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Synthesis of 1-Hexanol/Hexyl hexanoate Mixtures from Grape Pomace: Insights on Diesel Engine Performances at High Bio-Blendstock Loadings

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Abstract: The production of oxygenated bio-additives for traditional fuels represents a key challenge due to their depletion in the near-future and their positive contribution to the reduction in environmental pollution. The present study considers the synthesis of 1-hexanol/hexyl hexanoate mixtures, two oxygenated Diesel bio-additives produced through the hydrogenation of hexanoic acid, obtainable from the fermentation of a wide variety of waste biomasses. In our case, crude hexanoic acid was produced through the fermentation of grape pomace, an abundant Italian agrifood waste. Commercial 5 wt% Re/γ-Al_2O_3 was adopted for the catalytic hydrogenation of crude hexanoic acid, and the support acidity allowed the tuning of the reaction selectivity toward the formation of hexyl hexanoate, instead of 1-hexanol, reaching yields of 40 and 25 mol%, respectively. The effects of each bio-additive on Diesel engine performance and exhaust emissions (soot, nitrogen oxides, carbon monoxide, unburned hydrocarbons) were evaluated, highlighting noteworthy positive effects especially on the reduction in carbon monoxide and soot emissions, if compared with those of Diesel fuel alone. Similar promising performances were achieved by employing Diesel blend mixtures of 1-hexanol/hexyl hexanoate, mimicking typical compositions of the rhenium-catalyzed post-hydrogenation mixtures. Even in such cases, 1-hexanol/hexyl hexanoate mixtures can be blended with commercial Diesel fuel, up to high loadings currently not yet investigated (20 vol%), without altering the engine performances and, again, significantly lowering soot and carbon monoxide emissions by more than 40%. This work highlights the possibility of obtaining such oxygenated bio-additives starting from waste through to a fully sustainable process and proves their beneficial effects on the reduction in exhaust emissions with no changes in engine performance.

Keywords: waste biomass; rhenium catalyst; hydrogenation; oxygenated bio-additives; exhaust emissions

1. Introduction

The world is going through a radical phase of energy transition, due to both environmental and socio-economic factors, which will lead to a progressive transition from fossil to renewable energy sources. In the field of the light land transport sector (cars), the abandonment of propulsion systems based on the use of internal combustion engines (ICEs) in favor of electrification (if electricity comes from renewable sources) seems the preferred solution. On the contrary, within heavy land (trucks and trains), marine, and air transport sectors, a precise choice has still not been defined. For these last categories, on-board energy storage through batteries still appears practically inappropriate due to their high costs and

low energy/weight ratio, even if lithium batteries have increased rapidly in recent years, reaching an energy density up to 1.6 MJ/kg [1,2].

Given the still unresolved bottlenecks of the electrification route, great interest is still devoted to improving the physicochemical properties of traditional fuels by performing the appropriate blending of different traditional fuels. For example, some low-octane components of gasoline, such as naphtha from natural gas condensate, can be blended with octane enhancers, such as isooctene, MTBE, ethylbenzene, toluene, isopropylbenzene, and isopentane, to produce a higher-performing high-octane gasoline, in accordance with European technical requirements for motor gasoline [3]. Remarkably, such blends generally show a lower sooting tendency than the pristine gasoline fuel alone [4]. Therefore, the use of such octane enhancers is effective in improving the combustion properties of low-octane hydrocarbon fractions, at the same time contributing to improving the environmental issues [5].

A possible alternative to fossil fuels is represented by bio-fuels derived from the conversion of (ligno)cellulosic biomasses, reducing the net CO_2 emissions as well as CO and particulate matter emissions [6]. At the same time, energy-poor countries will benefit from biofuels, becoming progressively independent from the supply of oil and natural gas, by promoting the agricultural-forestry activities of the territory and achieving considerable economic advantages [7,8]. It is worth noting that the use of bio-fuels does not involve a drastic change in the distribution systems and use of energy, keeping the existing infrastructures almost unchanged. In recent years, there has been an ever-increasing interest in the development of second-generation bio-fuels (obtained from non-food matrices) [9] and their use in ICEs. Oxygenated bio-fuels are attracting great interest as suitable blending agents with fossil gasoline and Diesel fuels, generally showing improved engine performances, lower pollutant emissions, and improved fuel efficiency [10]. Nowadays, ethanol, produced by the fermentation of carbohydrate fractions in lignocellulosic biomasses [11], and bio-diesel, obtained from oil crops or through the fermentative route [12,13], represent two of the most investigated second-generation bio-fuels. Also among them, other oxygenated compounds, such as alcohols and esters obtainable from residual lignocellulosic biomasses, appear extremely promising for use in Diesel engines [14]. For instance, several studies have investigated the employment of light alcohols (methanol, ethanol, 2-butanol, *n*-butanol) [15–17] and esters (alkyl levulinates) [18,19] in blendstock with Diesel, but their synthesis should always fully respect the criteria of environmental and economic sustainability [20]. Moreover, when short-chain alcohols are directly blended with Diesel, miscibility issues are ascertained, together with low cetane number and low viscosity, which may cause ignition and lubrication problems [21]. Thus, longer alcohols and esters are more appealing, thanks to their higher heating values, cetane numbers, and better miscibility, that make them more suitable for Diesel blendstocks. Under this perspective, recently, 1-hexanol (HexOH) and hexyl hexanoate (HexHex) have been proposed as bio-additives for Diesel engines. Regarding HexOH, several works have employed it in blendstock with Diesel, studying the effect on combustion performance and emission characteristics under the direct-injection mode [22–24] but also under the reactivity-controlled compression (RCCI) mode [25]. On the other hand, the influence of injection timing and exhaust gas recirculation on engine performance has also been investigated [26,27], and some more in-depth aspects, such as the kinetics of internal combustion [28] and the optical diagnostic of spray, combustion, and flame characteristics [21], have been considered. However, all these studies confirm that the use of HexOH/Diesel blends in different percentages leads to a decrease in soot and CO emissions, while those of NOx and hydrocarbons (HC) generally increase, mainly due to an increase in the combustion ignition delay, together with an increase in the peak values of in-cylinder pressure and temperature, as a consequence of the low cetane number of HexOH.

Few studies have reported on the utilization of HexHex as a Diesel additive. Fioroni et al. analyzed the properties of over 400 potential blends to power Diesel engines, whereas only 25 show promising engine performances and 12 could be obtained for experimental

research and property validation, including HexHex [29]. In the specific case of HexHex, improvements in lubricity, oxidation stability, and biodegradability were ascertained, but more experimental data are still required to better demonstrate the use of HexHex for engine applications. Remarkably, in a very recent technical report of Vijayagopal et al. [30], a blend of 25 vol% HexHex with Diesel fuel was tested for the simulation on a Class 6 delivery truck with a 6.7 L Diesel engine and certification drive cycles with four different power trains (conventional, ISG, parallel hybrid, and series hybrid cases), to investigate fuel economy, emissions, and well-to-wheel greenhouse gas performance. The authors claimed good engine performances of the 25 vol% HexHex mixture, which were comparable with those of 100 vol% Diesel fuel. However, NOx emissions of the blends were higher than those of 100 vol% Diesel, whilst other emissions (CO, soot, and HC) were not studied by the authors. The latter aspects deserve further investigation, due to the strategic role of the reduction in these emissions from an environmental sustainability perspective. Moreover, other research proved the good compatibility of HexHex with the traditional engine components, including elastomers [31] and plastic infrastructures [32], thus highlighting the feasibility of its immediate utilization within the available Diesel engine, without the necessity of replacement of any of its parts.

It is worth noting that both HexOH and HexHex can be obtained through the hydrogenation of hexanoic acid, a medium-chain fatty acid originating from the anaerobic acidogenic fermentation of biomasses and wastes, such as food wastes [33–35], the organic fraction of municipal solid waste [35], acid whey [36], and solid-free thin stillage [37], involving the chain elongation process. According to this path, short-chain carboxylic acids, e.g., acetic and/or butyric acids, are elongated with carbons from a reduced molecule, such as ethanol or lactic acid, which can be generated in situ during the fermentation step or manually added. In this regard, the authors have recently proposed a new cascade bio-refinery scheme for the bio-conversion of grape pomace, as an abundant Italian agrifood waste biomass, involving the upgrade of the available ethanol fraction into hexanoic acid through an efficient anaerobic acidogenic fermentation process [38]. This new integrated process allowed the exploitation of the obtained hexanoic acid as the substrate for the synthesis of the HexOH/HexHex mixture, employable as a Diesel additive, and for the production of medium-chain polyhydroxyalkanoates, employable as bio-polymers.

