), reaching 98.9% conversion with 99.2% selectivity to alkanes, 79.6% of which corresponded to C₁₆ (entry 3, Table 3). The catalyst maintained high stability over four consecutive cycles, with no significant changes in conversion or product distribution.

As studies progressed toward more structurally complex fatty acids, zeolites incorporating mesoporous structures were also investigated. Liu et al. [117] examined oleic acid upgrading over core-shell Ni/ZSM-22-mesoSiO₂ catalysts. The well-defined mesoporous shell provided a large number of accessible Si-OH groups, enhancing oleic acid adsorption. The shell facilitated deoxygenation to octadecane and heptadecane, followed by isomerization and cracking over the ZSM-22 core, yielding 54.8% C₈-C₁₆ hydrocarbons and an iso/*n* ratio of 5.6 at 320 °C and 40 bar of initial H₂ (entry 4, Table 3). In an attempt to reduce risks associated with H₂ use, Liu et al. [118] reported the conversion of oleic acid over Pt/ZSM-5 nanosheets under a CO₂ atmosphere. They obtained around 80% C₈-C₁₆ hydrocarbon yield after 5 h at 320 °C. However, after three cycles, catalyst stability declined due to Pt leaching (entry 5, Table 3).

Other inorganic mesoporous catalysts have also been investigated for oleic acid upgrading into SAF-range hydrocarbons. Ayandiran et al. [24] evaluated Ti, Zr, and Sn-promoted Fe-Cu/SiO₂-Al₂O₃ catalysts (entry 6, Table 3). Sn-promoted systems showed

improved Fe–Cu synergy, enhanced textural properties, and higher selectivity toward the desired hydrocarbon range (76.8%).

Commercial carbon-based catalysts have also gained attention. Liu et al. [72] studied palmitic acid conversion over Pt/C with in situ H₂ generation using formic acid as solvent. At higher temperatures (above 340 °C) and reaction times, the reaction proceeded predominantly through the DCO₂ pathway, whereas milder conditions favored HDO (entry 7, Table 3). Despite the promising use of formic acid as a solvent to avoid the use of H₂, low palmitic acid conversion was obtained. Pt/C was also evaluated by Fu et al. [119] for converting several saturated and unsaturated fatty acids (lauric, palmitic, stearic, oleic, and linoleic acids) in aqueous phase without external H₂ (entry 8, Table 3). The authors observed that the DCO₂ rate for saturated fatty acids was independent of chain length, whereas C₁₈ unsaturated acids underwent DCO₂ more slowly.

Non-noble metals supported on carbon have also been explored. Zhong et al. [69] investigated stearic acid conversion using Fe–Ni catalysts encapsulated in graphitic carbon without using hydrogen. The synergistic interaction between Fe and Ni enhanced deoxygenation activity compared with their monometallic counterparts. The catalyst also maintained its performance after four consecutive runs, with almost 80% selectivity for *n*-C₁₇ (entry 9, Table 3). Moreover, commercial CNT-based catalysts were studied by Ding et al. [28] (Mo/CNT and Co–Mo/CNT) for palmitic acid conversion (entry 10, Table 3). The presence of MoO₂ and Mo₂C species improved HDO activity, while Co incorporation into the MoO₂ lattice generated Lewis acid sites and oxygen vacancies, increasing hexadecane selectivity from 1.3% (Mo/CNT) to 54.8% (Co–Mo/CNT). Despite the excellent HDO performance and high stability, no cracking into lighter molecules or isomerization of *n*-alkanes was observed. Similar behavior was reported by Duan et al. [27] using Ni/CNT catalysts for palmitic acid upgrading (entry 11, Table 3). More recently, Ferreira et al. [120] have compared Co–Mo supported on oxidized CNT (CNT_{ox}) under optimized conditions to assess the conversion of palmitic acid into alkanes (entry 12, Table 3). The results demonstrate excellent fatty acid deoxygenation into hexadecane, but no small alkanes and isomers compounds. This behavior is consistent with the higher reaction temperatures employed compared with the work of Ding et al. [28], which favor HDO pathways. The absence of isomers and lighter alkanes can also be attributed to the lack of strong acidic functionality in CNT-based supports, even in their oxidized state. Subsequently, the same metal phase was supported on a CNT–H–ZSM–5 composite to investigate the conversion of palmitic acid [121]. The catalysts showed promising results in terms of product distribution, with selectivities of 21.2% for iso-C₈–C₁₆ and 12.4% for *n*-C₈–C₁₆ (entry 13, Table 3). The incorporation of a strong acid component (zeolite H–ZSM–5) into the CNT support increased the number of acid sites, thereby enhancing performance in cracking and isomerization reactions.

5.2. Catalytic Conversion of Vegetable Oils

Vegetable oils are lipid-rich materials obtained from plants and seeds (e.g., soybean and sunflower oils) through mechanical pressing, solvent extraction, or combined processes [5]. Their elemental composition is predominantly carbon, hydrogen, and oxygen, with minor amounts of heteroatoms such as nitrogen and sulfur. The fatty acid profile of each oil varies depending on the source. For instance, jatropha oil is particularly rich in oleic and linoleic acids, whereas palm oil contains higher fractions of palmitic and oleic acids. Oils such as palm, palm kernel, soybean, coconut, rapeseed, sunflower, and jatropha are among the most widely investigated feedstocks for SAF production, largely due to their availability, established production chains, and suitable lipid profiles [5]. Considering the composition of different vegetable oils, several studies have investigated how properties

such as acidity, porosity, and metal nature influence the catalytic conversion of these substrates into hydrocarbons.

