

CATALYTIC HYDROGENATION OF CRUDE HEXANOIC ACID, EASILY OBTAINED BY ANAEROBIC FERMENTATION OF GRAPE POMACE

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ABSTRACT: The transition from fossil resources to renewable ones represents an urgent need. Biomasses are promising feedstocks, potentially exploitable through novel bio-catalytic processes, such as acidogenic fermentation to carboxylic acids, which can be further converted into more value-added bio-products through cascade chemical approaches, such as hydrogenation to corresponding alcohols/esters. In this work, the optimization of the hydrogenation of commercial hexanoic acid to 1-hexanol and hexyl hexanoate was first investigated. For this purpose, 5 wt% Re/C resulted active and selective towards 1-hexanol production. The same catalyst was further tested for the hydrogenation of crude hexanoic acid, obtained by fermentation of red and white grape pomaces. Hydrogenation of these crude hexanoic acid mixtures confirmed the promising performances of 5 wt% Re/C, achieving the complete substrate conversion with a prevailing selectivity to 1-hexanol (~58 mol%), rather than to hexyl hexanoate (~30 mol%). Moreover, the use of an acid support, such as Al₂O₃, markedly shifted the selectivity towards hexyl hexanoate (~51 mol%). This observation was further demonstrated by testing physical mixtures of 5 wt% Re/C and different amounts of acidic niobium phosphate. Based on these promising results, exploitation of grape pomace for 1-hexanol/hexyl hexanoate production, to use as bio-fuels or bio-solvents, represents a smart possibility.

Keywords: Biobased products, Biorefinery, Fermentation, Reduction, Liquid biofuel

1 INTRODUCTION

Biomass represents a key feedstock in the transition from fossil resources to renewable ones. It can be advantageously converted into bio-fuels and bio-chemicals through both biological and chemical pathways [1]. In this perspective, grape pomace, an abundant agro-industrial by-product deriving from the winemaking process, can be considered a promising starting feedstock to propose within a bio-refinery approach. About 9 Mt of grape pomace are globally produced every year, which can cause major disposal problems. On the other hand, these are rich in exploitable compounds, such as polyphenols and polysaccharides [2]. Nowadays, bio-refineries involving the employment of grape pomace as starting feedstock already exist, limitedly aimed at the production of ethanol, anthocyanins, polyphenols, levulinic acid and butyl levulinate [3-6]. Remarkably, ethanol present in the grape pomaces can be anaerobically fermented to give medium chain-length carboxylic acids (C₆-C₁₂), through reverse β -oxidation pathways [7,8]. Up to now, these carboxylic acids have been produced from natural fats and oils through physicochemical processes [9], which are more complex and expensive than the fermentative route. The composition of the carboxylic acids broth obtained by the fermentative route strongly depends on the employed bacterial strains. *Clostridium kluyveri*, *Eubacterium pyruvativorans*, *Eubacterium limosum* and *Megasphaera elsdeni* have been largely reported for the production of hexanoic acid-rich liquor, one of the most attractive medium chain-length carboxylic acids [7,10]. In fact, hexanoic acid has great industrial interest, finding use as bactericidal agent or potentially convertible into the corresponding alcohol, to use within the formulation of surfactants, plasticizers and bio-fuels. On this basis, the reduction of carboxylic acids to alcohols is a reaction of paramount importance in industrial chemistry [8,11-15].

Up to now, common strategies for the synthesis of alcohols from the carboxylic acids provide the employment of stoichiometric amount of metal hydrides [16] or, more recently, silanes [17,18], but safety issues and generation of stoichiometric amount of wastes represent the main drawbacks to still overcome. Catalytic reduction of carboxylic acids in the presence of molecular H₂ is proposed as atom-efficient route, resulting more attractive than the above-mentioned ones [19,20]. However, the catalytic hydrogenation of carboxylic acids results more difficult than that of the esters, because the interaction of carboxylic acids with the active metal center may lead to the catalyst deactivation [19]. Moreover, some side-reactions could take place during the hydrogenation of carboxylic acids to alcohols, such as *i*) decarboxylation of carboxylic acids to alkanes, *ii*) hydrogenolysis of the produced alcohols to alkanes [21]. In this context, esterification is not considered as a real undesired reaction, because esters are promising products, to use as lubricants, fragrances and diesel blendstocks [22,23]. Several transition metal-based homogeneous catalysts (Ru, Ir, Rh, Re, Co) have been proposed for the hydrogenation of carboxylic acids to alcohols [24] but, from a practical point of view, the employment of heterogeneous catalytic systems should be preferred, due to the easier work-up [25-28].

