








Article

Tunable Production of Diesel Bio-Blendstock by Rhenium-Catalyzed Hydrogenation of Crude Hexanoic Acid from Grape Pomace Fermentation

Domenico Licursi ¹, Anna Maria Raspolli Galletti ^{1,*}, Claudia Antonetti ¹, Gonzalo A. Martinez ², Emma Jones ², Lorenzo Bertin ^{2,3}, Nicola Di Fidio ¹, Sara Fulignati ¹, Gianluca Pasini ⁴ and Stefano Frigo ⁴

¹ Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy

² Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Via Terracini 28, 40131 Bologna, Italy

³ Institute of Environmental Engineering, Kaunas University of Technology, K. Donelaičio St. 73, 44249 Kaunas, Lithuania

⁴ Department of Energy, System, Territory and Construction Engineering (DESTEC), University of Pisa, Largo Lucio Lazzarino, 56122 Pisa, Italy

* Correspondence: anna.maria.raspolli.galletti@unipi.it; Tel.: +39-050-2219290

Abstract: The transition from fossil resources to renewable ones represents a pressing need. The acidogenic fermentation of biomass-derived ethanol to carboxylic acids represents a novel and smart possibility, opening the way for the production of further value-added bio-products through cascade chemical approaches. In this work, the hydrogenation of commercial hexanoic acid to give 1-hexanol/hexyl hexanoate mixtures was preliminary studied in the presence of commercial rhenium catalysts (Re₂O₇ and 5 wt% Re/C), which resulted as mainly active and selective towards 1-hexanol. On the other hand, the use of niobium phosphate as the acid co-catalyst markedly shifted the selectivity towards hexyl hexanoate. Moreover, 5 wt% Re/C and physical mixtures of (5 wt% Re/C + niobium phosphate) were further tested for the hydrogenation of crude hexanoic acid obtained through fermentation of white grape pomace, confirming the promising performance of these catalytic systems and their recyclability. For the first time, the employment of 1-hexanol/hexyl hexanoate mixtures as a diesel blendstock was evaluated, highlighting a significant reduction of soot and CO emissions, without any significant change in the engine performance. The promising properties of these oxygenated additives are favorable for the partial replacement of traditional fossil fuels, in accordance with the short-term goals of EU countries.

Keywords: grape pomace; carboxylic acids; rhenium catalysts; hydrogenation; diesel blendstock



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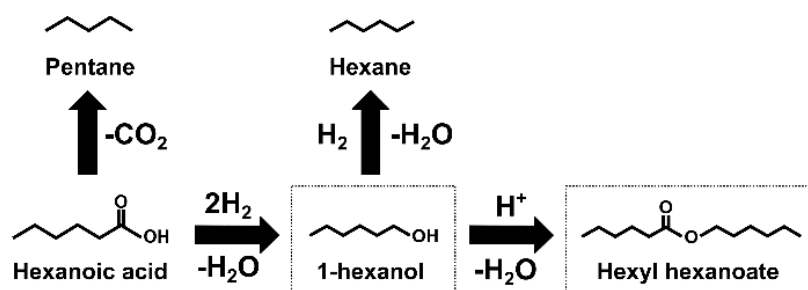


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1. Introduction

Biomass represents a key feedstock in the transition from fossil resources to renewable ones, to synthesize new biofuels and bio-chemicals through biological and/or chemical pathways [1]. The use of nonedible feedstocks is strategic for these goals, to not create any pressure on land use or hinder the supply of food [2]. From this perspective, grape pomace, an abundant agro-industrial waste derived from the winemaking process, is a promising feedstock to develop a bio-refinery approach. About 9 Mt of grape pomace are produced globally every year, these are valorized in centralized bio-refineries that obtain anthocyanins, polyphenols, and tartaric acid, but most of all distilled ethanol (e.g., for biofuel) [3]. Remarkably, ethanol distillation is an energy intensive process, e.g., 22% of the energy contained in the ethanol is consumed in the recovery process [4]. To date, the economic sustainability of grape pomace ethanol distillation had been based on subsidies from the government to distilleries. Within the framework of safety and sustainability by-design, an alternative route for ethanol valorization could represent an improvement,

towards a circular economy, or would represent a growth of the chemical portfolio in any case. In this line, the production of hexanoic acid from the ethanol contained in red grape pomace was recently reported: the anaerobic fermentation of grape pomace under chain elongation conditions (25 g/L of hexanoic acid) and a consecutive simple downstream procedure allowed obtaining ca. 90% pure hexanoic acid [5]. Such valorization represents an evolution of the carboxylate platform state of the art, i.e., demonstrating potential industrial technical feasibility through a proof-of-concept. In fact, hexanoic acid can be hydrogenated to 1-hexanol (HexOH), an industrially attractive chemical mainly used within the formulation of synthetic perfumes and detergents but also as a solvent, plasticizer, and, more recently, in diesel and gasoline blends [6,7]. Catalytic hydrogenation of carboxylic acids with molecular H₂ is industrially attractive [8,9] but difficult to achieve, because of the weak polarizability of their C=O group, thus showing a lower reactivity than ketones and aldehydes [10]. In addition, some side-reactions can take place, such as (i) decarboxylation of carboxylic acid to alkane, (ii) hydrogenolysis of the produced alcohol to alkane, (iii) esterification between the carboxylic acid and the produced alcohol [11], as summarized in Scheme 1:



Scheme 1. Possible reactions involved within hexanoic acid hydrogenation.

In the above scheme, in addition to HexOH, hexyl hexanoate (HexHex) has also been highlighted, because of its industrial importance to date, mainly for fragrance and lubricant production [12]. Remarkably, HexHex has been recently suggested by the United States Department of Energy as a potential blendstock candidate for use in diesel engines [13,14]. Based on the involved reactions (Scheme 1), the hydrogenation would require an active and robust metal, and rhenium can represent an interesting alternative to the most expensive noble metals (e.g., Pt, Pd, and Ru) [15–17]. Rhenium has several stable oxidation states (e.g., +3, +4, +6, +7), and a reduction step is required to obtain the hydrogenating forms, which predominantly include a mixture of +3 and +4 oxidation states, whilst its complete reduction is not feasible without harsh conditions [15,18–20]. Therefore, rhenium heptoxide (Re₂O₇) reduced in situ by H₂ in a suitable solvent has been proposed as an active catalyst for the hydrogenation of carboxylic acids [15,16]. Many studies involving bimetallic rhenium-based systems are available in the literature, with the most relevant related to the hydrogenation of hexanoic acid being summarized in Table 1; where they are compared with the best yields to HexOH obtained in this work, as discussed in the results section.

Table 1. Overview of the main relevant data on the hydrogenation of hexanoic acid to HexOH with rhenium catalysts.

Hexanoic Acid (g/L)	Catalyst	T (°C)	P (bar)	t (h)	Conversion (mol%)	HexOH Yield (mol%)	Ref.
n.a.	Re ₂ O ₇	200	188	2	n.a.	93	[16]
46.4	Re-Pt/TiO ₂	130	50	5	58	53	[21]
23.2	Re-Pd/C	130	20	18	n.a.	74	[22]
52.6	ReOx-Pd/SiO ₂	140	80	24	100	99	[11]
14.6	Re-Ni/TiO ₂	180	50	8	100	60	[23]
93	Re ₂ O ₇	220	115	1	100	70	This work
93	Re/C	220	115	3	100	62	This work

The use of bimetallic systems has been proposed to lower the reduction temperature of rhenium, exploiting the strong and close interaction between the two metals, thus improving the selectivity to alcohol [24–26]. Notwithstanding this, even with bimetallic noble metal/rhenium systems, which are expensive and not commercially available, the carboxylic acid hydrogenation remains difficult to perform, requiring harsh conditions, mainly in term of the H₂ pressure, reaction temperature, and/or time (Table 1).

