

Green Upgrading of Biodiesel Derived from Biomass Wastes [†]

Elissavet Emmanouilidou ^{1,2} , Alexandros Psalidas ¹ , Anastasia Lazaridou ^{1,2}, Sophia Mitkidou ^{1,2}
and Nikolaos C. Kokkinos ^{1,2,3,*} 

¹ Department of Chemistry, School of Sciences, Democritus University of Thrace, Ag. Loukas, 654 04 Kavala, Greece

² Petroleum Institute, Democritus University of Thrace, Ag. Loukas, 654 04 Kavala, Greece

³ Hephaestus Laboratory, School of Sciences, Democritus University of Thrace, Ag. Loukas, 654 04 Kavala, Greece

* Correspondence: nikokkinos@mwpc.gr; Tel.: +30-2510462294

[†] Presented at the 5th International Electronic Conference on Applied Sciences, 4–6 December 2024; Available online: <https://sciforum.net/event/ASEC2024>.

Abstract: The rising demand for edible oils underscores the potential of non-edible oils for biodiesel production. However, biodiesel's low oxidative stability (OS) and poor cold flow properties due to high unsaturation levels limit its use. This study aims to improve OS through the partial hydrogenation of polyunsaturated FAMES using a Ru-TPPTS biphasic catalytic system. GC-MS analysis showed that the pre-hydrogenated biodiesel contained over 85% of unsaturated FAMES, mainly linoleic (C18:2) and oleic acid (C18:1). Hydrogenation reduced C18:2 FAME content by over 70% while increasing stearic acid level (C18:0 FAME), significantly enhancing OS by more than 135%. Further optimization is needed to meet the required quality and performance standards.

Keywords: biodiesel; upgrade; hydrogenation; biphasic catalysis; biomass; waste cooking oil

1. Introduction

Transportation is a major contributor to global greenhouse gas (GHG) emissions, mainly due to the reliance on fossil fuel combustion. Biodiesel emerges as a sustainable alternative, capable of reducing lifecycle GHG emissions by up to 85%, contingent on feedstock and production processes [1]. Utilizing waste cooking oils (WCOs) as a biodiesel feedstock addresses critical challenges, including ethical concerns and land-use competition associated with food-based biofuels, while also offering economic advantages due to the lower cost of WCOs [2–4]. However, using WCOs for biodiesel production presents several challenges, particularly due to variations in oil composition, high free fatty acid (FFA) content, and impurities such as water, food residues, and oxidation byproducts. The fatty acid composition of WCOs varies depending on their source and prior usage, typically consisting of a mix of saturated, monounsaturated, and polyunsaturated fatty acids, with the latter contributing to oxidative instability and poor cold flow properties in the resulting biodiesel [5–7]. Several methods are available for biodiesel production, including transesterification, direct use and blending, micro-emulsion, and thermal cracking. Transesterification is the preferred method for biodiesel production from WCOs due to its efficiency, cost-effectiveness, and well-established industrial application. However, before transesterification, WCOs require purification steps such as filtration, degumming,



Academic Editor: Nunzio Cennamo

Published: 10 March 2025

Citation: Emmanouilidou, E.; Psalidas, A.; Lazaridou, A.; Mitkidou, S.; Kokkinos, N.C. Green Upgrading of Biodiesel Derived from Biomass Wastes. *Eng. Proc.* **2025**, *87*, 14. <https://doi.org/10.3390/engproc2025087014>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

and drying to remove contaminants. Additionally, oils with high acidity indices necessitate an esterification pre-treatment to reduce FFAs and prevent soap formation during transesterification [8].