Scaldaferri and Pasa [122] investigated the conversion of commercial soybean oil using different catalysts (ZSM-5, Pd/C, H- β , FCC, and NbOPO₄) under a H₂-free reaction. The first screening of catalysts showed that ZSM-5 yielded 76% of bio-gasoline (C₅–C₉), Pd/C and NbOPO₄ produced 62 and 50% of jet fuel (C₉–C₁₆), respectively, while H- β and FCC catalysts provided higher balanced yields among the products obtained. Despite the higher yield in jet fuel that Pd/C supplied, the aromatics content of 46% was above the desired ASTM limits. In contrast, 25% of aromatics was achieved using NbOPO₄. Furthermore, under the optimal conditions (350 °C, 10 bar of initial N₂, 5 h of reaction), the yields obtained for bio-gasoline, jet fuel, and green diesel (C₁₅–C₂₅) were 21%, 58%, and 37%, respectively (entry 1, Table 4).

Table 4. Results of the catalytic conversion of vegetable oils.

Entry	Feedstock	Catalyst	Experimental Set Up	Reaction Conditions	Catalyst:Oil	Solvent	Performance (%)	Ref.
1	Soybean oil	NbOPO ₄	Batch	350 °C, 10 bar ^a , 5 h	1:4	Solvent free	X = 90 Y _{C9-C16} = 58	[122]
2	Jatropha oil	HPMo-Ni/CNT	Fixed bed	330 °C, 30 bar ^b , LHSV ^c of 1 h ^{−1}	-	Solvent free	X = 98.2 Y _{C15-C18} = 86.7	[29]
3	Palm kernel oil	Pd/C	Batch	400 °C, autogenous pressure, 2 h	1:12.5	Solvent free	X = 96 S _{C8-C16} = 73	[123]
4	Palm olein	Pd/C	Batch	400 °C, autogenous pressure, 2 h	1:20	Solvent free	X = 99 S _{C8-C16} = 73	[124]
5	Palm oil	Ni-Fe/ZSM-5/SAPO-11	Batch	300 °C, 27 bar ^b , 2 h	1:5	<i>n</i> -heptane	X = 100 Y _{C8-C16} = 81.7	[80]
6	Palm oil	FeP/MCM-22	Batch	400 °C, 20 bar ^b , 3 h	1:100	cyclohexane	S _{C9-C14} = 78	[125]
7	Coconut oil	Ni/ZIF-67	Batch	350 °C, 30 bar ^b , 4 h	1:10	Solvent free	X = 99 S _{C8-C16} = 91.6	[126]
8	Palm oil	Ni/AC+Al ₂ O ₃	Batch	400 °C, autogenous pressure, 3 h	1:4	Solvent free	S _{C8-C16} = 77.2	[127]
9	Calophyllum inophyllum	Ni/ZrO ₂	Semi-batch	550 °C, 20 cm ³ min ^{−1} ^d , 2 h	1:100	Solvent free	S _{C8-C16} = 85.6	[128]

^a Initial N₂ pressure at room temperature; ^b Initial H₂ pressure at room temperature; ^c Liquid hourly space velocity; ^d Gas flow rate under atmospheric pressure.

The combination of redox and acid properties of NbOPO₄ led to the formation of different hydrocarbons, such as linear (38%) and branched alkanes (14%), cycloalkanes (1%), olefins (1%), and aromatics (36%) compounds. These results showed the potential for deoxygenation, cracking, and isomerization reactions under an N₂ atmosphere, reducing the costs and increasing the safety of the process. However, the aromatic content is still high for use as a drop in jet fuel. The authors proposed a mechanism (Figure 8) including the formation of cyclic and aromatic compounds, in which the generation of aromatics occurred to a large extent, likely through the dehydrogenation of pre-existing cyclic structures or via olefin cyclization [122].

Jatropha oil was used as feedstock to assess the production of liquid fuels over phosphomolybdic acid modified with Ni supported on CNT (HPMo-Ni/CNT) catalyst [29]. Under the optimal reaction conditions (330 °C, 30 bar, H₂/oil ratio of 800, and a liquid hourly space velocity of 1 h^{−1}), the process yielded 86.7% of green diesel (C₁₅–C₁₈) with a conversion of 98.2% (entry 2, Table 4). No significant cracking or isomerization was detected. The HPMo-Ni catalyst demonstrated excellent stability under the optimal conditions, maintaining the performance over five consecutive runs. However, a higher acidity would be required to enhance the production of C₈–C₁₆ hydrocarbons.

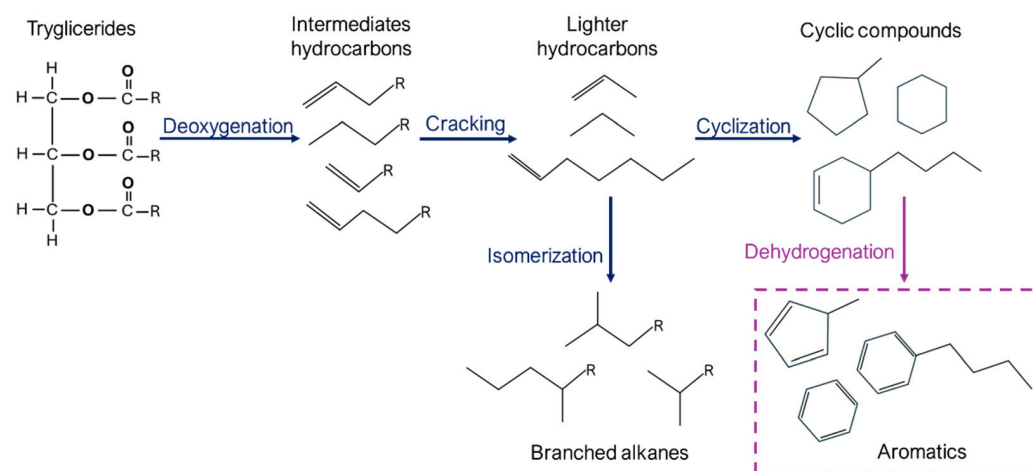


Figure 8. Reaction pathways to convert triglycerides over NbO_4PO_4 , focusing on the production of aromatics.

