

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

Domenico Licursi¹, Anna Maria Raspolli Galletti^{1,*}, Claudia Antonetti¹, Gonzalo A. Martinez², Emma Jones², Lorenzo Bertin², Nicola Di Fidio¹, Sara Fulignati¹, Gianluca Pasini³ and Stefano Frigo³

¹ Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124, Pisa, Italy; domenico.licursi@unipi.it, anna.maria.raspolli.galletti@unipi.it, claudia.antonetti@unipi.it, nicola.difidio@unipi.it, sara.fulignati@dcci.unipi.it

² Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, via Terracini 28, 40131, Bologna, Italy; gonzalo.martinez3@unibo.it, emma.jones2@unibo.it, lo-renzo.bertin@unibo.it

³ Department of Energy, System, Territory and Construction Engineering (DESTEC), University of Pisa, Largo Lucio Lazzarino, 56122, Pisa, Italy; gianluca.pasini@phd.unipi.it, stefano.frigo@unipi.it

* Correspondence: anna.maria.raspolli.galletti@unipi.it, Phone: +39 050 2219 290

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 to the production of even more 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 (Re_2O_7 and 5 wt% Re/C), which resulted active and selective mainly towards 1-hexanol. On the other hand, the use of niobium phosphate as the acid co-catalyst markedly shifted the selectivity towards hexyl hexanoate. 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 by fermentation of white grape pomace, confirming the promising performances of these catalytic systems and their recyclability. For the first time, the employ of 1-hexanol/hexyl hexanoate mixtures as diesel blendstock has been evaluated, highlighting a significant reduction of the soot and CO emissions, without any significant change in the engine performance. The promising properties of these oxygenated additives are favorable to the partial replacement of traditional fossil fuels, in accordance with the short-term goals of the EU countries.

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Last-name

Received: date

Accepted: date

Published: date

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



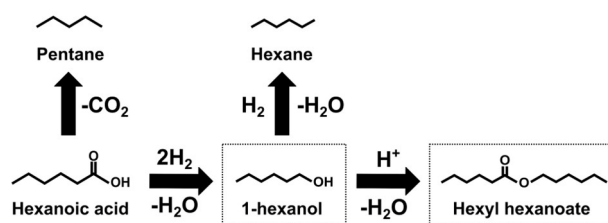
Copyright: © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: Grape pomace; Carboxylic acids; Rhenium catalysts; Hydrogenation; Diesel blendstock

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 without creating any pressure on land use and hindering the food supply [2]. In this perspective, grape pomace, an abundant agro-industrial waste deriving from the wine-making process, is a promising feedstock to develop a bio-refinery approach. About 9 Mt of grape pomace are globally produced every year, these are valorized in centralized bio-refineries that obtained anthocyanins, polyphenols, 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 ethanol contained energy is consumed in the recovery process [4]. So far, the economic sustainability of grape pomace ethanol distillation had been based on subsidies from the government to distilleries. In the framework of the so-called safety

and sustainable by-design, an alternative route for ethanol valorization could represent an improvement towards a circular economy or could 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 down-stream 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 the 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 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 could 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], summarized in Scheme 1:



Scheme 1. Possible reactions involved within hexanoic acid hydrogenation.

In the above scheme, in addition to HexOH, also hexyl hexanoate (HexHex) has been highlighted, because of its industrial importance, up to now mainly for fragrances and lubricants 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 should 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 highly 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 by far as the active catalyst for the hydrogenation of carboxylic acids [15,16]. Many studies involving bimetallic rhenium-based systems are available in the literature, the most relevant related to the hydrogenation of hexanoic acid being summarized in Table 1, where are compared with the best performances obtained in this work and discussed in the Results.

The use of bimetallic systems is 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 H₂ pressure, reaction temperature and/or time (Table 1).

From an applicative perspective, commercial rhenium monometallic systems should be preferred 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 lower formation of the unwanted alkanes (Scheme 1) [19,27].

Table 1. Overview of 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	ReO _x -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 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 adopting simple downstream processing. Raw starting substrates have been scarcely studied for hydrogenation reactions but a preliminary result on the hydrogenation of hexanoic acid ca. 90% pure obtained from red grape pomace fermentation recently suggested the viability of the proposed approach [5].

Now commercial Re₂O₇ and Re/C have been 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 respect to dry pre-reduction [28]. Moreover, the effect of the acidity, introduced 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 optimal identified reaction conditions were applied to the hydrogenation of crude hexanoic acid-rich liquor obtained from white grape pomace anaerobic fermentation, containing impurities as other carboxylic acids and water. The nature of this substrate has 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 has been evaluated for the first time as potential renewable diesel blendstock. The potential of HexOH as additive to automotive diesel fuel has already been highlighted in many other scientific publications [29,30], while much less interest has been devoted up to now to the adoption of HexHex as blendstock for diesel [31]. The present work shows for the first time the experimental results obtained fueling a Diesel engine with mixtures of Diesel fuel/HexOH/HexHex, with the perspective of partially replacing traditional fossil fuels, without modifying 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 the 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 the hexanoic acid hydrogenation, within a short time scale (within 3-5 hours) was performed. H₂ pressures of 60 and 115 bars have been investigated, working at 210 °C, thus preferring milder reaction conditions respect to these 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, the latter representing the main undesired by-product occurring mainly through the alcohol hydrogenolysis [11].

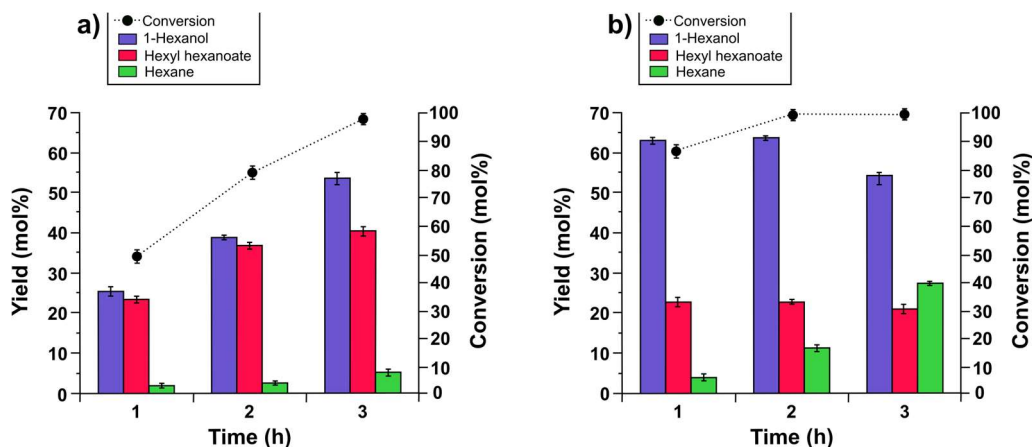


Figure 1. Influence of H₂ pressure on the pure hexanoic acid hydrogenation in the presence of Re₂O₇ at: a) 60 bar; b) 115 bar. Reaction conditions: T = 210 °C; substrate/Re ratio = 270 mol/mol.