From an application perspective, commercial rhenium monometallic systems are preferable over bimetallic ones, being easily available and much less expensive. Their catalytic activity can be increased by performing an appropriate pre-reduction, addressing the selectivity towards the hydrogenation products (e.g., the corresponding alcohol or a mixture of alcohol and its ester), with a lower formation of unwanted alkanes (Scheme 1) [19,27].

The choice of a commercial catalyst is strategic for developing industrial applications, especially those aimed at exploiting cheap crude carboxylic acid-based substrates working at high concentration and with a substrate as obtained from agro-industrial by-product fermentation and adopting simple downstream processing. Raw starting substrates have been little studied for hydrogenation reactions, but a preliminary result on the hydrogenation of ca. 90% pure hexanoic acid obtained from red grape pomace fermentation recently suggested the viability of the proposed approach [5].

Recently, commercial Re₂O₇ and Re/C were adopted as catalysts for studying the hydrogenation of commercial hexanoic acid. The effect of the wet pre-reduction of rhenium was investigated, adopting milder reaction conditions with respect to dry pre-reduction [28]. Moreover, the effect of the acidity, introduced by adopting physical mixtures of the rhenium catalyst with an acid co-catalyst, e.g., as (5 wt% Re/C + niobium phosphate (NbPO)), was also applied for tuning the composition of the alcohol/ester mixture. Afterwards, the identified optimal reaction conditions were applied to the hydrogenation of a crude hexanoic acid-rich liquor obtained from white grape pomace anaerobic fermentation, containing impurities as well as other carboxylic acids and water. The nature of this substrate determined the choice of using commercial and monometallic rhenium catalysts rather than ad hoc prepared and more expensive bimetallic systems. Moreover, the obtained mixture HexOH/HexHex was evaluated for the first time as a potential renewable diesel blendstock. The potential of HexOH as an additive to automotive diesel fuel has previously been highlighted in many other scientific publications [29,30], while much less interest has been devoted to the adoption of HexHex as a blendstock for diesel [31]. The present work shows, for the first time, experimental results obtained in fueling a diesel engine with mixtures of diesel fuel/HexOH/HexHex, from the perspective of partially replacing traditional fossil fuels, without changing the engine performance and achieving significant benefits in reducing soot and CO emissions.

2. Results

2.1. Hydrogenation of Pure Hexanoic Acid

2.1.1. Hydrogenation with Re₂O₇

Re₂O₇ was initially tested as the hydrogenation catalyst of commercial hexanoic acid, adopting a lower catalyst loading than that proposed by Broadbent et al. (0.6 wt% vs. 0.9 wt%, respectively), who reported that in situ reduction of Re₂O₇ took place during the reaction [16]. A preliminary study for the identification of the appropriate H₂ pressure to adopt in hexanoic acid hydrogenation, within a short time scale (within 3–5 h), was performed. H₂ pressures of 60 and 115 bars were investigated, working at 210 °C, thus preferring milder reaction conditions than those of Broadbent et al. [16]. According to our results (Figure 1), a lower H₂ pressure significantly slows down the reaction rate, advantageously improving the ester yield and limiting the hexane formation, with the latter representing the main undesired by-product, mainly occurring through alcohol hydrogenolysis [11].

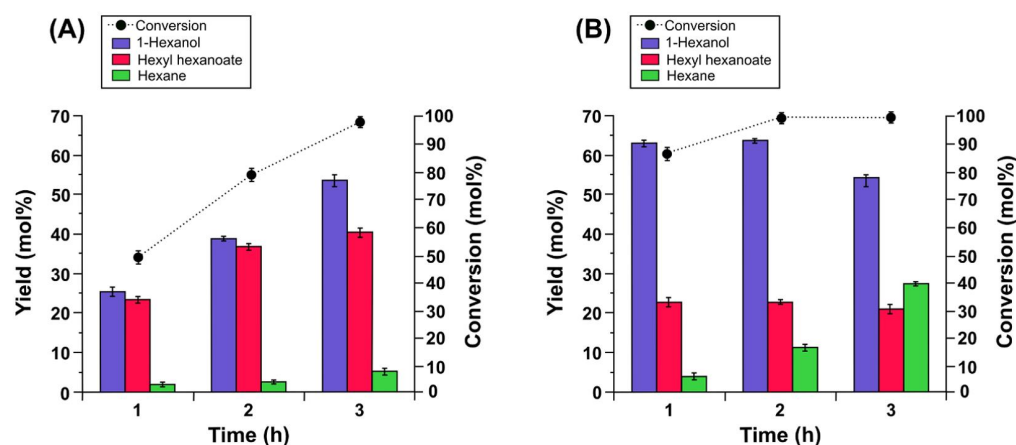


Figure 1. Influence of H₂ pressure on the pure hexanoic acid hydrogenation in the presence of Re₂O₇ at: (A) 60 bar; (B) 115 bar. Reaction conditions: T = 210 °C; substrate/Re ratio = 270 mol/mol.

To direct the reaction towards the preferential formation of HexOH, it is necessary to speed up the hexanoic acid conversion, thus preferably employing a higher H₂ pressure (115 bar). For the same purpose, the temperature was progressively increased from 180 to 220 °C, using the same catalyst loading (0.6 wt%, e.g., substrate/Re ratio = 270 mol/mol) and an H₂ pressure of 115 bar (Figure 2).

