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Posted Date: 7 September 2023

doi: 10.20944/preprints202309.0486.v1

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Article

Synthesis of 1-Hexanol/Hexyl Hexanoate Mixtures from Grape Pomace and Their Utilization as Bio-additive in Diesel Engine

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Abstract: The production of oxygenated bio-additives for traditional fuels represents a key challenge due to the depletion of fossil fuels in the next future and their contribution to environmental pollution. In this context, the present study considers the synthesis of different mixtures of 1-hexanol/hexyl hexanoate produced through the catalytic hydrogenation of hexanoic acid, a carboxylic acid obtainable from the fermentation of a wide variety of waste biomasses. In particular, crude hexanoic acid deriving from the fermentation of grape pomace, an abundant Italian agrifood waste, has been taken into consideration. The reaction was carried out with the commercial 5 wt% Re/γ-Al_2O_3 catalyst, whose acidity allowed the tuning of the reaction selectivity towards the preferential formation of hexyl hexanoate instead of 1-hexanol. As consequence, the tunable composition of the obtained 1-hexanol/hexyl hexanoate mixtures was leveraged for engine applications, thus allowing studying each component influence on the Diesel engine performances and verifying their synergistic effects. The engine experimental activity highlighted that both 1-hexanol and hexyl hexanoate, as well as their mixtures, can be used in Diesel engine with a commercial Diesel fuel up to high loadings (20 vol%) without altering engine performances and significantly lowering soot and CO emissions by more than 40%.

Keywords: grape pomace; hydrogenation; hexanol; hexyl hexanoate; diesel bio-additives; diesel engine performances

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. As regards the light land transport sector (cars), the abandonment of propulsion systems based on the use of internal combustion engines (ICEs) in favor of electrification (assuming that electricity comes from renewable sources) seems the preferred solution. On the contrary, heavy land (trucks and trains), marine and air transport sectors have not chosen yet what path must be taken. For these last categories, on-board energy storage through batteries still appears practically inappropriate, due to their high costs and low energy/weight ratio compared to liquid fuels, even if lithium batteries have increased rapidly in these last years, reaching an energy density up to 1.6 MJ/kg [1,2]. A possible alternative to fossil fuels is certainly represented by bio-fuels that, deriving from biomasses and preferentially from lignocellulosic wastes, allow making closed the carbon cycle thus reducing the net CO_2 emissions and can contribute to lowering also the CO and particulate matter emissions [3]. At the same time, this choice will make countries poor in energy sources independent

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from the supply of oil and natural gas by promoting the agricultural-forestry activities of the territory, with considerable economic advantages [4,5]. Noteworthy, the use of bio-fuels does not involve a drastic change in the distribution systems and use of energy, thus the existing infrastructures can remain unchanged. In the recent years, there has been an ever-increasing interest on the development of second-generation bio-fuels (obtained from non-food matrices) and their use in ICEs, as evidenced by the large scientific literature produced [6–9]. Among these ones, oxygenated compounds such as alcohols and esters obtained from residual lignocellulosic biomasses appear extremely promising for the use in Diesel engine [10–15], but their synthesis should always fully respect the criteria of environmental and economic sustainability [16]. Recently, 1-hexanol (HexOH) and hexyl hexanoate (HexHex) have been proposed as bio-additives for Diesel engine, despite few information of their effect on Diesel engine performances can be found in the scientific literature [24–31]. Overall, all these latest studies confirm that the use of HexOH/Diesel blends, in different percentages, leads to a decrease in soot and CO emissions, while NOx and hydrocarbons (HC) are generally increased, 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.

As aforementioned, few studies are reported on the utilization of HexHex as Diesel additive. Fioroni et al. analyzed the properties of over 400 potential blends to power Diesel engines, identifying only 25 of these ones whose properties met all requirements, and 12 could be obtained for experimental research and property validation, including HexHex [32]. Based on their low sooting index values, they are all expected to reduce particulate matter emissions from Diesel combustion. In the specific case of HexHex, improvement on lubricity, oxidation stability and biodegradability were ascertained but the authors evidenced that a more in-depth investigation is strictly necessary, especially for developing HexHex engine applications. Remarkably, in a very recent technical report of Vijayagopal et al. [33], a blend of 25 vol% HexHex with Diesel 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 like those of the 100 vol% Diesel fuel. However, NOx emissions require further evaluation, as these values resulted higher than those of pure Diesel, whilst other emissions (CO, soot and HC) were not studied by the authors. This last aspect surely deserves further study, due to the strategic role of the reduction of these emissions in an environmental sustainability perspective. Moreover, other research proved the compatibility of HexHex with the engine components, included elastomers [34] and plastic infrastructures [35], thus highlighting the feasibility of its immediate utilization within a Diesel engine, without the necessity of replacement of any of its parts.