Instead, 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 enhanced from 180 to 220 °C, using the same catalyst loading (0.6 wt%, e.g. substrate/Re ratio = 270 mol/mol) and the H₂ pressure of 115 bar (Figure 2).

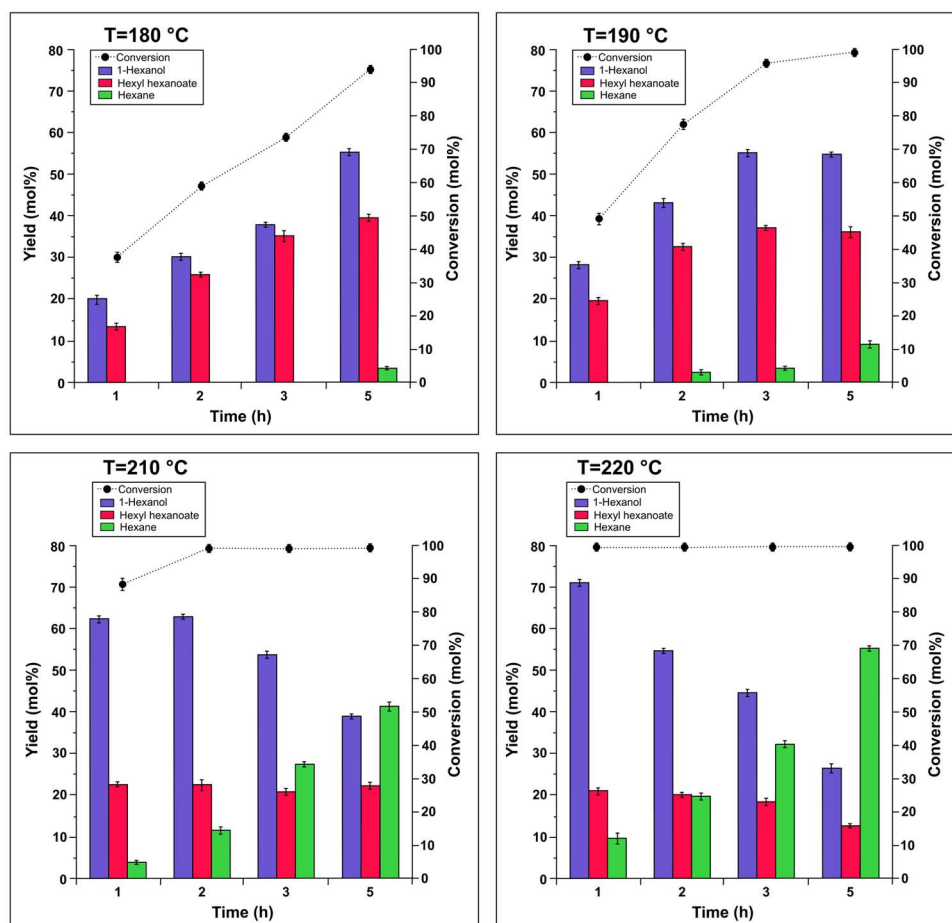


Figure 2. Effect of temperature on commercial hexanoic acid hydrogenation in the presence of Re_2O_7 . Reaction conditions: $P_{\text{H}_2} = 115$ bar; substrate/Re ratio = 270 mol/mol.

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 reached already after 1 hour of reaction, achieving the maximum HexOH and HexHex yields of about 70 and 20 mol%, respectively (Figure 2). On the other hand, at temperature higher than 210 °C and longer reaction times (Figure 2), the HexHex yield remains almost stable, whilst that in HexOH significantly decreases, leading to the 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 respect to Re_2O_7 , avoiding metal sintering, and making much easier catalyst recovery and recycle.

2.1.2. Hydrogenation with 5 wt% Re/C

Starting from the above results with Re_2O_7 , the monometallic 5 wt% Re/C was employed for further investigating the hexanoic acid hydrogenation. At the beginning, 5 wt% Re/C was characterized through ICP-OES, N_2 physisorption, TEM and H_2 -TPR techniques, finding that this catalyst has 4.8 wt% of rhenium content, 840 m^2/g of specific surface area, and 1.68 nm of rhenium average particle size, according to Figure 3.

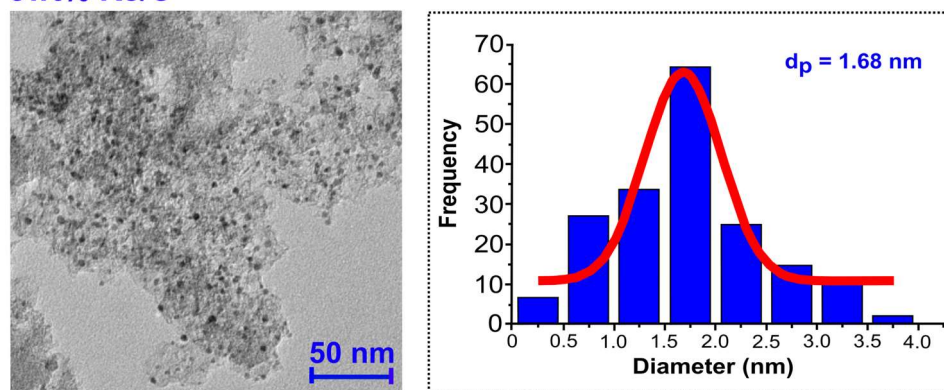
5wt% Re/C

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

Moreover, a maximum peak H_2 -TPR temperature at 400 °C was found (Figure 4), attributed to the complete reduction of the metal which is 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 reducible to 0 state [28,33].