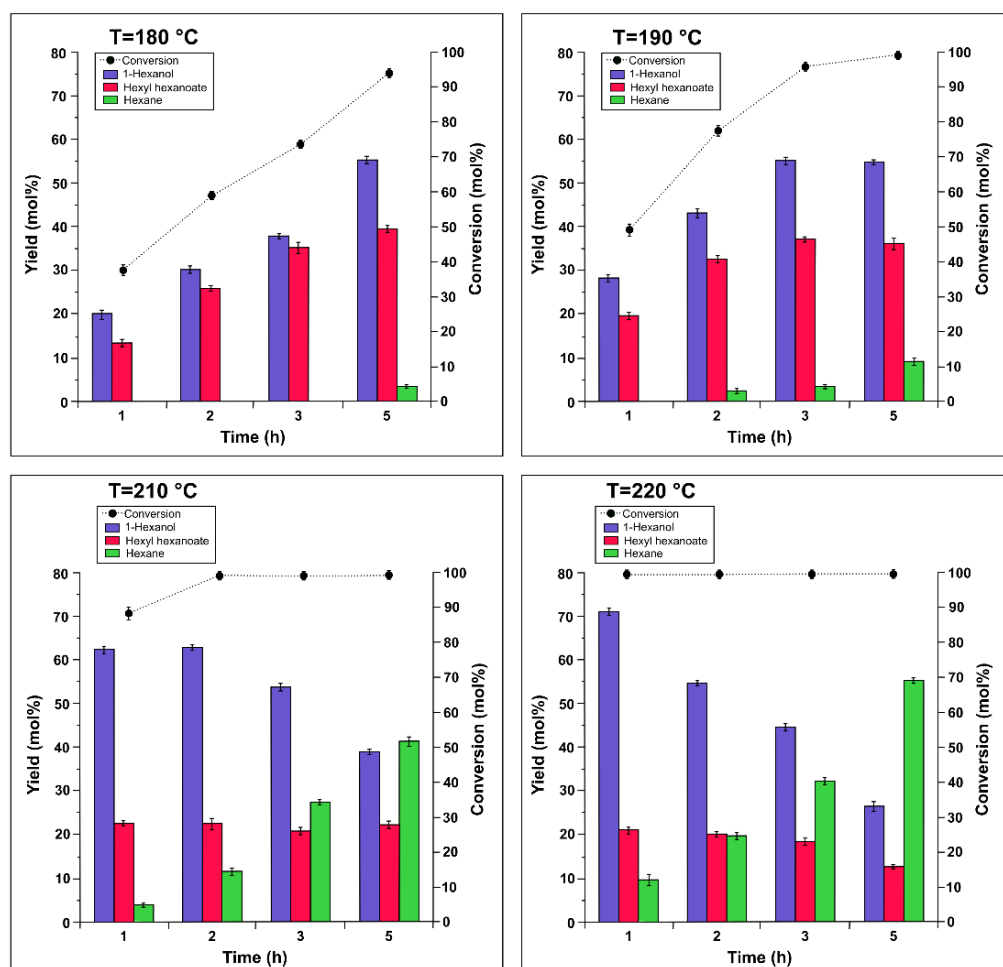


Figure 2. Effect of temperature on commercial hexanoic acid hydrogenation in the presence of Re₂O₇. Reaction conditions: P H₂ = 115 bar; substrate/Re ratio = 270 mol/mol.

The above data highlight the relevant improvement of the hexanoic acid conversion within the shorter reaction times at higher temperatures. Working at 220 °C, an almost complete substrate conversion was already reached after 1 h of reaction, achieving maximum HexOH and HexHex yields of about 70 and 20 mol%, respectively (Figure 2). On the other hand, at temperatures higher than 210 °C and longer reaction times (Figure 2), the HexHex yield remained almost stable, whilst that in HexOH significantly decreased, leading to undesired hexane formation. These results highlight the possibility of properly tuning the reaction conditions to address the selectivity towards an alcohol/ester mixture. This interesting result prompted us to perform an in-depth investigation of the hexanoic acid hydrogenation with the supported commercial system 5 wt% Re/C, with the aim of enhancing the catalytic activity with respect to Re₂O₇, avoiding metal sintering, and making catalyst recovery and recycling much easier.

2.1.2. Hydrogenation with 5 wt% Re/C

Starting from the above results with Re₂O₇, monometallic 5 wt% Re/C was employed to further investigate hexanoic acid hydrogenation. At the beginning, 5 wt% Re/C was characterized through ICP-OES, N₂ physisorption, TEM, and H₂-TPR techniques, finding that this catalyst had a 4.8 wt% rhenium content, 840 m²/g specific surface area, and 1.68 nm rhenium average particle size, as shown in Figure 3.

5wt% Re/C

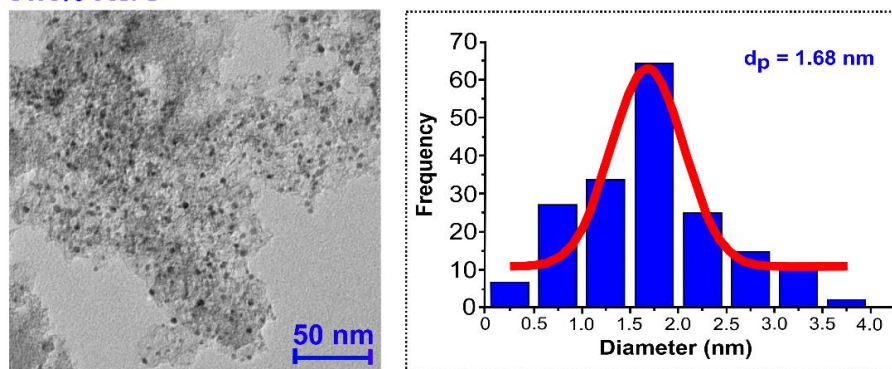


Figure 3. TEM picture of 5 wt% Re/C and the respective distribution of the Re particle sizes and the Gaussian fitting.

Moreover, the maximum peak H₂-TPR temperature was found at 400 °C (Figure 4), attributed to the complete reduction of the metal present in the sample with the highest oxidation state 7+ [32], this temperature being higher than those generally reported for other noble metals, confirming that Re is hardly reduced to the 0 state [28,33].

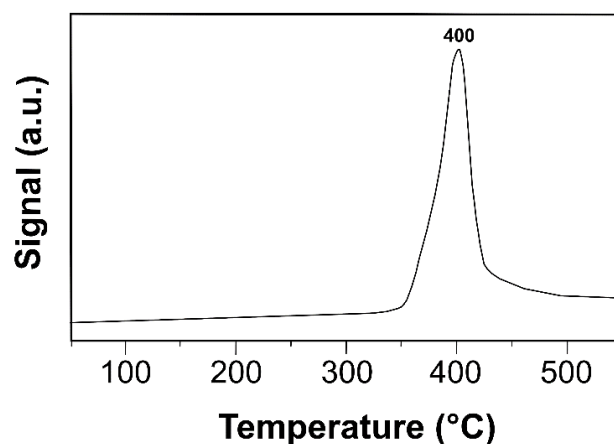


Figure 4. H₂-TPR profile of 5 wt% Re/C.

The received 5 wt% Re/C was preliminarily tested under the best reaction conditions identified for the Re_2O_7 catalyst ($T = 220\text{ }^\circ\text{C}$, $P \text{H}_2 = 115\text{ bar}$; substrate/Re ratio = 270 mol/mol), and a maximum hexanoic acid conversion of about 90 mol% was reached after 3 h (Figure 5A).