The innovative catalytic hydrogenation of hexanoic acid into HexOH and HexHex has been carried out in the presence of rhenium-based catalysts, with this metal being particularly active toward the hydrogenation of carboxylic acids [39,40], highlighting the good tunability of the reaction selectivity depending on the catalyst properties [41]. The 5 wt% Re/C catalyst was selective toward HexOH formation, whilst the addition of niobium phosphate (NbPO) as the acid co-catalyst caused a slowdown in substrate conversion but selectively catalyzed the esterification reaction between the unconverted hexanoic acid and the produced alcohol, thus improving the selectivity toward HexHex formation. The possibility of better tuning the reaction selectivity by modulating the catalyst properties is particularly attractive, especially if such mixtures of oxygenated compounds are blended with Diesel fuel. It is worth noting that when crude hexanoic acid recovered from the fermentation of grape pomace was employed as the substrate, the conversion was only slightly lower than that obtained by starting from the commercial hexanoic acid, while the selectivity parameter was almost unaffected. Remarkably, the proposed approach to produce HexOH/HexHex mixtures from the grape-pomace-derived hexanoic acid could be extended to a large variety of other waste feedstocks. The fuel properties of 10 vol% HexOH or HexHex mixtures as Diesel additive were investigated and, for the first time, a mixture of HexOH/HexHex composed by 5.2 vol% HexOH + 4.8 vol% HexHex was also tested. Such a composition is like that of the final crude mixture derived from the hydrogenation of hexanoic acid, carried out under the best reaction conditions, employing 5 wt% Re/C as the catalyst [41]. Remarkably, in this preliminary study, a significant reduction in the soot and CO emissions, without a significant change in the engine performances, was

ascertained, thus proving the potentialities of such HexOH/HexHex mixtures as new Diesel bio-additives.

Starting from these encouraging results, in the present work, the key role of the catalyst acidity is investigated more in-depth, aiming to selectively favor HexHex formation, starting from both commercial and crude grape-pomace-derived hexanoic acid and adopting a commercial 5 wt% Re/γ-Al$_2$O$_3$ catalyst. Afterward, our attention focuses on the study of the engine performances of HexOH/HexHex Diesel additives, taking into account a wider compositional range. High percentages of the HexOH/HexHex mixture, up to 20 vol%, in blend with commercial Diesel are proposed, investigating for the first time their effects on the engine performances and corresponding emissions. Our idea is to advantageously exploit the synergy between HexOH and HexHex, to improve the motor Diesel performances, with respect to their individual use. The present research activity is part of an even more ambitious goal, aimed at the development of last-generation ester bio-fuels, which was previously focused on butyl levulinate, the latter being identified as a very valuable Diesel additive [42,43]. The goal of these approaches is to valorize bio-esters as a new category of oxygenated bio-fuels to exploit for engine applications within the near-future, without the need to carry out significant technological changes on the available engines.

2. Materials and Methods

2.1. Materials

Hexanoic acid (>99%), hexane (>99%), hexyl hexanoate (>98%), 1-hexanol (>99%), *n*-octane (99%), methanol (>99%), and *n*-dodecane (>99%) were purchased from Sigma-Aldrich and employed as-received, whilst 5 wt% Re/γ-Al$_2$O$_3$ was provided by Riogen (Mantua, NJ, USA). Red and white grape pomaces, derived from wine production, were provided by Caviro Distillerie (Faenza, Italy) and employed as-received. Two different crude hexanoic acid-rich liquors were obtained starting from red or white grape pomaces, according to a previously reported procedure [38]. Briefly, the grape pomace was put into a 20 L plastic drum together with the acidogenic inoculum. At the end of the fermentation, the solid fraction was separated through filtration, whilst the liquid fraction was acidified with HCl up to pH = 2.2 and transferred into another bottle, where liquid phase separation took place. The upper phase included hexanoic acid, which was separated through overflow and centrifuged to remove suspended solids.

2.2. Catalyst Characterization

NH$_3$-TPD characterization was performed by adopting a Micromeritics TPDR Instrument. Samples were pre-heated at 500 °C under helium flow to remove possible trapped contaminants. Then, a flow (30 mL/min) of NH$_3$ (4 vol% in helium) was fed at 70 °C on the sample until saturation and, after a purge with pure helium, was carried out for 1 h. Subsequently, the sample was heated at 20 °C/min up to 900 °C, and NH$_3$ desorption was monitored through a TCD and a quadrupole MS.

A single-point Thermo Quest Surface Area Analyzer Qsurf S1 was employed for the determination of the Specific Surface Area (SSA) of the 5 wt% Re/γ-Al$_2$O$_3$ catalyst.

Transmission Electron Microscopy (TEM) analysis was performed in bright-field mode using a CM12 microscope (Philips, Amsterdam, The Netherlands), working at 120 keV, according to our previous work [44].

The rhenium content in the reaction mixtures was determined through ICP-OES analysis, employing an Optimum 7000 DV analyzer equipped with a CCD array detector, and an emission line of 221.43 nm was used.

2.3. Hydrogenation Reactions

Hydrogenation reactions were performed in a 300 mL stainless-steel Parr 4560 autoclave furnished with a P.I.D. controller 4843. The pre-reduction step, as well as the hydrogenation reaction, was performed according to our previous works [38,41]. Briefly, the catalyst (5 wt% Re/γ-Al$_2$O$_3$) was pre-reduced in methanol and then removed under

vacuum, and the reaction mixture was fed through suction and mechanically stirred. The reactor was pressurized by hydrogen and electrically heated. The pressure was kept constant during the reaction by automatically feeding hydrogen. At the end of the reaction, the reactor was cooled and depressurized, the spent catalyst was removed through filtration under argon atmosphere, and the reaction mixture was analyzed through GC-FID chromatography, according to the procedure reported in our previous work [41]. The analyses were performed in triplicate and the reproducibility was within 5%. On the other hand, the recovered spent catalyst was properly washed and recycled following the procedure described above.

2.4. Engine Setup

To verify the effectiveness of the HexOH/HexHex mixtures as Diesel bio-additive, a small direct injected Diesel engine (Lombardini-Kohler engines–Reegio Emilia–Italy) was employed, whose main characteristics are shown in Table 1.

Table 1. Experimental engine characteristics.

Engine Type	Lombardini 9LD 625/2
Number of cylinders	2
Cooling system	Forced air
Displacement (cm³)	1248
Bore (mm)	95
Stroke (mm)	88
Compression ratio	17.5:1
Max rotational speed (rpm)	3000
Power @ 3000 rpm (kW)	21
Max Torque @ 2200 rpm (Nm)	29.4
Fuel injection system	Direct-Mechanic

The Diesel engine was coupled with a Borghi & Saveri eddy current brake for the performance analysis. An eddy current brake for engine testing consists of a conductive non-ferromagnetic metal disk, directly connected to the engine crank shaft, which moves through the magnetic field created by an electromagnet. When the disk moves through such a magnetic field, the electromagnet exerts a drag force on the metal, which opposes its motion due to the circular electric currents ("eddy currents"), which are induced by the magnetic field within the metal. The electromagnet allows the braking force to be varied. When no current is passed through the electromagnet windings, no braking force is allowed. When current is passed through the electromagnet windings, a magnetic field is created, whereas greater currents in the windings lead to greater eddy currents and stronger braking force.

An AVL gravimetric fuel balance was used to measure online the fuel consumption, while an AVL DiTest Gas1000 (AVL List GmbH–Graz–Austria) was adopted for the analyses of the pollutant emissions. The particulate matter was measured using an AVL smoke meter (model 415 S). A Kistler pressure sensor (Kistler Group–Winterthur–Switzerland) model 6052/C was suitably positioned on the cylinder head for the acquisition of the indicated cycle and the analysis of the engine combustion, together with an AVL encoder and an AVL Indimodul data acquisition system (model 622). A K-type thermocouple was located at the engine exhaust to verify the steady-state conditions reached. A detailed picture of the Lombardini-Kohler 9LD 625/2 on a test bench is shown in Figure 1. After stabilization of the target operating conditions, data were collected and analyzed. The variability in the obtained results was within 5%.

