

Catalytic Upgrading of Biodiesel by Partial Hydrogenation of Its FAME Composition: A Systematic Review

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Abstract: Biodiesel is one of the most popular biofuels as it is a promising substitute for conventional diesel fuel, but for now, it cannot be used as a stand-alone fuel due to its low oxidative stability. For this reason, there have been efforts to upgrade biodiesel in the last few years through the partial hydrogenation of its fatty acid methyl esters (FAMES). This procedure succeeds in resolving the problem of low oxidative stability, but in some cases, a new issue arises as non-selective hydrogenation deteriorates the fuel's cold flow properties, which are crucial for vehicle's operation without damaging the vehicle's engine. More specifically, the problem of deteriorated cold flow properties is caused by the formation of trans-monounsaturated and fully saturated FAMES during the hydrogenation reaction. Hydrogenated biodiesels are preferred to contain more cis-monounsaturated FAMES because these are considered to have the best combination of high oxidative stability and good cold flow properties. As a result, various systems and methods have been tested to achieve selective partial hydrogenation of biodiesel FAMES. In this review article, the catalytic systems and processes that stood out in various research studies are presented, and the factors that lead to the best possible outcome are investigated and discussed.

Keywords: biofuels; biodiesel; catalytic upgrading; partial hydrogenation; green energy; FAME



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1. Introduction

The need that has emerged in recent decades to reduce dependence on fossil fuels due to their environmental impact has led to increased interest in developing biofuels (biodiesel, bio-oil, bio-jet fuel, etc.) [1–4]. One of the biofuels that stands out is biodiesel, which is considered a potential alternative to conventional diesel because of its many advantages, such as zero contribution to carbon dioxide increase, higher cetane number, lower carbon monoxide and unburned hydrocarbon emissions, and in addition, it is biodegradable and less toxic [2,5–11].

However, there is a pressing need to identify appropriate non-edible oil sources and develop catalysts with bifunctional site properties that are easily recyclable. These catalysts should efficiently facilitate the one-pot conversion process. Additionally, given the abundance of transition metals in the Earth's crust and their diverse chemical properties, catalysts based on transition metals play a pivotal role in initiating the creation of active intermediates from hydroxyl or carbonyl groups in biomass [12]. According to Li et al. [13], a biomass-derived hydrophobic catalyst (FDCA/SA-Hf) exhibited significant potential in the realm of heterogeneous acid-mediated catalysis, particularly in the context of biodiesel production from non-edible oils. Wang et al. [14] successfully synthesized and applied one-pot conversion of *Euphorbia lathyris* L. seed oil to biodiesel, a bifunctional acid heterogeneous catalyst with high efficiency and recyclability. In another study, Chen et al. [15] applied a novel Lewis–Brønsted bifunctional catalytic material for the direct conversion of *Jatropha curcas* oil into biodiesel, where the catalyst exhibited commendable activity and

demonstrated the ability to be effectively reused. Additionally, biodiesel and biorefining precursors, such as 5-hydroxymethylfurfural (HMF), have gained increased attention in sustainable liquid/solid biomass valorization. Deep eutectic solvents (DESs), valued for their low cost, high tunability, long-term sustainability, and minimal environmental impact, are widely acknowledged as promising alternatives to conventional solvents in the industrial production of both biodiesel and HMF [16].

Nevertheless, biodiesel has noteworthy disadvantages that limit its wider application and, at present, it can only be used in mixtures with conventional diesel [17]. These disadvantages include its low oxidative stability (OS) and poor cold flow properties [10,11]. These fuel properties depend on the fatty acid methyl esters (FAMES) of which biodiesel is composed and, in particular, their degree of unsaturation [3,10,18,19]. The more polyunsaturated FAMES the fuel contains, the better its cold flow properties. Still, it has lower oxidative stability [7,17,20], resulting in the production of ketones, aldehydes, acids, and peroxides during storage due to oxidation, which are undesirable products as they degrade the properties of the fuel [3,5,6]. In contrast, the higher the percentage of saturated FAMES in biodiesel, the higher the oxidative stability but the worse the cold flow properties [6,18,21,22], leading to vehicle engine problems [5]. The FAMES considered the best compromise between satisfactory cold flow properties and high oxidative stability are cis-monounsaturated FAMES [23].

When biodiesel is produced, its FAMES consist of the corresponding fatty acids of the oils and fats used as feedstock [10,21,24,25]. Thus, the fuel is composed of a mixture of polyunsaturated, monounsaturated, and saturated FAMES in such proportions that it cannot be used as a fuel itself, but as a blend with conventional diesel. Specifically, two primary challenges are linked with applying pure biodiesel in compression ignition (CI) engines: inadequate cold flow characteristics and thermal stability. The first issue significantly affects the starting performance of CI engines, especially in situations with sub-zero environmental conditions, while the second issue is crucial for storing biodiesel for an extended duration. Therefore, utilizing diesel and biodiesel blends is a common method used to enhance biodiesel properties and leverage its advantages. Compression ignition (CI) engines can seamlessly accommodate blends containing up to 30% biodiesel mixed with diesel fuel without requiring any modifications [26]. Using biodiesel to a greater extent requires an upgrade.

The upgrading of biodiesel is achieved through the partial hydrogenation of polyunsaturated FAMES [22,27], with as much selectivity as possible toward cis-monounsaturated FAMES to obtain the highest possible oxidative stability and, at the same time, to maintain good cold flow properties as much as possible. The hydrogenation process can be performed by two methods that differ in hydrogen supply. The most common is that the hydrogen is supplied directly as molecular hydrogen in gaseous form, while the other is that the hydrogen is provided by a compound that acts as a donor during the reaction, which is called catalytic transfer hydrogenation [5,28]. Achieving the ideal result through partial hydrogenation presents challenges. During the hydrogenation of polyunsaturated FAMES, the monounsaturated FAMES present in biodiesel are also hydrogenated [29], so there is a risk of creating biodiesel with a large amount of saturated FAMES, which will not have the desired properties. Then, in parallel with hydrogenation, the isomerization of cis-monounsaturated FAMES to their trans isomers occurs, degrading the fuel quality by giving it sub-standard cold flow properties [21,30]. The extent to which these undesirable reactions take place depends significantly on the catalytic system used and the conditions chosen to carry out hydrogenation. Thus, for the successful upgrading of biodiesel, it is necessary to find a catalytic system and conditions that not only hydrogenate polyunsaturated FAMES to cis-monounsaturated FAMES but, at the same time, do not favor isomerization and complete hydrogenation.

The catalysts for upgrading biodiesel are mostly metal particles supported on porous materials consisting of carbon, silicon, or aluminum materials. The metals most commonly met in catalytic systems are Pd, Pt, and Ni, while there are few reports of attempted

upgrading using metals such as Rh and Cu. However, despite all of the development and research in biodiesel upgrading, there is still a need to find more effective catalysts to enable biodiesel use either in blends with conventional diesel in higher proportions or as a stand-alone fuel without posing any risk to the vehicle engine. Therefore, the current systematic review will present the factors that influence the hydrogenation outcome of biodiesel from the perspective of the catalytic system and reaction conditions and highlight those that lead closer to the desired outcome. In addition, a separate section of this review summarizes the partial hydrogenation of biodiesel using a biphasic aqueous/organic catalyst system. This green method has the advantages of easy recovery, reuse of the catalyst, and reduces the use of organic solvents [31–34].