On this basis, the present work investigates the hydrogenation of hexanoic acid, carried out in the presence of commercial heterogeneous rhenium catalysts. Rhenium is cheaper than the other noble metals (Pt, Pd and Ru), is particularly active and selective in converting carboxylic acids to alcohols and poorly susceptible to catalytic poisoning and deactivation [26]. Up to now, it has been proposed especially as bimetallic systems or as Re₂O₇, as shown in Table 1.

Table I: Overview of main relevant data on the hydrogenation of hexanoic acid to 1-hexanol with rhenium catalysts.

[Hexanoic acid] (g/L)	Catalyst	T (°C)	P (bar)	t (h)	Conversion (mol%)	1-Hexanol yield (mol%)	Ref.
n.a.	Re ₂ O ₇	200	188	2	n.a.	93	29
46.4	Re-Pt/TiO ₂	130	50	5	58	53	30
23.2	Re-Pd/C	130	20	18	n.a.	74	31
52.6	ReO _x -Pd/SiO ₂	140	80	24	100	99	21
14.6	Re-Ni/TiO ₂	180	50	8	100	60	32

n.a. = not-available.

Harsher reaction conditions, in terms of temperature and hydrogen pressure, are generally required to obtain good 1-hexanol yields, despite bimetallic catalytic systems are active also at milder reaction conditions, thanks to the synergistic effect between rhenium and other metals [33]. However, commercial monometallic catalysts should be preferred over bimetallic ones for cost and practical reasons [34]. On this basis, in the present work, commercial Re/C and Re/Al₂O₃ have been adopted as catalysts firstly for the hydrogenation of commercial hexanoic acid, then for the hydrogenation of a crude hexanoic acid-rich liquor obtained from red or white grape pomace fermentation. So far, real fermented broths have been scarcely considered for this application, and most of the hydrogenation studies have been performed on model compounds, for greater simplicity. Noteworthy, Lee *et al.* [35] investigated the hydrogenation of butyric acid-rich liquor deriving from fermentation of glucose, working at 265 °C and 25 bar of H₂, in the presence of the bimetallic Ru-Sn/ZnO catalyst, reaching the maximum 1-butanol yield of 98 mol%. However, the adopted butyric acid was not directly hydrogenated from the crude fermented broth, but it was preliminarily purified by distillation under reduced pressure. Remarkably, the hydrogenation of fermented hexanoic acid-rich liquor has been described only in a recent our publication. In this research, a preliminary study on the hydrogenation of a crude hexanoic acid-rich liquor deriving from grape pomace fermentation has been carried out, working at 180 °C and 115 bar of H₂ with 5 wt% Re/C, obtaining a mixture of 1-hexanol/hexyl hexanoate, which has been proposed as a promising diesel blendstock [7]. Further developing this approach, the present work aims the more deeply investigation of this path, studying the influence of the catalyst properties and reaction conditions on the selectivity towards 1-hexanol and/or hexyl hexanoate production.

2 EXPERIMENTAL

2.1 Materials

Hexanoic acid (>99%), *n*-dodecane (>99%), hexane (>99%), hexyl hexanoate (>98%), 1-hexanol (>99%), methanol (>99%) and *n*-octane (99%) were purchased by Sigma-Aldrich. 5 wt% Re/Al₂O₃ and 5 wt% Re/C were obtained by Riogen. Niobium phosphate (NbPO) was provided from CBMM (Companhia Brasileira de Metalurgia e Mineração) and used after treatment at 255 °C for 6 h under high vacuum. Grape pomace was kindly provided by Caviro Distillerie (Faenza, Italy), deriving from red and white wine production, and used without any pre-treatment. Crude hexanoic acid-rich liquor was produced through acidogenic fermentation of red and white grape pomace, according to our previous work [7].