Other types of vegetable oils have also been extensively studied, especially those derived from palm, due to their high availability and high saturated fatty acid content. Why et al. [123] studied the production of SAF from palm kernel oil. The authors tested different commercial catalysts such as V_2O_5 and Pd/C . The study showed that the Pd/C catalyst was the most favorable for converting the oil, yielding approximately 96% of liquid product with a $\text{C}_8\text{--C}_{16}$ selectivity of 73% (entry 3, Table 4). The same group subsequently expanded their investigation to the production of jet fuel from various palm-based renewable feedstocks (e.g., palm olein, palm kernel oil) through deoxygenation [124]. In this later work, they tested a broader set of catalysts (e.g., CaO , zeolite, V_2O_5 , Pd/C , TiO_2) under the previous study's reaction conditions. Despite the use of different feedstocks, the best catalytic performance was achieved with Pd/C for both palm olein and palm kernel oil, with a $\text{C}_8\text{--C}_{16}$ hydrocarbon selectivity of 73% in each case (entry 4, Table 4). In both studies of the group, Pd/C presented similar catalytic performance for distinct vegetable oils, despite the use of different catalyst-to-substrate ratios. This suggests that the reaction outcomes do not strongly depend on either the catalyst loading or the chemical composition of the oil.

More recent approaches have evaluated bifunctional materials based on zeolites, in which acidity and metal activity act synergistically. Khan et al. [80] investigated the use of Ni and Fe supported on ZSM-5/SAPO-11 zeolites, reporting a $\text{C}_8\text{--C}_{16}$ yield of 81.7% from palm oil (entry 5, Table 4). The authors observed a synergistic effect between Ni and Fe, increasing the active metal sites (as evidenced by hydrogen temperature-programmed reduction). Moreover, moderate acidity contributed to higher conversion and $\text{C}_8\text{--C}_{16}$ selectivity via stronger adsorption of carbonaceous species on the catalyst's surface, while the mesoporous structure improved diffusion and promoted cracking on Brønsted and Lewis acid sites. The results also showed a significant selectivity to aromatic compounds (18%).

The importance of the textural characteristics of the support is also evident in studies with micro- and mesoporous materials, as demonstrated by Tanwongwan et al. [125]. The authors examined the hydrocracking of palm oil using iron phosphide (FeP) supported on zeolites and mesoporous materials synthesized from natural silicon and aluminum sources (entry 6, Table 4). The authors prepared microporous (MCM-22 and MCM-36) and mesoporous supports (MCM-41 and MCM-48) via hydrothermal synthesis and demonstrated that the microporous material exhibited higher acidity and micropore surface area than the mesoporous materials. Among them, MCM-22 showed superior acidity, which strongly influenced catalytic performance. FeP supported on MCM-22 delivered the best results, achieving around 33% liquid hydrocarbon yield and 78% selectivity toward the $\text{C}_8\text{--C}_{16}$ fraction. The excellent performance of FeP/MCM-22 was attributed to its high acidity, thermal

stability, and uniform FeP dispersion enabled by its microporous framework. Reusability tests further revealed enhanced catalytic performance over three consecutive cycles, with liquid hydrocarbon yields increasing to 50% and bio-jet selectivity stabilizing at 83%.

Nugroho et al. [126] evaluated the catalytic conversion of coconut oil over a Ni-supported zeolitic imidazole framework-67 catalyst (Ni/ZIF-67), a subclass of a metal-organic framework. The authors achieved a hydrocarbon yield of 99.0% and a C₈–C₁₆ paraffins selectivity of 91.6% at 350 °C for 4 h under 30 bar of initial H₂ (entry 7, Table 4). The superior activity was attributed to the coexistence of multiple acidic sites and strong basicity, which facilitated C–O bond cleavage predominantly through DCO₂/DCO pathways. However, a minimal number of isomers was produced, and after the second consecutive reaction, the catalyst's activity decreased due to pore blockage by soft coke.

A recent study by Ahmad et al. [127] investigated the catalytic conversion of palm oil using Ni supported on activated carbon (Ni/AC) physically mixed with Al₂O₃, aiming to produce SAF-range hydrocarbons without external hydrogen input. The addition of alumina significantly increased the concentration of medium and strong-acid sites, which promoted selective deoxygenation. Under optimized conditions, the catalyst achieved a liquid yield of 45.5%, with selectivity of 77.2% in the C₈–C₁₆ range (entry 8, Table 4). Product distribution analysis indicated that DCO and DCO₂ were the dominant pathways, confirming that the in situ-generated hydrogen was sufficient to drive deoxygenation in the absence of external H₂; however, the liquid yield was low compared to other studies in the literature. The improvement in acidity provided by Al₂O₃ also enhanced catalyst activity and shifted the reaction toward SAF-range hydrocarbons while minimizing thermal cracking, but lower liquid yield was produced.

Saviola et al. [128] investigated the hydroconversion of non-edible oils—*Calophyllum inophyllum* (CIO) and *Pongamia pinnata* (PPO)—to produce SAF-range hydrocarbons using Ni/ZrO₂ and Mo/ZrO₂ catalysts. The results demonstrate the predominance of metallic Ni and MoO₃ species on each catalyst surface. Hydrotreatment was performed in a semi-batch reactor under atmospheric hydrogen flow for 2 h. Ni/ZrO₂ showed the highest catalytic activity and selectivity toward C₈–C₁₆ hydrocarbons, particularly for CIO, whose fatty acid profile (C₁₆–C₂₂) favored jet-range product formation compared to PPO (C₁₆–C₂₄). Under optimal conditions, Ni/ZrO₂ yielded 55.4% of total liquid products, with 85.6% SAF selectivity from CIO (entry 9, Table 4). For PPO, the same catalyst led to a 51.3% increase in liquid hydrocarbons yield and 77.1% of SAF selectivity. In contrast, Mo/ZrO₂ exhibited lower SAF-range selectivity but higher HDO activity, leading to an increased formation of green diesel fractions.

Despite the studies involving raw vegetable oils, the growing demand for more sustainable and economically viable sources has directed attention to lipid waste, especially WCO. Thus, the next section discusses the catalytic conversion of WCO, highlighting the chemical particularities of this substrate and its impact on the activity and stability of catalysts.