Various systems and methods have been explored to achieve selective partial hydrogenation of biodiesel FAMES, including heterogeneous and homogeneous catalytic approaches, different metal catalysts, and biphasic reaction systems. Stathis et al. [9] investigated the partial hydrogenation of polyunsaturated FAMES of linseed oil under mild reaction conditions employing water-soluble Pt/TPPTS (trisodium triphenylphosphine-3,3', 3'-tri sulfonate) catalysts. The iodine value (IV) was significantly reduced while maintaining a low trans-C18:1 ester content, whereas the traditional Ni-based partial hydrogenation of soybean oil resulted in substantially higher trans-fat formation at comparable IV reductions. Bouriazos et al. [10] employed water-soluble Rh-, Ru-, and Pd-TPPTS complexes for the partial hydrogenation of polyunsaturated FAMES of linseed, sunflower, *Cynara cardunculus*, and soybean oils. The results indicated that Rh/TPPTS catalytic complexes in green aqueous/organic biphasic systems achieved high selectivity for monounsaturated (C18:1) esters, producing first-generation biodiesel with enhanced oxidative stability, improved energy and environmental performance, and a low pour point. Zuo et al. [11] conducted ultrasonic-assisted catalytic transfer hydrogenation of biodiesel produced from cottonseed oil, utilizing Raney Ni as the catalyst, isopropanol as the hydrogen donor, and water as the solvent. Under the optimum conditions, the selectivity of trans-C18:1 and the IV value of biodiesel were reduced while also decreasing the yield of C18:0 and shortening the hydrogenation time, demonstrating that ultrasonic assistance is an efficient intensification method. Notably, biphasic reaction systems have been studied for first-generation biodiesel production utilizing edible feedstocks. Nevertheless, further development of biphasic catalytic hydrogenation systems should also be pursued for non-edible feedstocks. This study explores partial hydrogenation in aqueous/organic biphasic catalytic systems as an innovative and environmentally friendly approach to selectively hydrogenate polyunsaturated FAMES into cis-monounsaturated FAMES derived from waste-biomass feedstocks, like WCO [12,13]. The work aims to enhance biodiesel fuel properties, focusing on oxidative stability, as biodiesel exhibits low oxidative stability due to its high concentration of unsaturated fatty acid methyl esters (FAMES), especially polyunsaturated compounds.

2. Materials and Methods

A flow diagram of the process steps is illustrated in Figure 1. Waste cooking oil (WCO) obtained from a local restaurant was used as the primary feedstock for biodiesel production. The WCO sample was pretreated at 110 °C for 1 h, followed by filtration. As the acid value was found to be less than 2 mg KOH/g, the oil was directly subjected to transesterification under optimal conditions: reaction time of 1 h, 1 wt% sodium hydroxide (NaOH) catalyst, a methanol-to-oil molar ratio of 6:1, and a reaction temperature of 65 °C. All chemicals used were of analytical grade. The resulting biodiesel was characterized to evaluate its properties in accordance with EN ISO standard procedures [14]. The composition of fatty acid methyl esters (FAMES) in the biodiesel was further analyzed using gas chromatography–mass spectrometry (GC-MS) [15]. The analysis was conducted using an Agilent 6890N gas chromatograph system (Agilent Technologies, Santa Clara, California) integrated with an MSD 5975B mass spectrometer detector and a DB-XXLB capillary column. Helium served as the carrier gas at a 1.3 mL/min flow rate. The samples were diluted in n-hexane at a 1:100 ratio and introduced in split mode with a 1:100 split ratio. A 2 µL aliquot of each sample was injected using an Agilent 7683 auto-injector (Agilent Technologies, Santa Clara, CA, USA). The temperature program was initiated at 80 °C, held for 1 min, then increased at 15 °C/min to 180 °C, where it remained for 10 min. Subsequently, the temperature

was risen to 320 °C at 8 °C/min and maintained for 2 min, resulting in a total run time of 37.17 min. Compound identification was performed based on structural characteristics, utilizing the NIST MS Search V2.0 spectrum library and bibliographic data. Concentrations were determined by calculating the relative area percentages of the detected peaks.