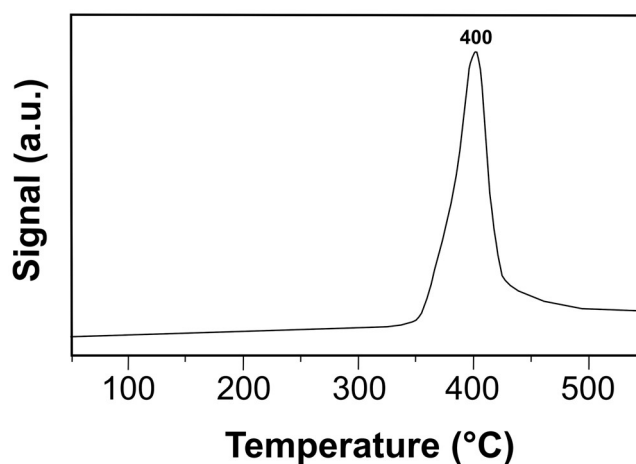
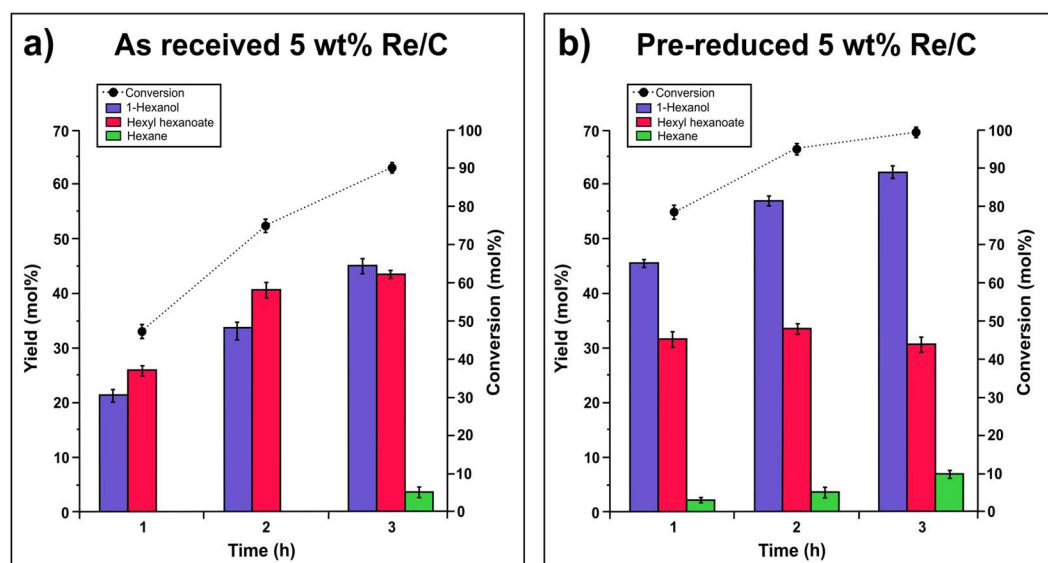


Figure 4. H_2 -TPR profile of 5 wt% Re/C.

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



187

Figure 5. Effect of pre-reduction on commercial hexanoic acid hydrogenation, in the presence of 5 wt% Re/C. Reaction conditions: T = 220 °C; P H₂ = 115 bar; substrate/Re ratio = 270 mol/mol.

188

189

The reaction proceeds more slowly than that with Re₂O₇ (Figure 2), and an almost equimolar mixture of HexOH/HexHex was obtained after 3 hours, due to the lower activity of 5 wt% Re/C, indicative of a more difficult *in-situ* reducibility of 5 wt% Re/C. Literature reports that rhenium is active for hydrogenation reactions as a mixture of oxidized species, but generally a pre-reduction step allows to reduce the average oxidation state of the Re species, mainly up to the active states 3+ and 4+ [15]. Therefore, a wet pre-reduction was adopted for improving the activity of the 5 wt% Re/C, adopting a much milder temperature (180 °C), e.g. more sustainable conditions, if compared with the traditional dry method (at least 400 °C) [34]. This choice is further supported by the well-known difficulty in obtaining the 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). XPS spectrum of the as received 5 wt% Re/C reveals the sole presence of Re⁷⁺, 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 shows the presence of Re⁷⁺, but in lower amount (43%), because additional bands are found at 41.4 and 43.1 eV, which are characteristic of Re³⁺ (30 %) and Re⁴⁺ (27%) species, respectively [32,35].

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

207

208

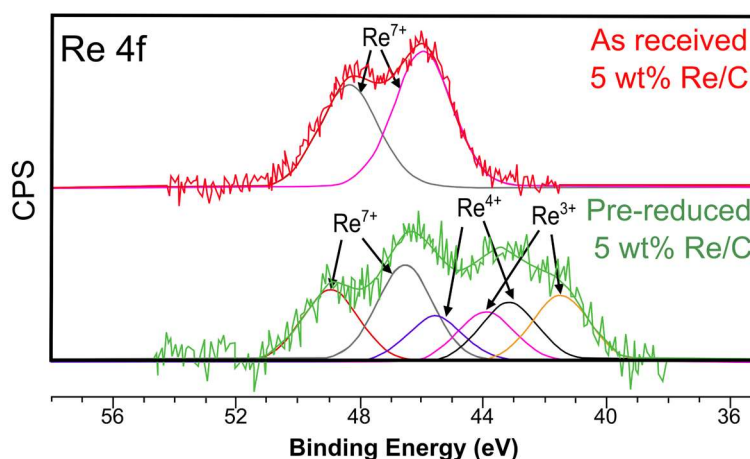


Figure 6. XPS spectra of fresh and pre-reduced commercial 5 wt% Re/C.

209

210

The effectiveness of this mild pre-reduction on the catalytic performances was evidenced by the comparison of the performances between the hydrogenation carried out with the as-received and pre-reduced 5 wt% Re/C, adopting the same reaction conditions (Figure 5). In fact, the complete conversion of the hexanoic acid was achieved after 3 hours, with maximum HexOH and HexHex yields of 62 mol% and 31 mol%, respectively, when the pre-reduced 5 wt% Re/C catalyst was employed. Also the spent catalyst was 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 occurs during substrate hydrogenation, this improving the catalytic activity of 5 wt% Re/C system.