5.3. Catalytic Conversion of Waste Cooking Oil

Second-generation feedstocks like WCO represent a promising lipid source, offering an effective route to valorize waste via HEFA. WCO costs far less than refined vegetable oil, and it has emerged as a substitute for conventional vegetable oils in liquid fuel production. Waste oils from restaurants and processed animal fats are cheaper options compared to edible oils such as sunflower, canola, and soybean [129]. During frying, oils can reach temperatures of about 160–200 °C, which can trigger oxidation, hydrolysis, isomerization, and polymerization reactions. These degradation processes can significantly influence the oil's behavior during the HEFA process [130]. Several techniques can be used to improve

WCO quality, such as filtration, vacuum distillation, membrane adsorption, neutralization of acid compounds, degumming, among others [131]. According to some studies in the literature, filtration is the most typical pre-treatment to retain any residual solids contained in the WCO [21]. Degumming is also largely employed as a pre-treatment to remove mainly phospholipids, sulfur, and nitrogen traces in WCO [110]. This process involves treating the oil with heated water, a saline solution, or a dilute acidic aqueous solution [131].

Considering the relevance of WCO valorization, numerous research groups have focused on upgrading this residue, primarily for biodiesel production via transesterification [132–134]. However, with transesterification technologies already well established and the growing global demand for SAF, WCO has increasingly emerged as a key feedstock for bio-jet fuel production through the HEFA process.

Following this trend, several studies have investigated its catalytic conversion into SAF-range hydrocarbons using different reactor configurations, catalysts, and process conditions. Le-Phuc et al. [135] investigated the catalytic cracking of high acid value waste cooking oils using different types of spent fluid catalytic cracking (FCC) catalysts. In this study, WCO with acid values ranging from 6 to 22 mg KOH g^{−1} was processed in a lab-scale FCC reactor at temperatures between 450 and 520 °C. The authors demonstrated that from 480 °C onward, all tested spent FCC catalysts could convert WCO into liquid fuels with near-zero acidity. Under the optimized conditions, total product yield reached 83–86 wt.%, with product distributions of 25–29 wt.% of diesel, 40–42 wt.% of gasoline and 14–18 wt.% of liquid petroleum gases (LPG), while coke formation remained low (5–6 wt.%) (entry 1, Table 5). Increasing the reaction temperature to 520 °C enhanced cracking severity, promoting the conversion of diesel molecules into gasoline and LPG. Additionally, the presence of ZSM-5 in one of the SFCC catalysts increased LPG and propylene formation. Despite these results, the study did not mention any formation of SAF-range products but highlighted the importance of FCC and ZSM-5-based catalysts in cracking reactions.

Table 5. Results of the catalytic conversion of WCO.

Entry	Catalyst	Experimental Set Up	Reaction Conditions	Catalyst:WCO	Solvent	Performance (%)	Ref.
1	Spent FCC	FCC-unit (bench scale)	480 °C, 1 bar	3.5:1	Solvent free	Y _{LPG} = 14–18 Y _{gasoline} = 40–42 Y _{diesel} = 25–29	[135]
2	Ni-MoS ₂ /Al ₂ O ₃	Fixed-bed	420 °C, LHSV of 1 h ^{−1} , 10 bar ^a	-	Solvent free	X = 96.6 S _{C8-C16} = 55.6	[21]
3	Ni-MoS ₂ /Al ₂ O ₃ -SiO ₂	Fixed-bed	350 °C, WHSV of 1.1 h ^{−1} , 60 bar ^a	-	Solvent free	X = 86.69 S _{C8-C16} = 74.8	[136]
4	Ni-Co/SBA-15-SH	Semi-batch	350 °C, 2 h, 5 bar ^b	1:20	Solvent free	S _{C8-C16} = 92	[137]
5	Ni-Co/TiO ₂	Batch	350 °C, 3 h, 1 bar ^b	3:100	Solvent free	S _{C8-C16} = 44.5	[138]
6	Ni/PO ₄ -ZrO ₂	Semi-batch	350 °C, 2 h, atmospheric pressure	-	Solvent free	Y _{C8-C16} = 54.7	[139]
7	Ni/Al ₂ O ₃	Batch	350 °C, 1 h, 6 bar ^b	1:200	Solvent free	Y _{C8-C16} = 80.2	[140]
8	Pt-Fe ₂ O ₃ -ZrO ₂	Batch	375 °C, 4.5 h, 10 bar ^a	1:20	Solvent free	Not specified	[141]
9	Co-Mo/CNT	Batch	350 °C, 5 h, 70 bar ^a	1:10	<i>n</i> -decane	X = 100 S _{C8-C16} = 15.4	[64]
10	Mo ₂ C /CNF	Fixed-bed	350 °C, 70 bar ^a , WHSV of 0.05 mL _{WCO} g _{cat} ^{−1} min ^{−1}	-	<i>n</i> -decane	Y _{C15-C18} = 87	[110]
11	Ni ₂ P/AC	Fixed-bed	300 °C, 1 bar ^a , GHSV ^c of 2.33 min ^{−1}	1:10	<i>n</i> -heptane	X = 89 Y _{C15-C18} = 77.4	[142]
13	Co-Mo/CNT+H-ZSM-5	Fixed-bed	325 °C, 70 bar ^a , WHSV of 0.05 g _{WCO} g _{cat} ^{−1} min ^{−1}	-	<i>n</i> -decane	S _{C8-C16} = 30.6	[143]

^a Initial H₂ pressure at room temperature; ^b Initial N₂ pressure at room temperature; ^c Gas hourly space velocity.

Later, Verma et al. [21] conducted a comprehensive reaction parameters optimization study over a commercial sulfided Ni-Mo/ Al_2O_3 catalyst using a filtered WCO with 320 and 390 ppm of N and S, respectively. Under optimal conditions, the catalyst achieved 96.6% WCO conversion and 55.6% selectivity to SAF-range hydrocarbons, with a remarkable isomer yield of 82.9% and an iso/*n* ratio of 4.8 (entry 2, Table 5). The jet fraction consisted mainly of paraffins (43.6%), followed by naphthenes (8.2%) and very low aromatic content (3.73%). Heteroatom removal was almost complete (99.9% of N, 94.3% of S, and 99.9% of O) during hydroprocessing.