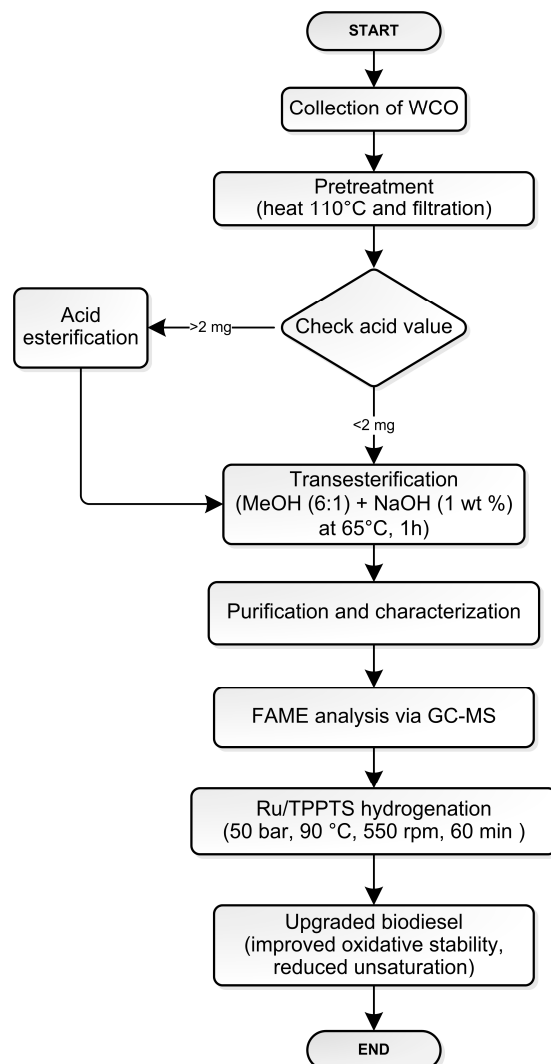


Figure 1. Flow diagram of the process steps.

The hydrogenation reaction was conducted in a 100 mL batch reactor (Autoclave Engineers, Erie State, US) under controlled conditions, where the catalyst interacted with the WCO biodiesel to selectively reduce the degree of unsaturation in the FAMEs. The Ru/TPPTS (ruthenium-tris (3-sulfonate phenyl) phosphine) catalyst was synthesized in situ to enable a direct interaction with the FAMEs in the WCO biodiesel. The molar ratio of TPPTS/Ru was 4.0066, with a catalyst concentration equal to 174.9 ppm and a volume ratio of organic/aqueous phase equal to 1. The reactor was purged with hydrogen, pressurized to 50 bar, and heated to 90 °C. The reaction mixture was stirred at 550 rpm for 60 min under these controlled conditions.

3. Results

The biodiesel yield was determined to be 87.3%. The primary measured properties of the WCO biodiesel sample before being hydrogenated are summarized in Table 1. As shown, the calculated density falls within the acceptable range of 0.86–0.91 g·cm^{−3}, as per EN ISO 12185 [14]. Additionally, the acid number is below the maximum limit of

0.5 mg KOH·g⁻¹, indicating good quality and minimal presence of free fatty acids. This reduces the risk of corrosion in engine parts [16]. The cold filter plugging point (CFPP) value is well below the country-specific maximum limit of +5 °C, making the biodiesel suitable for colder climates. A low CFPP demonstrates adequate cold-flow properties, minimizing the risk of filter clogging in low temperatures [17]. However, the oxidative stability is significantly below the minimum requirement per EN 14112 [14]. This is a critical issue, as poor oxidative stability can lead to fuel degradation during storage, with the formation of gums and sediments that can damage engines [18].

Table 1. WCO biodiesel properties before biphasic hydrogenation.