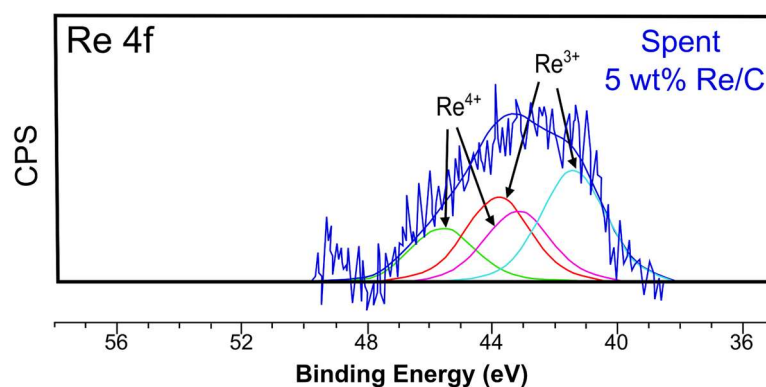
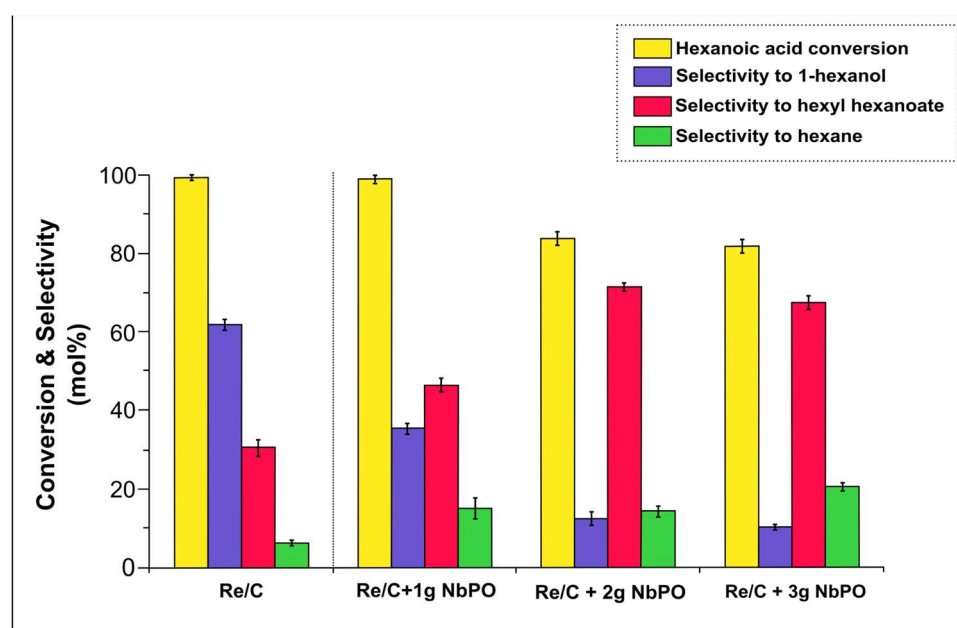


Figure 7. XPS spectra of spent commercial 5 wt% Re/C.

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 Lewis acidity assigned to unsaturated Nb^{5+} sites, while Brønsted acidity is mainly originated by P-OH groups and, in lesser extent, by Nb-OH sites [36]. The water-tolerant NbPO is characterized by a specific surface area of 133 m^2/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 have been tested for hexanoic acid hydrogenation, aimed at maximizing the ester formation, 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 already adopted for pre-reduced 5 wt% Re/C system (220 °C, 115 bar, 3 h) and the corresponding data are reported in Figure 8.



237

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.

238

239

240

The results confirm that the presence of acidity markedly favors the ester formation. A moderate slowdown of the hexanoic acid conversion was ascertained by increasing the NbPO amount, 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%), keeping low the hexane selectivity (<15 mol%). On the other hand, the increase of NbPO amount up to 3 g did not further improve the ester selectivity, rather enabling the hexane formation and making stirring difficult. Therefore, the proper acidity of the catalytic system plays a key role to address the selectivity of the reaction towards esterification, favoring the preferential production of HexHex.

241

242

243

244

245

246

247

248

249

250

251

252

2.2. Hydrogenation of crude hexanoic acid

253

The hydrogenation was then performed on a real crude hexanoic acid, obtained through the anaerobic fermentation of the white grape pomace. In our preliminary study [5], the first results on hydrogenation of hexanoic acid from fermented red grape pomace with 5 wt% Re/C, were showed. However, wine making process also produces white grape pomace which, differently from the red one, 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 on the chemical composition of the corresponding fermented liquors and the proposed cascade process should be robust, i.e. poorly 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 by GC-FID technique and resulted appreciably higher than that of the corresponding liquor deriving 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 to identify, in addition to hexanoic acid as the main target compound, only 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 most performing Re-based catalysts, addressed to the more selective production of

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

HexOH (5 wt% Re/C) and of HexHex (physical mixture of 5 wt% Re/C+ 2 g of NbPO),
adopting the best identified reaction. The obtained results are reported in Figure 9:

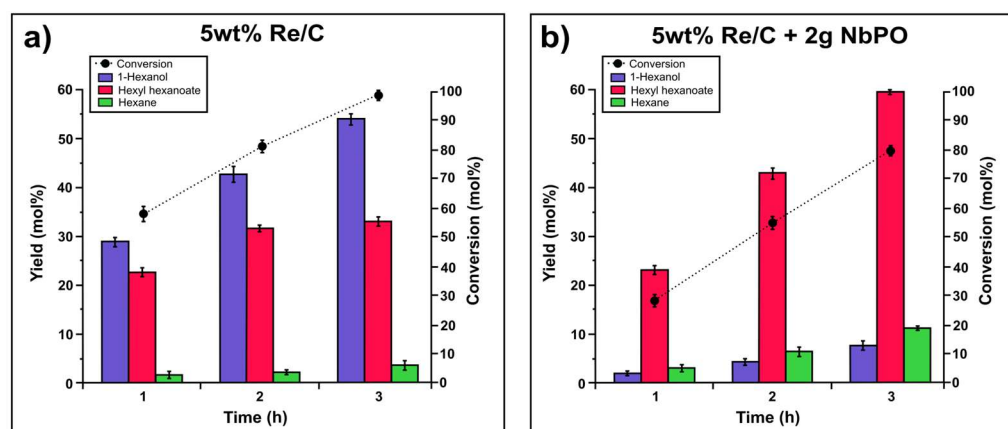


Figure 9. Hydrogenation of crude hexanoic acid from white grape pomace with (a) 5 wt% Re/C and (b) physical mixture [5 wt% Re/C + 2 g NbPO]. Reaction conditions: T = 220 °C; P H₂ = 115 bar; substrate/Re ratio of 270 mol/mol.