Noteworthy, 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 involving the chain elongation process [19–23]. According to this mechanism, short-chain carboxylic acids, e.g. acetic and/or butyric acids, are elongated with carbons from a reduced molecule as ethanol or lactic acid, which can be generated in-situ during the fermentation or added by outside. In this regard, the authors have recently proposed a new cascade bio-refinery scheme for the bio-conversion of an abundant Italian agrifood waste as grape pomace, involving the upgrading of the ethanol fraction into hexanoic acid by the anaerobic acidogenic fermentation process [17]. This new integrated process allowed the exploitation of the obtained hexanoic acid as substrate for the synthesis of HexOH/HexHex mixture, employable as 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, being this metal particularly active in the hydrogenation of carboxylic acids [36,37], and evidenced the tunability of the reaction selectivity depending on the catalyst properties [18]. In fact, the 5 wt% Re/C catalyst resulted selective towards the HexOH formation, whilst the addition of niobium phosphate (NbPO) as acid co-catalyst caused the slowdown of the substrate conversion but selectively catalyzed the esterification reaction between the unconverted hexanoic acid and the produced alcohol, thus improving the selectivity towards HexHex. The possibility of tuning the reaction selectivity by modulating the catalyst properties is particularly attractive when these mixtures are applied as new oxygenated bio-additive for Diesel engines. Noteworthy, 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 starting from the commercial hexanoic acid, while the selectivity of the hydrogenation resulted unaffected. On this basis, the proposed approach to produce HexOH/HexHex mixtures from the crude hexanoic acid obtained by exploiting grape pomace as the starting feedstock could be extended to a large variety of other wastes. Moreover, the fuel properties of 10 vol% HexOH or HexHex mixtures as Diesel additive were investigated and for the first time also a mixture of HexOH/HexHex composed by 5.2 vol% HexOH + 4.8 vol% HexHex was tested, a composition representative of that of the final mixture deriving from the hydrogenation of hexanoic acid in the presence of 5 wt% Re/C as the catalyst [18]. It is remarkable that in this preliminary study a significant reduction of the soot and CO emissions, without notable change in the engine performances, was ascertained, thus proving the potentialities of these HexOH/HexHex Diesel bio-additives.

Starting from these encouraging preliminary results, in the present work the key role of the catalyst acidity, e.g. the possibility of selectively favoring the HexHex formation starting from both commercial and crude hexanoic acid obtained from grape pomace, has been investigated more in depth, adopting a commercial 5 wt% Re/γ-Al_2O_3 catalyst. Afterwards, attention has been focused on the engine performances of HexOH/HexHex Diesel additives, evaluating a wider compositional range. High percentages of the HexOH/HexHex mixture, up to 20 vol%, have been adopted together with commercial Diesel, investigating for the first time their influence on the engine performances and emissions. By this way, it will be possible to exploit the synergy between HexOH and HexHex, to improve the motor Diesel performances respect to their individual use. The present research activity is part of uneven more ambitious goal, aimed at the development of last generation ester bio-fuels, which was previously focused on butyl levulinate, identified as a very valuable diesel additive [38,39]. 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%) have been purchased by Sigma-Aldrich and employed as received, whilst 5 wt% Re/γ-Al_2O_3 was provided by Riogen. Red and white grape pomaces, deriving from the wine production, were provided by Caviro Distillerie and employed as received. Two different crude hexanoic acid rich liquors were obtained starting from red or white grape pomaces according to the previous reported procedure [17]. 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 by filtration, whilst the liquid fraction was acidified with HCl up to pH 2.2 and transferred into another bottle where the liquid phase separation took place. The upper phase included hexanoic acid that was separated by overflow and centrifugated to remove suspended solids.

2.2. Catalyst characterization

NH_3-TPD characterization was performed 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.

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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_2O_3 catalyst.

Transmission Electron Microscopy (TEM) analysis was performed in bright field mode with a CM12 microscope (Philips), working at 120 keV, according to our previous work [40].

The rhenium content in the reaction mixtures was determined through ICP-OES analysis employing an Optimum 7000DV 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, were performed according to our previous works [17,18]. Briefly, the catalyst (5 wt% Re/γ-Al_2O_3) was pre-reduced in methanol, then the solvent was removed under vacuum and the reaction mixture was fed by suction and mechanically stirred. The reactor was pressurized with 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 by filtration under argon atmosphere and the reaction mixture was analyzed through GC-FID chromatography, according to the procedure reported in our previous work [18]. 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 Diesel engine model 9LD 625/2) 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 AVL gravimetric fuel balance was used to online measure the fuel consumption, while for pollutant emissions an AVL DiTest Gas1000 was adopted. The particulate matter was measured with an AVL smoke meter (model 415 S). A Kistler pressure sensor (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). An exhaust gas K-type thermocouple was located at the engine exhaust to verify the steady state conditions reach. A detail of the Lombardini-Kohler 9LD 625/2 on the test bench is shown in Figure 1. After stabilization in each operating condition, data were collected and analyzed.

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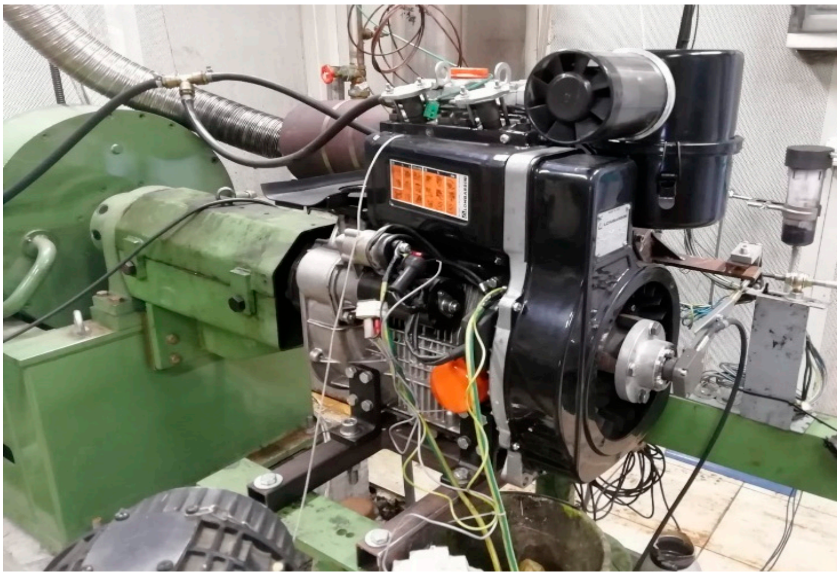

Figure 1. Lombardini-Kohler 9LD 625/2 on the test bench.