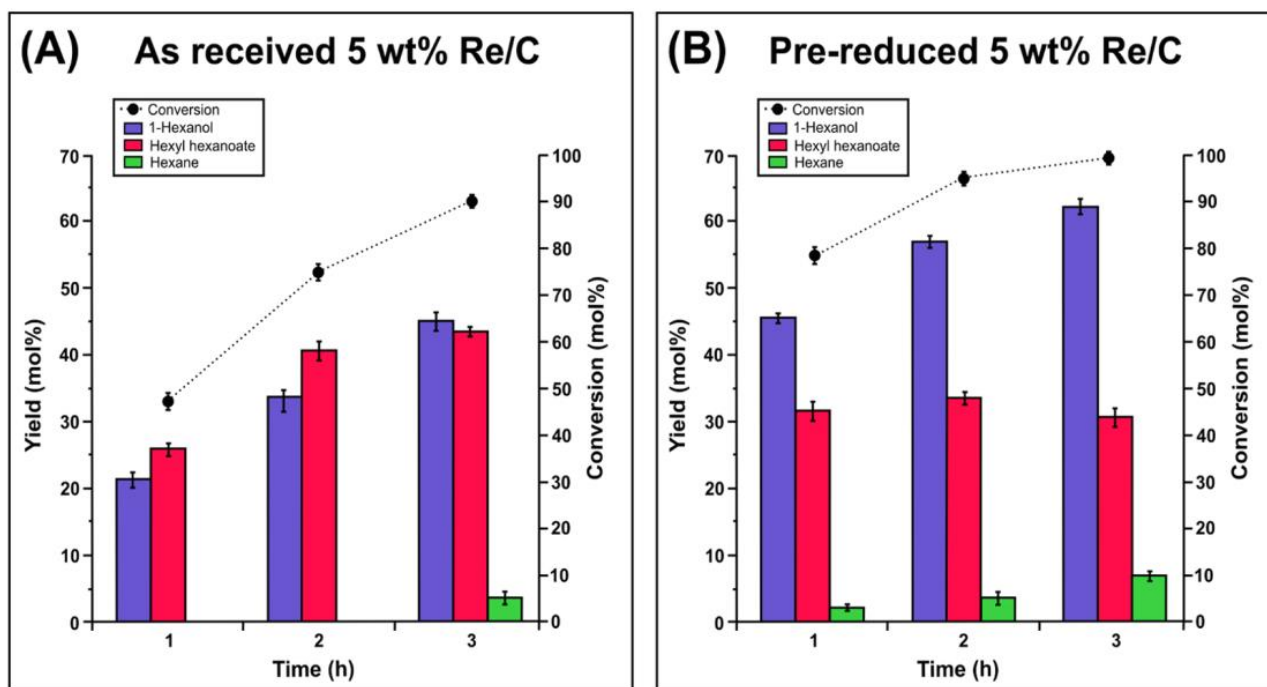


Figure 5. Effect of pre-reduction on commercial hexanoic acid hydrogenation, in the presence of 5 wt% Re/C used as received (A) or pre-reduced (B). Reaction conditions: $T = 220\text{ }^\circ\text{C}$; $P \text{H}_2 = 115\text{ bar}$; substrate/Re ratio = 270 mol/mol.

The reaction proceeded more slowly than that with Re_2O_7 (Figure 2), and an almost equimolar mixture of HexOH/HexHex was obtained after 3 h, due to the lower activity of 5 wt% Re/C, indicative of a more difficult in situ reducibility of 5 wt% Re/C. The literature reports that rhenium is active for hydrogenation reactions as a mixture of oxidized species, but generally a pre-reduction step allows reduction of the average oxidation state of the Re species; generally, up to the active states 3+ and 4+ [15]. Therefore, a wet pre-reduction was adopted to improve the activity of the 5 wt% Re/C, adopting a much milder temperature ($180\text{ }^\circ\text{C}$); i.e., more sustainable conditions if compared with the traditional dry method (at least $400\text{ }^\circ\text{C}$) [34]. This choice was further supported by the well-known difficulty in obtaining completely reduced rhenium, even under particularly severe conditions [18]. XPS spectroscopy was used to evaluate the oxidation state of rhenium within the as received and pre-reduced catalyst under our wet conditions, thus demonstrating the effectiveness of the proposed approach (Figure 6). The XPS spectrum of the as received 5 wt% Re/C revealed the sole presence of Re^{7+} , with the 4d_{7/2} component centered at about 45.9 eV; in agreement with the results of Rozmysłowicz et al. [20]. After the pre-reduction, XPS analysis (Figure 6) still showed the presence of Re^{7+} , but in lower amounts (43%), because additional bands were found at 41.4 and 43.1 eV, which are characteristic of Re^{3+} (30%) and Re^{4+} (27%) species, respectively [32,35].

The effectiveness of this mild pre-reduction on the catalytic performances was evidenced by the comparison of the performance between the hydrogenation carried out with the as received and pre-reduced 5 wt% Re/C, and adopting the same reaction conditions (Figure 5). In fact, complete conversion of the hexanoic acid was achieved after 3 h, with maximum HexOH and HexHex yields of 62 mol% and 31 mol%, respectively, when the pre-reduced 5 wt% Re/C catalyst was employed. The spent catalyst was also characterized by XPS analysis, confirming the presence of Re^{3+} (41%) and Re^{4+} (59%) species (Figure 7), thus

proving that the reduction of all the Re^{7+} species occurred during substrate hydrogenation, improving the catalytic activity of the 5 wt% Re/C system.

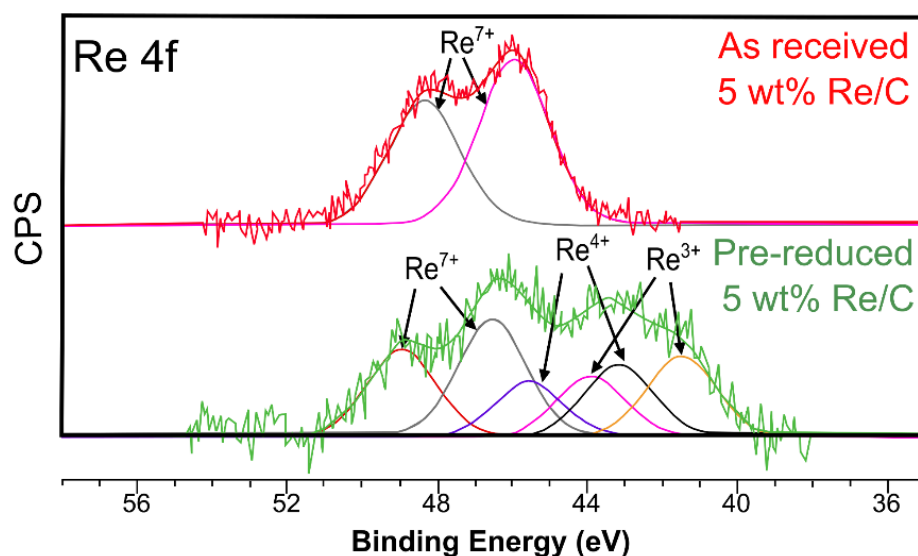


Figure 6. XPS spectra of fresh and pre-reduced commercial 5 wt% Re/C.

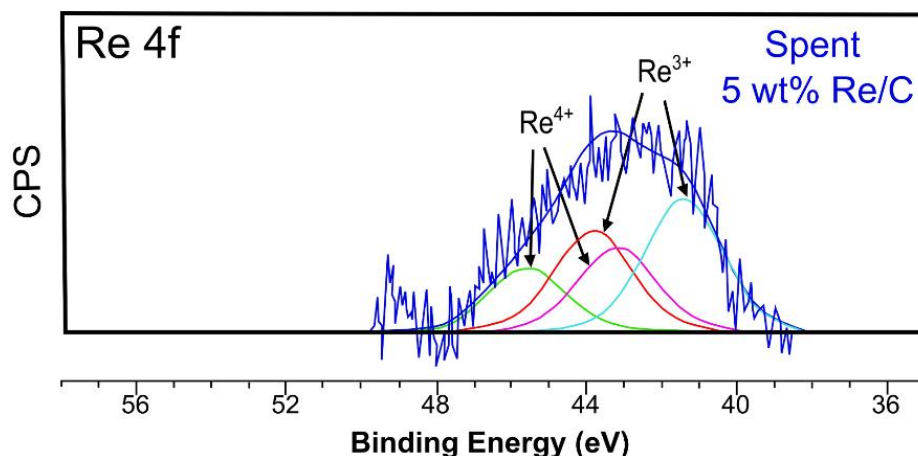


Figure 7. XPS spectra of spent commercial 5 wt% Re/C.