Remarkably, when crude hexanoic acid obtained from fermentation of white grape pomace was employed as the substrate, the conversion was only slightly lower than that ascertained for the pure hexanoic acid. The selectivity behaviors towards HexOH and HexHex agree with those achieved in the hydrogenation of commercial hexanoic acid (compare Figure 9 with Figure 5 and Figure 8), thus proving the tunability and the robustness of the adopted catalytic systems. In both cases, hexane formation was kept low, highlighting the successful optimization of the reaction conditions. The reaction mixture deriving 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 employed catalytic systems was demonstrated up to five recycling tests (Figure 10), a relevant characteristic for the successive scale-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 catalytic systems during the filtration, recovery and recycling steps, rather than due to rhenium leaching from the catalysts.**

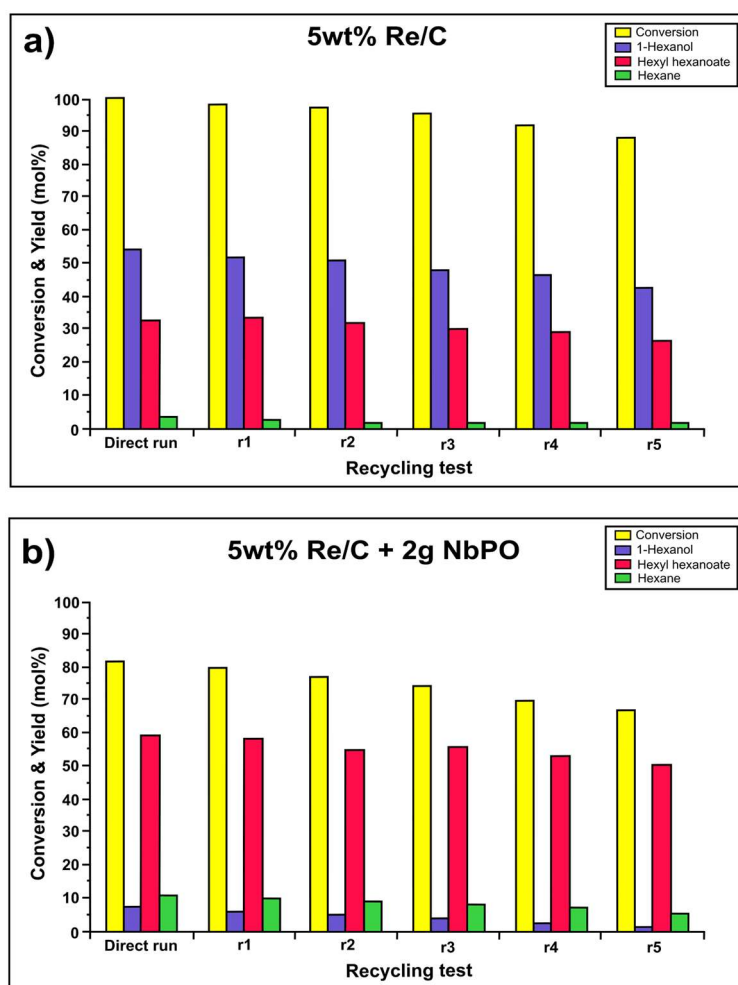


Figure 10. Recyclability tests of: a) 5 wt% Re/C; b) physical mixture [5 wt% Re/C + 2 g NbPO] employed in the hydrogenation of crude hexanoic acid from white grape pomace. Reaction conditions: T = 220 °C; P H₂ = 115 bar; t = 3 h; substrate/Re ratio of 270 mol/mol.

This was confirmed by the ICP analysis showing that the Re content in the reaction mixtures recovered at the end of the fifth recycle was below the detection limit, indicating that 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 has been 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 have confirmed the absence of further hydrogenation products.

2.3. Engine tests 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 90vol% of Diesel fuel, without any phase separation. The resulting blend has been tested in the experimental engine and compared with Diesel fuel alone and with the 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 have been employed as reference to better understand the influence of the single components, alcohol and ester, on engine performance 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 mixtures previously described have been utilized at maximum loads and different rpm, i.e. at 1500, 2000 and 2500 rpm, whilst injection timing was maintained fixed along the experimentation. As reported in Figure 11a, the use of different blending with Diesel does not significantly affect the power-rpm curve of the employed engine. The HexOH/HexHex mixtures employed for the tests resulted only in a slightly lower power: since the fuel volumetric flow is 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. Remarkably, 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 molecule (compared to Diesel), and to the presence of oxygen, which enhances the carbon complete oxidation during combustion [40]. As evidenced in Figure 11c, HC emissions result higher when Diesel combustion is realized within 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 enough time for realizing HC oxidation). In our case, the ascertained delay combustion (higher HC formation), caused by the HexHex, could be 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 (respect to that of Diesel) only slightly enhances NO_x emissions (Figure 11d), thus indicating that the maximum combustion temperature moderately increases in the case of the diesel-HexHex/HexOH blendstocks. Here, the ignition delay increases the amount of fuel required within the first part of the combustion process and, consequently, the release rate of the combustion heat. Lastly, a significative reduction of the 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 is due to the lower carbon content (lower C/H ratio) of the employed mixtures, which reduces the carbon availability for soot formation, and the oxygen promotes the oxidation processes. Moreover, the lower boiling points of the oxygenated compounds lead to a kind of “droplet explosion” once the fuel mixture is introduced in a hot environment [41,42], improving fuel atomization and mixing, thus leading to the combustion completion of the carbon-based molecules.