3. Results

3.1. Hydrogenation of hexanoic acid with 5 wt% Re/γ-Al_2O_3

In our previous work [18], it was found that 5 wt% Re/C catalyzed the hydrogenation of hexanoic acid towards the selective formation of HexOH up to the 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, such as the commercial 5 wt% Re/γ-Al_2O_3. Generally, a commercial catalyst should be preferred, being widely available on the market, and produced in a constant and repeatable way. Before the catalytic runs, 5 wt% Re/γ-Al_2O_3 was characterized through N_2 physisorption and TEM techniques, showing the specific surface area of 220 m^2/g and the rhenium average particle size of about 3.85 nm (Figure 2a), respectively. Moreover, the acidic properties of the catalyst were evaluated by NH_3-TPD analysis, that highlighted the presence of a large peak between 200–800 °C (Figure 2b) demonstrating the high amount of total acid sites (552 μmol/g) that are characterized mainly by high strength, in agreement with the literature [41].

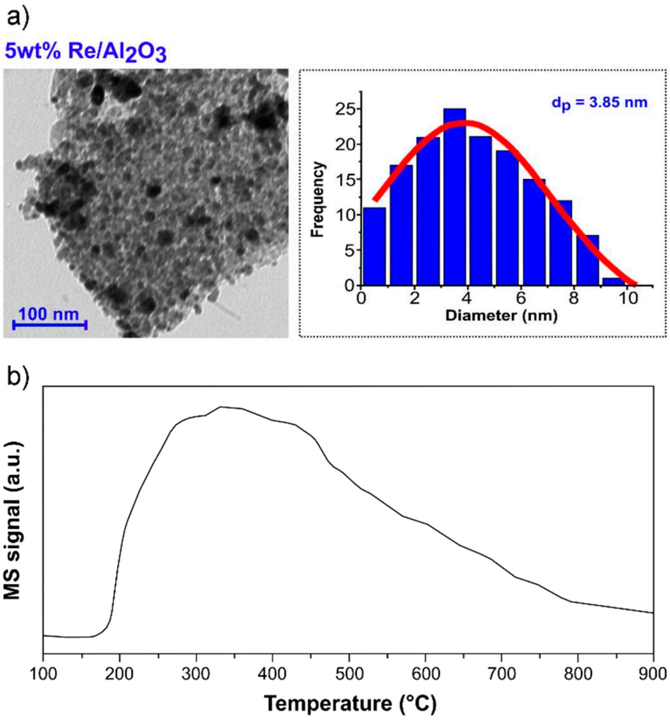

Figure 2. (a) TEM picture and the respective distribution of the Re particle sizes and (b) NH_3-TPD profile of 5 wt% Re/Al_2O_3.

We have already found that a wet pre-reduction of 5 wt% Re/C allowed the Re^{+7} reduction to the species of lower valence, mainly Re^{+3} and Re^{+4}, thus improving the hydrogenating activity of the bulk metal [18]. Under this perspective, also 5 wt% Re/γ-Al_2O_3 was 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 under the reaction conditions already adopted for the 5 wt% Re/C catalyst. The obtained results are compared in Figure 3.

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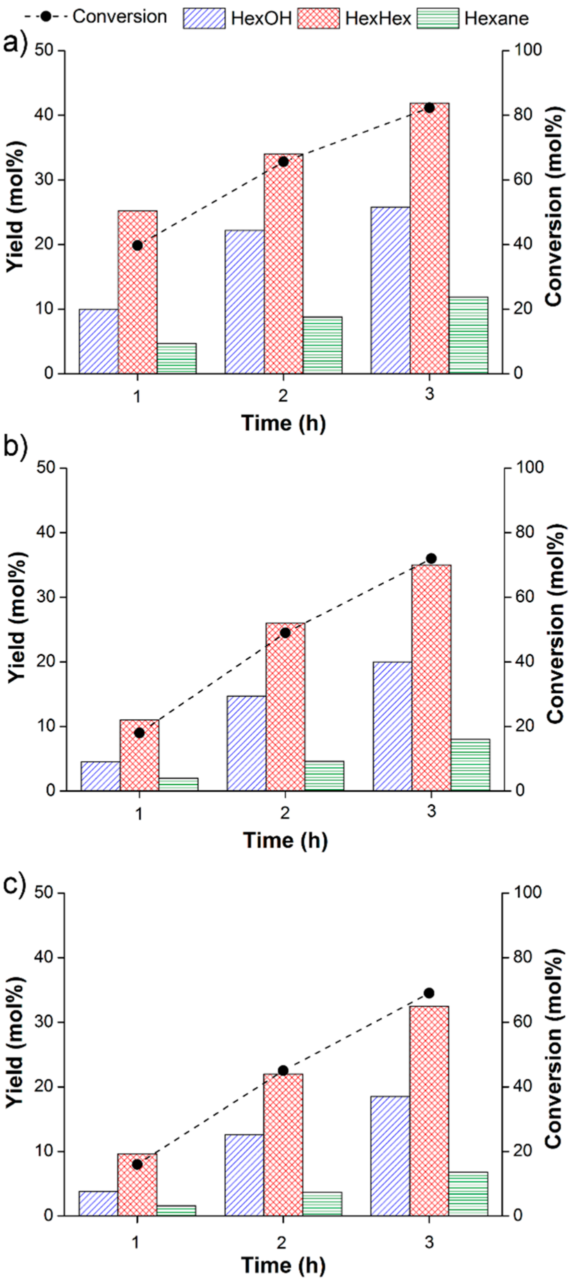