Property	Measured Value	Specs EN 14214	Test Method
Density at 15 °C, g·cm ⁻³	0.8868	0.86–0.91	EN ISO 12185
Acid number, mg KOH·g ⁻¹	0.40	<0.5	EN ISO 14104 [14]
CFPP, °C	−2.0	Country Specific Max. +5 °C	EN 116 [14]
Oxidative stability at 110 °C, h	0.34	>6	EN 14112

The GC-MS analysis indicated that the most abundant FAMES identified in the pre-hydrogenated biodiesel sample were unsaturated FAMES, as shown in Figure 2. Specifically, C18:2 and C18:1 methyl esters were found to constitute 48% and 39% of the FAMES, respectively, making up more than 85% of the total FAME content. This indicates that the biodiesel is predominantly composed of unsaturated fatty acids, which are typical of biodiesels derived from vegetable or WCOs.

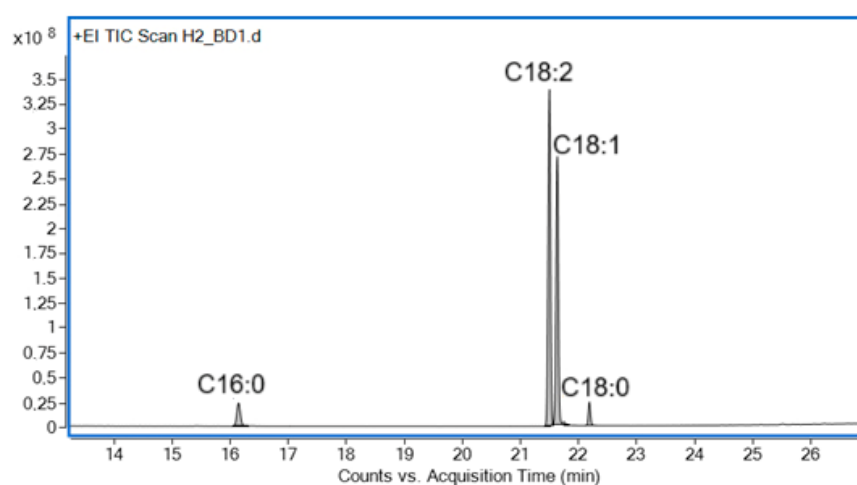


Figure 2. GC-MS chromatograph of pre-hydrogenated biodiesel.

Partial hydrogenation is crucial because it aims to reduce the unsaturation of fatty acid esters without creating trans fats, which are undesirable in biodiesel. The biphasic system could potentially enhance reaction control, minimize byproduct formation, and improve catalyst recovery and reusability. Figure 3 illustrates the formation of two distinct layers following the biphasic hydrogenation of the WCO biodiesel. The separation process was highly efficient, with the hydrogenated biodiesel forming one layer (upper), and the catalyst remaining in the aqueous phase (lower layer), enabling the straightforward recovery and reuse of the catalyst.

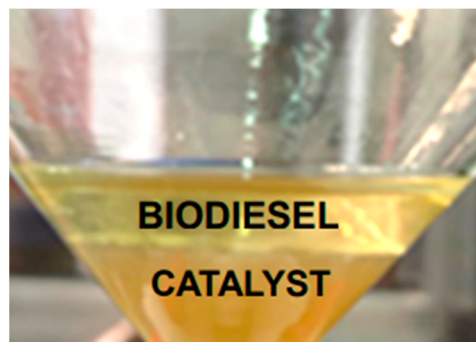


Figure 3. Hydrogenated biodiesel (upper layer) and aqueous phase with the Ru/TPPTS catalyst (lower layer).

The hydrogenated WCO biodiesel sample was further subjected to GC-MS analysis and OS measurement. As shown in Figure 4, the process significantly reduced the unsaturated linoleic acid (C18:2) methyl ester content by more than 70%, resulting in a final percentage of approximately 13.9%. Additionally, the content of stearic acid (C18:0) methyl ester showed a significant increase, reaching a final percentage of 30.4%, compared to the initial value of 4.1%.