Figure 1. Lombardini-Kohler 9LD 625/2 on the test bench.

3. Results

3.1. Hydrogenation of Hexanoic Acid with 5 wt% Re/γ-Al$_2$O$_3$

In our previous work [41], it was found that 5 wt% Re/C catalyzed the hydrogenation of hexanoic acid toward the selective formation of HexOH, up to a yield of 62 mol%, whilst the addition of NbPO as the acid co-catalyst markedly increased the HexHex yield, up to about 60 mol% (corresponding to a selectivity of 70 mol%). Considering that the use of physical mixtures of different catalysts is not suitable for industrial applications, in this work, we propose a supported rhenium catalyst that combines both hydrogenating and acidic properties, a commercial 5 wt% Re/γ-Al$_2$O$_3$. Generally, such a commercial catalyst should be preferred over ad hoc synthesized ones, given the wider availability of the former, which is produced in a constant and repeatable way. Before the catalytic runs, 5 wt% Re/γ-Al$_2$O$_3$ was characterized through N$_2$ physisorption and TEM techniques, showing a specific surface area of 220 m^2/g and a rhenium average particle size of about 3.85 nm (Figure 2a). Moreover, the acidic properties of the catalyst were evaluated through NH$_3$-TPD analysis, highlighting the presence of a large peak between 200 and 800 °C (Figure 2b) and thus demonstrating the high amount of total acid sites (552 μmol/g) that are mainly characterized by high-strength, in agreement with the literature findings [45].
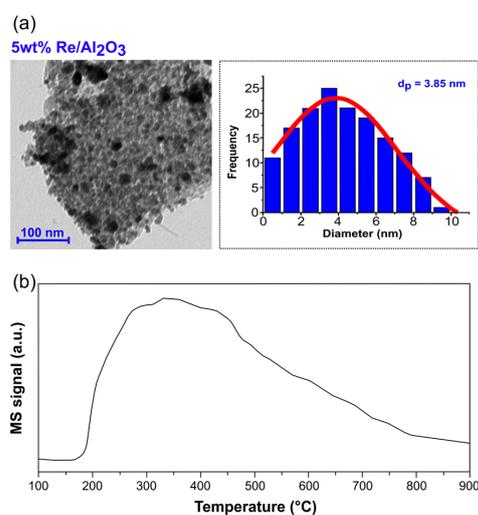

Figure 2. (**a**) TEM image and the respective distribution of the Re particle sizes and (**b**) NH$_3$-TPD profile of 5 wt% Re/Al$_2$O$_3$.

We have previously found that a wet pre-reduction of 5 wt% Re/C allowed the Re^{+7} reduction to a species of lower valence, mainly Re^{+3} and Re^{+4}, thus improving the hydrogenating activity of the bulk metal [41]. Under this perspective, 5 wt% Re/γ-Al$_2$O$_3$ was also pre-reduced and employed in the hydrogenation of both commercial hexanoic acid and crude hexanoic acid obtained from the anaerobic fermentation of red and white grape pomaces, working under the reaction conditions already identified for the 5 wt% Re/C catalyst. The obtained results are compared in Figure 3.
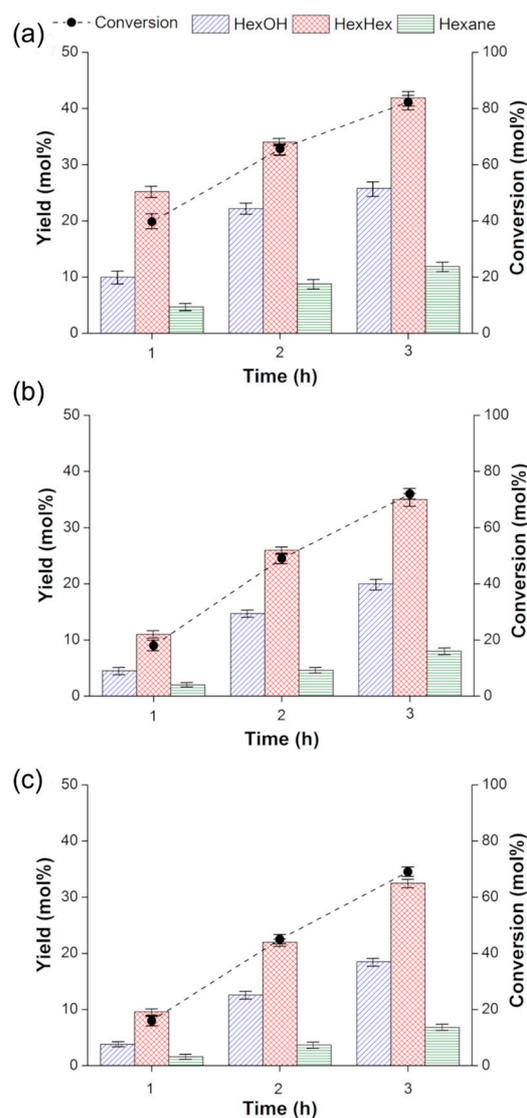
Figure 3. Hydrogenation of (**a**) commercial hexanoic acid, (**b**) crude hexanoic acid derived from fermented white grape pomace, and (**c**) crude hexanoic acid derived from fermented red grape pomace, always in the presence of pre-reduced 5 wt% Re/γ-Al$_2$O$_3$. Reaction conditions: T = 220 °C; P$_{H2}$ = 115 bar; substrate/Re molar ratio of 270 mol/mol.

The conversion of commercial hexanoic acid with the pre-reduced 5 wt% Re/γ-Al$_2$O$_3$ (Figure 3a) was slightly lower than that previously achieved with the pre-reduced 5 wt% Re/C (about 85 mol% vs. 100 mol%, respectively, after 3 h), leading to HexOH and HexHex yields of 25 and 40 mol% respectively, instead of 60 and 30 mol% ascertained with the 5 wt% Re/C system. The slowdown of hexanoic acid conversion can be ascribed to the lower specific surface area of 5 wt% Re/γ-Al$_2$O$_3$, if compared with that of 5 wt% Re/γ-Al$_2$O$_3$ (e.g., 220 vs. 840 m^2/g, respectively). This moderation of the catalyst activity, in synergy with the presence of the support acidity, enabled the simultaneous esterification between

the unreacted substrate and the produced HexOH, thus improving the selectivity toward HexHex formation. The ascertained results confirm the tunability of the composition of the final reaction mixture, depending on the catalyst characteristics, thus allowing the evaluation of different alcohol/ester mixtures for engine tests. Moreover, a limited formation of hexane was ascertained in the presence of 5 wt% Re/γ-Al$_2$O$_3$, in agreement with the results achieved with the 5 wt% Re/C catalyst [41].

Afterward, crude hexanoic acid derived from the anaerobic fermentation of white and red grape pomaces was proposed as the real substrate. The purity degree of hexanoic acid in the fermentation liquors was already investigated in our previous works, through GC-FID and GC-MS chromatographic techniques [38,41]. Hexanoic acid purity was higher in the liquor derived from the fermentation of the white grape pomace, rather than from the red one (93 and 87 wt%, respectively). The GC-MS analysis highlighted the presence of few carboxylic acids (C4–C8) in the crude-fermented white grape pomace, which were present in higher amounts in the crude-fermented red grape pomace. This different composition of the substrates might lead to relevant consequences on the hydrogenation process. Remarkably, in our proposed cascade process, only slight differences have been observed as a consequence of the hydrogenation of such substrates, thus highlighting the robustness of the proposed process. In fact, only a slight decrease in conversion was observed, but a higher selectivity toward HexHex was confirmed, together with a low formation of hexane (Figure 3b,c).