2. Method

The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) [35] protocol was followed to conduct this systematic review (Figure 1). The Scopus database was used to find the literature. The search was conducted from 1 July 2023 to 1 August 2023 by searching for article titles, abstracts, and keywords with the keywords ‘partial AND biodiesel AND hydrogenation’, without filtering for the publication dates of the articles. The total search results included 86 articles, of which 27 were removed before screening because they had irrelevant titles compared to the review’s topic. Of the 59 articles left for screening, 7 were excluded because it was evident from their abstracts that they did not deal with the partial hydrogenation of biodiesel FAMES, while an attempt was made to retrieve the remaining 52 articles. Of these 52 articles, 6 could not be retrieved because they were not accessible. Finally, of the 46 remaining articles, 7 were rejected because their data did not fulfill the research purpose.

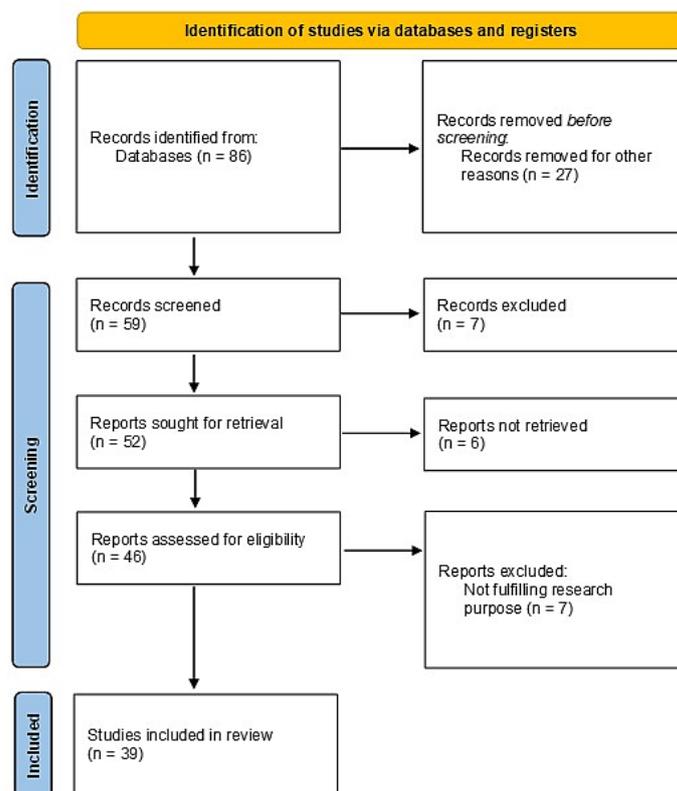


Figure 1. Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flow diagram for the systematic review.

3. Results and Discussion

Table 1 summarizes the key data derived from studies in which catalytic upgrading of biodiesel was carried out. In several studies, more than one catalyst was examined. Nevertheless, only the most effective catalyst was listed in Table 1.

Table 1. Studies investigating the catalytic partial hydrogenation of biodiesel.

Feedstock	Method/Catalyst	Reaction Conditions	Upgrade	Highlights	Ref.
Biodiesel derived from Kemiri Sunan oil	Partial hydrogenation/NiMo/C nanocrystal catalyst Catalyst/oil mass ratio: 1%	Batch reactor Temperature: 110 °C Pressure: 4 bar Stirring rate: 800 rpm Time: 3 h	Conversion of polyunsaturated FAMES: 20.41% Selectivity to monounsaturated FAMES: 8.87%	Low activity and selectivity at operating conditions	[17]
Soybean oil	Simultaneous transesterification and partial hydrogenation under supercritical methanol/Cu in powder form Catalyst/oil mass ratio: 10%	Stainless steel autoclave Temperature: 320 °C Pressure: 20 MPa Stirring rate: 1000 rpm Time: 0.5 h Methanol/oil molar ratio: 45:1	OS (h): 8.5 (4.6) IV (g/100 g): 78 (121.3) CN: 59.4 (47.5) CFPP (°C): −1.5 (−3.1)	Production and upgrade of biodiesel were achieved in a single step	[24]
Biodiesel derived from palm oil	Partial hydrogenation/Pd/C (biomass nanoporous carbon) activated with H ₃ PO ₄ Catalyst/oil mass ratio: 0.1%	Semi-batch reactor Temperature: 80 °C Pressure: 0.5 MPa Stirring rate: 700 rpm Time: 0.75 h	Conversion of polyunsaturated FAMES: 90% Selectivity to monounsaturated FAMES: 84% OS (h): 65 (13) CP (°C): 16 (14)	Low-cost nanoporous carbon from cattail flower proved to be an effective catalyst support	[36]
Biodiesel derived from soybean oil	Partial hydrogenation/Pd/Zr-SBA-15 (Zr/Si = 0.07) Catalyst/oil mass ratio: 0.75%	Semi-batch reactor Temperature: 100 °C Pressure: 4 bar Time: 2 h	Conversion of polyunsaturated FAMES: 80% after 1.8 h OS (h): 53 (2) CP (°C): 7 (2) PP (°C): 3 (0)	The presence of Zr in the catalyst's surface increased its activity	[7]
Biodiesel derived from jatropha oil	Catalytic transfer hydrogenation (CTH)/Raney-Ni Catalyst dosage: 8%wt	Microwave chemical reactor Temperature: 85 °C Stirring rate: 400 rpm Time: 0.83 h Hydrogen donor: isopropyl alcohol 24 g	Mass conversion ratio of 18:2 FAMES: 91.98%wt Selectivity to monounsaturated FAMES: 63% IV (g/100 g): 70.21 (97.08)	Microwave heating increased activity and selectivity of CTH	[28]
Biodiesel derived from soybean oil	Partial hydrogenation/Pd/SiO ₂ (Q30) Catalyst/oil mass ratio: 1%	Batch reactor Temperature: 120 °C Pressure: 4 bar Stirring rate: 1000 rpm Time: 2.5 h	OS (h): 30.4 (1.4) CP (°C): 6 (1)	Pd catalyst proved more suitable for partial hydrogenation than Pt and Ni catalysts	[18]
Biodiesel derived from rapeseed oil	Partial hydrogenation/Pd/SiO ₂ (Q30) 0.3 g catalyst 180 mL biodiesel	Semi-batch reactor Temperature: 80 °C Pressure: 0.3 MPa Stirring rate: 1000 rpm Time: 1 h	Conversion of polyunsaturated FAMES: 91.6% OS (h): 39 (1.9) CP (°C): 11 (−3) PP (°C): 5 (−11)	Pd catalyst proved more suitable for the partial hydrogenation than Pt and Ni catalysts	[19]

Table 1. Cont.