In addition to these advances, Racha et al. [136] provided further insight into the catalytic upgrading of WCO through a two-step reaction: hydroprocessing route followed by isomerization. The authors also tested bimetallic Ni-Mo as a metal phase (Mo in its sulfide form) but supported on mixed Al_2O_3 - SiO_2 oxides. The study focused on how the Al_2O_3 : SiO_2 ratio influences textural properties, metal-support interactions, and the formation of active MoS_2 phases. Among the evaluated formulations, the catalyst supported on Al_2O_3 - SiO_2 with a 70:30 ratio showed the best performance during the HDO step, achieving 86.69% conversion of degummed WCO and 74.8% selectivity to SAF-range hydrocarbons under relatively mild conditions (entry 3, Table 5).

Recent advances in Ni- and NiCo-based catalysts have demonstrated their strong potential for converting WCO into SAF. Razak et al. [137] showed that bimetallic Ni-Co catalysts supported on SBA-15 exhibit enhanced activity when the support is functionalized with -SH groups, which improves surface area, pore size, and acidity. Metal load was also a key factor in the performance, since excessive metal loading (10 wt.%) reduced accessibility to active sites, whereas the Ni-Co/SBA-15-SH catalyst achieved the best performance under H_2 -free reaction, producing 80% hydrocarbon yield with 92% SAF selectivity (entry 4, Table 5). Also under hydrogen-free conditions, Goh et al. [138] developed a Ni-Co/ TiO_2 catalyst capable of efficiently deoxygenating WCO, achieving 83.13% deoxygenation and 44.5% selectivity to jet fuel under optimized parameters identified by Box-Behnken methodology (entry 5, Table 5).

Focusing on monometallic Ni systems, Saviola et al. [139] synthesized Ni supported on PO_4 - ZrO_2 nanocatalysts, reporting superior acidity, dispersion, and activity compared to conventional wet impregnation. Their optimal catalyst 1 wt.% Ni/ PO_4 - ZrO_2 yielded 54.7% of SAF (entry 6, Table 5). After five consecutive runs, SAF yield slightly declines to 41.1%. A different approach was explored by Khan et al. [140], who proposed a synergistic thermocatalytic process coupling catalytic cracking with in situ hydrogen production, using a Ni/ Al_2O_3 catalyst. Under optimized conditions, the process yielded 80.2% of C_8 - C_{16} , with minimal coke (1%), offering a cost-effective dual-output route aligned with circular economy goals (entry 7, Table 5).

Beyond Ni- and Co-based systems, several studies have explored alternative catalytic formulations for WCO upgrading. Jamil et al. [141] developed a novel Pt- Fe_2O_3 - ZrO_2 catalyst with elevated acidity, porosity, and metal dispersion, enabling 91.3% of total deoxygenation and the formation of hydrocarbons in the diesel and aviation ranges (entry 8, Table 5).

Although carbon-based catalysts remain scarce in the hydroprocessing of WCO, the available studies clearly demonstrate their strong potential. Ferreira et al. [65] evaluated Ni(Co)-Mo bimetallic catalysts supported on CNT and CNT_{ox} for WCO upgrading. Characterization results showed the presence of MoO_2 species in all evaluated catalysts, as well as mixed Co-Mo oxides. Additionally, no significant differences in the total acidity of the catalysts supported on pristine CNT and oxidatively treated CNT were identified. This was reflected in the similar performance observed during the screening of the prepared materials. The Ni-Mo/ CNT_{ox} catalyst showed no deactivation after four consecutive

reactions, reaffirming the excellent stability of carbon-based catalysts in hydrotreatment reactions. The presence of Co led to the production of isomers in the range of the C₈–C₁₆ (entry 9, Table 5). However, the catalysts were more selective to the green diesel range (around 70%), confirming the higher capacity for deoxygenating triglycerides and less capability to crack high molecules into small ones.

Muñoz-Arjona et al. [110] showed that Mo₂C supported on CNF (Mo₂C/CNF) is highly effective for HDO, first using stearic acid as a model compound and then applying the catalyst to real WCO in a trickle-bed reactor. At 350 °C, Mo₂C/CNF achieved up to 87 mol.% C₁₅–C₁₈ hydrocarbons, predominantly through the direct HDO route, but with minimal cracking (entry 10, Table 5). Earlier work by Pham et al. [142] also demonstrated the viability of carbon support, using activated-carbon-supported nickel phosphides (Ni₂P/AC) for atmospheric-pressure HDO of WCO. The authors achieved more than 85% oxygen removal and produced mainly *n*-alkanes in the C₁₅–C₁₉ range (entry 11, Table 5). Ribeiro et al. [143] investigated the conversion of WCO using a physical mixture of Co-Mo/CNT and H-ZSM-5 in continuous and discontinuous modes. A high content of aromatics was obtained with these catalysts in the reaction performed in batch (around 75% of selectivity). On the other hand, the physical mixture provided a higher selectivity in C₈–C₁₆ hydrocarbons when performed in a fixed-bed reactor (entry 12, Table 5), showing the importance of aligning catalyst properties with suitable reaction systems to maximize the selectivity in the desired products.

Based on the compilation of the main results reported in the literature, there remains significant room for the development of carbon-based catalysts, particularly those based on CNT. Important knowledge gaps persist regarding how modifications to the surface chemistry of these materials, especially the introduction of acidic functional groups through nitric acid oxidation, can influence product selectivity within the C₈–C₁₆ hydrocarbon range. Furthermore, the literature demonstrates that metal-supported carbon catalysts exhibit excellent performance in deoxygenation reactions via HDO, with Mo standing out as an effective active metal phase. Nevertheless, the promotion of cracking and isomerization reactions remains limited when carbon-based catalysts are employed. Beyond surface acidity modification, the incorporation of acidic solids (such as zeolites), either through simple physical mixtures or the formation of hybrid materials, has been scarcely explored, highlighting the need for further systematic investigations.