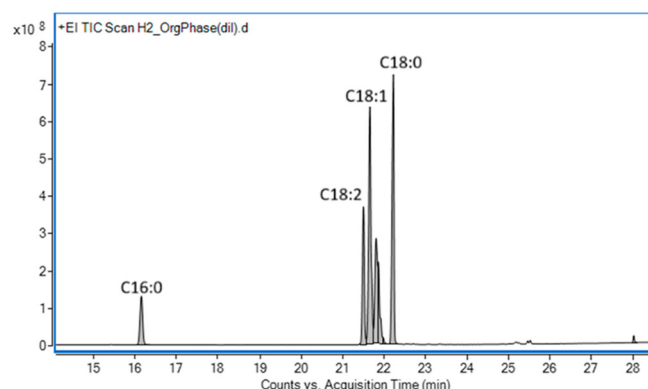


Figure 4. GC-MS chromatograph of hydrogenated WCO biodiesel sample.

This compositional change improved the oxidative stability of the biodiesel, enhancing it to 0.80 h. This indicates that the hydrogenation of biodiesel using the biphasic system improved the oxidative stability by more than 135%. This is a significant improvement, suggesting that the process effectively reduces the vulnerability of biodiesel to oxidation.

4. Discussion

The biodiesel produced from WCO generally met most of the EN 14214 standards [14]. This includes parameters such as density, acid number, flash point ($>120^{\circ}\text{C}$), CFPP, and water content ($<500\text{ mg/kg}$), which aligned with the EN 14214 standards for biodiesel quality. However, OS remained a significant challenge in its practical application. OS is closely linked to the degree of unsaturation in the FAMES present in biodiesel [6]. The antioxidant capacity of FAMES plays a crucial role in determining the ease of their oxidation. Saturated FAMES, such as methyl stearate (C18:0) and methyl palmitate (C16:0), possess no double bonds, which significantly enhances their oxidative stability and resistance to degradation. In contrast, unsaturated FAMES, like methyl oleate (C18:1) and methyl linoleate (C18:2), contain one or more double bonds, which can serve as sites for oxidative reactions, leading to rapid degradation [19,20]. As the percentage of unsaturated FAMES in the WCO biodiesel surpassed 85%, the fuel became increasingly susceptible to oxidative degradation. This heightened susceptibility resulted in its oxidative stability falling below

the minimum threshold required by the EN 14214 standard [14]. This observation highlights a critical issue in biodiesel production: achieving an appropriate balance between the degree of unsaturation and the fuel's oxidative stability. While unsaturated FAMES contribute to the desirable characteristics of biodiesel, such as improved fuel properties and renewable sourcing, excessive unsaturation compromises its storage stability and long-term usability [21].

The Ru-TPPTS biphasic catalytic hydrogenation system proved to be highly effective in modifying the composition of biodiesel derived from WCO. This catalytic system presents an efficient and environmentally friendly approach for altering the FAME profile of biodiesel. During hydrogenation, unsaturated FAMES are converted to their saturated counterparts, theoretically improving their oxidative stability. However, the degree of hydrogenation and the specific reaction conditions (such as temperature, pressure, and catalyst type) play a significant role in determining the extent of this improvement. By selectively hydrogenating polyunsaturated FAMES, the system reduces the number of double bonds, which directly contributes to an improvement in oxidative stability. The observed reduction in linoleic acid (C18:2) FAME levels indicates a decrease in the unsaturation of the biodiesel, which is a key factor in enhancing its oxidative stability. Furthermore, the increase in stearic acid (C18:0) FAME, a saturated FAME, suggests a shift toward a more stable and less reactive fuel composition. For biodiesel to meet OS parameters, the hydrogenation process must not only reduce the levels of polyunsaturated FAMES but also ensure that the resulting saturated FAMES possess OS. Further optimization of the hydrogenation process is essential to meet the EN 14112 specification, which outlines the requirements for the OS of biodiesel. Additionally, while hydrogenation may enhance OS, it is important to note that excessive hydrogenation can lead to the formation of unwanted byproducts or alter the beneficial properties of biodiesel. Optimizing the process will involve carefully controlling the extent to which polyunsaturated FAMES are hydrogenated to ensure that the biodiesel attains the desired level of oxidative stability without compromising other crucial fuel properties. Striking the right balance between oxidative stability and factors such as fuel efficiency, cold flow properties, and overall performance is key to meeting regulatory standards and ensuring biodiesel's viability for long-term, practical use in engines [6].