Feedstock	Method/Catalyst	Reaction Conditions	Upgrade	Highlights	Ref.
Biodiesel derived from soybean oil	Partial hydrogenation/Pd/MCM-41 Catalyst/oil mass ratio: 0.5%	Semi-batch reactor Temperature: 100 °C Pressure: 0.4 MPa Stirring rate: 500 rpm Time: 4 h	Conversion of polyunsaturated FAMEs: 93.4 Selectivity to cis-monounsaturated FAMEs: 55.2% OS (h): 11.71 (1.94) CP (°C): 15 (4)	Catalysts with small particle sizes presented higher selectivity	[21]
Biodiesel derived from rapeseed oil	Partial hydrogenation/Pd/SiO ₂ (Q ₃₀) Catalyst/oil mass ratio: 0.2%	Semi-batch reactor Temperature: 80 °C Pressure: 0.3 MPa Stirring rate: 1000 rpm Time: 1 h	OS (h): 38.98 (1.89) CP (°C): 11 (−3) PP (°C): 5 (−11)	Non-porous and microporous supports improved selectivity	[37]
Biodiesel derived from poultry fat	Hydrogenation/4%wt Pd/C catalyst B113W from Sigma Aldrich, St. Louis, MO, USA Catalyst/oil mass ratio: 3.9%	Laboratory reactor model Parr 4575 Temperature: 120 °C Pressure: 4 atm Time: 2 h	OS (h): 11.8 (0.71) CN: 58.4 (47.3)	The hydrogenated product was unsuitable for cold weather conditions	[38]
Soybean oil	Simultaneous transesterification and catalytic transfer hydrogenation (CTH) under supercritical methanol/ 0.5%wt Pd/ZSM-5 Catalyst/oil mass ratio: 0.05%	Batch reactor Temperature: 300 °C Pressure: 10 MPa Horizontal shaking: 0.85 Hz Time: 0.5 h Methanol/oil molar ratio: 45:1	OS (h): 8 (4.6) CN: 60.5 (50) CFPP (°C): −4.1 (−3.8)	High-quality biodiesel was obtained in a single step and short time	[39]
Biodiesel derived from soybean oil	Partial hydrogenation/Pd-Ba/SiO ₂ Catalyst/oil mass ratio: 1%	Semi-batch reactor Temperature: 80 °C Pressure: 4 bar Stirring rate: 500 rpm Time: 4 h	OS (h): 11.8 (2.2) CP (°C): 5.3 (4) PP (°C): 0 (−2)	Catalyst with proper basicity presented higher activity	[23]
Biodiesel derived from soybean oil	Partial hydrogenation/Pd-Mg/SiO ₂ Catalyst/oil mass ratio: 1%	Batch reactor Temperature: 80 °C Pressure: 4 bar Stirring rate: 1000 rpm Time: 4 h	OS (h): 11 (2) CP (°C): 10 (7) CFPP (°C): −2 (−6)	Catalysts with higher basicity presented higher selectivity	[8]
Soybean oil	Simultaneous transesterification and partial hydrogenation under supercritical methanol, without the use of H ₂ gas/Cu Catalyst/oil mass ratio: 10%	Batch reactor Temperature: 300 °C Pressure: 20 MPa Horizontal shaking: 0.85 Hz Time: 0.5 h Methanol/oil molar ratio: 45:1	OS (h): 6.3 (4.6) CN: 66.1 (50.6) CFPP (°C): −3.9 (−4.6)	High-quality biodiesel was obtained in a single step	[40]
Biodiesel derived from jatropha oil	Oxygen-assisted hydrogenation/Pd/γ-Al ₂ O ₃	Up-flow fixed bed reactor Temperature: 100 °C Pressure: 0.5 MPa Time: 2 h	Conversion of polyunsaturated FAMEs: 89% OS (h): 13.2 (0.8) PP (°C): 13 (3)	Co-feeding of O ₂ reduced the deactivation rate Drawback: not an economically feasible method	[41]

Table 1. Cont.

Feedstock	Method/Catalyst	Reaction Conditions	Upgrade	Highlights	Ref.
Biodiesel derived from palm oil	Partial hydrogenation/Ni/C Catalyst/oil mass ratio: 5%	Batch reactor Temperature: 120 °C Pressure: 6 bar Stirring rate: 200 rpm Time: 2.5 h	Yield of monounsaturated FAMES: 9.87% Selectivity to monounsaturated FAMES: 10.58 OS (h): 10.3 (9.75) IV (g/100 g): 82.38 (91.78) CN: 55.59 (52.51)	Low activity and selectivity	[42]
Biodiesel model from pure compounds	Partial hydrogenation/5.7%wt Pd/C commercial catalyst 50 mg Catalyst 1 mL FAME mixture	Schlenck tube Temperature: 50 °C Pressure: 1 atm Time: 1 h Solvent: 5 mL n-heptane	Conversion of polyunsaturated FAMES: 82.9% Yield of monounsaturated FAMES: 81.1% Selectivity to monounsaturated FAME: 97.8% Selectivity to cis-monounsaturated FAMES: 51.5%	Successful partial hydrogenation was achieved under uncommonly mild conditions using n-heptane as solvent	[43]
Biodiesel derived from tobacco seed oil	Partial hydrogenation/5.7%wt Pd/C commercial catalyst	Schlenck tube Temperature: 15 °C Pressure: 0.1 MPa Stirring rate: 300 rpm Time: 1 h Solvent: 5 mL n-heptane	Conversion of 18:2-FAMES: 97% Yield of monounsaturated FAMES: 91.3% Selectivity to monounsaturated FAMES: 94.1% Selectivity to cis-monounsaturated FAMES: 43% OS (h): 61.8 (4.3) IV (g/100 g): 82.9 (145.6) CN: 55 (40.8) CP (°C): -2.8 (-2.7) PP (°C): -9.8 (-9.8) CFPP (°C): -6.4 (-12.4)	Successful partial hydrogenation was achieved under uncommonly mild conditions using n-heptane as a solvent	[44]
Biodiesel model from pure compounds	Catalytic transfer hydrogenation using NaBH ₄ as hydrogen donor/Ni-La-B Catalyst/oil mass ratio: 10%wt	Three-neck glass flask Temperature: 85 °C Time: 2.5 h Hydrogen donor: 1.14 g NaBH ₄	Conversion of 18:2-FAMES: 95.4% OS (h): 35.3 (4.1) IV (g/100 g): 76.1 (151.9)	NaBH ₄ was an effective hydrogen donor for the CTH process	[45]
Biodiesel derived from jatropha oil	Partial hydrogenation/Ni/Bentonite Catalyst/oil mass ratio: 3.33%wt	Temperature: 200 °C Pressure: 0.3 MPa Stirring rate: 400 rpm Time: 1 h	Conversion of 18:2-FAMES: 75% OS (h): 18 (6.5) CP (°C): 0.8 (0.8) CFPP (°C): 10 (-3.5)	The catalyst did not show any decrease in its activity after 5 uses	[46]

Table 1. Cont.