6. Catalytic Upgrading of Plastic Waste

In addition to lipid-based feedstocks, other second-generation sources have gained increasing attention as complementary routes to meet the growing demand for SAF. Although WCO represents an attractive low-cost and low-carbon feedstock, its limited availability is insufficient to sustain large-scale SAF production [52]. In this context, alternative feedstocks such as plastic waste emerge as promising candidates due to their high hydrocarbon content, wide availability, and the urgent need for environmentally responsible disposal pathways.

Global plastic consumption has increased significantly over recent decades, leading to a substantial rise in plastic waste generation. This growing volume places significant pressure on waste management systems and represents an environmental concern. Since 1950, approximately 6.3 billion tons of plastic have been produced worldwide, of which only about 9% has been recycled [144].

From creation to disposal, plastic has detrimental consequences on the ecosystem. Its end of life causes a number of issues, including the release of toxic gases through incineration, the formation of microplastics during degradation in the environment or in landfills, which have an impact on human and animal health, and contribute to landfill overload due to its prolonged degradation time, even though its production involves the

consumption of fossil resources and the emission of GHG [14]. In this context, promoting an appropriate and sustainable end-of-life destination for plastics is crucial to minimize environmental damage and ensure long-term ecological balance.

There are several classification systems for different types of plastics, which mainly depend on the stage of the plastic life cycle considered. One of the most widely used systems is the resin identification code (RIC), designed for both the use and end-of-life phases and commonly found on consumer packaging. Developed to support recycling processes, RIC originated the ASTM D7611/D7611M-20. This system defines standardized symbols and numerical codes for six packaging plastics: polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) (all numbered from one to six, while code seven is reserved for other polymers) [145].

Overall, plastics are distinguished by their chemical composition, with each polymer consisting of repeating monomer units. Figure 9 illustrates the RIC and the condensed molecular formula of each polymer. They are composed mainly of C and H atoms and, in some cases, heteroatoms like O and Cl. Their C–C bonds can be cleaved by hydrogenolysis reactions in the presence of hydrogen pressure, temperature, and a metal-supported catalyst [13,146]. The produced hydrocarbons can undergo cracking and isomerization reactions. In this perspective, plastics are attractive feedstocks for jet fuel production due to their chemical structure and the urgency to give a final disposition to plastic waste.

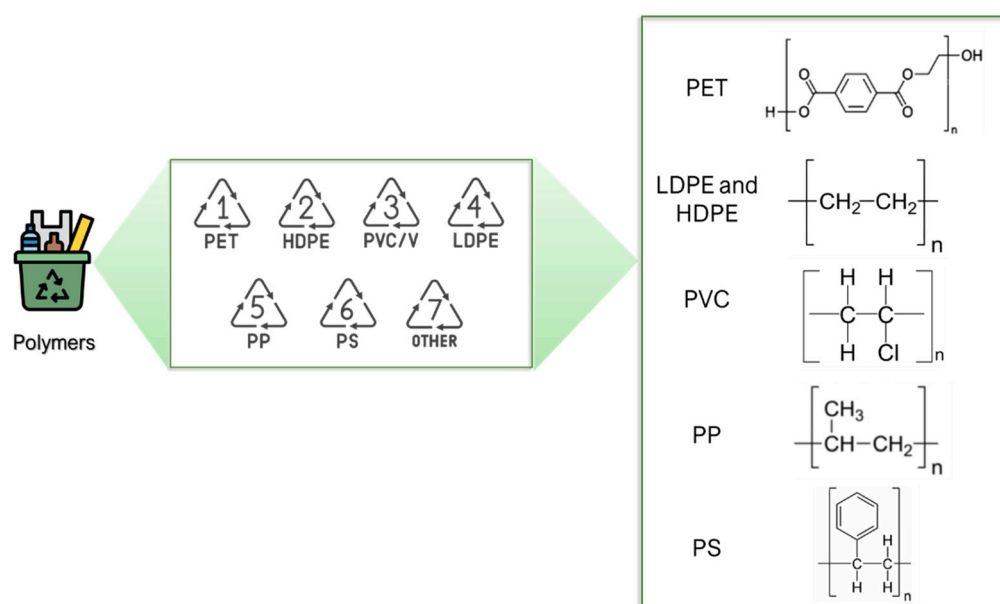


Figure 9. Plastic recycling RICs and their molecular formula.

The production of aviation fuel from plastic residues is not yet consolidated as one of the technologies defined by the ASTM. However, advances regarding the development of a new technological route to convert plastics have been recently debated by the ASTM Committee D02 on Petroleum Products, Liquid Fuels and Lubricants. The proposed standard route, plastic-to-jet synthetic kerosene with aromatics (PtJ-SKA), admits that the feedstock is a waste plastic processed oil made from post-consumer waste plastic mainly composed of LDPE, HDPE, and PP [147]. Consequently, studies involving the conversion of these feedstocks have been emerging in recent years. The most widely produced industrial polymers are LDPE and HDPE, and, therefore, they are also the most commonly studied in the literature [12]. From a process point of view, their conversion could be approached by applying catalytic systems analogous to those used in the upgrading of lipid-based feed-

stocks to SAF, adapting reaction conditions and catalyst formulations to accommodate the polymeric nature of plastics. However, it is important to note that, while lipid conversion is mainly governed by deoxygenation pathways, the conversion of polyolefins involves hydrogenolysis at metal sites and cracking reactions over both metal and acid sites.