Figure 3. Hydrogenation of: a) commercial hexanoic acid, b) crude hexanoic acid deriving from fermented white grape pomace and c) crude hexanoic acid deriving from fermented red grape pomace with pre-reduced 5 wt% Re/γ-Al_2O_3. Reaction conditions: T=220 °C; P_{H2}= 115 bar; substrate/Re molar ratio of 270 mol/mol.

Hexanoic acid conversion ascertained with the pre-reduced 5 wt% Re/γ-Al_2O_3, starting from commercial hexanoic acid (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 5 wt% Re/C. The slowdown of hexanoic acid conversion can be addressed to the lower specific surface area of 5 wt% Re/γ-Al_2O_3 than that of 5 wt% Re/γ-Al_2O_3 (e.g. 220 vs 840 m^2/g, respectively). This, in synergy with the acidity of the support γ-Al_2O_3, enabled the simultaneous esterification between the unreacted substrate and the produced HexOH, thus improving the selectivity towards HexHex. The ascertained results confirm the tunability of the reaction mixture composition depending on the catalyst characteristics, allowing the achievement of the more suitable alcohol/ester mixtures for engine tests. Moreover, as previously found, a limited formation of hexane was ascertained also in the presence of 5 wt% Re/γ-Al_2O_3.

Crude hexanoic acid derived from anaerobic fermentation of white and red grape pomaces was then studied as the real substrate. The purity of hexanoic acid in the fermentation liquors has been already investigated in our previous works through GC-FID and GC-MS chromatography [17,18]. We found that the hexanoic acid purity was higher in the liquor derived from the fermentation of the white grape pomace than from the red one, being 93 and 87 wt% respectively. The GC-MS analysis highlighted the presence of only few carboxylic acids (C4–C8) in the crude fermented white grape pomace, which were present also in the crude fermented red grape pomace but in higher amount. This different composition of the substrates might have relevant consequences on the hydrogenation process, but in our proposed cascade process only little differences have been observed between the results ascertained starting from the three different substrates, thus highlighting the robustness of the process. In fact, only a slight decrease of conversion was observed but the higher selectivity towards HexHex, rather than HexOH, was confirmed together with a low formation of hexane (Figures 3b and 3c).

Also the chemical stability of the adopted catalyst is of paramount relevance to consider the whole process really robust and scalable, thus the spent catalysts recovered at the end of the hydrogenation of commercial hexanoic acid, crude hexanoic acid deriving from fermented white and red grape pomaces were recycled in three following tests (Figure 4). The catalyst resulted stable during the recycling tests for each of the investigated substrate, showing to be suitable for the successive scale-up starting also from real wastes. In fact, only a slight decrease of 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. In fact, a relevant rhenium leaching has been excluded by the ICP analysis of the reaction mixtures where the Re content was below the detection limit.