5. Conclusions

The catalytic upgrading of biodiesel through partial hydrogenation in aqueous/organic biphasic systems represents an exciting area of research in renewable energy. This approach enhances fuel properties, contributing to the development of cleaner and more sustainable energy solutions. The results of the Ru-TPPTS biphasic catalytic hydrogenation system demonstrate its effectiveness in altering the composition of waste cooking oil (WCO) biodiesel. The process notably reduced the proportion of unsaturated linoleic acid (C18:2) methyl ester by over 70% and increased the proportion of saturated stearic acid (C18:0) methyl ester. As a result, oxidative stability (OS) was significantly improved by more than 135%, demonstrating the positive impact of biphasic hydrogenation on enhancing biodiesel stability. Although the study successfully highlights the impact of biphasic hydrogenation on biodiesel composition, further research is needed in several key areas. Optimization of the hydrogenation process, including reaction conditions and catalyst performance, remains crucial for maximizing efficiency and selectivity. Additionally, a comprehensive economic assessment of hydrogenation's impact on biodiesel production costs is necessary to evaluate its feasibility for large-scale implementation. These advancements will help improve biodiesel production and its application, ensuring its competitiveness in the renewable energy sector.

Author Contributions: Conceptualization, N.C.K.; methodology, N.C.K., A.P., E.E. and S.M.; validation, N.C.K., E.E. and S.M.; formal analysis, N.C.K., A.P., E.E. and S.M.; investigation, A.P.; data curation, A.L.; writing—original draft preparation, N.C.K., A.P., E.E., A.L. and S.M.; writing—review and editing, N.C.K., S.M. and A.L.; supervision, N.C.K. and S.M.; project administration, N.C.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Special thanks are due to the Petroleum Research Institute at Democritus University of Thrace, Greece, for its research support.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CFPP	Cold Filter Plugging Point
FAME	Fatty Acid Methyl Ester
GC-MS	Gas Chromatography–Mass Spectrometry
OS	Oxidative Stability
WCO	Waste Cooking Oil
TPPTS	Trisodium Triphenylphosphine-3,3', 3'-Tri Sulfonate