Feedstock	Method/Catalyst	Reaction Conditions	Upgrade	Highlights	Ref.
Biodiesel derived from palm oil	Partial hydrogenation/30%wt Ni/Electrospun silica fiber 0.4 g catalyst	Continuous fixed bed reactor Temperature: 140 °C Pressure: 1 bar Time 4 h Biodiesel feed rate: 0.44 g min ⁻¹	Conversion of 18:2-FAMES: 71.3% OS (h): 23 (16) PP (°C): 20 (16) FP (°C): 184 (184)	The catalyst was not stable enough for commercial application	[47]
Commercial biodiesel	Partial hydrogenation/Pd/activated carbon Catalyst/oil mass ratio: 1.5%	Semi-batch reactor Temperature: 120 °C Pressure: 0.4 MPa Stirring rate: 500 rpm Time: 1.5 h	Conversion of polyunsaturated-FAMES: 94.5% OS (h): 32.5 (1.49) CP (°C): 23 (16) PP (°C): 22 (16)	Hydrogenation in batch-type reactor was more selective than in continuous flow-type reactor	[48]
Biodiesel derived from soybean oil	Partial hydrogenation/in situ sulfur poisoned Pd-Pt/MCM-41(1:1) Catalyst/oil mass ratio: 1%	Semi-batch reactor Temperature: 100 °C Pressure: 0.4 MPa Stirring rate: 500 rpm Time: 4 h Additional sulphur content: 2 ppm	OS (h): 65 (0.6) CP (°C): 7 (2)	Bimetallic Pd-Pt (1:1) catalyst was more active than Pd and Pt catalysts. Poisoned Pd-Pt/MCM-41(1:1), catalyst presented higher selectivity.	[49]
Biodiesel derived from soybean oil	Partial hydrogenation/Pd/Pd/ImS3-12@Al ₂ O ₃ in BMIM-NTf ₂ ionic liquid 1.3 μmol Pd 6 mL biodiesel	Stainless steel autoclave Temperature: 27 °C Pressure: 75 atm Stirring rate: 500 rpm Time: 4 h 1 mL BMIM-NTf ₂	OS (h): 28 (<1)	The catalyst was obtained easily and showed good recyclability due to phase separation between ionic liquids and hydrogenated products	[30]
(a) Biodiesel derived from used cooking oils and (b) Biodiesel derived from fats from rendering plants	Hydrogenation/Nickel catalyst B113W from Degussa Ni content: 0.4%wt Hydrogen content: 5%wt	Laboratory autoclave Temperature: 180 °C Pressure: 400 kPa Time: (a) 2 h and (b) 3 h	OS (h): (a) 93.6 (3.9) and (b) 35.3 (1.3)	Hydrogenation increased biodiesel's oxidative stability	[50]
Biodiesel derived from palm oil	Partial hydrogenation/0.5wt% Pd/SBA-15	Fixed bed reactor Temperature: 100 °C Pressure: 0.3 MPa TOS: 28 h 0.37 g min ⁻¹ biodiesel	Conversion of polyunsaturated FAMES: 36.4% Selectivity to cis-monounsaturated FAMES: 86.4% OS (h): 27.9 (19.4) CP (°C): 13 (12) PP (°C): 12 (12)	Catalyst with high metal dispersion, weak acidity framework, and fast molecular diffusion presented higher activity and selectivity	[51]
Biodiesel derived from palm oil	Partial hydrogenation/1%wt Pd/SBA-15 Catalyst/oil mass ratio: 0.3%	Batch reactor Temperature: 80 °C Pressure: 0.5 MPa Stirring rate: 1000 rpm	OS (h): 28 (5.1) CP (°C): 17 (13) PP (°C): 16 (13)	Catalyst with higher Pd particle dispersion and well-ordered pore channels exhibited higher activity and tolerance to impurities	[27]

Table 1. Cont.

Feedstock	Method/Catalyst	Reaction Conditions	Upgrade	Highlights	Ref.
Biodiesel derived from soybean oil	Partial hydrogenation using DBD plasma reactor/Raney-Nickel Catalyst/oil mass ratio: 3%	DBD plasma reactor Temperature: 25 °C Pressure: 0.1 MPa Time: 1.5 h Circulation flow rate: 40 mL/min Working Voltage: 17.68 kV	Conversion of polyunsaturated FAMEs: 57.04% Selectivity to monounsaturated FAMEs: 77.75%	Successful biodiesel upgrade at room temperature and atmospheric pressure in the DBD plasma reactor	[29]
Biodiesel derived from palm oil	Partial hydrogenation/Pd/SBA-15 Pd/oil mass ratio: 6.67×10^{-5}	Batch-type reaction system Temperature: 80 °C Pressure: 0.5 MPa Stirring rate: 1000 rpm	Conversion of polyunsaturated FAMEs: 90% after 0.3 h	The Pd/SBA-15 prepared catalyst presented higher activity and selectivity than the commercial Pd/C catalyst	[52]
Biodiesel derived from linseed oil	Partial hydrogenation in biphasic aqueous/organic system/Rh/TPPTS TPPTS/Rh molar ratio: 4 C=C/Rh molar ratio: 500	Autoclave Temperature: 80 °C Pressure: 10 bar Stirring rate: 770–850 rpm Time: 2 h	Selectivity to monounsaturated FAMEs: 79.8%	Easy catalyst by simple two-phase separation. Activity remained at the same level after consecutive runs	[53]
Biodiesel derived from soybean oil	Partial hydrogenation in biphasic aqueous/organic system / Rh/TPPTS TPPTS/Rh molar ratio: 5 C=C/Rh molar ratio: 2500	Autoclave Temperature: 120 °C Pressure: 10 bar Stirring rate: 770 rpm Time: 0.17 h	Increase in monounsaturated FAMEs (mol%): 68.6 (26.6)	Activity and selectivity remained at the same levels after three consecutive runs	[31]
Biodiesel derived from soybean oil	Partial hydrogenation in biphasic aqueous/organic system/Pd/BPhDS BPhDS/Pd molar ratio: 1 C=C/Pd molar ratio: 10,000	Autoclave Temperature: 120 °C Pressure: 20 bar Stirring rate: 620–850 rpm Time: 0.08 h	Selectivity to monounsaturated FAMEs: 78.4%	The use of water-soluble nitrogen-containing ligands increased the catalytic activity	[32]
FAMEs mixture derived from linseed oil	Partial hydrogenation in biphasic aqueous/organic system/Pt/TPPTS TPPTS/Pt molar ratio: 12 C=C/Pt molar ratio: 1000	Autoclave Temperature: 60 °C Pressure: 30 bar Stirring rate: 700 rpm Time: 0.33 h	IV: 85 (202)	Very low selectivity to trans-monounsaturated and saturated FAMEs. Drawback: the catalyst decomposed	[54]

Values in parentheses are the initial values of biodiesel properties before hydrogenation. In the case of simultaneous transesterification and partial hydrogenation, the values in parentheses are the values of the properties of the biodiesel produced under the same conditions but not hydrogenated. (OS) Oxidative Stability, (IV) Iodine Value, (CN) Cetane Number, (CFPP) Cold Filter Plugging Point, (CP) Cloud Point, (PP) Pour Point.

In Table 1, the upgrade column presents the biodiesel's properties before and after partial hydrogenation. The values in parentheses show the initial values of the biodiesel's properties before hydrogenation. In the case of simultaneous transesterification and partial hydrogenation, the values in parentheses present the values of the biodiesel's properties

under the same conditions but not hydrogenated. Moreover, the conversion, selectivity, and yield are presented in the same table. CP, CFPP, and PP are cold flow properties, and their increase is not desirable due to the resulting biodiesel's quality downgrade. In addition, IV is a value that must be decreased after upgrading. On the contrary, increases in OS and CN values are preferable, as they enhance product quality. Hence, a successful upgrading method ought to increase the OS and CN values with the least possible increase in cold flow properties.

3.1. Catalytic System

3.1.1. Heterogeneous Catalytic System

Most catalytic systems designed so far consist of metal particles supported on solid supports, with the metals most commonly tested being Pd, Pt, and Ni. In studies conducted using catalysts of these three metals and comparing them in terms of their activity and selectivity, Pd has emerged as the most active among the three, while Ni is the least active [8,18,19]. In addition, Pd was also reported to lead to the isomerization of cis-monounsaturated FAMES to trans isomers to a greater extent [19,48]. As for Pt, it has been observed to favor the complete hydrogenation of FAMES, resulting in the production of biodiesel with higher amounts of saturated FAMES [18,19]. Due to the above, Pd is of great interest as a catalyst for the partial hydrogenation of biodiesel.