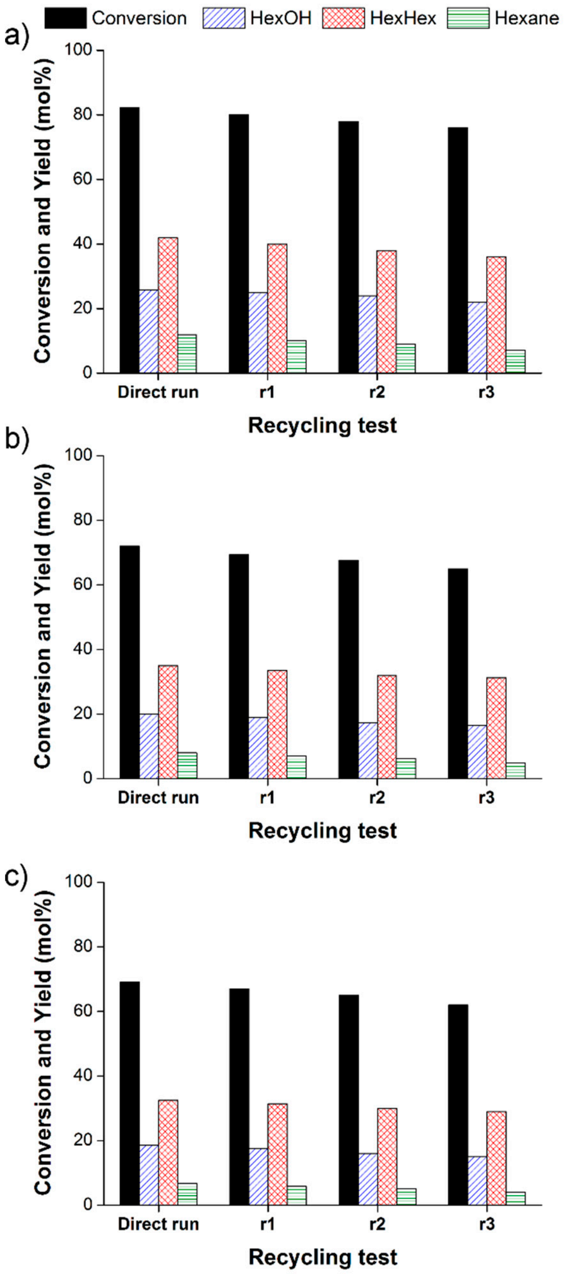

Figure 4. Recyclability tests of 5 wt% Re/γ-Al_2O_3 in the hydrogenation of: a) commercial hexanoic acid, b) crude hexanoic acid deriving from fermented white grape pomace and c) crude hexanoic acid deriving from fermented red grape pomace. Reaction conditions: T=220 °C; P_{H2}= 115 bar; t= 3 h; substrate/Re molar ratio of 270 mol/mol.

3.2. Additives definition for engine tests

Given the promising preliminary results on the use of 10 vol% HexOH+HexHex as additives with the Diesel fuel [18], it was decided to enhance the amount of the oxygenated additives and investigate a wider compositional range that reproduces the composition of the mixtures obtained from the previous hydrogenation runs with 5 wt% Re/C and those obtained in the present work with 5 wt% Re/γ-Al_2O_3. Preliminary engine tests showed that mixtures up to 30 vol% of HexOH with Diesel fuel led to a strong variability on engine combustion, caused by the very low cetane number of HexOH (equal to 23, as reported in Table 3) that led to an inacceptable ignition delay (≈ 10–11° crank angle). Consequently, the maximum percentage of oxygenated additive was set at 20 vol%, which is anyway a very promising loading if compared with the values reported generally in the literature for other bio-additives [39,42–44]. On this basis, nine mixtures were tested and compared with the utilization of Diesel fuel alone and their compositions are reported in Table 2. It is worthwhile to underline that the prepared mixtures proved to be stable (no stratification) until the completion of the experiments (several weeks).

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

Table 3. Main characteristics 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
Latent Heat of Vaporisation (kJ/kg)	270-375	486	NA
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

The main chemical-physical characteristics of the Diesel and the two utilized oxygenated additives (HexOH and HexHex) are reported in Table 3 [18,32,45].

3.3. Engine tests with HexOH or HexHex with Diesel fuel

To better understand the effect of the single oxygenated additives on the engine performance, a first experimental campaign has been 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 performance concerning power and main pollutant emissions, at full load and different engine speed, are reported in Figure 5 and 6, respectively, and compared with the utilization of 100 vol% Diesel fuel. Injection timing was not changed along the experimentation.

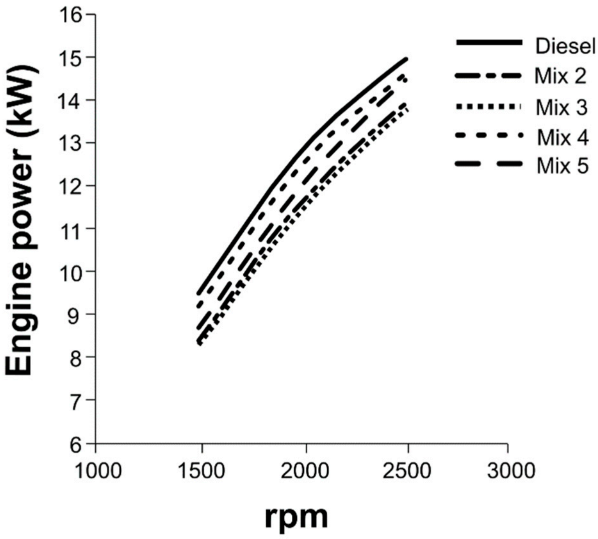

Figure 5. Engine power utilizing the HexOH- or HexHex-Diesel additives reported in Table 2.