2.1.3. Hydrogenation in the Presence of NbPO as the Acid Co-Catalyst

The possibility of shifting the selectivity towards HexHex formation was evaluated by adopting commercial NbPO as the acid co-catalyst. This protonic solid is characterized by a Lewis acidity assigned to unsaturated Nb^{5+} sites, while the Brønsted acidity is mainly originated by P-OH groups and, to a lesser extent, by Nb-OH sites [36]. The water-tolerant NbPO is characterized by a specific surface area of $133 \text{ m}^2/\text{g}$ and a total acidity of 0.33 mmol/g , with a predominant fraction of low-medium strength sites and a relatively smaller fraction of stronger sites [37,38]. Several physical mixtures of pre-reduced 5 wt% Re/C with different amounts of NbPO were tested for hexanoic acid hydrogenation, aiming at maximizing the ester formation and thus simplifying the screening of the appropriate (acid) catalyst dosage. The hydrogenation of hexanoic acid with 5 wt% Re/C + NbPO was carried out under the same conditions as previously adopted for the pre-reduced 5 wt% Re/C system ($220 \text{ }^\circ\text{C}$, 115 bar, 3 h), and the corresponding data are reported in Figure 8.

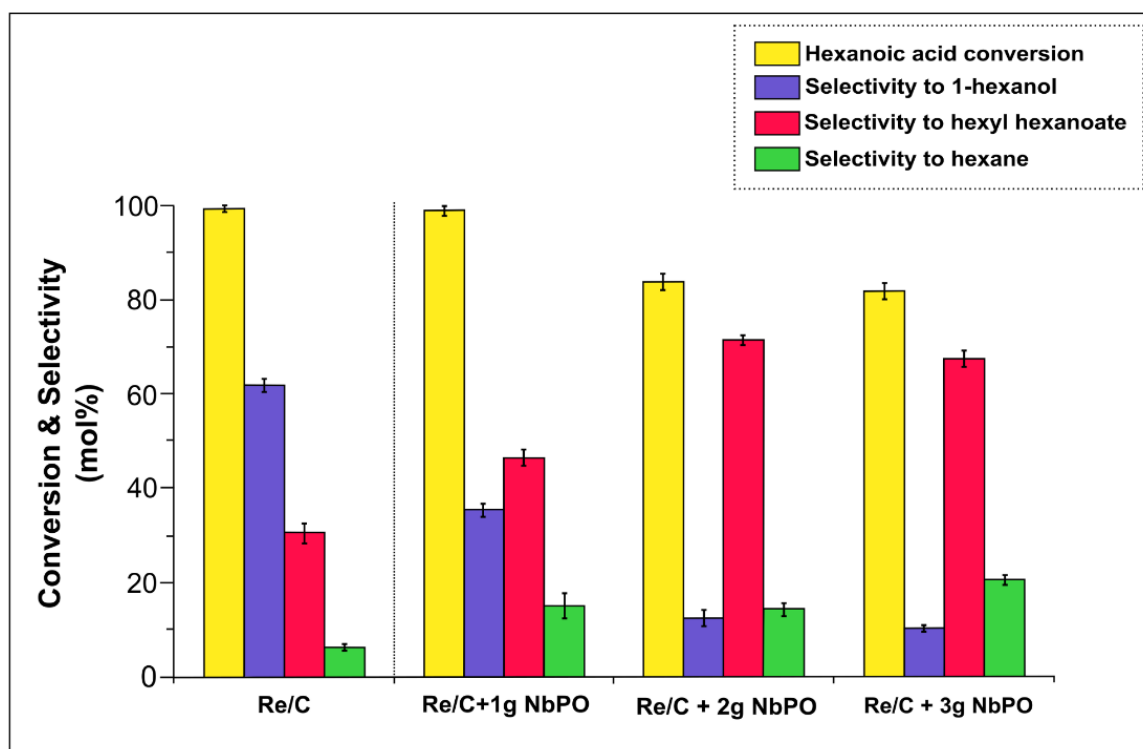


Figure 8. Effect of the acidity of the proposed acidic catalytic systems towards the hydrogenation of commercial hexanoic acid. Reaction conditions: $T = 220\text{ }^{\circ}\text{C}$; $P\text{ H}_2 = 115\text{ bar}$; $t = 3\text{ h}$; substrate/Re ratio of 270 mol/mol.

The results confirmed that the presence of acidity markedly favored the ester formation. A moderate slowdown of the hexanoic acid conversion was ascertained by increasing the amount of NbPO, probably due to lower stirring efficiency and diffusion limitations in the slurry, but a much more relevant improvement of the HexHex selectivity was obtained. In particular, the physical mixture composed of 5 wt% Re/C + 2 g of NbPO led to the highest HexHex selectivity of about 70 mol% (corresponding to a yield of about 60 mol%), while keeping the hexane selectivity low (<15 mol%). On the other hand, the increase of NbPO up to 3 g did not further improve the ester selectivity, rather enabling hexane formation and making stirring difficult. Therefore, the proper acidity of the catalytic system plays a key role in addressing the selectivity of the reaction towards esterification, favoring the preferential production of HexHex.

2.2. Hydrogenation of Crude Hexanoic Acid

Hydrogenation was then performed on a real crude hexanoic acid, obtained through anaerobic fermentation of white grape pomace. In our preliminary study [5], the first results on the hydrogenation of hexanoic acid from fermented red grape pomace with 5 wt% Re/C were produced. However, the wine making process also produces white grape pomace that, differently from the red pomace, does not undergo alcoholic fermentation, thus resulting poorer in ethanol and richer in fermentable sugars [39]. The compositional differences of the biomasses might have relevant repercussions for the chemical composition of the corresponding fermented liquors, and the proposed cascade process should be robust, i.e., not dependent on compositional variations of the fermented crude liquor. Anaerobic fermentation of white grape pomace was carried out under the previously reported reaction conditions [5]. Hexanoic acid purity was determined using the GC-FID technique and resulted as appreciably higher than that of the corresponding liquor derived from red grape pomace fermentation (93 vs. 87 wt% for white and red grape pomace, respectively). GC-MS analysis of the crude fermented white grape pomace allowed identification, in addition to hexanoic acid as the main target compound, only a few carboxylic acids in the

range C4–C8 as the minor compounds (Figure S1 and Table S1). Hydrogenation of the crude fermented white grape pomace was carried out with the best performing Re-based catalysts, addressed to the more selective production of HexOH (5 wt% Re/C) and of HexHex (physical mixture of 5 wt% Re/C+ 2 g of NbPO), and adopting the best identified reaction parameters. The obtained results are reported in Figure 9:

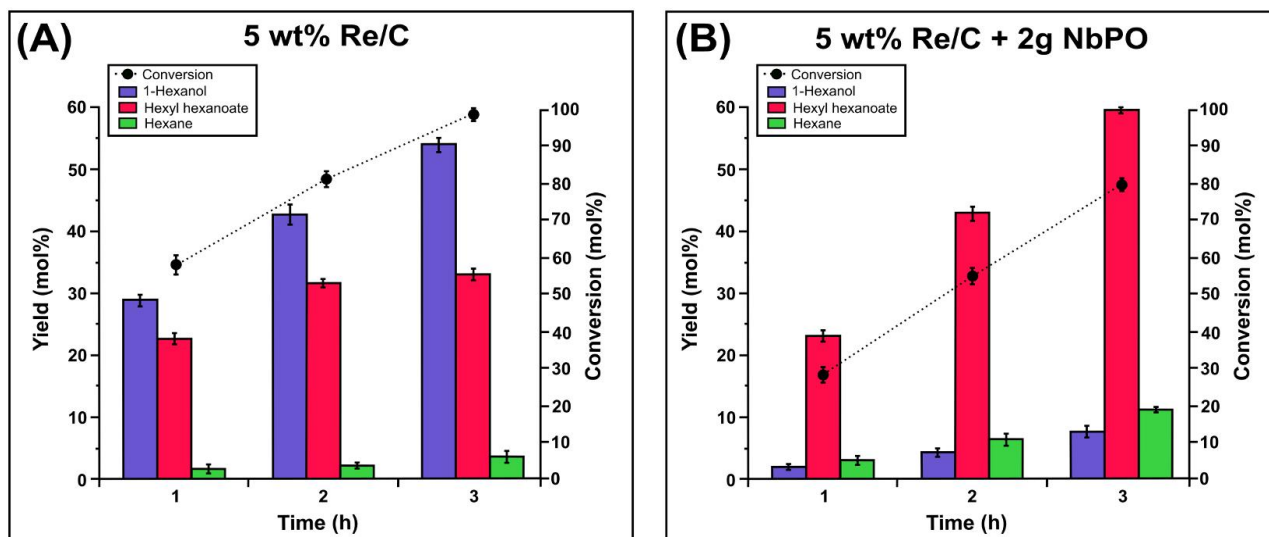


Figure 9. Hydrogenation of crude hexanoic acid from white grape pomace with (A) 5 wt% Re/C and (B) physical mixture (5 wt% Re/C + 2 g NbPO). Reaction conditions: T = 220 °C; P H₂ = 115 bar; substrate/Re ratio of 270 mol/mol.

Remarkably, when crude hexanoic acid obtained from the fermentation of white grape pomace was employed as the substrate, the conversion was only slightly lower than that obtained for the pure hexanoic acid. The selectivity behaviors towards HexOH and HexHex agreed with those achieved in the hydrogenation of commercial hexanoic acid (compare Figure 9 with Figures 5 and 8), thus proving the tunability and the robustness of the adopted catalytic systems. In both cases, the hexane formation was kept low, highlighting the successful optimization of the reaction conditions. The reaction mixture derived from white grape pomace hydrogenation shows the presence of HexOH, butyl butanoate, HexHex, and hexyl octanoate (Figure S2 and Table S2). The chemical stability of both catalytic systems employed was demonstrated in up to five recycling tests (Figure 10), a relevant characteristic for the successive scaling up of this process. In fact, it was possible to observe only a slight decrease of the hexanoic acid conversion with the progress of the recycling tests, mainly due to the partial loss of the catalyst during the filtration, recovery, and recycling steps, rather than due to rhenium leaching from the catalysts.

This was confirmed by the ICP analysis, showing that the Re content in the reaction mixtures recovered at the end of the fifth recycling was below the detection limit, indicating that the leaching of Re was negligible for both catalytic systems (5 wt% Re/C and the physical mixture 5 wt% Re/C and NbPO). The absence of rhenium leaching was further confirmed by removal of bulk 5 wt% Re/C from the reaction mixture recovered after 3 h of hydrogenation of crude hexanoic acid from white grape pomace (Figure 9A). The addition of fresh hexanoic acid to the recovered reaction mixture and the continuation of the reaction for other 3 h confirmed the absence of further hydrogenation products.

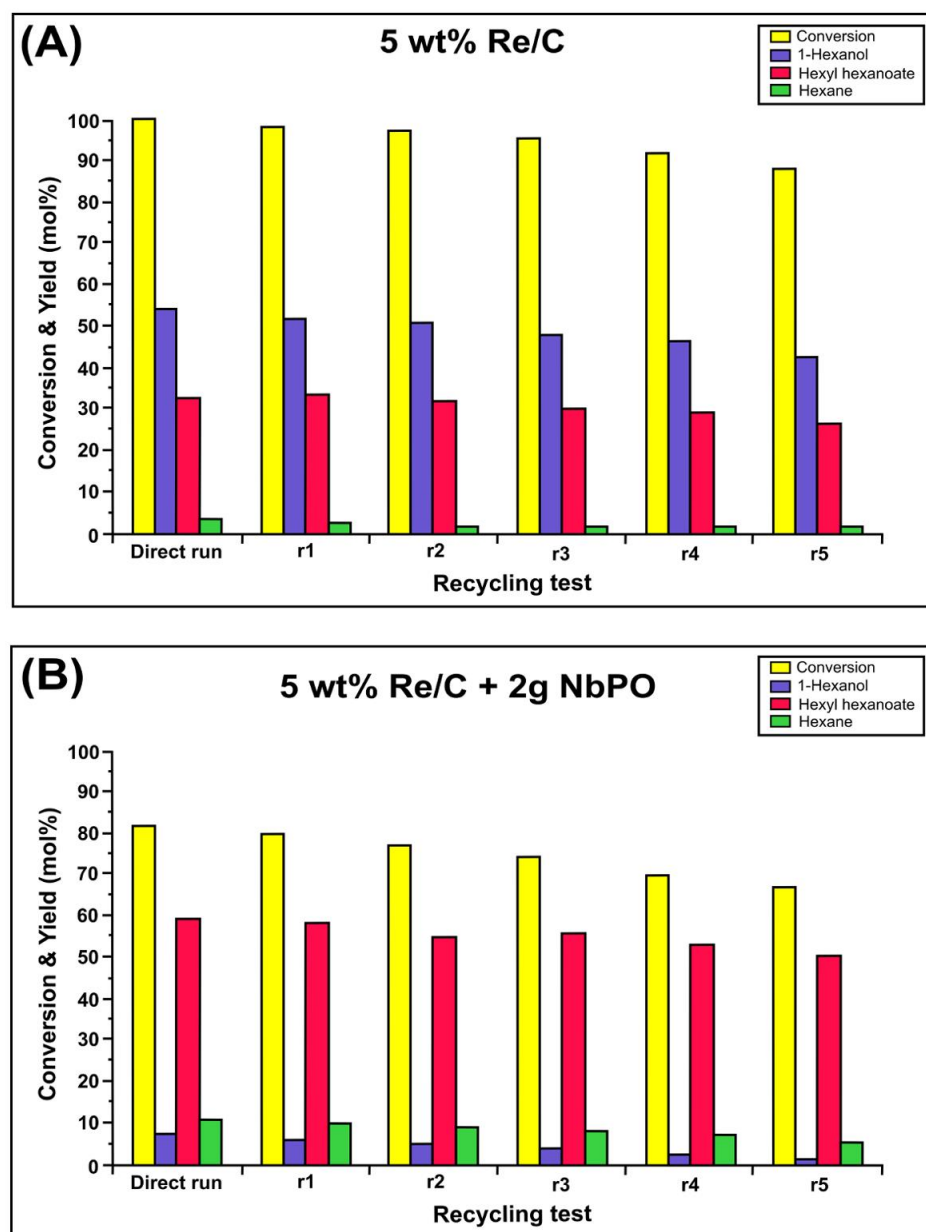


Figure 10. Recyclability tests of: (A) 5 wt% Re/C; (B) physical mixture (5 wt% Re/C + 2 g NbPO) employed in the hydrogenation of crude hexanoic acid from white grape pomace. Reaction conditions: $T = 220\text{ }^{\circ}\text{C}$; $P\text{ H}_2 = 115\text{ bar}$; $t = 3\text{ h}$; substrate/Re ratio of 270 mol/mol.