Apart from the type of metal, the activity and selectivity of the catalyst are influenced by the size of the metal particles on the surface of the support. Numwong et al. [21] reported that tri- and di-unsaturated FAMES interact with the metal particle surface more strongly than monounsaturated FAMES due to the presence of more double bonds. In the same study, it was found that the catalyst with the smallest particle size had the highest selectivity for cis-monounsaturated FAMES, while as the size increased, the activity increased but the selectivity decreased. These results are in agreement with those of other studies, which report that larger particles increase the activity but promote the isomerization of cis-monounsaturated isomers to trans [8,18]. Numwong et al. [21] explained these observations by proposing that, on the one hand, larger particles have a larger planar surface with which FAMES can interact more strongly, resulting in increased activity. On the other hand, monounsaturated FAMES interact more with the catalyst and favor isomerization and production of saturated products. Furthermore, the activity of the catalyst is also related to the distribution of metal particles on the surface of the support, as it has been reported that catalysts with a higher dispersion of metal particles exhibit higher activity [7,19,27,51].

In addition, a parameter that plays an important role in both the activity of the system and selectivity of the reaction, again influencing the interaction being developed between the unsaturated FAMES and the catalyst, is the acidity of its surface. Thus, there are reports that catalysts with a more acidic nature exhibit greater activity [36,40,47]. Thunyaratchatanon et al. [7], in a study where Pd/Zr-SBA-15 catalysts were used with different amounts of Zr to study how its presence would affect catalyst performance, observed that all of them were more active than the simple Pd/SBA-15 catalyst, and this was attributed to the increase in acidity of the catalysts due to the presence of Zr. Also, interestingly, up to the Zr/Si = 0.07 ratio, the activity increased as the amount of Zr increased, after which a decrease was observed due to the development of such strong interactions that the adsorbed FAMES did not desorb. As a result, they reduced the accessibility to other FAMES. In addition, the increase in Zr also increased the amount of monounsaturated trans isomers in the final product. These results are consistent with the findings of Chen et al. [51] that catalysts with moderately and strongly acidic natures led to lower selectivity toward cis isomers compared to a weakly acidic catalyst. Similarly, in experiments using modified Pd-Mg/SiO₂ and Pt-Mg/SiO₂ catalysts, which exhibited a more basic nature compared to plain Pd/SiO₂ and Pt/SiO₂ catalysts, it was found that Mg-modified catalysts exhibited higher activity and higher selectivity for cis-monounsaturated FAMES [8]. This improvement was attributed to the increase in electron density induced by the presence of Mg, resulting in a weaker interaction between the already hydrogenated

FAMEs and the catalyst, easier desorption, and no isomerization of cis to trans isomers taking place. In contrast, in a study using Pd-Ca/SiO₂, Pd-Na/SiO₂, and Pd-Ba/SiO₂ catalysts, which also increased the basic character of the catalyst, it was observed that Pd-Ca/SiO₂ and Pd-Na/SiO₂ catalysts had significantly lower activity than the simple Pd/SiO₂ catalyst, while the Pd-Ba/SiO₂ catalyst showed higher activity and also the highest selectivity toward the formation of trans-monounsaturated FAMEs [23]. This difference in results was due to the difference in the number of base particles around the Pd particles, as while these elements differ in atomic weight, in all cases, the catalysts had 4%wt of base metal. Thus, in the case of Na and Ca, the effect of the bases was so strong that the interaction between the FAMEs and the catalyst was reduced to the point that the activity of the respective catalysts was reduced. On the other hand, the amount of Ba used was appropriate, so the basicity of the catalyst was increased to such an extent that it served in the desorption of the hydrogenated FAMEs without hindering the adsorption of the remaining FAMEs, thus increasing the activity of the catalyst. Therefore, the optimal catalyst selection depends on the desired balance between activity and selectivity. Particularly, catalysts with acidic characteristics tend to promote higher activity but may lead to lower selectivity toward cis isomers. On the other hand, catalysts with a more basic nature can exhibit higher selectivity for cis-monounsaturated FAMEs. Consequently, if maximizing activity is a priority and some trans isomers are acceptable, an acidic catalyst may be preferred. Conversely, if achieving high selectivity for cis-monounsaturated FAMEs is crucial, a catalyst with a more basic nature might be the better choice.

In addition, the result of partial hydrogenation is influenced by the morphology of the support carrier. Numwong et al. [37], studying the effect of SiO₂ pore size using Pd/SiO₂ catalysts, observed that small and large pores had lower activity than intermediate-sized pores but increased selectivity towards cis-monounsaturated FAMEs. The explanation given for these results was that the different pore size affected the probability of contact of FAMEs with the active sites. Specifically, they reported that the existence of small pores prevented FAMEs from accessing the active sites within them, resulting in FAMEs contacting only the active sites located on the outer surface of the catalyst, thus limiting activity. In the cases of intermediate-sized and large pores, FAME molecules could enter, but the probability of contacting a catalytic center was lower as the size increased, resulting in the difference observed. Phumpradit et al. [47] also reported the effect of support morphology by comparing a non-porous Ni/electrospun silica fiber catalyst with a porous Ni/porous silica ball. From the results, it was found that the fibrous catalyst showed higher activity and higher selectivity for cis-monounsaturated FAMEs. This observation was attributed to the higher accessibility offered by the non-porous morphology of the fibrous catalyst (also, the fibrous catalyst possessed a more acidic nature, which enhanced its activity). Therefore, in order to lead partial hydrogenation to the desired outcome, the morphology of the support carrier needs to be studied.

3.1.2. Reaction Conditions in Heterogeneous Catalytic Systems

Many studies have investigated how reaction conditions affect the outcome of biodiesel upgrading, so it is worth mentioning the effects of changing each hydrogenation parameter.

First, the parameter for which there are most reports is temperature. All studies agree that an increase in temperature favors the isomerization of cis-monounsaturated FAMEs into trans [8,43,45–48] because the formation of trans isomers is thermodynamically favored [8,39]. Moreover, it has often been reported that higher temperature leads to greater conversion to fully saturated FAMEs [43,46,48] and increases the reaction speed [45,46]. Hence, in order to achieve the best possible compromise between reaction speed and selectivity to cis-monounsaturated FAMEs, the preferred temperature is in the range of 80–120 °C, as shown in Table 1.

Pressure is another parameter that affects the result of hydrogenation. Numwong et al. [48] reported that increasing the pressure increased the conversion of polyunsaturated FAMEs, but at the same time, the amount of trans-monounsaturated FAMEs increased.

These findings are similar to those of Phumpradit et al. [41], according to which higher pressure increased the amount of trans-monounsaturated and fully hydrogenated FAMES in biodiesel. Furthermore, in the case of Zhu et al. [46], it has only been reported that increasing the pressure led to a higher reaction rate, while Thunyaratchatanon et al. [18] reported that by increasing the pressure while decreasing the temperature, the isomerization of cis to trans isomers occurred at a lower rate.

In general, solvents find extensive application at every stage of a catalytic process, encompassing catalyst synthesis, the catalytic reaction itself, and frequently, the purification of the end product. Several solvent properties affect the performance of a catalytic process, such as polarity and hydrogen-bond donating and accepting abilities. Selecting the appropriate solvent is often crucial to achieving high catalytic activity and selectivity. According to the results shown in Table 1, in most cases, no solvent is used for partial hydrogenation of FAMES [55]. Quaranta and Cornacchia [43] only tested n-heptane as a solvent and, using a commercial Pd/C catalyst, successfully carried out the hydrogenation of a mixture of FAMES under very mild conditions. In particular, they observed that compared to tests without solvent or using MeOH, DMC, and THF as solvents, hydrogenation with n-heptane was faster and cis to trans isomerization occurred to a lesser extent. The effectiveness of n-heptane as a solvent was also shown in a study by Quaranta et al. [44], in which the reaction was faster and a higher quality biodiesel was obtained using n-heptane compared to the solvent-free test. This effect of n-heptane was attributed to its low viscosity and weak interaction with the catalyst, which did not hinder reactant access.

