



## **Optimization of Biodiesel and Biofuel Process**

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Currently in the European Union (EU) there is an intense debate on the limits to acquire the European Green Deal, to make Europe the first climate neutral continent in the world [1]. In this context, a priority objective is the reduction of the  $CO_2$  emissions of new cars and vans, 55% reduction of emissions from cars by 2030, 50% reduction of emissions from vans by 2030 and 0 emissions from new cars by 2035, to achieve in this way the carbon neutrality set for 2050. Furthermore, the Commission also promotes the growth of the market for zero- and low- emissions vehicles. In this sense, these vehicles are usually associated with the use of electric motor cars. It is also proposing to promote sustainable aviation fuels, imposing an obligation for planes to take on sustainable blended fuels for all departures from EU airports. To ensure the maritime sector contribution to economy decarbonization, the Commission will also set targets for major ports to serve vessels with onshore power, reducing the use of polluting fuels, that also harm local air quality. In this context, the E-fuel have been defined as all fuel produced by renewable electricity, made from some renewable sources (hydro, wind or solar) with low carbon emissions [2]. Moreover, biomass is featured with carbon neutrality, which makes clean biomass-based fuel (b-fuel) production through gasification very attractive in future energy systems [3]. These E-fuels are also known as electrofuels, power-fuels, or electricity-based synthetic fuels, and are fuels that can be used in any engine of current cars, trucks, or airplanes, without make any change or modification to said engines. In summary, E-fuels are those organic compounds, synthesized from renewable raw materials and green hydrogen that can easily replace the current fossil fuels. At the present time,  $CO_2$  captured from either fossil sources (e.g., industrial plants) or the atmosphere (biomass or direct air capture, DAC) is considered the raw material to obtain different E-fuels [4].

Indeed, there is currently a huge effort to obtain E-fuels through different  $CO_2$  hydrogenation processes, since they can be added to the existing infrastructure and be used in conventional vehicles, especially for heavy duty vehicles, that predictably should have a worse behavior working with electric engines [5]. In this connection, the main studied E-fuels can be subdivided into three main groups [6]: Hydrocarbons, Alcohols (methanol, ethanol) and Ethers (DME). In general, due to their molecular weight distribution, density, boiling points and similar high-octane number, all they are compounds capable of operating, pure or in the form of mixtures with fossil fuels, in Spark Ignition (SI) engines [7]. However, obtaining E-fuels capable of operating in Compression Ignition (CI) engines, it is not a sufficiently studied process at present, since only the conventional Fischer-Tropsch (FT) process, which operates with a mixture of CO with  $H_2$  (syngas), allows obtaining mixtures of hydrocarbons of proper Cetane Number (CN) [8]. However, Fuels derived from Fischer-Tropsch (FT) processes, exhibits a high fraction of n-alkanes and poor cold flow properties, so that they need an additional hydrocracking and hydroisomerization upgrading processes, designed to reach an optimal compromise between cold-flow properties and auto-ignition quality in the diesel fuel [9]. That is why, in order to obtain suitable E-fuels to operate in conventional diesel CI engines, it is necessary to resort to operating with fuels obtained from secondary processes, carried out with E-fuels such as DME or methanol. In



Citation: Luna, D.; Estevez, R. Optimization of Biodiesel and Biofuel Process. *Energies* **2022**, *15*, 5917. https://doi.org/10.3390/en15165917

Received: 26 July 2022 Accepted: 12 August 2022 Published: 15 August 2022

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**Copyright:** © 2022 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/). this sense, it is being investigated Polyoxymethylene Dimethyl Ethers (PODE), a liquid oxygenated oligomer, (PODE), a liquid oxygenated oligomer [10]. However, regardless of the potential efficiency of this E-diesel, given the need for an additional synthesis process (which implies an increase in the production cost of the PODE), the Hydrotreated Vegetable Oils (HVO), has the higher potential to emerge as an alternative fuel to mineral diesel due to its favorable properties [11]. When green hydrogen is used in the treatment process, since vegetable oils are renewable, it can be concluded that it is an E-fuel, 100% renewable, with a higher energy density [12]. Taking into account that aircrafts require high energy density fuels, synthetic aviation fuels (SAFs) are basically also obtained from Hydrotreated Vegetable Oils (HVO) [13].