The chemical stability of the adopted catalyst is of paramount relevance to develop a robust and scalable process. On this basis, the spent catalysts were recovered at the end of the hydrogenation of commercial hexanoic acid and crude hexanoic acid derived from fermented white and red grape pomaces, and they were recycled in the three following tests (Figure 4). The catalyst stability was always ascertained, demonstrating its true usefulness for the future scale-up of this reaction. In fact, only a slight decrease in hexanoic acid conversion was observed with the progress of the recycling tests, mainly caused by the partial loss of the catalyst during its separation and recycling steps. Significant rhenium leaching was excluded by the ICP analysis of the reaction mixtures, whereas the Re content was below the detection limit.
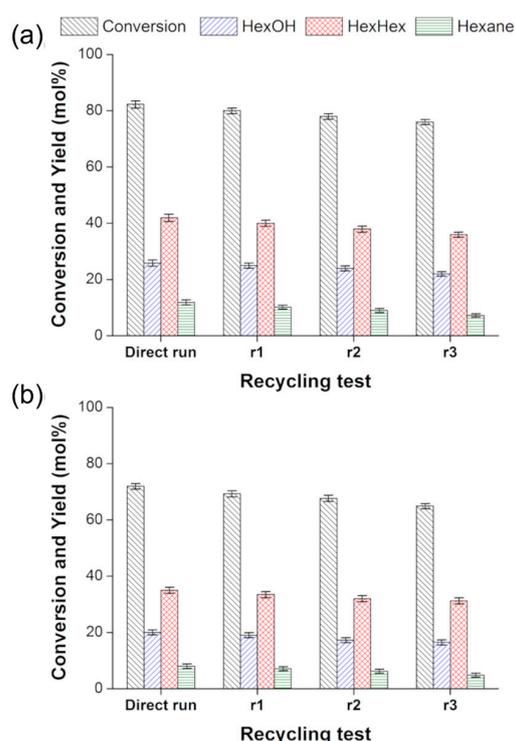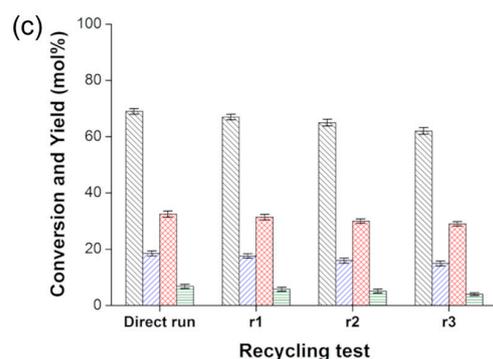

Figure 4. *Cont.*

Figure 4. Recyclability tests of 5 wt% Re/γ-Al$_2$O$_3$ for the hydrogenation of (**a**) commercial hexanoic acid, (**b**) crude hexanoic acid derived from fermented white grape pomace, and (**c**) crude hexanoic acid, always derived from fermented red grape pomace. Reaction conditions: T = 220 °C; P$_{H2}$ = 115 bar; t = 3 h; substrate/Re molar ratio of 270 mol/mol.

3.2. Additives Definition for Engine Tests

Given the promising preliminary results obtained by the use of 10 vol% HexOH + HexHex as additives for Diesel fuel [41], the amount of the oxygenated additives was consequently enhanced, representing a wider compositional range, in agreement with the typical compositions of the mixtures obtained after the hydrogenation runs with 5 wt% Re/C and 5 wt% Re/γ-Al$_2$O$_3$. On this basis, nine mixtures were tested and compared with pure Diesel fuel (Table 2). Remarkably, these mixtures were stable for several weeks after the completion of the experiments, not showing appreciable stratification. Preliminary engine tests revealed that mixtures up to 30 vol% of HexOH with Diesel fuel led to a strong variability in the engine combustion, ascribed to the very low cetane number of HexOH (equal to 23, as reported in Table 3), giving an inacceptable ignition delay (≈10–11° crank angle). Consequently, the maximum percentage of oxygenated additive was set at 20 vol%, which represents a very high loading if compared with those typically employed for other bio-additives [43,46–48].

Table 2. Composition of the tested mixtures.

Mix	HexOH (vol%)	HexHex (vol%)	Diesel (vol%)	HexOH/HexHex (mol/mol)
1	0	0	100	Not applicable
2	10	0	90	Not applicable
3	0	10	90	Not applicable
4	20	0	80	Not applicable
5	0	20	80	Not applicable
6	5.2	4.8	90	2/1
7	3.5	6.5	90	1/1
8	2.1	7.9	90	1/2
9	7	13	80	1/1
10	4.2	15.8	80	1/2

The main physicochemical properties of the Diesel and the two utilized oxygenated additives (HexOH and HexHex) are reported in Table 3 [29,41,49].

Table 3. Main physicochemical properties of the utilized fuels.

	Diesel	HexOH	HexHex
Density (g/cm^3)	0.837	0.815	0.863
Cinematic Viscosity (at 40 °C—cSt)	≈2.7	3.64	2.37
Self-Ignition Temperature (°C)	≈300	285	NA [a]
Latent Heat of Vaporization (kJ/kg)	270–375	486	NA [a]

Table 3. *Cont.*

	Diesel	HexOH	HexHex
Flash Point (°C)	55	63	99
Cetane number (CN)	>50	23	40
Boiling point @1barA (°C)	180–360	157	245
Lower Heating Value (MJ/kg)	≈43	39	35

[a] NA= not available.

3.3. Engine Tests with HexOH or HexHex with Diesel Fuel

To better understand the effect of the single oxygenated additives on the corresponding engine performances, the first experimental campaign was carried out with 10 vol% and 20 vol% of HexOH and HexHex, individually considered as Diesel additives (mixtures 2, 3, 4, 5 described in Table 2). Engine performances, in terms of power and main pollutant emissions at full load and different engine speeds, are reported in Figures 5 and 6, respectively, whereas engine performances with 100 vol% Diesel fuel are reported as references. The injection timing was not changed during this experiment.
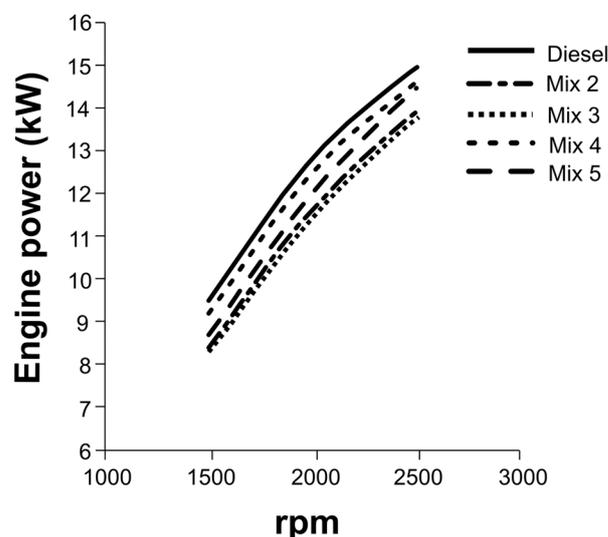
Figure 5. Engine power utilizing the HexOH- or HexHex-Diesel additives reported in Table 2.

As reported in Figure 5, the use of different Diesel additives did not significantly affect the engine performances. In fact, the tested mixtures led to a slightly lower power than that of 100 vol% Diesel, probably due to the reduced LHV of test mixtures (fuel volumetric flow was kept constant). Moreover, despite the marked CN difference between HexOH and HexHex (Table 3), the use of such oxygenated components with Diesel up to 20 vol% led to analogous advantages over 100 vol% Diesel fuel, in terms of pollutant emissions.

As reported in Figure 6a, an appreciable decrease in the CO emissions can be observed, with better results at higher bio-additive concentrations (20 vol% HexOH and 20 vol% HexHex). This behavior can be explained considering the higher H/C ratio in HexOH and HexHex (compared to 100 vol% Diesel), and the presence of oxygen in these molecules, which enhances the carbon oxidation during the combustion stage [50].