Different catalysts have been developed to convert plastic into liquid fuels. Noble metals such as Ru have a special role in hydrogenolysis reactions and are mostly applied in polymer reactions. Commercial Ru/C was studied by Jia et al. [148], Rorrer et al. [149], and Chen et al. [146] to convert HDPE and LDPE into liquid fuels. The results showed great performance of this catalyst, with a 99–100% conversion and selectivity of 60% in C₈–C₁₆ (entry 1, Table 6), a liquid yield of 45% (entry 2, Table 6), and selectivity of 57% in C₁₂–C₂₀ (entry 3, Table 6). Despite differences in the use of Ru/C, some consistent trends can be observed. Complete conversion is achieved in all cases, confirming its high activity for hydrogenolysis. However, product distribution depends strongly on reaction conditions. Higher temperatures and shorter times favor C₈–C₁₆ hydrocarbons, whereas milder conditions require longer reaction times and tend to produce heavier fractions or lower liquid yields.

Table 6. Results of the catalytic conversion of different polymers ^a.

Entry	Polymer	Catalyst	Reaction Conditions	Catalyst:Polymer	Solvent	Performance (%)	Ref.
1	HDPE	Ru/C	220 °C, 1 h, 60 bar ^b	1:5	<i>n</i> -hexane	X = 99 S _{C8-C16} = 60	[148]
2	LDPE	Ru/C	200 °C, 16 h, 20 bar ^b	1:28	<i>n</i> -octadecene	X = 100 Y _{liquid} = 45	[149]
3	LDPE	Ru/C	175 °C, 76 h, 82 bar ^b	1:10	Solvent free	X = 100 S _{C12-C20} = 57	[146]
4	LDPE	Ru/milled-ZSM-22	290 °C, 2 h, 50 bar ^b	1:10	Solvent free	Y _{liquid} = 80.7	[150]
5	LDPE	Ru/CeO ₂	240 °C, 8 h, 60 bar	1:34	Solvent free	X = 99 Y _{C5-C21} = 84	[19]
6	LDPE	Ru/WZR	250 °C, 2 h, 50 bar ^b	1:40	Solvent free	X = 99 S _{C8-C16} = 33	[151]
7	LDPE	Pt/Al-MCM-48	300 °C, 4 h, 40 bar ^b	1:10	Solvent free	X = 99.3 S _{C9-C15} = 85.9	[97]
8	HDPE	Ni-Hβ	250 °C, 20 h, 30 bar ^b	3:4	Solvent free	X = 95 S _{C8-C16} = 80	[152]
9	LDPE	Ni/SiO ₂	280 °C, 4 h, 30 bar ^b	1:5	Solvent free	X = 100 Y _{C5-C22} = 81.2	[153]
10	HDPE	H-USY	300 °C, 1 h, 20 bar ^b	1:4	Solvent free	X = 60 S _{C7-C12} = 48 S _{C13-C20} = 50	[154]
11	LDPE	Pt/WO ₃ /ZrO ₂ + HY	250 °C, 1 h, 30 bar ^b	1:10	Solvent free	X = 100 S _{C8-C16} = 31	[20]
12	LDPE	Pt-Ru/TMSN + H-β	260 °C, 2 h, 10 bar ^b	1:5	Solvent free	X = 100 S _{C4-C8} = 75.6	[155]
13	LDPE	Ru/CNT _{ox} + H-Y	325 °C, 3 h, 30 bar	1:10	Solvent free	X = 99 S _{C8-C16} = 80	[156]

^a All the catalytic systems were done in batch mode; ^b Initial H₂ pressure at room temperature.

Other supports beyond carbon have also been investigated to enhance the catalytic performance. Cheng et al. [150] reported a maximum liquid yield of 80.7% from LDPE using Ru/milled-ZSM-22 at 290 °C, highlighting the role of zeolitic acidity in promoting controlled chain cracking (entry 4, Table 6). Nakaji et al. [19] achieved nearly complete conversion (99%) and liquid yield in C₅–C₂₁ of 84% from LDPE using Ru/CeO₂ (entry 5, Table 6). However, these high liquid yields were obtained under relatively severe conditions, requiring a long reaction time (8 h) and high hydrogen pressure (60 bar), which may limit their industrial applicability. Using Ru supported on W and Zr (Ru/WZR), Wang

et al. [151] reported nearly complete LDPE conversion with significant selectivity toward C₈–C₁₆ hydrocarbons (33%) and other range fuel hydrocarbons (entry 6, Table 6).

Pt- and Ni-based catalysts have also been investigated for PE conversion. Liu et al. [97] reported 99.3% LDPE conversion using Pt/Al-MCM-48, with high selectivity toward the jet fuel range, achieving 85.9% of products in the C₉–C₁₅ fraction at 300 °C (entry 7, Table 6). The mesoporous Al-MCM-48 support with moderate acidity contributed to effective diffusion and controlled chain scission, limiting cracking to lighter alkanes. In contrast, Ni-based catalysts have been explored as lower-cost alternatives, although they often require longer reaction times or more severe conditions. Zhang et al. [152] achieved 95% HDPE conversion with 80% selectivity in the C₈–C₁₆ range using Ni-H β after 20 h (entry 8, Table 6). Zhao et al. [153] reported complete LDPE conversion over Ni/SiO₂, with 81.2% in total liquid products in the C₅–C₂₂ range (entry 9, Table 6).

The use of zeolitic catalysts as single-component systems has also been reported. Costa et al. [154] investigated H-USY (Si/Al = 15) for HDPE conversion, achieving 60% conversion at 300 °C. The product distribution was relatively balanced between the C₇–C₁₂ (48%) and C₁₃–C₂₀ (50%) fractions (entry 10, Table 6). It reflects the ability of zeolites to produce a wide range of alkanes, but with limited conversion. To overcome the limitations of zeolite-only systems, combined bifunctional catalytic systems, mixing metal and acid functions, have been proposed [157,158]. Liu et al. [20] reported complete LDPE conversion using Pt/WO₃/ZrO₂ combined with HY, although the product distribution was shifted toward lighter hydrocarbons, with 52% selectivity in the C₅–C₇ range (entry 11, Table 6). Similarly, Wang et al. [155] achieved full LDPE conversion using bimetallic Pt-Ru supported on trimethylsilylated micro-mesoporous silica nanocomposite (Pt-Ru/TMSN) combined with H- β , with predominant selectivity (75.6%) toward the C₄–C₈ fraction (entry 12, Table 6). Although mild conditions were employed, particularly the lower H₂ pressure (10 bar), the use of a bimetallic noble-metal catalyst remains a limitation from a cost perspective. Finally, Ferreira et al. [156] investigated Ru/CNT_{ox} physically mixed with H-Y zeolite (entry 13, Table 6). The catalytic system was notable for its ability to selectively produce jet fuel-range hydrocarbons under solvent-free and relatively mild conditions (325 °C, 3 h, 30 bar H₂). Under these conditions, it achieves a 50% liquid yield, with approximately 80% corresponding to C₈–C₁₆ hydrocarbons. In addition, the system promotes a significant level of isomerization (iso/n = 4–9) and shows high conversion and strong robustness when processing real plastic residues. Moreover, in the same study, the use of Ru/CNT_{ox} alone was insufficient to crack heavier hydrocarbons (C₁₇–C₃₀) into the jet fuel range, highlighting the key role of additional acid functionality provided by the zeolite in promoting cracking and isomerization reactions.