We therefore have that, despite the potential capacity of electric motors and E-fuels to replace a very important part of the fossil fuels currently used in transport, vegetable oils are essential for obtaining certain fuels, for their use in heavy duty vehicles and aviation transport. Of course, the potential sustainability problems associated with the large-scale production of the necessary raw materials, with the use of the land to produce food or fuel, must be clearly resolved using non-edible raw materials, such as castor oil, or recycled used oils [14]. However, assuming that vegetable oils are an essential part of the process for decarbonization of the transportation sector, due to incompatibilities that electric engines or E-fuels exhibit for being applied to heavy-duty fleets and air transports. However, assuming that vegetable oils are an essential part of the transportation of the transportation sector, due to incompatibilities or E-fuels exhibit for being applied to heavy-duty fleets and air transports. However, assuming that vegetable oils are an essential part of the process for decarbonization of the transportation sector, due to incompatibilities that electric engines or E-fuels exhibit for being applied to heavy-duty fleets and air transports. However, assuming that vegetable oils are an essential part of the process for decarbonization of the transportation sector, due to incompatibilities that electric engines or E-fuels exhibit for being applied to heavy-duty fleets and air transports, it must be considered that, apart from conventional biodiesel, there is currently a great diversity of biofuels that have vegetable oils as raw material [15].

In this Special Issue, a series of papers are collected trying to contribute to this effort, to enable the substitution of fossil fuels, in the greatest proportion possible in this transition period, which could be extended even for several decades. Thus, some research works are collected here that provide solutions to make the manufacture of conventional biodiesel more viable or that provide solutions for the reuse of glycerol, which is currently being produced in conventional biodiesel production plants, Table 1.

**Table 1.** Summary of the articles published in the Special Issue Optimization of Biodiesel and Biofuel Process.

| Published Articles   | Reference |
|--|-----------|
| Ecodiesel, a biodiesel-like biofuels that avoid the glycerol production is obtained by using Rhizomucor miehei<br>Lipase Supported on Inorganic Solids.  | [16]      |
| Performance and Emission Quality Assessment of blends of gasoline and a straight oil, such as castor oil in a Diesel Engine  | [17]      |
| A review on the use of residual glycerol obtained in the synthesis of biodiesel, through the preparation of oxygenate additives for fuel, by the heterogeneous etherification reaction of glycerol with alcohols or olefins  | [18]      |
| Use of glycerol as raw material to produce H <sub>2</sub> by a Photo-Production process by using a Nickel-Doped TiO <sub>2</sub> catalyst  | [19]      |
| Optimization of an enzymatic heterogeneous process to produce Biodiesel Using Waste Cooking Oil as Feedstock.  | [20]      |
| The behavior of triple mixtures: diethyl ether (DEE), straight vegetable oils (SVOs) and fossil diesel, is studied in a current compression ignition (CI) engine, to implement the replacing of fossil fuels with others of a renewable nature.  | [21]      |
| In this study a much cheaper and simpler method called high vacuum fractional distillation (HVFD) has been used as an alternative to produce high-quality refined biodiesel and to improve the manufacturing process.  | [22]      |
| This study evaluates ethyl acetate (EA) as a solvent of two straight vegetable oils (SVOs), castor oil (CO), and sunflower oil (SO), to obtain EA/SVO double blends that can be used directly as biofuels, or along with fossil diesel (D) in triple blends, in the current compression-ignition (C.I.) engines. | [23]      |

In summary, in this Special Issue, articles that address the obtaining of renewable synthetic diesel fuel from triglycerides to make possible the smooth transition from the current state, in which diesel engines operate with fossil fuels, to a new situation in which diesel engines will work employing solely renewable biofuels have been included. Thus, in addition to conventional biodiesel, obtained by catalytic or enzymatic transesterification of triglycerides, all the research providing effective solutions to allow the use of fats and oils as biofuels in diesel engines, without having to perform any modification in them. These synthetic biofuels, without being E-diesel, they are clean biomass-based fuel (B-fuel) and achieve 100% of atom efficiency, because neither glycerol nor any byproduct is obtained. Thus, the overall production process of the biofuel is simplified in large extension. Finally, it must be considered that, in general, they are processes ready for immediate application, in keeping with the urgency that the fuels decarbonization process currently requires.