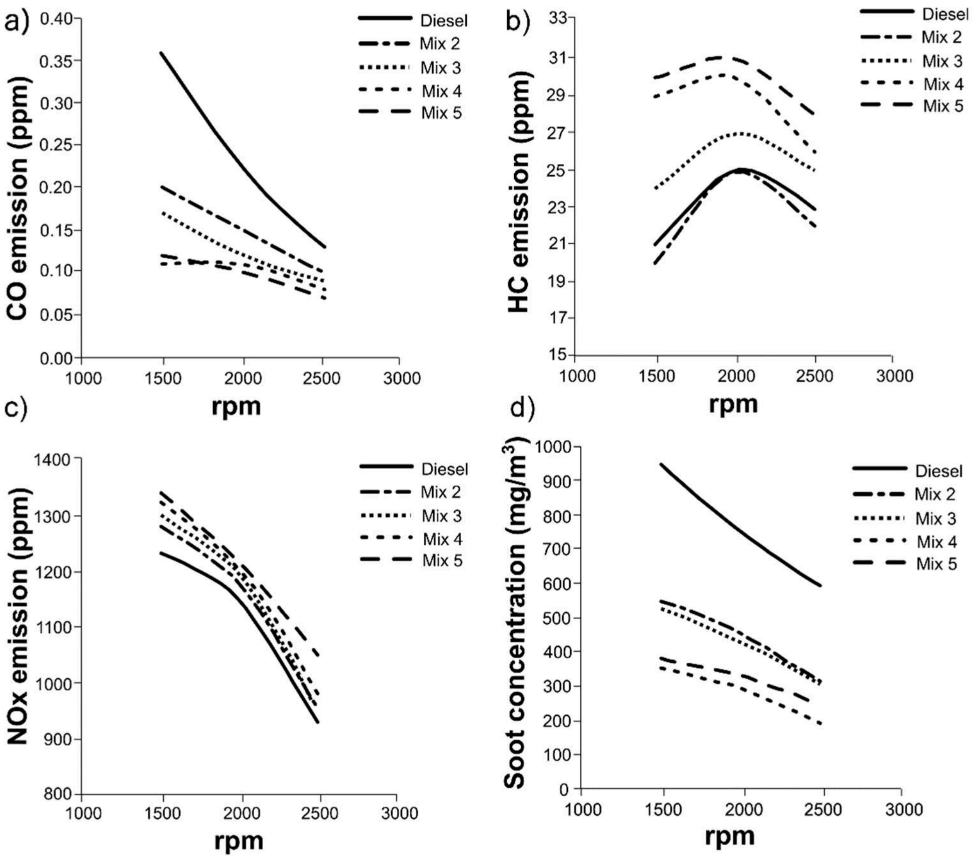

Figure 6. Engine emissions of: a) CO; b) HC; c) NOx and d) soot, utilizing the HexOH- or HexHex-Diesel additives reported in Table 2.

As reported in Figure 5, the use of different Diesel additives did not significantly affect the engine performance. In fact, the tested mixtures led to slightly lower power, probably due to the reduced LHV of test mixtures with respect to the fossil Diesel fuel, given that the fuel volumetric flow is constant. Moreover, despite the marked difference in CN between HexOH and HexHex (Table 3), the use of these two components with Diesel up to 20 vol% led to analogous substantial advantages in pollutant emissions respect to the fossil Diesel fuel.

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As reported in Figure 6a, a decrease in the CO emissions can be observed, with better values at higher bio-additives 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 Diesel, and to the presence of oxygen in these molecules, which enhances the carbon complete oxidation during combustion [46].

Figure 6b shows that HC emissions follow a different trend with an evident increase at higher concentration of HexOH and HexHex. This behavior could be addressed to the lower CN of HexHex and, especially, of HexOH that, retarding 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 2-3 CA° with the utilization of 20 vol% HexOH and 20 vol% HexHex), thus justifying such behavior. Certainly, in addition to the 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 with respect to Diesel fuel, 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 this kind of oxygenated alcohols. The scientific literature about the influence of oxygenated alcohols on the HC emissions, is contrasting, whereas authors found an increase [25,28], or a decrease [24,47]. This may be due to the different type of employed engines, which imply different types and setting of the fuel injection systems, a different internal flow field and therefore different mixing processes in the combustion chamber.

On the other hand, NOx emissions of HexOH-Diesel and HexHex-Diesel mixtures show a slight increase respect to Diesel fuel (Figure 6c), also at the highest bio-additive loadings (20 vol%), thus indicating that the maximum combustion temperature moderately increase with their utilization. Also this can be addressed to the lower CN values of HexOH and HexHex respect to Diesel fuel that, retarding the combustion ignition, lead to an increase of the fuel mass involved during the first phase of the combustion process (the injection timing is fixed with respect to crank angle position), which can be approximated to a constant volume combustion process [46], with higher peak of the in-cylinder pressure and temperature (see Figure 9). In addition, the fuel bonded oxygen, which characterizes the employed oxygenated bio-additive, increases the local oxygen concentration thus promoting NOx formation [24].

Finally, a significant reduction of the soot emissions was observed (Figure 6d), with a reduction of roughly 50% at higher rpm. This can be ascribable to the lower carbon content of HexOH and HexHex respect to Diesel fuel, which reduces the carbon availability for soot formation, and to the oxygen bonds of additives, that promote the oxidation processes. Moreover, the reduced boiling point of the oxygenated mixtures improves not only droplets evaporation [31], but also leads to a sort of "droplet explosion" when the fuel is sprayed in a hot ambient [48,49], increasing fuel atomization and mixing, thus enhancing the combustion completion of eventual soot particles.

3.4. Engine tests with mixtures of HexOH/HexHex with Diesel fuel

Once the pure components have been tested, the experimental activity was dedicated to analyzing the behavior of HexOH/HexHex mixtures added, in various percentage (vol%), to Diesel fuel (mixtures 6–10 described in Table 2). Engine performances concerning power and main pollutant emissions, at full load and different engine speed, are reported in Figures 7 and 8, respectively, and compared with the utilization of Diesel fuel only.

Performance and emissions trends observed utilizing mixtures of HexOH/HexHex confirm those of mixtures of pure components previously reported. 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, these last with the highest differences at highest concentration (mix 9 and 10 in Table 2).