These studies demonstrate that combined catalytic systems are of interest for polymer conversion because the separation of metal and acid functions allows improved control of hydrocracking reactions. According to these authors, acid sites promote C–C bond cleavage and the formation of olefin intermediates, while metal sites enable H₂ activation and hydrogenation, limiting olefin accumulation. The balance between these functions is critical, as high acidity favors cracking reactions, whereas insufficient metal activity reduces hydrogenation efficiency. Further investigation into combining metal-supported catalysts with zeolites is needed, with particular interest in the use of CNT as support for the metallic phase alongside acidic solids.

Compared to HEFA, the catalytic upgrading of plastic waste presents additional technical and economic challenges, since HEFA is currently at a more advanced technology readiness level. Plastic conversion generally involves less uniform feedstocks and less predictable reaction pathways, which complicates process control and product selectivity. In particular, the cleavage of C–C bonds during plastic hydrocracking may produce a

broad product distribution, requiring additional separation and upgrading steps [159]. The process often requires relatively high temperatures and hydrogen pressures, leading to increased energy consumption and higher operating costs. Catalyst deactivation, mainly due to coke formation, metal sintering, and the presence of additives or heteroatom-containing contaminants in real mixed-plastic waste streams, also represents an important limitation. From an economic perspective, the demand for high-pressure hydrogen, the dependence on noble metal catalysts, feedstock pretreatment requirements, and the costs associated with product separation significantly affect process viability [160]. These challenges highlight the need for more selective and robust catalytic systems, improved heat management, and integrated process designs to enable large-scale production of plastic-derived SAF.

Although the addressed processes show promising performance at the laboratory scale, their scale-up remains challenging and depends strongly on reactor configuration. High hydrogen pressures and long reaction times increase operational complexity and raise safety concerns. In addition, the overall energy demand can be very high due to heating, cooling, and hydrogen compression and recycling, which significantly affect process efficiency. The need to separate and recompress unreacted hydrogen, together with broad product distributions, further increases process costs [160]. These aspects highlight that, beyond catalyst performance, process integration and energy efficiency remain critical limitations for large-scale implementation.

7. Conclusions and Future Perspectives

This work summarizes recent advances in the conversion of lipid feedstocks and plastic waste into the jet fuel range. Particular attention was given to hydroprocessing reactions, including deoxygenation, cracking, and isomerization, and the design of bifunctional heterogeneous catalysts capable of producing C₈–C₁₆ hydrocarbons, particularly highlighting the potential of carbon materials as supports.

In general, non-noble transition metals have shown a strong tendency to promote the deoxygenation pathway via HDO. In studies involving model compounds derived from lipid sources, catalysts supported on zeolites have demonstrated excellent deoxygenation and isomerization capabilities. However, several studies have reported limited catalyst stability due to coke deposition on the active sites of the zeolite pores. In contrast, carbon-based materials such as AC and CNT have been employed as catalyst supports, showing high catalytic performance and improved stability in consecutive reaction cycles. Nevertheless, these materials generally exhibit a lower intrinsic capacity for cracking and isomerization reactions. A similar trend has been observed in the catalytic conversion of vegetable oils and WCO, where mesoporous carbon-based materials such as CNT and CNF, as well as other mesostructured supports including metal oxides and mesoporous silicas, have been explored. In addition, the combination of supported catalysts with solid materials presenting moderate to high acidity has recently attracted attention, particularly for the catalytic upgrading of polyolefins into jet-fuel-range hydrocarbons. However, unlike lipid-derived feedstocks, the conversion of plastic polymers frequently relies on the use of noble metals due to the hydrogenolysis reactions required for C–C bond cleavage in polymer chains. In this context, developing non-noble transition metal catalysts with sufficient hydrogenolysis activity to replace noble metals remains a key challenge, particularly under milder hydrogen pressures and with complex plastic feedstocks.

Overall, the catalytic systems used for the conversion of lipid-based feedstocks share several similarities with those employed for upgrading plastic waste into liquid fuels, including jet fuel. This parallel suggests promising opportunities for the development of hybrid catalytic systems, such as composite materials or physical mixtures, that combine mesoporous carbon-based supports (e.g., CNT and CNF) with solids of moderate acidity,

including alumina, mesoporous silicas, and moderately acidic zeolites. In particular, controlling the proportion of carbon-based materials and acid components is critical, as higher fractions of acid supports favor cracking and isomerization, whereas higher carbon content enhances metal dispersion and catalyst stability.

Exploring strategies for in situ hydrogen production could prove useful in reducing the external demand for hydrogen, although most current studies still face limitations in terms of conversion efficiency and selectivity. In particular, achieving high C₈–C₁₆ selectivity at reduced hydrogen pressures (lower than 30 bar) remains a critical target for improving process viability. The design of such multifunctional catalytic systems may contribute to improving hydrocarbon selectivity, catalyst stability, and process efficiency, ultimately supporting the large-scale production of SAF from oils and improving technologies to convert plastic residues into jet fuel.

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