**Author Contributions:** D.L. and R.E. contributed equally to the design, developing, implementation, and the delivery of the Special Issue. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors are thankful to Spanish MICINN through the PID2019-104953RB-I00 Project, Junta de Andalucía and FEDER funds (P18-RT-4822) and UCO-FEDER (1264113-RMINECO-ENE2016-81013-R (AEI/FEDER, EU)).

Acknowledgments: The authors are thankful for the technical assistance of staff at Central Service for Research Support (SCAI) and Institute of Nanochemistry (IUNAN) of the University of Córdoba.

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

## References

- 1. Wolf, S.; Teitge, J.; Mielke, J.; Schütze, F.; Jaeger, C. The European Green Deal—More Than Climate Neutrality. *Intereconomics* 2021, 56, 99–107. [CrossRef] [PubMed]
- Lindstad, E.; Lagemann, B.; Rialland, A.; Gamlem, G.M.; Valland, A. Reduction of maritime GHG emissions and the potential role of E-fuels. *Transp. Res. Part D* 2021, 101, 103075. [CrossRef]
- Salbrechter, K.; Schubert, T. Combination of b-Fuels and e-Fuels—A Technological Feasibility Study. *Energies* 2021, 14, 5250. [CrossRef]
- Ramirez, A.; Sarathy, M.; Gascon, J. CO<sub>2</sub> Derived E-Fuels: Research Trends, Misconceptions, and Future Directions. *Trends Chem.* 2020, 2, 785–795. [CrossRef]
- Schemme, S.; Breuer, J.L.; Maximilian Köller, M.; Meschede, S.; Walman, F.; Samsun, R.C.; Peters, R.; Stolten, D. H<sub>2</sub>-based synthetic fuels: A techno-economic comparison of alcohol, ether and hydrocarbon production. *Int. J. Hydrogen Energy* 2020, 45, 5395–5414. [CrossRef]
- 6. Schemme, S.; Breuer, J.L.; Samsun, R.C.; Peters, R.; Detlef Stolten, D. Promising catalytic synthesis pathways towards higher alcohols as suitable transport fuels based on H<sub>2</sub> and CO<sub>2</sub>. *J. CO<sub>2</sub> Util.* **2018**, 27, 223–237. [CrossRef]
- Boot, M.D.; Tian, M.; Hensen, E.J.M.; Sarathy, S.M. Impact of fuel molecular structure on auto-ignition behavior–Design rules for future high-performance gasolines. *Prog. Energy Combust. Sci.* 2017, 60, 1–25. [CrossRef]
- 8. De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S.A.; Jaramillo, T.F.; Sargent, E.H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, *6438*. [CrossRef]
- Pleyer, O.; Vrtiška, D.; Straka, P.; Vráblík, A.; Jencík, J.; Šimácek, P. Hydrocracking of a Heavy Vacuum Gas Oil with Fischer– Tropsch Wax. *Energies* 2020, 13, 5497. [CrossRef]
- 10. Lin, Q.; Tay, K.L.; Yu, W.; Zong, Y.; Wenming Yang, W.; Rivellini, L.-H.; Ma, M.; Lee, A.K.Y. Polyoxymethylene dimethyl ether 3 (PODE3) as an alternative fuel to reduce aerosol pollution. *J. Clean. Prod.* **2021**, *285*, 124857. [CrossRef]
- 11. Swiderski, E.; Stengel, B.; Pinkert, F.; Buchholz, B. Influence of E-fuels on Flame Structures and Combustion Processes of Large Diesel Engines. *MTZ Worldw.* 2022, *83*, 54–61. [CrossRef]
- 12. Hunicz, J.; Mikulski, M.; Shukla, P.C.; Geca, M.S. Partially premixed combustion of hydrotreated vegetable oil in a diesel engine: Sensitivity to boost and exhaust gas recirculation. *Fuel* **2022**, 307, 121910. [CrossRef]
- 13. Cabrera, E.; Melo de Sousa, J.M. Use of Sustainable Fuels in Aviation—A Review. Energies 2022, 15, 2440. [CrossRef]
- 14. Osorio-González, C.S.; Gómez-Falcon, N.; Sandoval-Salas, F.; Saini, R.; Brar, S.K.; Avalos-Ramírez, A. Production of Biodiesel from Castor Oil: A Review. *Energies* **2020**, *13*, 2467. [CrossRef]
- 15. Estevez, R.; Aguado-Deblas, L.; López-Tenllado, F.J.; Luna, C.; Calero, J.; Romero, A.A.; Bautista, F.M.; Luna, D. Biodiesel is dead: Long life to advanced biofuels. A 2 comprehensive critical review. *Energies* **2022**, *15*, 3173. [CrossRef]