Figure 6b shows that HC emissions follow a different trend, showing a more marked increase at higher concentrations of HexOH and HexHex. This behavior could be ascribed to the lower CN of HexHex and, especially, of HexOH that, upon reducing combustion ignition, leaves less time to complete the oxidation of the hydrocarbons. However, in-cylinder pressure analysis did not evidence marked differences in ignition delay between the utilization of the mixtures and the Diesel fuel alone (at maximum of 2–3 CA° with the utilization of 20 vol% HexOH and 20 vol% HexHex), thus justifying such behavior. Besides such differences in CN values, other physical/chemical mechanisms are involved

in HC formation, such as the different boiling and flash point temperatures of HexOH and HexHex, which could influence the HC oxidation rate. In addition, this behavior can be influenced by the characteristics of the gas analyzer, which is not calibrated for these kinds of oxygenated alcohols. Concerning the influence of oxygenated alcohols on the HC emissions, the available literature reports contrasting results, e.g., an increase [23,26] or a decrease [22,51] in HC emissions. This may be due to the different types of employed engines, which imply different types and settings of the fuel injection systems, a different internal flow field, and different mixing processes involved within the combustion chamber.
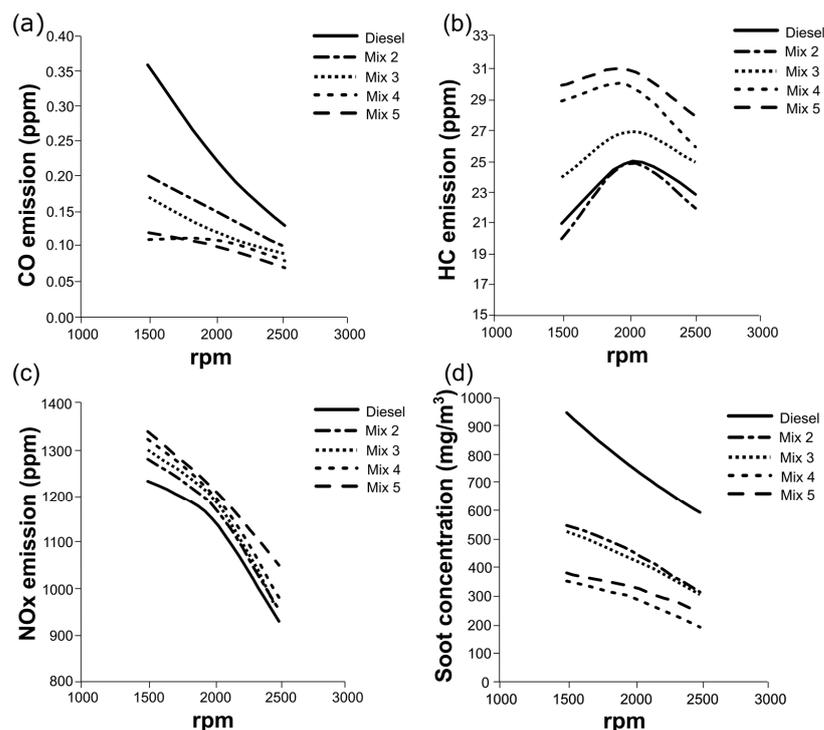
Figure 6. Engine emissions of (**a**) CO, (**b**) HC, (**c**) NOx, and (**d**) soot, utilizing the HexOH- or HexHex-Diesel additives reported in Table 2.

On the other hand, NOx emissions of HexOH-Diesel and HexHex-Diesel mixtures show a slight increase over 100 vol% Diesel fuel (Figure 6c), also at the highest bio-additive loadings (20 vol%), thus indicating that the maximum combustion temperature moderately increases with their utilization. This finding can be again ascribed to the lower CN values of HexOH and HexHex (in comparison with 100 vol% Diesel fuel) that, upon reducing the combustion ignition, lead to an increase in the fuel mass involved during the first phase of the combustion process (the injection timing is fixed with respect to crank angle position). This can be approximated to a constant-volume combustion process [50], with a presumably higher peak of in-cylinder pressure and temperature. In addition, the fuel-bonded oxygen, which characterizes the employed oxygenated bio-additive, increases the local oxygen concentration, thus promoting NOx formation [22].

Lastly, a significant reduction in soot emissions was observed (Figure 6d), with a reduction of roughly 50%, at higher rpm. This achievement is ascribed to the lower carbon content of HexOH and HexHex with respect to 100 vol% Diesel fuel, which reduces the carbon availability for soot formation, and to the oxygen bonds of additives, which promote the oxidation processes. Moreover, the reduced boiling point of the oxygenated mixtures not only improves droplet evaporation [21] but also leads to a sort of "droplet explosion" when the fuel is sprayed into a hot ambient [52,53], increasing fuel atomization and mixing and thus enhancing the combustion completion of the resulting soot particles.

3.4. Engine Tests with Mixtures of HexOH/HexHex with Diesel Fuel

After having tested the pure oxygenated components, the next step in the experiment was focused on the analysis of the behavior of HexOH/HexHex mixtures, added in various percentages (vol%), to Diesel fuel (mixtures 6–10 described in Table 2). Engine performances, in terms of power and pollutant emissions, at full load and different engine speed, are reported in Figures 7 and 8, respectively, and compared with the utilization of 100 vol% Diesel.
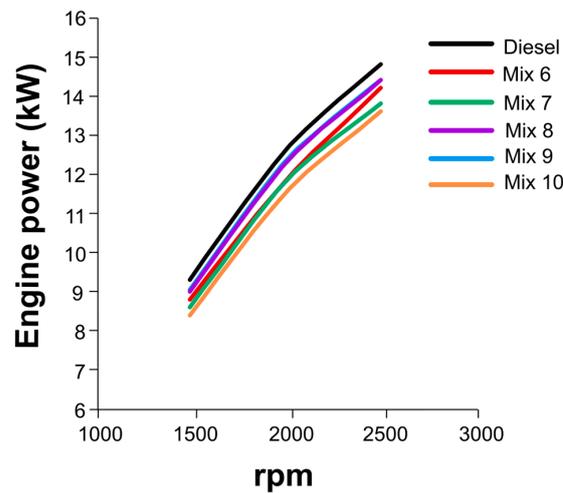
Figure 7. Engine power utilizing the HexOH/HexHex-Diesel additives reported in Table 2.
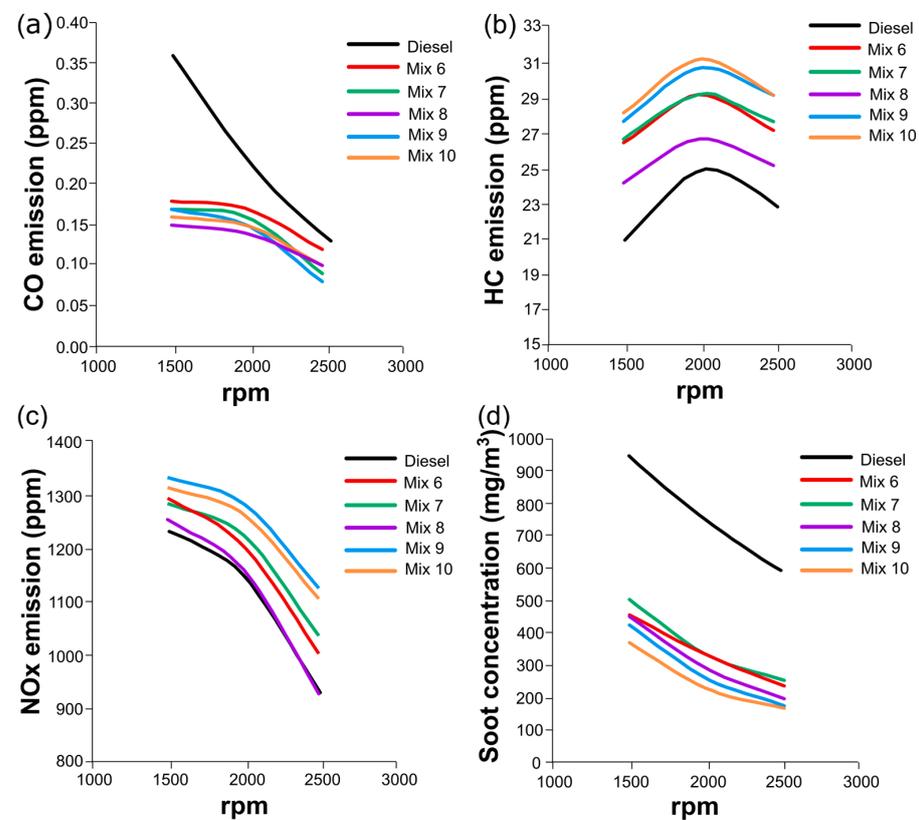
Figure 8. Engine emissions of (**a**) CO, (**b**) HC, (**c**) NOx, and (**d**) soot, utilizing the HexOH/HexHex-Diesel additives reported in Table 2.