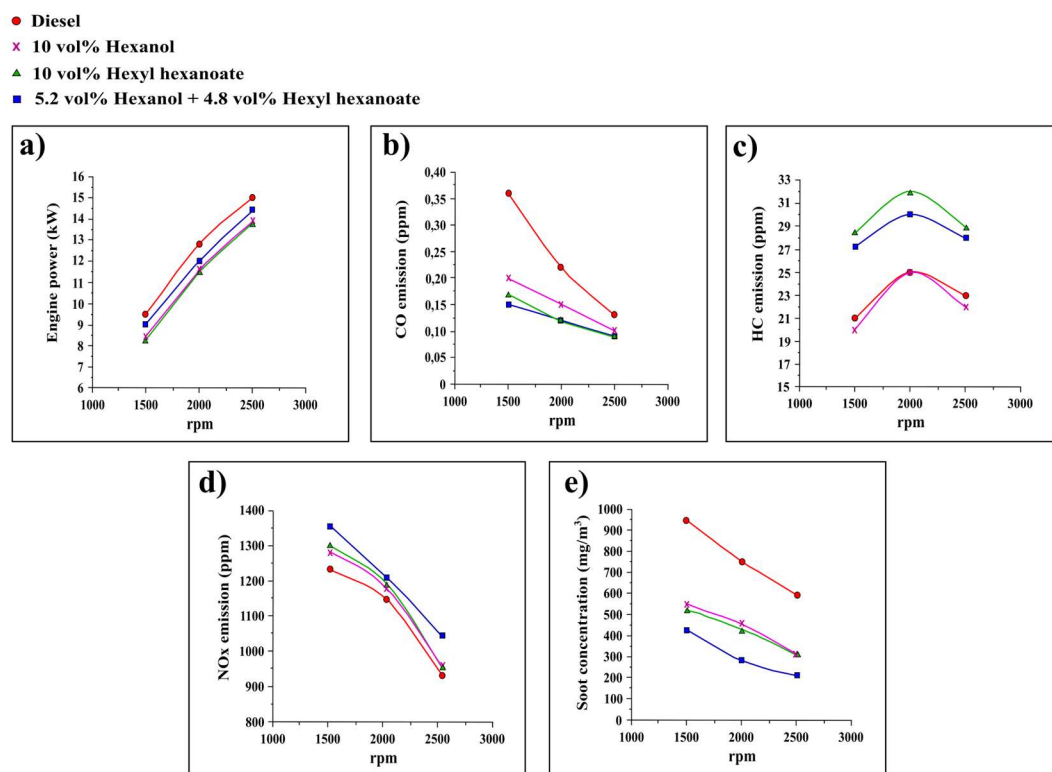


Figure 11. Engine performances, in term of a) engine power; b) CO emission; c) HC emission; d) NO_x emission and e) soot emission, all evaluated at the maximum load.

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. 5 wt% Re/C was provided by Riogen, whilst NbPO by CBMM (Companhia Brasileira de Metalurgia e Mineração) and used after treatment at 255 °C for 6 h under high vacuum.

Grape pomace, deriving 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 the previously reported procedure slightly modified. Briefly, the white grape pomace was fed into a leaching process with water which allowed to obtain: 1) the ethanol solution (30 g/L) to be fermented for hexanoic acid production; and 2) the grape pomace that could be further valorized through conventional process (tartaric acid, seed oil extraction; out of the focus of this work). Thereafter, the ethanol solution was fermented and hexanoic acid was extracted as previously reported [5]. The obtained crude hexanoic acid was later characterized.

3.2. Catalyst characterization

Temperature programmed reduction by H₂ (H₂-TPR) was performed in an AutoChem II apparatus (Micromeritics). 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, 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 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), 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 by inductively coupled plasma-optical emission spectrometry (ICP-OES), using an Optima 7000 DV (PerkinElmer) analyser equipped with a CCD array detector and the 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 equipped with a P.I.D. controller (4848). 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 any 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, pressure being held constant by automatically feeding more hydrogen. At the end of the reaction, the reactor was rapidly cooled at room temperature, depressurized and the reaction mixture was filtered to remove the catalyst and finally analysed 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 to the same procedure as adopted for the direct run.

3.4. Product analysis

The liquid samples were analyzed using GC-FID (DANI GC1000) 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 the 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; 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 the 5%.

The identification of the compounds of interest was performed by GC-MS (Agilent 7890B-5977A), equipped with a HP-5MS column (30 m \times 0.25 mm \times 0.25 μ m). Helium was adopted as carrier gas, with the flow rate of 1 mL/min. 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; 270 °C for 1 min.

3.5. Engine experimental setup

A Lombardini-Kohler Diesel engine model 9LD 625/2, whose specifications have been previously reported has been utilised and coupled with a Borghi&Saveri eddy current brake with rpm/Torque controller. Emission analysis was performed as previously reported [45].

4. Conclusions

In this work, the hydrogenation of commercial hexanoic acid has been 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 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 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, deriving 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 the commercial hexanoic acid, even after up to five recycle runs, thus highlighting the robustness of the process, the proper choice of the catalyst resulting strategic to modulate the composition of the final mixture. Engine tests confirm the potentiality of these mixtures as novel diesel bio-blendstocks, able to reduce the emissions of particulate and CO without any significant increasing of NO_x emission or changing in engine performance, thus contributing to meet the greenhouse gases emission reductions target and to the partial replacement of traditional fossil fuels, in accordance with the short-term goals of the EU countries.

Supplementary Materials: The following supporting information can be downloaded at: 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.

Author Contributions: The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding: This research was funded by the project VISION PRIN 2017 FWC3WC_002 funded by MIUR.

Acknowledgments: The authors thank the PRIN 2017-Project VISION “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).

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

References

- 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. Doi: 10.1016/j.biortech.2021.126195.
- Capodaglio, A.G.; Bolognesi, S. Ecofuel feedstocks and their prospects. In *Advances in eco-fuels for a sustainable environment*; Azad, K., Ed.; Woodhead Publishing: Cambridge, United Kingdom, 2019; pp. 15–51. Doi: 10.1016/B978-0-08-102728-8.00002-4.
- Chowdhary, P.; Gupta, A.; Gnansounou, E.; Pandey, A.; Chaturvedi, P. Current trends and possibilities for exploitation of grape pomace as a potential source for value addition. *Environ. Pollut.* **2021**, *278*, 116796. Doi: 10.1016/j.envpol.2021.116796.
- Ingledeu, W.M. *The alcohol textbook: a reference for the beverage, fuel and industrial alcohol industries*, Nottingham University Press, Nottingham, 5th ed, 2009.
- 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. Doi: 10.1039/d2gc00044j.