2.3. Engine Test Results

A mixture of 5.2 vol% of HexOH + 4.8 vol% of HexHex, corresponding to a molar ratio of about 2/1 mol/mol, was selected as a model of the reaction mixture obtained in the hydrogenation performed in the presence of pre-reduced Re/C (Figure 5B). This mixture (10 vol%) was added to 90 vol% of diesel fuel, without any phase separation. The resulting blend was tested in an experimental engine and compared with diesel fuel alone, and with two mixtures of the single components with diesel, i.e., 10 vol% of HexOH with 90% diesel fuel (10HexOH) and 10% HexHex with 90 vol% diesel fuel (10HexHex). These last two mixtures were employed as a reference to better understand the influence of the single components, alcohol, and ester on the engine performance when adopting the same conditions.

The main physicochemical properties of the used fuels are reported in Table 2.

Table 2. 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
Flash Point (°C)	55	63	102
Cetane Number (CN)	>50	23	40
Boiling Point (°C)	180–360	157	205
Lower Heating Value (MJ/Kg)	≈43	39	35

The previously mixtures described were utilized at maximum loads and different rpm, i.e., at 1500, 2000 and 2500 rpm, whilst the injection timing was maintained fixed during the experimentation. As reported in Figure 11A, the use of different blends with diesel did not significantly affect the power–rpm curve of the employed engine. The HexOH/HexHex mixtures employed for the tests only resulted in a slightly lower power: since the fuel volumetric flow was constant, due to the volumetric injection system, the lower power can be explained by the reduced LHV of the employed mixtures with respect to the diesel fuel. Notably, the use of the HexOH/HexHex mixtures led to a decrease in the CO emissions, as reported in Figure 11B, mainly owing to the higher H/C ratio in the fuel molecules (compared to diesel), and to the presence of oxygen, which enhanced the carbon complete oxidation during combustion [40]. As evidenced in Figure 11C, the HC emission results were higher when diesel combustion was realized with the co-presence of HexHex, rather than HexOH. This behavior is apparently in contrast with the higher cetane number of HexHex (if compared with that of HexOH), whilst a decrease in HC formation should be expected (given by the shorter combustion delay, resulting in sufficient time to realize HC oxidation). In our case, the ascertained delay combustion (higher HC formation), caused by the HexHex, could have been due to its self-ignition properties, mainly defined by its higher boiling point and flash point temperature. On the other hand, the lower cetane number of HexOH and HexHex (with respect to that of diesel) only slightly increased the NO_x emissions (Figure 11D), thus indicating that the maximum combustion temperature was moderately increased in the case of the diesel–HexHex/HexOH blendstocks. Here, the ignition delay increased the amount of fuel required within the first part of the combustion process and, consequently, the release rate of the combustion heat. Finally, a significant reduction in soot emissions was ascertained in the case of the diesel–HexOH–HexHex blendstocks (Figure 11E), achieving a reduction of about 50% at higher rpm. This noteworthy result was due to the lower carbon content (lower C/H ratio) of the employed mixtures, which reduced the carbon available for soot formation, and the oxygen promoted the oxidation processes. Moreover, the lower boiling points of the oxygenated compounds led to a kind of “droplet explosion”, once the fuel mixture was introduced into a hot environment [41,42], improving fuel atomization and mixing, thus leading to complete combustion of the carbon-based molecules.

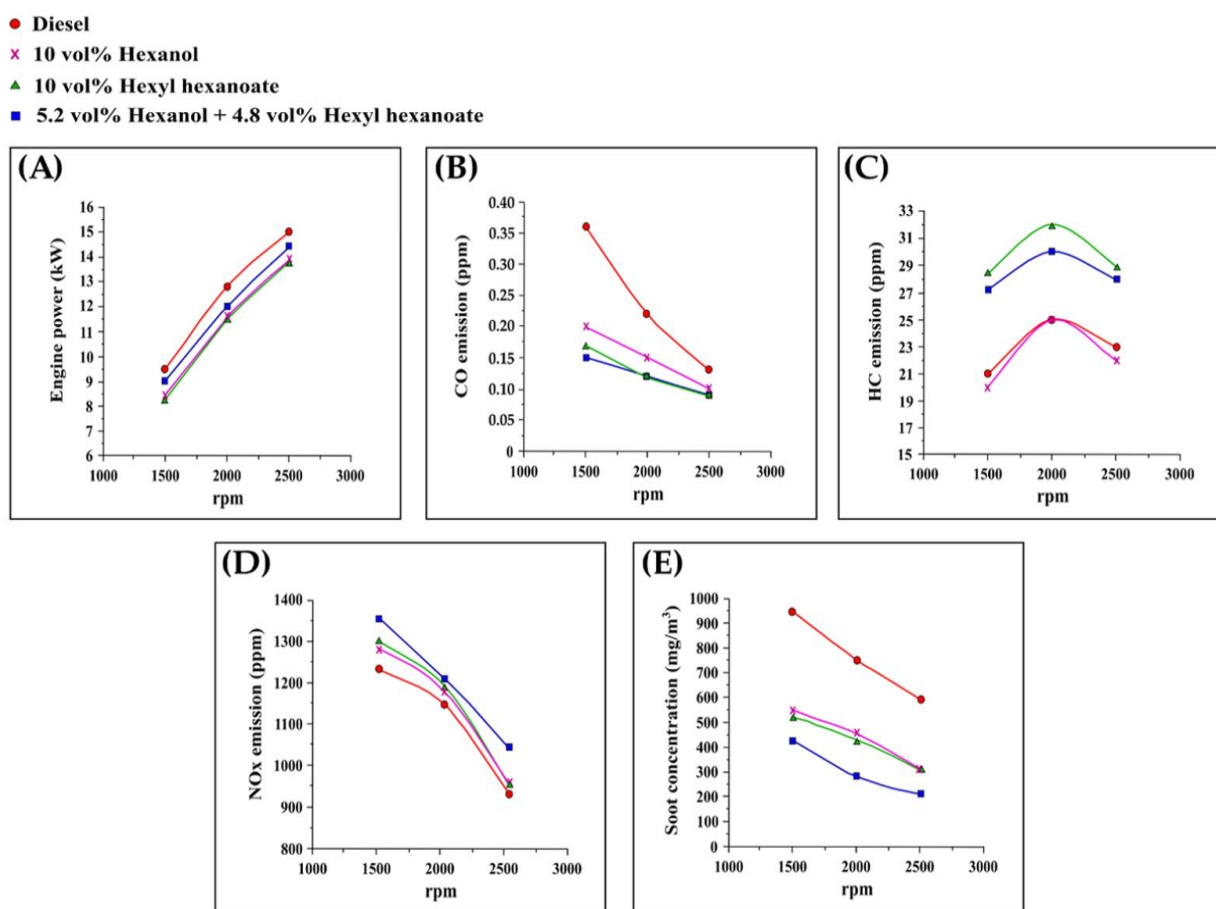


Figure 11. Engine performance, in terms of (A) engine power; (B) CO emission; (C) HC emission; (D) NO_x emission, and (E) soot emission, all evaluated at the maximum load.