Engine power and emission trends with mixtures of HexOH/HexHex agree with the previously reported trends for the mixtures composed of pure components. Therefore,

comparing the results obtained utilizing the mixtures and the Diesel fuel alone, it is possible to note a slight decline in engine power, an increase in HC and NOx emissions, and a marked reduction in soot and CO emissions, with the latter having the highest differences at the highest concentration (mix 9 and 10 in Table 2).

3.5. Engine Combustion Analysis

The in-cylinder pressure signal was acquired and properly utilized to analyze the engine combustion behavior. Once the engine was stabilized in the target operating condition, 100 cycles were acquired and averaged to calculate several combustion-related parameters, such as MFB50, which is the crank angle (CA°) where 50% of the fuel mass is burned per cycle, and COV_{imep}, which is the coefficient of variation of the in-cylinder mean effective pressure [50]. The MFB50 gives indications concerning the combustion speed, while COV_{imep} allows the analysis of the cyclic regularity of the engine. Figure 9 shows the comparison of pressure behavior at 2000 rpm and full load utilizing the mixtures reported in Table 2, whilst Figure 10 reports the MFB50 and COV_{imep} for the same mixtures. Remarkably, according to Figure 9, the higher peak of in-cylinder pressure is typical of a constant-volume combustion process, as previously stated, The pressure trend of the mixtures is very similar, with only small differences at the maximum pressure value, due to the different calorific value of the mixtures. Therefore, the analysis of the pressure data confirms that the use of HexOH-HexHex mixtures, up to 20 vol%, does not significantly alter the combustion trend with respect to the use of Diesel fuel alone, thus making their use in normal production engines feasible.
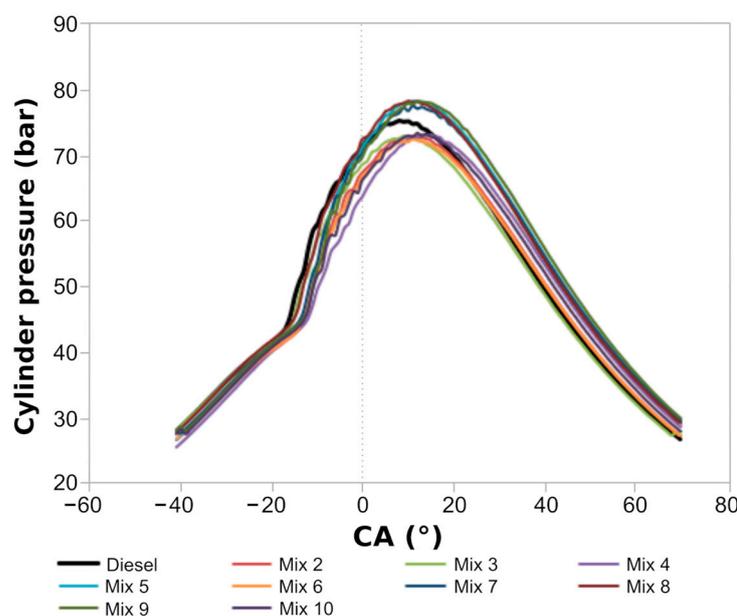

Figure 9. In-cylinder pressure behavior at full load and 2000 rpm, utilizing the various mixtures.

The calculated MFB50 (Figure 10a) highlights that the utilization of the mixtures led to an increase in combustion delay, as expected, with the highest value ($\approx$2.5 CA°) ascertained with the use of 20 vol% HexOH (mix 4). Remarkably, the combustion delays of all the mixtures are reasonable, and such delays can be easily reduced by acting on the fuel injection timing. Engine combustion variability is correlated with COV_{imep}, as shown in Figure 10b. Engine cyclic variability is acceptable for all the tested mixtures, showing values around 1%, with the worst results obtained using 20 vol% HexOH (mix 4), as predicted.
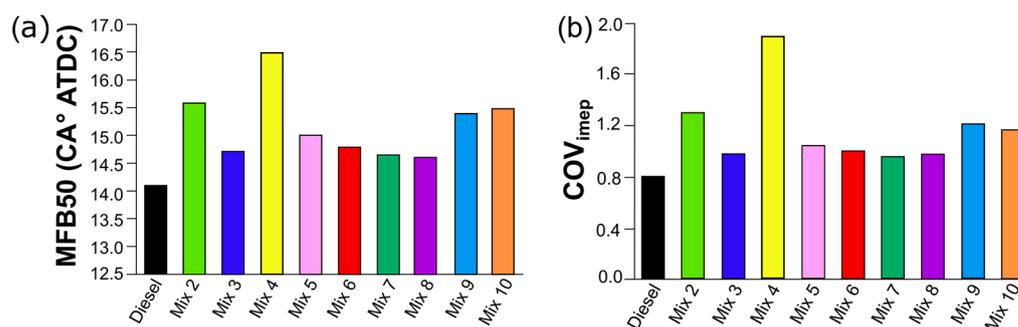
Figure 10. MFB50 and COV_{imep} at full load and 2000 rpm, utilizing the various mixtures.

4. Conclusions

The present study investigated the synthesis of two novel oxygenated bio-additives, e.g., 1-hexanol and hexyl hexanoate, through rhenium-catalyzed hydrogenation of crude hexanoic acid, with the latter obtained from the anaerobic fermentation of grape pomace, an abundant Italian agrifood waste. The catalyst acidity was exploited to better tune the final composition of 1-hexanol/hexyl hexanoate mixtures toward the formation of hexyl hexanoate. For this purpose, a commercial 5 wt% Re/γ-Al_2O_3 was adopted, promoting the esterification between the unconverted hexanoic acid and 1-hexanol, with the latter obtained from the carboxylic acid hydrogenation, leading to the highest hexyl hexanoate yield of about 40 mol%. The 5 wt% Re/γ-Al_2O_3 catalyst was stable up to three recycle runs, thus highlighting the robustness of the proposed cascade process.

The effects of each bio-additive on Diesel engine performance and exhaust emissions (soot, nitrogen oxides, carbon monoxide, unburned hydrocarbons) were carefully evaluated, highlighting noteworthy positive effects especially on the reduction in carbon monoxide and soot emissions (up to 40%), if compared with those of Diesel fuel alone.

Similar promising performances were achieved by employing Diesel blend mixtures of 1-hexanol/hexyl hexanoate, mimicking typical compositions of the rhenium-catalyzed post-hydrogenation mixtures. Remarkably, high loadings of these bio-additives (up to 20 vol%) were employed in such formulations, without the occurrence of significant changes in engine combustion characteristics and performances (in terms of cyclic variability and power). Moreover, such blends have shown excellent stability over time (stratifications are not evident even after weeks of storage), while their compatibility with the polymers used for the fuel distribution system must be carefully evaluated over the long term.

Definitely, 1-hexanol/hexyl hexanoate Diesel blends could remarkably improve the quality of combustion in Diesel engines, highlighting the possibility of obtaining such oxygenated bio-additives through fully sustainable and well-tunable conversion processes.