- Juan Calero, J.; Diego Luna, D.; Luna, C.; Bautista, F.M.; Hurtado, B.; Romero, A.A.; Posadillo, A.; Estevez, R. Rhizomucor miehei Lipase Supported on Inorganic Solids, as Biocatalyst for the Synthesis of Biofuels: Improving the Experimental Conditions by Response Surface Methodology. *Energies* 2019, *12*, 831. [CrossRef]
- 17. Estevez, R.; Aguado-Deblas, L.; Posadillo, A.; Hurtado, B.; Bautista, F.M.; Hidalgo, J.M.; Luna, C.; Calero, J.; Romero, A.A.; Luna, D. Performance and Emission Quality Assessment in a Diesel Engine of Straight Castor and Sunflower Vegetable Oils, in Diesel/Gasoline/Oil Triple Blends. *Energies* **2019**, *12*, 2181. [CrossRef]
- 18. Estevez, R.; Aguado-Deblas, L.; Luna, D.; Bautista, F.M. An Overview of the Production of Oxygenated Fuel Additives by Glycerol Etherification, Either with Isobutene or tert-Butyl Alcohol, over Heterogeneous Catalysts. *Energies* **2019**, *12*, 2364. [CrossRef]
- 19. Hidalgo-Carrillo, J.; Martin-Gomez, J.; Morales, J.; Espejo, J.C.; Urbano, F.J.; Marinas, A. Hydrogen Photo-Production from Glycerol Using Nickel-Doped TiO<sub>2</sub> Catalysts: Effect of Catalyst Pre-Treatment. *Energies* **2019**, *12*, 3351. [CrossRef]
- Touqeer, T.; Mumtaz, M.W.; Mukhtar, H.; Irfan, A.; Akram, S.; Shabbir, A.; Rashid, U.; Nehdi, I.A.; Choong, Y.T.S.Y. Fe<sub>3</sub>O<sub>4</sub>-PDA-Lipase as Surface Functionalized Nano Biocatalyst for the Production of Biodiesel Using Waste Cooking Oil as Feedstock: Characterization and Process Optimization. *Energies* 2020, *13*, 177. [CrossRef]
- Aguado-Deblas, L.; Hidalgo-Carrillo, J.; Bautista, F.M.; Luna, D.; Luna, C.; Calero, J.; Posadillo, A.; Romero, A.A.; Estevez, R. Diethyl Ether as an Oxygenated Additive for Fossil Diesel/Vegetable Oil Blends: Evaluation of Performance and Emission Quality of Triple Blends on a Diesel Engine. *Energies* 2020, 13, 1542. [CrossRef]
- Ijaz, B.; Hanif, M.A.; Rashid, U.; Zubair, M.; Mushtaq, Z.; Nawaz, H.; Choong, T.S.Y.; Nehdi, I.A. High Vacuum Fractional Distillation (HVFD) Approach for Quality and Performance Improvement of *Azadirachta indica* Biodiesel. *Energies* 2020, 13, 2858. [CrossRef]
- Aguado-Deblas, L.; Estevez, R.; Hidalgo-Carrillo, F.J.; Bautista, F.B.; Luna, C.; Calero, J.; Posadillo, A.; Romero, A.A.; Luna, D. Outlook for Direct Use of Sunflower and Castor Oils as Biofuels in Compression Ignition Diesel Engines, Being Part of Diesel/Ethyl Acetate/Straight Vegetable Oil Triple Blends. *Energies* 2020, *13*, 4836. [CrossRef]