3. Materials and Methods

3.1. Materials

Hexanoic acid (>99%), n-dodecane (>99%), hexane (>99%), hexyl hexanoate (>98%), 1-hexanol (>99%), methanol (>99%), n-octane (99%), and Re₂O₇ were purchased by Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The 5 wt% Re/C was provided by Riogen (Riogen, Mantua, NJ, USA), whilst NbPO was from CBMM (Compahia Brasileira de Metalurgia e Mineração, Araxá, Minas Gerais, Brazil) and used after treatment at 255 °C for 6 h, under high vacuum.

Grape pomace, derived from white wine production, was kindly provided by Caviro Distillerie (Faenza, Italy) and used without any pre-treatment. Crude hexanoic acid-rich liquor was produced from white grape pomace, according to a previously reported procedure, slightly modified. Briefly, the white grape pomace was fed into a leaching process with water, which allowed (1) the ethanol solution (30 g/L) to be fermented for hexanoic acid production; and (2) the grape pomace to be further valorized through conventional processes (tartaric acid, seed oil extraction; outside of the scope of this work). Thereafter, the ethanol solution was fermented and hexanoic acid was extracted as previously reported [5]. The obtained crude hexanoic acid was characterized later.

3.2. Catalyst Characterization

Temperature programmed reduction by H₂ (H₂-TPR) was performed in an AutoChem II apparatus (Micromeritics, Norcross, GA, USA). The catalyst was firstly treated at 300 °C under He flow of 50 mL/min for 30 min, for the removal of impurities. After cooling to 50 °C, the carrier gas was switched to 5 vol% H₂/Ar, with a flow of 40 mL/min. When the baseline was stable, the temperature was increased up to 800 °C, with a heating rate

of 10 °C/min. The amount of consumed H₂ was measured with a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) measurements were conducted with a VSW TA10 twin anode (VSW Scientific Instruments, Manchester, UK), adopting the X-ray AlK α source (emission: 10 mA, voltage 10 kV), and a hemispherical electron energy analyzer VSW HA100.

A single point ThermoQuest Surface Area Analyzer Qsurf S1 (ThermoQuest, Mississauga, Canada) was used for specific surface area (SSA) analysis of the supported rhenium catalysts, according to the experimental procedure reported in our previous work [43].

Transmission electron microscopy (TEM) measurements in bright field mode were conducted with a CM12 microscope (Philips, Amsterdam, The Netherlands), operating at 120 keV, as previously reported [44].

The rhenium content, both in the as received catalyst and in the liquid sample collected at the end of the recycle runs, was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES), using an Optima 7000 DV (PerkinElmer, Waltham, MA, USA) analyzer equipped with a CCD array detector, and an emission line of 221.43 nm was adopted.

3.3. Hydrogenation Procedure

Hydrogenation reactions were carried out in a 300 mL stainless steel Parr 4560 autoclave (Parr Instrument Company, Moline, IL, USA) equipped with a P.I.D. controller (4848). Then, 5 wt% Re/C was pre-reduced in methanol (180 °C, 90 bar of H₂, 6 h) as previously reported [5], whilst Re₂O₇ was directly employed, without a pre-reduction step. The reaction mixture was stirred using a mechanical overhead stirrer. The reactor was pressurized with hydrogen up to the selected value, determined at a reaction temperature, with the pressure being held constant by automatically feeding more hydrogen. At the end of the reaction, the reactor was rapidly cooled to room temperature and depressurized, and the reaction mixture was filtered to remove the catalyst and finally analyzed through GC/FID and GC/MS chromatography. For the recycling tests, the spent catalyst was recovered by filtration under argon atmosphere, properly washed, and recycled following the same procedure as adopted for the direct run.

3.4. Product Analysis

The liquid samples were analyzed using a GC-FID (DANI GC1000, Dani Instruments S.P.A., Cologno Monzese, Italy) equipped with a HP-PONA column (20 m \times 0.2 mm \times 0.5 μ m). N₂ was employed as the carrier gas with a flow rate of 1 mL/min. Both injector and detector were kept at 250 °C, and the following temperature program was employed for the chromatographic runs: 150 °C for 5 min; 12 °C/min up to 200 °C; 200 °C for 2 min; 15 °C/min up to 250 °C; and 250 °C for 10 min. The moles of analytes were calculated from the calibration with standard solutions. The analyses were carried out in triplicate and the reproducibility of the technique was within 5%.

The identification of the compounds of interest was performed by GC-MS (Agilent 7890B-5977A, Agilent Technologies, Santa Clara, CA, USA), equipped with a HP-5MS column (30 m \times 0.25 mm \times 0.25 μ m). Helium was adopted as the carrier gas, with a flow rate of 1 mL/min. The injector and detector were kept at 250 and 280 °C, respectively, and the following temperature program was employed for the chromatographic runs: 60 °C for 1 min; 10 °C/min up to 200 °C; 200 °C for 2 min; 5 °C/min up to 220 °C; 220 °C for 20 min; 10 °C/min up to 270 °C; and 270 °C for 1 min.

3.5. Engine Experimental Setup

A Lombardini-Kohler Diesel engine model 9LD 625/2 (Lombardini, Reggio Emilia, Italy), whose specifications were previously reported, was utilized and coupled with a Borghi & Saveri eddy current brake with rpm/Torque controller (Borghi & Saveri, Bologna, Italy). A 30 emission analysis was performed as previously reported [45].

4. Conclusions

In this work, the hydrogenation of commercial hexanoic acid was investigated for the synthesis of 1-hexanol/hexyl hexanoate mixtures, employing different rhenium heterogeneous catalysts. The activity of the reaction was enhanced by a mild pre-reduction step, while the selectivity of the reaction was strongly affected by the acidic properties of the overall catalytic systems. In fact, under the same reaction conditions, the selectivity of the 5 wt% Re/C catalyst was mainly addressed towards 1-hexanol, whilst the employment of a rhenium-based acid catalytic system, such as a physical mixture (5 wt% Re/C + niobium phosphate), significantly shifted the selectivity towards hexyl hexanoate formation. Catalytic hydrogenation of the crude hexanoic acid, derived from acidogenic fermentation of white grape pomace without any purification, with 5 wt% Re/C and with the physical mixture (5 wt% Re/C + niobium phosphate) gave similar results to those achieved with commercial hexanoic acid, even after up to five recycle runs, thus highlighting the robustness of the process, with the proper choice of catalyst being important to modulate the composition of the final mixture. Engine tests confirmed the potential of these mixtures as novel diesel bio-blendstocks, able to reduce the emissions of particulate and CO, without any significant increase of NO_x emissions or change in engine performance, thus contributing to meeting greenhouse gas emission reduction targets and to the partial replacement of traditional fossil fuels, in accordance with the short-term goals of EU countries.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/xxx/s1>, Figure S1: Total ion chromatogram (TIC) of crude fermented white grape pomace; Figure S2: Total ion chromatogram (TIC) of post-hydrogenated white grape pomace; Table S1: Products identified in the crude fermented white grape pomace; Table S2: Products identified in the crude fermented white grape pomace.

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