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Nomenclature

CA°	crank angle
CCD	charge coupled device
CN	cetane number
COV$_{imep}$	coefficient of variation of the indicated mean effective pressure
GC-FID	gas chromatography–flame ionization detector
GC-MS	gas chromatography–mass spectrometry
HC	hydrocarbon
HexHex	hexyl hexanoate
HexOH	1-hexanol
ICEs	internal combustion engines
ICP-OES	inductively coupled plasma–optical emission spectroscopy
ISG	integrated starter generator
LHV	lower heating value
MFB50	mass fraction burned 50%
NbPO	niobium phosphate
TCD	temperature conductivity detector
TEM	transmission electron microscopy
TPD	temperature-programmed desorption

References

1. Volumetric Energy Density of Lithium-Ion Batteries Increased by More Than Eight Times between 2008 and 2020. Available online: https://www.energy.gov/eere/vehicles/articles/fotw-1234-april-18-2022-volumetric-energy-density-lithium-ion-batteries (accessed on 30 August 2023).
2. IEA. Global EV Outlook 2022. Available online: https://www.iea.org/reports/global-ev-outlook-2022 (accessed on 30 August 2023).
3. Abdellatief, T.M.M.; Ershov, M.A.; Kapustin, V.M. New recipes for producing a high-octane gasoline based on naphtha from natural gas condensate. *Fuel* **2020**, *276*, 118075. [CrossRef]
4. Al Shebli, M.N.; Raj, A.; Elkadi, M.; Anjum, D.; Pena, G.D.J.; Prabhu, A. Fuel oxygenation as a novel method to reduce sooting propensity of fuels: An investigation with gasoline surrogate fuels. *Fuel* **2022**, *324*, 124562. [CrossRef]
5. Abdellatief, T.M.M.; Ershov, M.A.; Kapustin, V.M.; Abdelkareem, M.A.; Kamil, M.; Olabi, A.G. Recent trends for introducing promising fuel components to enhance the anti-knock quality of gasoline: A systematic review. *Fuel* **2021**, *291*, 120112. [CrossRef]
6. Azad, K. *Advances in Eco-Fuels for a Sustainable Environment*; Elsevier: Amsterdam, The Netherlands, 2019.
7. Rodionova, M.V.; Poudyal, R.S.; Tiwari, I.; Voloshin, R.A.; Zharmukhamedov, S.K.; Nam, H.G.; Zayadan, B.K.; Bruce, B.D.; Hou, H.J.M.; Allakherdiev, S.I. Biofuel production: Challenges and opportunities. *Int. J. Hydrog. Energy* **2017**, *42*, 8450–8461. [CrossRef]
8. Florin, M.J.; van de Ven, G.W.J.; van Ittersum, M.K. What drives sustainable biofuels? A review of indicator assessments of biofuel production systems involving small holder farmers. *Environ. Sci. Policy* **2014**, *37*, 142–157. [CrossRef]
9. Kumar, B.; Verma, P. Biomass-based biorefineries: An important architype towards a circular economy. *Fuel* **2021**, *288*, 119622. [CrossRef]
10. AlNazr, H.A.; Ahmad, N.; Ahmed, U.; Mohan, B.; Jameel, A.G.A. Predicting physical properties of oxygenated gasoline and diesel range fuels using machine learning. *Alex. Eng. J.* **2023**, *76*, 193–219. [CrossRef]
11. Pramanik, A.; Sinha, A.; Chaubey, K.K.; Hariharan, S.; Dayal, D.; Bachheti, R.K.; Bachheti, A.; Chandel, A.K. Second-generation bio-fuels: Strategies for employing degraded land for climate change mitigation meeting United Nation-sustainable development goals. *Sustainability* **2023**, *15*, 7578. [CrossRef]

12.　Alalwan, H.A.; Alminshid, A.H.; Aljaafari, H.A.S. Promising evolution of biofuel generations. Subject review. *Renew. Energy Focus* **2019**, *28*, 127–139. [CrossRef]

13.　Murugapoopathi, S.; Ramachandran, T.; Rajaganapathy, C. Theoretical performance on energy and exergy analysis of methyl esters of rubber seed oil fuelled on supercharged VCR engine. *Environ. Dev. Sustain.* **2022**. [CrossRef]

14.　Ashokkumar, V.; Venkatkarthick, R.; Jayashree, S.; Chuetor, S.; Dharmaraj, S.; Kumar, G.; Chen, W.H.; Ngamcharussrivichai, C. Recent advances in lignocellulosic biomass for biofuels and value-added bioproducts—A critical review. *Biores. Technol.* **2022**, *344*, 126195. [CrossRef] [PubMed]

15.　Çelebi, Y.; Aydın, H. An overview on the light alcohol fuels in diesel engines. *Fuel* **2019**, *236*, 890–911. [CrossRef]

16.　Vargün, M.; Özsezen, A.N. Evaluation of the effect of the fuel injection phase on the combustion and exhaust characteristics in a diesel engine operating with alcohol-diesel mixtures. *Energy* **2023**, *270*, 126975. [CrossRef]

17.　Musyoka, S.K.; Khalil, A.S.G.; Ookawara, S.A.; Elwardany, A.E. Effect of C4 alcohol and ester as fuel additives on diesel engine operating characteristics. *Fuel* **2023**, *341*, 127656. [CrossRef]

18.　Wu, P.; Miao, C.; Zhuang, X.; Li, W.; Tan, X.; Yang, T. Physicochemical characterization of levulinate esters with different alkyl chain lengths blended with fuel. *Energy Sci. Eng.* **2023**, *11*, 164–177. [CrossRef]

19.　Zhuo, C.; Xueqin, L.; Zhiwei, W.; Yantao, Y.; Tanglei, S.; Taoli, H.; Peng, L.; Yanling, L.; Youqing, W.; Tingzhou, L.; et al. Techno-economic and whole life cycle assessment of ester fuels production from agricultural waste via hydrothermal liquefaction. *Ind. Crops Prod.* **2023**, *192*, 116096. [CrossRef]

20.　Bartling, A.W.; Benavides, P.T.; Phillips, S.D.; Hawkins, T.; Singh, A.; Wiatrowski, M.; Tan, E.C.D.; Kinchin, C.; Ou, L.; Cai, H.; et al. Environmental, economic, and scalability considerations of selected bio-derived blendstocks for mixing-controlled compression ignition engines. *ACS Sustain. Chem. Eng.* **2022**, *10*, 6699–6712. [CrossRef]

21.　Li, G.; Dai, J.; Liu, Z.; Lee, T.H.; Zhang, C. Optical study on spray, combustion and flame characteristics of n-hexanol/diesel blends under various diesel engine-like conditions. *Fuel* **2022**, *325*, 124941. [CrossRef]

22.　Yan, J.; Gao, S.; Zhao, W.; Lee, T.H. Study of combustion and emission characteristics of a diesel engine fueled with diesel, butanol-diesel and hexanol-diesel mixtures under low intake pressure conditions. *Energy Convers. Manag.* **2021**, *243*, 114273. [CrossRef]

23.　Santhosh, K.; Kumar, G.N. Effect of injection time on combustion, performance and emission characteristics of direct injection CI engine fuelled with equi-volume of 1-hexanol/diesel blends. *Energy* **2021**, *214*, 118984. [CrossRef]

24.　Nour, M.; Sun, Z.; El-Seesy, A.I.; Li, X. Experimental evaluation of the performance and emissions of a direct-injection compression-ignition engine fueled with n-hexanol–diesel blends. *Fuel* **2021**, *302*, 121144. [CrossRef]

25.　Thomas, J.J.; Sabu, V.R.; Basrin, G.; Nagarajan, G. Hexanol: A renewable low reactivity fuel for RCCI combustion. *Fuel* **2021**, *286*, 119294. [CrossRef]

26.　De Poures, M.V.; Sathiyagnanam, A.P.; Rana, D.; Kumar, B.R.; Saravanan, S. 1-hexanol as a sustainable biofuel in DI diesel engines and its effect on combustion and emissions under the influence of injection timing and exhaust gas recirculation (EGR). *Appl. Therm. Eng.* **2017**, *113*, 1505–1513. [CrossRef]

27.　Seelam, N.; Gugulothu, S.K.; Reddy, R.V.; Burra, B. Influence of hexanol/hydrogen additives with diesel fuel from CRDI diesel engine with exhaust gas recirculation technique: A special focus on performance, combustion, gaseous and emission species. *J. Clean. Prod.* **2022**, *340*, 130854. [CrossRef]

28.　Thomas, J.J.; Manojkumar, C.V.; Sabu, V.R.; Nagarajan, G. Development and validation of a reduced chemical kinetic model for used vegetable oil biodiesel/1-hexanol blend for engine application. *Fuel* **2020**, *273*, 117780. [CrossRef]