6. Kumar, N.; Pali, H.S.; Sonthalia, A.S. Higher alcohols as diesel engine fuel. In *Advances in energy and combustion, green energy and technology*; Gupta, A.K.; De, A.; Aggarwal, S.K.; Kushari, A.; Runchal, A.K. (Eds.); Springer Nature Singapore Pte Ltd, 2022; pp. 157–174. Doi: 10.1007/978-981-16-2648-7_7. 486–488
7. Yaman, H.; Doğan, B.; Yeşilyurt, M.K.; Erol, D. Application of higher-order alcohols (1-hexanol-C6 and 1-heptanol-C7) in a spark-ignition engine: Analysis and assessment. *Arab. J. Sci. Eng.* **2021**, *46*, 11937–11961. Doi: 10.1007/s13369-021-05765-7. 489–490
8. Cui, X.; Li, Y.; Topf, C.; Junge, K.; Beller, M. Direct ruthenium-catalyzed hydrogenation of carboxylic acids to alcohols. *Angew. Chem. Int. Ed.* **2015**, *54*, 10596–10599. Doi: 10.1002/anie.201503562. 491–492
9. Tamura, M.; Nakagawa, Y.; Tomishige, K. Recent development of heterogeneous catalysts for hydrogenation of carboxylic acids to their corresponding alcohols. *Asian J. Org. Chem.* **2020**, *9*, 126–143. Doi: 10.1002/ajoc.201900667. 493–494
10. Ralphs, K.; Collins, G.; Manyar, H.; James, S.L.; Hardacre, C. Selective hydrogenation of stearic acid using mechanochemically prepared titania-supported Pt and Pt–Re bimetallic catalysts. *ACS Sustainable Chem. Eng.* **2022**, *10*, 6934–6941. Doi: 10.1021/acssuschemeng.1c07595. 495–496
11. Takeda, Y.; Nakagawa, Y.; Tomishige, K. Selective hydrogenation of higher saturated carboxylic acids to alcohols using a Re–O_x–Pd/SiO₂ catalyst. *Catal. Sci. Technol.* **2012**, *2*, 2221–2223. Doi: 10.1039/C2CY20302B. 498–499
12. Dudu, A.I.; Lăcătuș, M.A.; Bencze, L.C.; Paizs, C.; Toșa, M.I. Green Process for the enzymatic synthesis of aroma compounds mediated by lipases entrapped in tailored sol-gel matrices. *ACS Sustainable Chem. Eng.* **2021**, *9*, 5461–5469. Doi: 10.1021/acssuschemeng.1c00965. 500–502
13. Gaspar, D.J. Top 13 Blendstocks derived from biomass for mixing-controlled compression-ignition (Diesel) engines: Biblendstocks with potential for lower emissions and increased operability. PNNL-31421, 2021, Pacific Northwest National Laboratory, Richland, WA. 503–505
14. 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.; Bidy, M.; Tao, L.; Young, A.; Brown, K.; Li, S.; Zhu, Y.; Snowden-Swan, L.J.; Mevawala, C.R.; Gaspar, D.J. Environmental, economic, and scalability considerations of selected bio-derived blendstocks for mixing-controlled compression ignition engines. *ACS Sustainable Chem. Eng.* **2022**, *10*, 6699–6712. Doi: 10.1021/acssuschemeng.2c00781. 506–509
15. 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. *Eur. J. Inorg. Chem.* **2021**, *39*, 4043–4065. Doi: 10.1002/ejic.202100459. 510–512
16. Broadbent, H.S.; Campbell, G.C.; Bartleyand, W.J.; Johnson, J.H. Rhenium and its compounds as hydrogenation catalysts. III. Rhenium heptoxide. *J. Org. Chem.* **1959**, *24*, 1847–1854. Doi: 10.1021/jo01094a003. 513–514
17. Broadbent, H.S.; Bartley, W.J. Rhenium catalysts. VII. Rhenium(VI) oxide. *J. Org. Chem.* **1963**, *28*, 2345–2347. Doi: 10.1021/jo01044a046. 515–516
18. Toyao, T.; Ting, K.W.; Hakim Siddiki, S.M.A.; Touchy, A.S.; Onodera, W.; Maeno, Z.; Ariga-Miwa, H.; Kanda, Y.; Asakura, K.; Shimizu, K. Mechanistic study of the selective hydrogenation of carboxylic acid derivatives over supported rhenium catalysts. *Catal. Sci. Technol.* **2019**, *9*, 5413–5424. Doi: 10.1039/C9CY01404G. 517–519
19. Gothe, M.L.; Pérez-Sanz, F.J.; Braga, A.H.; Borges, L.R.; Abreu, T.F.; Bazito, R.C.; Gonçalves, R.V.; Rossi, L.M.; Vidinha, P. Selective CO₂ hydrogenation into methanol in a supercritical flow process. *J. CO₂ Util.* **2020**, *40*, 101195. Doi: 10.1016/j.jcou.2020.101195. 520–522
20. Rozmysłowicz, B.; Kirilin, A.; Aho, A.; Manyar, H.; Hardacre, C.; Wärnå, J.; Salmi, T.; Murzin, D.Y. Selective hydrogenation of fatty acids to alcohols over highly dispersed ReO_x/TiO₂ catalyst. *J. Catal.* **2015**, *328*, 197–207. Doi: 10.1016/j.jcat.2015.01.003. 523–524
21. Suknev, A.; Zaikovskii, V.; Kaichev, V.; Paukshtis, E.; Sadvovskaya, E.; Bal'zhinimaev, B. The nature of active sites in Pt–ReO_x/TiO₂ catalysts for selective hydrogenation of carboxylic acids to alcohols. *J. Energy Chem.* **2015**, *24*, 646–654. Doi: 10.1016/j.jechem.2015.09.003. 525–527
22. Ullrich, J.; Breit, B. Selective hydrogenation of carboxylic acids to alcohols or alkanes employing a heterogeneous catalyst. *ACS Catal.* **2018**, *8*, 785–789. Doi: 10.1021/acscatal.7b03484. 528–529
23. Liu, K.; Pritchard, J.; Lu, L.; van Putten, R.; Verhoeven, M.W.G.M.; Schmitkamp, M.; Huang, X.; Lefort, L.; Kiely, C.J.; Hensen, E.J.M.; Pidko, E.A. Supported nickel-rhenium catalysts for selective hydrogenation of methyl esters to alcohols. *Chem. Commun.* **2017**, *53*, 9761–9764. Doi: 10.1039/c7cc04759b. 530–532
24. Yoshino, K.; Kajiwarra, Y.; Takaishi, N.; Inamoto, Y.; Tsuji, J. Hydrogenation of carboxylic acids by rhenium-osmium bimetallic catalyst. *JAOCs* **1990**, *67*, 21–24. Doi: 10.1007/BF02631383. 533–534
25. Behr, A.; Brehme, V.A. Bimetallic-catalyzed reduction of carboxylic acids and lactones to alcohols and diols. *Adv. Synth. Catal.* **2002**, *344*, 525–532. Doi: 10.1002/1615-4169(200207)344:5<525::AID-ADSC525>3.0.CO;2-U. 535–536
26. Haus, M.O.; Meledin, A.; Leiting, S.; Louven, Y.; Roubicek, N.C.; Moos, S.; Weidenthaler, C.; Weirich, T.E.; Palkovits, R. Correlating the synthesis, structure, and catalytic performance of Pt–Re/TiO₂ for the aqueous-phase hydrogenation of carboxylic acid derivatives. *ACS Catal.* **2021**, *11*, 5119–5134. Doi: 10.1021/acscatal.0c05612. 537–539
27. Liu, S.; Simonetti, T.; Zheng, W.; Saha, B. Selective hydrodeoxygenation of vegetable oils and waste cooking oils to green diesel using a silica-supported Ir–ReO_x bimetallic catalyst. *ChemSusChem* **2018**, *11*, 1446–1454. Doi: 10.1002/cssc.201800321. 540–541
28. Šivec, R.; Huš, M.; Likozar, B.; Grilc, M. Furfural hydrogenation over Cu, Ni, Pd, Pt, Re, Rh and Ru catalysts: ab initio modeling of adsorption, desorption and reaction micro-kinetics. *Chem. Eng. J.* **2022**, *436*, 135070. Doi: 10.1016/j.cej.2022.135070. 542–543