3.1.3. Resistance and Deactivation of Heterogeneous Catalysts

The processes leading to the deactivation of heterogeneous catalysts are diverse. These processes can be categorized into six fundamental mechanisms of catalyst deterioration: (a) poisoning, (b) fouling, (c) thermal degradation, (d) formation of vapor compounds and/or leaching with the transport from the catalyst surface or particle, (e) vapor–solid and/or solid–solid reactions, and (f) attrition/crushing. Different deactivation mechanisms may dominate depending on the reaction and catalyst system, and multiple factors can act synergistically to influence catalyst performance [56]. Catalysts containing highly active transition metals as central components find extensive application across diverse industrial settings for chemical synthesis and conversion processes. Sulfur-containing species possess highly toxic properties and are frequently encountered in industrial processes. Therefore, enhancing the sulfur resistance of metal catalysts presents a challenging task [57].

During biodiesel upgrading, the main threats to catalysts are the sulfur species contained in the feedstock, which are adsorbed into the catalyst and deactivate it by hindering the adsorption of FAMES on the surface of the catalyst [18,27,41,49]. The vulnerability of each catalyst depends on various features, such as the acidity of the catalyst surface and metal particle size [49]. Specifically, Thunyaratchatanon et al. [18] reported that catalysts with large metal particles on their surface were deactivated faster than those with small particles. In addition, the presence of sulfur species in the feedstock not only leads to gradual deactivation but also affects the selectivity of the catalyst. Chen et al. [27] reported that the selectivity of the Pd catalyst was negatively affected in biodiesel with a higher sulfur species concentration. On the contrary, Na Rungsi et al. [49] used a bimetallic Pd-Pt/MCM-41 catalyst with a Pd-to-Pt ratio of 1 and observed that the addition of more sulfur-containing compounds in the feedstock increased the selectivity to cis-monounsaturated FAMES. It was suggested that this was due to the absorption of sulfur species on stronger catalytic sites where full hydrogenation was more likely to take place. Furthermore, it is worth mentioning that a possible solution to address the catalyst deactivation problem was proposed by Mochizuki et al. [41], who found that the catalyst was regenerated *in situ* when molecular oxygen was simultaneously added during the reaction by removing deactivating impurities.

3.1.4. Aqueous/Organic Biphasic Catalytic Systems

For the partial hydrogenation of biodiesel, the biphasic catalytic systems tested are of aqueous/organic phases. The aqueous phase contains an organometallic catalyst, while the organic phase consists of the FAMES destined for partial hydrogenation and an organic solvent, if needed. Such a system has the advantage of easy and quantitative recovery of the catalyst by simple two-phase separation, thanks to the non-miscibility of the aqueous/organic phase, and therefore easy catalyst reuse [31,32,54].

The organometallic catalysts used consist of a metal that acts as the catalytic center and ligands assembled around it. The common catalyst used in two-phase catalysis studies is Rh/TPPTS [31,32,53,54], while tests have also been performed with Ru, Pd, and Pt catalytic metals with the TPPTS ligand [32,54], as well as systems with Pd metal catalyst and TPPTS, EDTANa₄, DTPPA, and BPhDS ligands [32]. According to Stathis et al. [54], who investigated the partial hydrogenation of methyl esters derived from linseed oil using Rh/TPPTS, Pd/TPPTS, and Pt/TPPTS catalysts, the Rh catalyst showed the highest catalytic activity and highest selectivity toward the formation of fully saturated FAMES. The Pd catalyst showed the highest conversion to monounsaturated FAMES and highest formation of trans-monosaturated FAMES. On the other hand, the Pt catalyst showed the lowest activity and by far the lowest selectivity for the formation of trans-monosaturated and fully saturated FAMES. At the same time, in comparing two-phase catalytic partial hydrogenation with a heterogeneous catalyst, partial hydrogenation with Pt/Al₂O₃ catalyst was also tested, and the results showed that the heterogeneous catalyst had higher activity but favored the production of fully saturated FAMES to a much greater extent. Thus, the Pt/TPPTS catalyst seems attractive due to its significant selectivity toward the desired product, but it has the disadvantage that it decomposes more easily than the others, forming metallic Pt, the presence of which increases the formation of fully saturated FAMES.

In their research, Bouriazos et al. [32] tested different types of ligands in a biphasic system with Pd as the catalytic metal. In particular, they compared the TPPTS ligand, which is the common ligand used in partial biphasic hydrogenation, with nitrogenous EDTANa₄, DTPPA, and BPhDS ligands, all of which gave the system higher activity than the TPPTS ligand, with the BPhDS ligand achieving the highest activity.

Along with the choice of organometallic catalyst, the following parameters play an important role in the efficiency of two-phase catalysis: the presence of surfactants, pH, the use of an organic solvent, the molar ratio of ligand to catalytic metal, the molar ratio of C=C units to catalytic metal, temperature, and pressure.

Starting with the presence of surfactants, this is important to prevent the catalyst from decomposing and forming metal aggregates [32]. However, in the partial hydrogenation of FAMES, the addition of surfactants is not required if the feedstock already contains surfactants, as for example in various vegetable oil lecithins [31,53]. In addition, there is a different optimum pH for the reaction to take place for different feedstocks. For instance, there are reports that the activity increased by changing the pH from neutral to acidic in the partial hydrogenation of FAMES derived from sunflower oil [31,53], while in the partial hydrogenation of FAMES derived from linseed oil, the highest activity was achieved when the reaction was carried out at neutral pH [31]. Furthermore, the organic solvent parameter is also dependent on the feedstock. Bouriazos et al. [53] reported that the partial hydrogenation of FAMES derived from sunflower oil had no significant difference whether or not an organic solvent was used. Whereas in the case of FAMES derived from linseed oil, several organic solvents were used, and the one that gave the highest activity in the system was diethyl ether. In addition, it has been reported that the water-to-organic solvent ratio is an influential parameter. Bouriazos et al. [31] observed that higher activity and selectivity to monounsaturated-FAMES were achieved when a water-to-n-hexane ratio of 30/10 was used. A possible explanation was that the micelle, formed from the surfactants, was better stabilized at that ratio.

Furthermore, the molecular ratio of ligand to catalytic metal seems to play a triple role in the catalytic system by affecting its activity, selectivity, and protection against decomposition.

In particular, the ratio reduces the system's activity as it increases [31,54] and reduces the system's selectivity for trans-monosaturated FAMES [54]. Stathis et al. [54] suggested a possible explanation for this observation, attributing it to the increased competition that arises between ligand and substrate for coordination around the catalytic center when the amount of free ligand molecules increases. It is also reported that decomposition was prevented for the Pt/TPPTS catalyst when the ligand-to-catalytic metal molar ratio was above a threshold [54]. Then, increasing the molar ratio of C=C units to catalytic metal increases the activity and selectivity of the system [31,32,53,54]. The proposed explanation for this is that stereochemical hindrance is created around the catalytic center. Finally, temperature and pressure are two important factors that act in the same way as in the conventional partial hydrogenation discussed earlier. That is, increasing these parameters increases the speed of the reaction but favors the formation of undesirable products [31,54].