References

- Kokkinos, N.; Emmanouilidou, E.; Sharma, S. *Waste-To-Biofuel Production for the Transportation Sector*; Springer: Berlin/Heidelberg, Germany, 2024; pp. 99–122.
- Ramos, M.; Dias, A.P.S.; Puna, J.F.; Gomes, J.; Bordado, J.C. Biodiesel Production Processes and Sustainable Raw Materials. *Energies* **2019**, *12*, 4408. [\[CrossRef\]](#)
- Suzihaque, M.U.H.; Alwi, H.; Kalthum Ibrahim, U.; Abdullah, S.; Haron, N. Biodiesel production from waste cooking oil: A brief review. *Mater. Today Proc.* **2022**, *63*, S490–S495. [\[CrossRef\]](#)
- Cerón Ferrusca, M.; Romero, R.; Martínez, S.L.; Ramírez-Serrano, A.; Natividad, R. Biodiesel Production from Waste Cooking Oil: A Perspective on Catalytic Processes. *Processes* **2023**, *11*, 1952. [\[CrossRef\]](#)
- Shin, H.-Y.; Ryu, J.-H.; Bae, S.-Y.; Kim, Y.C. Biodiesel production from highly unsaturated feedstock via simultaneous transesterification and partial hydrogenation in supercritical methanol. *J. Supercrit. Fluids* **2013**, *82*, 251–255. [\[CrossRef\]](#)
- Lin, C.-Y. Effects of the Degree of Unsaturation of Fatty Acid Esters on Engine Performance and Emission Characteristics. *Processes* **2022**, *10*, 2161. [\[CrossRef\]](#)
- Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol.* **2005**, *86*, 1059–1070. [\[CrossRef\]](#)
- Wan Osman, W.N.A.; Rosli, M.H.; Mazli, W.N.A.; Samsuri, S. Comparative review of biodiesel production and purification. *Carbon Capture Sci. Technol.* **2024**, *13*, 100264. [\[CrossRef\]](#)
- Stathis, P.; Stavroulaki, D.; Kaika, N.; Krommyda, K.; Papadogianakis, G. Low trans-isomers formation in the aqueous-phase Pt/TPPTS-catalyzed partial hydrogenation of methyl esters of linseed oil. *Appl. Catal. B Environ.* **2017**, *209*, 579–590. [\[CrossRef\]](#)
- Bouriazos, A.; Vasilou, C.; Tschla, A.; Papadogianakis, G. Catalytic conversions in green aqueous media. Part 8: Partial and full hydrogenation of renewable methyl esters of vegetable oils. *Catal. Today* **2015**, *247*, 20–32. [\[CrossRef\]](#)
- Zuo, L.; Wang, J.; Mei, D.; Adu-Mensah, D.; Gao, Y. Ultrasonic-assisted catalytic transfer hydrogenation of cottonseed biodiesel using Raney-Ni catalyst in aqueous environment. *Chem. Eng. J.* **2022**, *437*, 135193. [\[CrossRef\]](#)
- Psalidas, A.; Emmanouilidou, E.; Kokkinos, N. Catalytic Upgrading of Biodiesel by Partial Hydrogenation of Its FAME Composition: A Systematic Review. *Energies* **2023**, *17*, 561. [\[CrossRef\]](#)
- Kokkinos, N.C. Modeling and simulation of biphasic catalytic hydrogenation of a hydroformylated fuel. *Int. J. Hydrog. Energy* **2021**, *46*, 19731–19736. [\[CrossRef\]](#)
- Wieselburg, B. Review on Biodiesel Standardization World-Wide. 2004. Available online: <https://task39.ieabioenergy.com/wp-content/uploads/sites/37/2013/05/Review-on-Biodiesel-Standardization.pdf>. (accessed on 10 March 2024).

15. Emmanouilidou, E.; Lazaridou, A.; Mitkidou, S.; Kokkinos, N. A comparative study on biodiesel production from edible and non-edible biomasses. *J. Mol. Struct.* **2024**, *1306*, 137870. [[CrossRef](#)]
16. Lopresto, C.G.; De Paola, M.G.; Calabrò, V. Importance of the properties, collection, and storage of waste cooking oils to produce high-quality biodiesel—An overview. *Biomass Bioenergy* **2024**, *189*, 107363. [[CrossRef](#)]
17. Dwivedi, G.; Jain, S.; Sharma, M.P. Impact analysis of biodiesel on engine performance—A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4633–4641. [[CrossRef](#)]
18. Pullen, J.; Saeed, K. An overview of biodiesel oxidation stability. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5924–5950. [[CrossRef](#)]
19. Wang, W.; Liu, H.; Li, F.; Wang, H.; Ma, X.; Li, J.; Zhou, L.; Xiao, Q. Effects of unsaturated fatty acid methyl esters on the oxidation stability of biodiesel determined by gas chromatography-mass spectrometry and information entropy methods. *Renew. Energy* **2021**, *175*, 880–886. [[CrossRef](#)]
20. Masudi, A.; Muraza, O.; Jusoh, N.W.C.; Ubaidillah, U. Improvements in the stability of biodiesel fuels: Recent progress and challenges. *Environ. Sci. Pollut. Res.* **2023**, *30*, 14104–14125. [[CrossRef](#)] [[PubMed](#)]
21. Kumar, N. Oxidative stability of biodiesel: Causes, effects and prevention. *Fuel* **2017**, *190*, 328–350. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.