29. 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. Doi: 10.1016/j.enconman.2021.114273. 544
545
30. 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. Doi: 10.1016/j.energy.2020.118984. 546
547
31. Fioroni, G.; Fouts, L.; Luecke, J.; Vardon, D.; Huq, N.; Christensen, E.; Huo, X.; Alleman, T.; McCormick, R.; Kass, M.; Polikarpov, E.; Kukkadapu, G.; Whiteside, R.A. Screening of potential biomass-derived streams as fuel blendstocks for mixing controlled compression ignition combustion. SAE Technical Paper 2019,2019-01-0570. 548
549
32. Muchave, G.J.; Netto, L.D.S.; 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. Dev. Res.* **2020**, *10*, 42266–42278, Doi: 10.37118/ijdr.20421.11.2020. 550
551
33. Di, X.; Li, C.; Lafaye, G.; Especel, C.; Epron, F.; Liang, C. Influence of Re-M interactions in Re-M/C bimetallic catalysts prepared by a microwave-assisted thermolytic method on aqueous-phase hydrogenation of succinic acid. *Catal. Sci. Technol.* **2017**, *7*, 5212–5223. Doi: 10.1039/c7cy01039g. 552
553
554
555
34. Tudorache, M.; Opris, C.; Cojocaru, B.; Apostol, N.G.; Tirsoaga, A.; Coman, S.M.; Parvulescu, V.I.; Duraki, B.; Krumeich, F.; van Bokhoven, J.A. Highly efficient, easily recoverable, and recyclable Re-SiO₂-Fe₃O₄ catalyst for the fragmentation of lignin. *ACS Sustain. Chem. Eng.* **2018**, *6*, 9606–9618. Doi: 10.1021/acssuschemeng.7b04294. 556
557
558
35. Ma, L.; Yan, L.; Lu, A.; Ding, Y. Effect of Re promoter on the structure and catalytic performance of Ni-Re/Al₂O₃ catalysts for the reductive amination of monoethanolamine. *RSC Adv.* **2018**, *8*, 8152–8163. Doi: 10.1039/c7ra12891f. 559
560
36. Armaroli, T.; Busca, G.; Carlini, C.; Giuttari, M.; Raspolli Galletti, A.M.; Sbrana, G. Acid sites characterization of niobium phosphate catalysts and their activity in fructose dehydration to 5-hydroxymethyl-2-furaldehyde. *J. Mol. Catal. A. Chem.* **2000**, *151*, 233–243. Doi: 10.1016/S1381-1169(99)00248-4. 561
562
37. Licursi, D.; Antonetti, C.; Fulignati, S.; Giannoni, M.; Raspolli Galletti, A.M. Cascade strategy for the tunable catalytic valorization of levulinic acid and γ -valerolactone to 2-methyltetrahydrofuran and alcohols. *Catalysts*, **2018**, *8*, 277. Doi: 10.3390/catal8070277. 563
564
565
38. Antonetti, C.; Melloni, M.; Licursi, D.; Fulignati, S.; Ribechini, E.; Rivas, S.; Parajó, J.C.; Cavani, F.; Raspolli Galletti, A.M. Microwave-assisted dehydration of fructose and inulin to HMF catalysed by niobium and zirconium phosphate catalysts. *Appl. Catal. B: Env.* **2017**, *206*, 364–377. Doi: 10.1016/j.apcatb.2017.01.056. 566
567
568
39. Kalli, E.; Lappa, I.; Bouchagier, P.; Tarantilis, P.A.; Skotti, E. Novel application and industrial exploitation of winery by-products. *Bioresour. Bioprocess.* **2018**, *5*, 46. Doi: 10.1186/s40643-018-0232-6. 569
570
40. Internal combustion engine fundamentals. 2nd ed.; Hetwood, J.B., Ed.; McGraw-Hill Education, 2018. 571
572
41. 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. Doi: 10.1038/s41598-017-09663-7. 573
574
42. 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. Doi: 10.1080/00102208008952383. 575
576
43. Licursi, D.; Antonetti, C.; Fulignati, S.; Vitolo, S.; Puccini, M.; Ribechini, E.; Bernazzani, L.; Raspolli Galletti, A.M. In-depth characterization of valuable char obtained from hydrothermal conversion of hazelnut shells to levulinic acid. *Biores. Technol.* **2017**, *244*, 880–888. Doi: 10.1016/j.biortech.2017.08.012. 577
578
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.e1–390.e9. Doi: 10.1016/j.jiec.2021.04.057. 579
580
45. 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. Doi:10.3390/catal10050509. 581
582
583
584
585
586
587