29.　Fioroni, G.; Fouts, L.; Luecke, J.; Vardon, D.; Huq, N.; Christensen, E.; Huo, X.; Alleman, T.; McCormick, R.; Kass, M.; et al. Screening of potential biomass-derived streams as fuel additives for mixing controlled compression ignition combustion. *SAE Int. J. Adv. Curr. Prac. Mobil.* **2019**, *1*, 1117–1138. [CrossRef]

30.　Vijayagopal, R.; Curran, S.; Deter, D.; Longman, D. *Evaluating Class 6 Delivery Truck Fuel Economy and Emissions using Vehicle System Simulations for Conventional and Hybrid Powertrains and Co-Optima Fuel Blends*; SAE Technical Paper 2022-01-1156; SAE International: Warrendale, PA, USA, 2022. [CrossRef]

31.　Kass, M.D.; Janke, C.J.; Connatser, R.M.; Lewis, S. Compatibility of biologically derivable alcohols, alkanes, esters, ketones, and an ether as diesel blendstocks with fuel system elastomers. *Energy Fuels* **2021**, *35*, 4979–4996. [CrossRef]

32.　Kass, M.; Janke, C.; Nafziger, E. *Impact of Biodiesel, Renewable Diesel, 1-Octanol, Dibutoxymethane, n-Undecane, Hexyl Hexanoate and 2-Nonanone with Infrastructure Plastics as Blends with Diesel*; SAE Technical Paper 2022-01-0487; SAE International: Warrendale, PA, USA, 2022. [CrossRef]

33.　Nzeteu, C.O.; Trego, A.C.; Abram, F.; O'Flaherty, V. Reproducible, high-yielding, biological caproate production from food waste using a single-phase anaerobic reactor system. *Biotechnol. Biofuels* **2018**, *11*, 108. [CrossRef]

34.　Gazzola, G.; Braguglia, C.M.; Crognale, S.; Gallipoli, A.; Mininni, G.; Piemonte, V.; Rossetti, S.; Tonanzi, B.; Gianico, A. Biorefining of food waste through the anaerobic conversion of endogenous lactate into caproate: A fragile balance between microbial substrate utilization and product inhibition. *Waste Manag.* **2022**, *150*, 328–338. [CrossRef]

35.　Cheah, Y.K.; Vidal-Antich, C.; Dosta, J.; Mata-Álarez, J. Volatile fatty acid production from mesophilic acidogenic fermentation of organic fraction of municipal solid waste and food waste under acidic and alkaline pH. *Environ. Sci. Pollut. Res.* **2019**, *26*, 35509–35522. [CrossRef]

36. Duber, A.; Jaroszynski, L.; Zagrodnik, R.; Chwialkowska, J.; Juzwa, W.; Ciesielski, S.; Oleskowicz-Popiel, P. Exploiting the real wastewater potential for resource recovery—n-caproate production from acid whey. *Green Chem.* **2018**, *20*, 3790–3803. [CrossRef]
37. Carvajal-Arroyo, J.M.; Candry, P.; Andersen, S.J.; Props, R.; Seviour, T.; Ganigué, R.; Rabaey, K. Granular fermentation enables high rate caproic acid production from solid-free thin stillage. *Green Chem.* **2019**, *21*, 1330–1339. [CrossRef]
38. Martinez, G.A.; Puccio, S.; Domingos, J.M.B.; Morselli, E.; Gioia, C.; Marchese, P.; Raspolli Galletti, A.M.; Celli, A.; Fava, F.; Bertin, L. Upgrading grape pomace contained ethanol into hexanoic acid, fuel additives and a sticky polyhydroxyalkanoate: An effective alternative to ethanol distillation. *Green Chem.* **2022**, *24*, 2882–2892. [CrossRef]
39. Bacchiocchi, R.; De Maron, J.; Tabanelli, T.; Bianchi, D.; Cavani, F. Supported rhenium catalysts for the hydrogenation of levulinic acid derivatives: Limits and potential. *Sustain. Energy Fuels* **2023**, *7*, 671–681. [CrossRef]
40. Gothe, M.L.; Silva, K.L.C.; Figueredo, A.L.; Fiorio, J.L.; Rozendo, J.; Manduca, B.; Simizu, V.; Freire, R.S.; Garcia, M.A.S.; Vidinha, P. Rhenium–A tuneable player in tailored hydrogenation catalysis. *Eur. J. Inorg. Chem.* **2021**, *39*, 4043–4065. [CrossRef]
41. Licursi, D.; Raspolli Galletti, A.M.; Antonetti, C.; Martinez, G.A.; Jones, E.; Bertin, L.; Di Fidio, N.; Fulignati, S.; Pasini, G.; Frigo, S. Tunable production of diesel bio-blendstock by rhenium-catalysed hydrogenation of crude hexanoic acid from grape pomace fermentation. *Catalysts* **2022**, *12*, 1550. [CrossRef]
42. Antonetti, C.; Gori, S.; Licursi, D.; Pasini, G.; Frigo, S.; López, M.; Parajó, J.C.; Raspolli Galletti, A.M. One-pot alcoholysis of the lignocellulosic *Eucalyptus nitens* biomass to *n*-butyl levulinate, a valuable additive for diesel motor fuel. *Catalysts* **2020**, *10*, 509. [CrossRef]
43. Frigo, S.; Pasini, G.; Caposciutti, G.; Antonelli, M.; Raspolli Galletti, A.M.; Gori, S.; Costi, R.; Arnone, L. Utilisation of advanced biofuel in CI internal combustion engines. *Fuel* **2021**, *297*, 120742. [CrossRef]
44. Fulignati, S.; Antonetti, C.; Wilbers, E.; Licursi, D.; Heeres, H.J.; Raspolli Galletti, A.M. Tunable HMF hydrogenation to furan diols in a flow reactor using Ru/C as catalyst. *J. Ind. Eng. Chem.* **2021**, *100*, 390.e1. [CrossRef]
45. Muchave, G.J.; de S. Netto, L.D.; Almeida, J.M.A.R.; Aranda, D.A.G. Synthesis of fatty alcohols by hydrogenation of palm esters using rhenium-based catalysts supported on niobia, alumina and titania. *Int. J. Develop. Res.* **2020**, *10*, 42266–42278. [CrossRef]
46. Babu, D.; Anand, R. Effect of biodiesel-diesel-n-pentanol and biodiesel-diesel-n-hexanol blends on diesel engine emission and combustion characteristics. *Energy* **2017**, *133*, 61–76. [CrossRef]
47. Huo, X.; Huq, N.A.; Stunkel, J.; Cleveland, N.S.; Starace, A.K.; Settle, A.E.; York, A.M.; Nelson, R.S.; Brandner, D.G.; Fouts, L.; et al. Tailoring diesel bioblendstock from integrated catalytic upgrading of carboxylic acids: A "fuel property first" approach. *Green Chem.* **2019**, *21*, 5813–5827. [CrossRef]
48. Yusuff, A.S.; Dada, T.; Olateju, I.I.; Azeez, T.M.; Azeez, S.O. Experimental investigation of influence of methyl, ethyl and methyl-ethyl ester blends of used cooking oil engine performances and emissions. *Energy Convers. Manag. X* **2023**, *17*, 100346. [CrossRef]
49. Kumar, B.R.; Saravanan, S. Use of higher alcohol biofuels in diesel engines: A review. *Renew. Sustain. Energy Rev.* **2016**, *60*, 84–115. [CrossRef]
50. Heywood, J.B. *Internal Combustion Engine Fundamentals*, 2nd ed.; McGraw-Hill Education: New York, NY, USA, 2018.
51. Herreros, J.M.; Jones, A.; Sukjit, E.; Tsolakis, A. Blending lignin-derived oxygenate in enhanced multi-component diesel fuel for improved emissions. *Appl. Energy* **2014**, *116*, 58–65. [CrossRef]
52. Rao, D.C.K.; Karmakar, S.; Basu, S. Atomization characteristics and instabilities in the combustion of multi-component fuel droplets with high volatility differential. *Sci. Rep.* **2017**, *7*, 8925. [CrossRef] [PubMed]
53. Lasheras, J.C.; Fernandez-Pello, A.C.; Dryer, F.L. Experimental observations on the disruptive combustion of free droplets of multicomponent fuels. *Combust. Sci. Technol.* **1980**, *22*, 195–209. [CrossRef]