It is also important to note that all of the two-phase systems used for the partial hydrogenation of FAMES, with the exception of the Pt/TPPTS catalyst, were robust, did not decompose, remained in the aqueous phase, and showed the same levels of activity when reused in continuous catalytic cycles [31,32,53].

3.2. Partial Hydrogenation Methods

3.2.1. Conventional Partial Hydrogenation

The phrase conventional partial hydrogenation in this article means the hydrogenation of biodiesel carried out using a heterogeneous catalyst and supplying the hydrogen required for the reaction in gaseous form as molecular H₂. An illustration of this method is given in Figure 2. As shown in Table 1, conventional partial hydrogenation is the most common process that has been applied so far for the partial hydrogenation of biodiesel. Since there are a large number of experiments using this method, some subcategories can be distinguished according to their metal, support, or other characteristics.

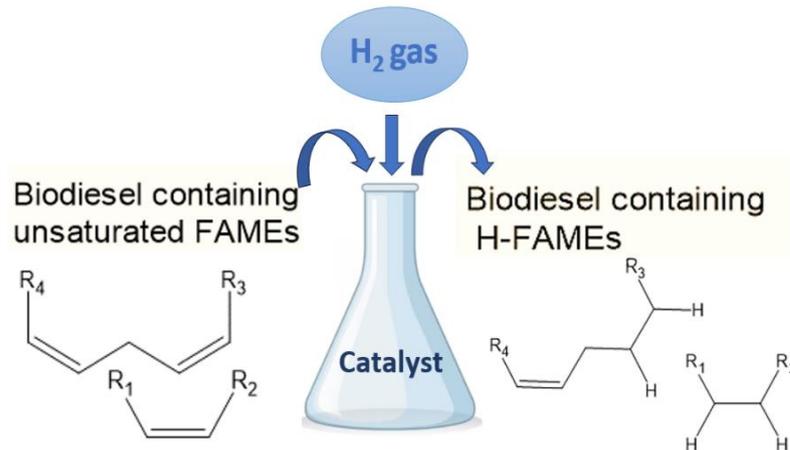


Figure 2. The conventional partial hydrogenation process.

The first subcategory is that of Ni catalysts. Simple Ni catalysts have the lowest activity (for example, NiMo/C and Ni/C [17,42]) and do not reach conversion levels such that significant upgrading can be achieved. However, with some modifications, such as the use of different supports, they have the potential to be significantly improved, as shown by the investigations of Zhu et al. [46] and Phumpradit et al. [47], who respectively used Ni/bentonite and Ni/electrospun silica fiber catalysts and were able to achieve conversions of 75% and 71.3%.

The next subcategory of this method is Pd catalysts, which have emerged as the most active and prevailed as the most effective in most studies (Table 1). Since a large number of different Pd catalysts have been used, they can also be divided into subcategories.

Starting with Pd catalysts with silicate support (such as SiO₂, SBA-15, and MCM-41), it is observed that these catalysts achieve high conversions leading to high oxidative stability,

completing the main objective of biodiesel upgrading. Nevertheless, these catalysts do not have high enough selectivity not to significantly degrade the cold flow properties of the feedstock. As a result, the cold flow properties of a biodiesel close to the specification limits may be deteriorated to the point that it is unsuitable for use after the partial hydrogenation process.

Then, there are Pd catalysts with carbon support. These catalysts reach high conversions and oxidative stability, like silica-supported catalysts. Moreover, they do not have such high selectivity to not alter the biodiesel's cold flow properties after the upgrading process.

Then, of interest are Pd catalysts to which a metal such as Ba or Mg has been added to give the catalyst's surface a more basic character so that it has the appropriate electron density to provide the best possible interaction with FAMES. Such catalysts were created by Thunyaratchanon et al. [8] and Thunyaratchanon et al. [23] and had increased selectivity, thus achieving both objectives of biodiesel upgrading: increasing oxidative stability without significant deterioration of cold flow properties.

3.2.2. Catalytic Transfer Hydrogenation

Catalytic transfer hydrogenation differs from conventional partial hydrogenation in how the hydrogen necessary for the reaction is supplied, as shown in Figure 3. Instead of being supplied as pure molecular hydrogen H_2 in gaseous form, the hydrogen is supplied through compounds that act as hydrogen donors [28,45]. The usual hydrogen donors are formates, formic acid, and alcohols. In particular, among alcohols, those preferred are secondary alcohols as they are the most active [28].

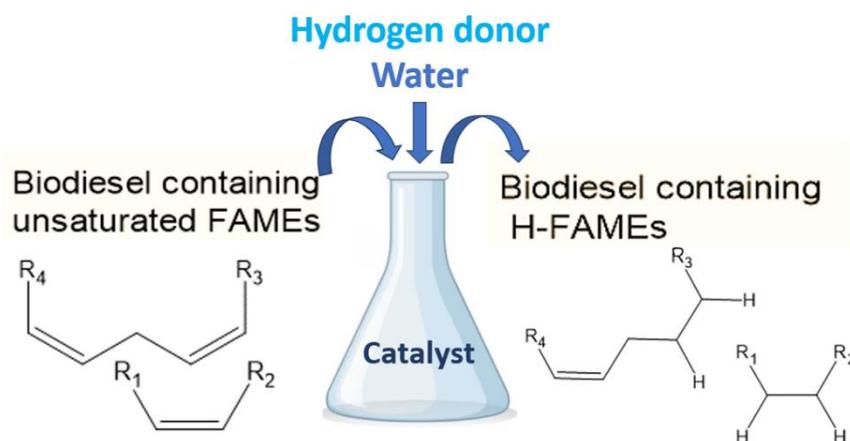


Figure 3. The catalytic transfer hydrogenation process.

This different method of hydrogen transfer offers economical and practical advantages. This occurs because it does not require the use of expensive and explosive pure hydrogen gas and does not require so many safety measures for the storage and transportation of the compounds used as hydrogen donors [28,45]. Moreover, this method has economic advantages, as Ni catalysts are cheaper than catalysts of noble metals such as Pd and Pt. Finally, it is important to mention that partial hydrogenation by this method occurs under mild conditions (atmospheric pressure and relatively low temperatures) [28,45].

3.2.3. Simultaneous Transesterification and Partial Hydrogenation under Supercritical Methanol

As its name suggests, in this process, biodiesel production co-occurs through the transesterification reaction and its upgrading through partial hydrogenation under supercritical conditions for methanol and in the presence of a catalyst suitable for hydrogenation. An important feature of this method is that it does not require a supply of hydrogen to the reaction mixture since methanol plays a dual role under supercritical conditions and in the presence of a catalyst. Apart from being a reactant in the transesterification reaction, it also acts as a hydrogen donor due to its decomposition without negatively affecting the reaction yield [24,39,40]. According to Lee et al. [40], in addition to methanol, the glycerol produced

by the transesterification reaction decomposes and also acts as a hydrogen donor, which is advantageous as it reduces the amount of glycerol in the final mixture after completion of the reaction. A simplified diagram of this process is shown in Figure 4.