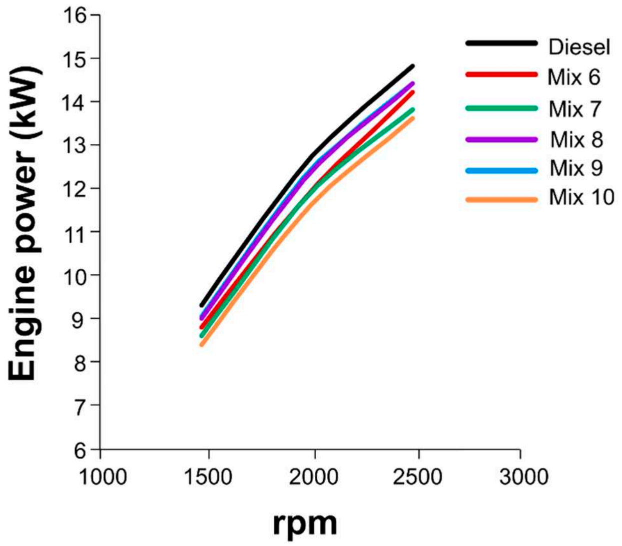

Figure 7. Engine power utilizing the HexOH/HexHex-Diesel additives reported in Table 2.

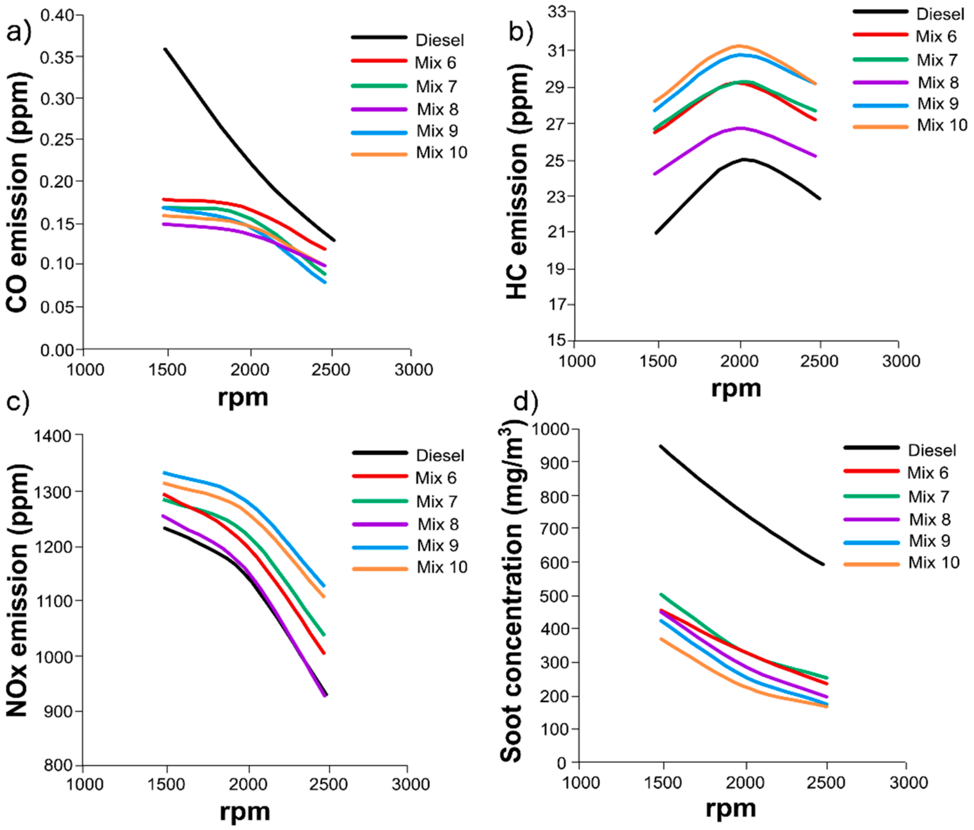

Figure 8. Engine emissions of: a) CO; b) HC; c) NOx and d) soot, utilizing the HexOH/HexHex-Diesel additives reported in Table 2.

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 one operating condition, 100 cycle were acquired and averaged to calculate several combustion related parameters, such as the MFB50, that is the crank angle (CA°) at which 50% of the fuel mass is burned per cycle, and the COV_{imep}, that is the coefficient of variation of the in-cylinder mean effective pressure [46]. The MFB50 gives indications concerning the combustion speed, while the COV_{imep} allows to analyze 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.

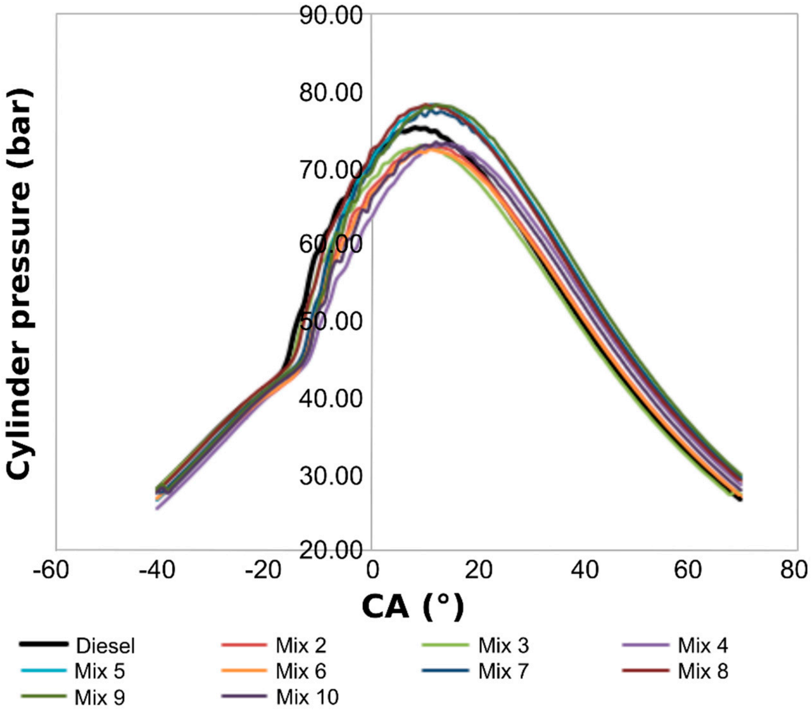

Figure 9. In-cylinder pressure behavior at full load and 2000 rpm, utilizing the various mixtures.