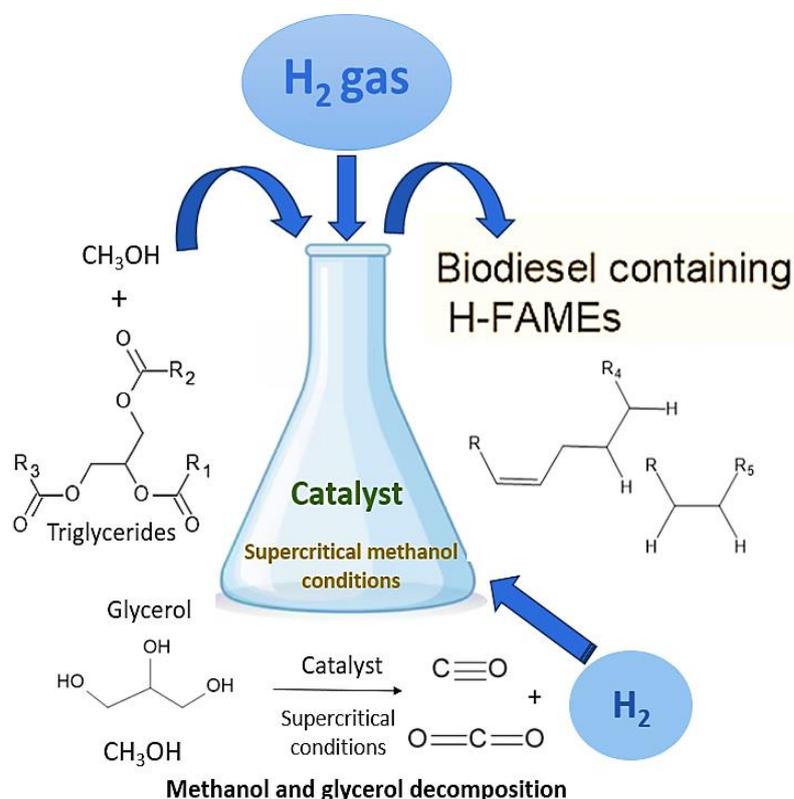


Figure 4. Simultaneous transesterification and partial hydrogenation method under supercritical methanol conditions.

It is interesting to note that, as shown in Table 1, biodiesel obtained with this method has improved oxidative stability and no significant difference in its cold flow properties compared to non-hydrogenated biodiesel. Therefore, the production of good quality biodiesel can be achieved in a single step via this method. A negative aspect of this method is that the temperature used is close to the decomposition temperature of FAMES [24,39,40]. Therefore, there is a risk of product loss if it is not handled correctly.

3.2.4. Partial Hydrogenation in Biphasic Aqueous/Organic Systems

With this method, partial hydrogenation occurs in a biphasic aqueous/organic catalytic system, with the catalyst located in the aqueous phase while the FAMES of biodiesel are in the organic phase, as shown in Figure 5. A very important feature of this method is the quantitative recovery of the catalyst with simple two-phase separation and its recyclability for continuous catalytic cycles without significantly reducing its activity and selectivity [31,53,54]. It is also worth mentioning the combination of high catalytic activity and selectivity that this system offers when operated under appropriate conditions, resulting in a very short time needed to produce the desired products. For instance, Bouriazos et al. [32] used the Pd/BPhDS organometallic catalyst in a two-phase system, achieving a TOF of 71 300 h⁻¹ in just 5 min, and the amount of monounsaturated FAMES increased from 22.5 mol% to 78.4 mol% in biodiesel derived from soybean oil.

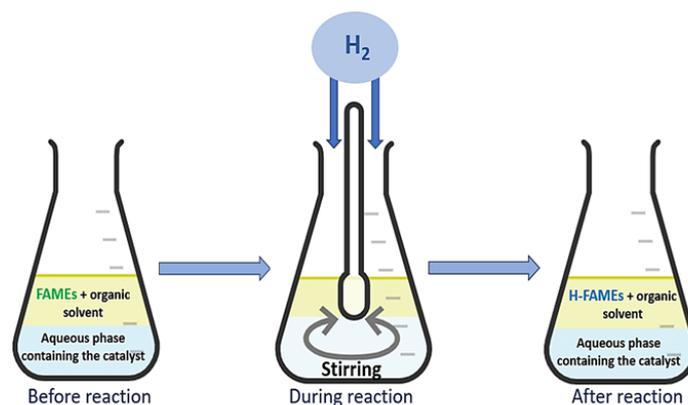


Figure 5. Biphasic aqueous/organic catalytic process.

3.3. Biodiesel Purification

Biodiesel purification can be achieved through several methods, with water washing being the most commonly utilized industrial process. The purification of biodiesel can also be accomplished through a dry washing process, employing solid sorbents like ion exchange resins, silica, activated carbon, and other adsorbents. This method is characterized by its speed, ease of integration into industrial plants, and cost-effectiveness [58]. Additionally, inorganic and polymeric membranes offer an alternative approach for biodiesel purification. These membranes act as selective barriers, effectively retaining the contaminants in biodiesel [59].

While hydrogenation is primarily aimed at improving biodiesel quality and meeting certain standards, it can also be considered a purification step as it removes impurities and improves specific fuel properties. However, separation of the catalyst from biodiesel after hydrogenation is a critical step in the overall process. The choice of a suitable separation method depends on various factors, including the nature of the catalyst, the reaction conditions, and the desired purity of the final biodiesel product. Separation of the catalyst from biodiesel in the final stage may not always be achieved through simple filtration. Hydrogenation processes often involve finely dispersed catalyst particles, which may be challenging to effectively separate using conventional filtration methods. Separation of the catalyst from biodiesel after hydrogenation typically involves additional steps, and the choice of method depends on the specific catalyst and process conditions [60].

4. Conclusions

In conclusion, this review underscores catalytic upgrading of biodiesel via partial hydrogenation of its fatty acid methyl ester composition for the first time, focusing on the applied catalytic systems. While efforts have focused on addressing challenges like low oxidative stability and poor cold flow properties, investigating unconventional methods is a significant departure from conventional approaches. Simultaneous transesterification and partial hydrogenation under supercritical methanol has emerged as a promising approach to enhance both oxidative stability and cold flow properties. Applying partial hydrogenation within a biphasic aqueous/organic system introduces a high turnover frequency and facilitates efficient catalyst recovery, presenting a novel solution in biodiesel upgrading. Future prospects for catalytic upgrading of biodiesel appear promising, considering the ongoing research and development in the field. Continued research into innovative catalysts and catalytic systems can lead to enhanced efficiency, selectivity, and overall performance in biodiesel upgrading. Additionally, exploring greener solvents, energy-efficient methods, and catalysts derived from renewable resources could minimize the environmental impact of biodiesel production. Overall, ongoing innovation and a holistic approach to addressing environmental and economic challenges shape a promising outlook for the biodiesel upgrading process.

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Nomenclature

BMIM-NTf ₂	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
BPhDS	Bathophenanthrolinedisulfonic acid disodium salt
CFPP	Cold Filter Plugging Point
CI	Compression Ignition
CN	Cetane Number
CP	Cloud Point
DBD	Dielectric-Barrier Discharge
DESs	Deep Eutectic Solvents
DTPPA	Diethylenetriaminepentakis(methyl-phosphonic acid)
EDTANa ₄	Ethylenediaminetetraacetic acid tetrasodium salt
FAMES	Fatty Acid Methyl Esters
H-FAMES	Hydrogenated Fatty Acid Methyl Esters
HMF	5-hydroxymethylfurfural
ImS3-12	3-(1-dodecyl-3-imidazolium)propanesulfonate
IV	Iodine Value
MCM-41	Mobil Composition of Matter No. 41
OS	Oxidative Stability
PP	Pour Point
SBA-15	Santa Barbara Amorphous-15
TOF	Turn Over Frequency
TPPTS	Triphenylphosphinetrisulfonic acid trisodium salt

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