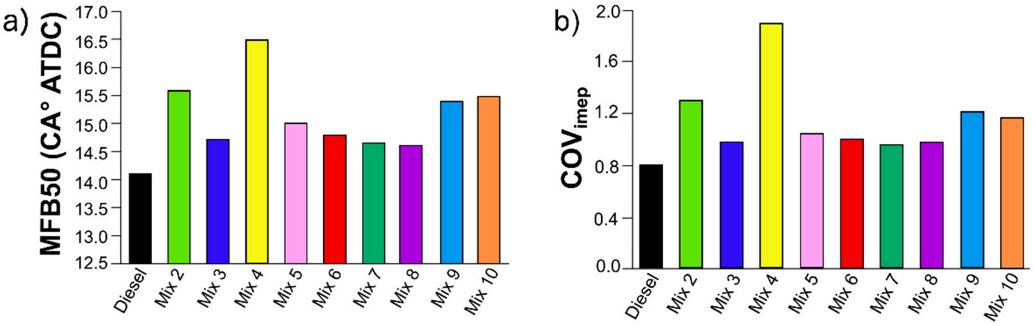

Figure 10. MFB50 and COV_{imep} at full load and 2000 rpm, utilizing the various mixtures.

Pressure trend is very similar when passing from one mixture to an another one, with small differences only in the maximum pressure value caused by 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 compared to the use of Diesel fuel alone, thus making their use not problematic in normal production engines.

The calculated MFB50 (Figure 10a) highlights that, as to be expected, the mixtures utilization led to an increase in combustion delay, with the highest value (≈ 2.5 CA°) ascertained with the use of 20 vol% HexOH (mix 4). However, it is worthwhile to underline that all the mixtures combustion delays are not excessive, therefore this problem can be easily solved by acting on the fuel injection timing. Engine combustion variability is correlated to COV_{imep}, whose evaluation is shown in Figure 10b. Engine cyclic variability is acceptable for all the mixtures tested, with values around 1% and with the worst results obtained as a result of using 20 vol% HexOH (mix 4), as predictable.

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4. Conclusions

The present study investigated the synthesis of second-generation oxygenated bio-additives, such as 1-hexanol (HexOH) and hexyl hexanoate (HexHex), through rhenium catalyzed hydrogenation of crude hexanoic acid, easily obtained from the anaerobic fermentation of an abundant agrifood waste as the grape pomace. The composition of HexOH/HexHex mixtures depended on the catalyst characteristics and in particular the acidity had a key role. Therefore, a commercial catalyst having acid properties, as the 5 wt% Re/γ-Al_2O_3, allowed to selectively favor the HexHex formation promoting the esterification between the unconverted hexanoic acid and HexOH. Noteworthy, similar results were obtained starting not only from commercial hexanoic acid but also from crude one obtained from white and red grape pomace fermentation and the catalyst resulted stable up to three recycle runs, thus highlighting the robustness of the process. Afterwards, mixtures of HexOH and HexHex with different compositions were prepared and added up to 20 vol% to a commercial Diesel fuel, in order to investigate the possibility of exploiting their synergy to improve the performances of a Diesel engine. The tests proved that the employment of HexOH/HexHex mixtures as Diesel bio-additives effectively decreased CO and soot emissions, these last up to 40%, respect to the use of Diesel fuel alone, with a modest increase of NOx and HC emissions without significative changes in engine combustion characteristics and performances (cyclic variability, power). The blends have shown excellent stability over time (stratifications are not evident even after weeks of storage), while compatibility with the polymers used for the fuel distribution system must be carefully evaluated over the long term. In conclusion, the second-generation bio-additives presented in this work can contribute to the reduction of greenhouse gas emissions and to the partial replacement of traditional fossil fuels, in agreement with the increasingly pressing regulations of the EU countries.

Author Contributions: Conceptualization, S.F. (Stefano Frigo), A.M.R.G. and G.P.; methodology, S.F. (Stefano Frigo), A.M.R.G., S.F. (Sara Fulignati), L.B., G.P.; formal analysis: S.F. (Stefano Frigo), A.M.R.G., S.F. (Sara Fulignati), D.L., G.A.M., L.B. and G.P.; writing-original draft preparation, S.F. (Stefano Frigo), A.M.R.G., S.F. (Sara Fulignati) and G.P.; writing-review and editing, S.F. (Stefano Frigo), A.M.R.G., S.F. (Sara Fulignati), D.L., G.A.M., L.B. and G.P.; supervision, S.F. (Stefano Frigo), A.M.R.G. and G.P.

Acknowledgments: The authors thank the project VISION PRIN 2017 “Development and promotion of the levulinic acid and carboxylate platforms by the formulation of novel and advanced PHA-based biomaterials and their exploitation for 3D printed green-electronics applications” (code FWC3WC_002) funded by MUR and the project NEST “Network 4 Energy Sustainable Transition” (code PE0000021) funded by the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 – Call for tender No. 1561 of 11.10.2022 of MUR, funded by the European Union – NextGenerationEU.

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

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