2.2 Hydrogenation reaction

Before the reaction, rhenium catalysts were pre-reduced according to the procedure reported in a previous our work [36]. Briefly, the pre-reduction was carried out in a 300 mL stainless steel Parr 4560 autoclave equipped with a P.I.D. controller. The heterogeneous catalyst (~1 g), previously dried under vacuum, was introduced into the autoclave, which was closed, and conditioned by five vacuum-nitrogen cycles. Then, 80 mL of deaerated methanol were introduced into the autoclave by suction. The autoclave was pressurized with H₂ up to 90 bar, determined at the temperature of 180 °C, and maintained at this temperature for 6 h. At the end of the treatment, the reactor was cooled down up to room temperature, H₂ was evacuated, and methanol was removed under high vacuum. Subsequently, the reaction mixture (9.3 g of commercial hexanoic acid/ crude hexanoic acid-rich liquor in 100 ml of *n*-octane) and the internal standard (*n*-dodecane) were introduced into the autoclave by suction. The reactor was pressurized with H₂ up to 115 bar, determined at the reaction temperature, and the pressure was held constant by feeding external H₂. The reaction was monitored by periodically sampling the reaction mixture through a dip tube and the collected liquid samples were analyzed by GC-FID and GC-MS.

2.3 Product analysis

The liquid samples were analyzed using GC-FID (DANI GC1000) equipped with a HP-PONA column (20 m × 0.2 mm × 0.5 μm). 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 based on the calibration with standard solutions. The analyses were carried out in triplicates 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 × 0.25 mm × 0.25 μm). 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.

2.4 Catalyst characterization

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.

3 RESULTS AND DISCUSSION

In our previous work [7] it was found that the pre-reduction of the 5 wt% Re/C catalyst was necessary for improving the subsequent hydrogenation of commercial hexanoic acid. The use of 5 wt% Re/C as the catalyst and 115 bar of H₂ led to complete substrate conversion with selectivities to hexyl hexanoate and 1-hexanol of about 50 and 27 mol%, respectively, after 9 h at 180 °C. Now, this pre-reduced catalyst was further characterized by XPS spectroscopy and compared with the corresponding fresh one. XPS spectrum of the commercial raw 5 wt% Re/C shows the presence of two signals of Re in its maximum oxidation state (+7), with the 4f_{7/2} binding energy centred at about 45.9 eV (Fig. 1) [37]. On the other hand, after the catalyst pre-reduction, the presence of Re (+7), as well as of other Re species of lower oxidation states, such as Re (+3) and (+4), at 41.4 and 43.1 eV, respectively [38,39], is confirmed (Fig. 1).

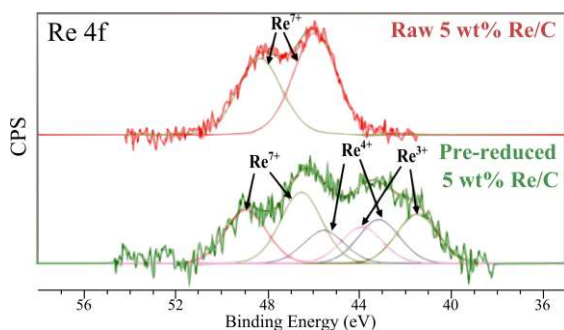


Figure 1: XPS spectra of fresh and pre-reduced commercial 5 wt% Re/C.

Definitely, XPS characterization has demonstrated the successful pre-reduction of 5 wt% Re/C catalyst, as desired.

Then, in order to speed up the conversion parameter, a higher temperature (220 °C) was employed, keeping constant both the H₂ pressure and the 5 wt% Re/C amount (substrate/Re ratio of 270 mol mol⁻¹). Remarkably, now the substrate conversion was almost complete after only 3 hours, achieving selectivities to hexyl hexanoate and 1-hexanol of about 30 and 60 mol%, respectively, as shown in Fig. 2. Respect to our previous work [7] now the reaction is faster, thus resulting more selective towards 1-hexanol production, rather than to hexyl hexanoate. The choice of a higher reaction temperature represents a useful way to simply tune the reaction towards the selective production of 1-hexanol. On the other hand, lower temperatures are desired for selectively enabling the reaction between the unconverted

carboxylic acid and the corresponding formed alcohol, thus improving the selectivity to the hexyl hexanoate product. Hexane represents the main reaction by-product, deriving from over-hydrogenation of 1-hexanol. Its formation did not occur at lower temperatures [7] but its formation was always limited, achieving a final selectivity lower than 10 mol%. Based on this promising result, this reaction was then performed on a real substrate, in the perspective of developing industrial applications. In this context, red grape pomace has been upgraded into hexanoic acid-rich liquor by direct anaerobic fermentation. This crude fermented liquor has been proposed as the real hexanoic acid-rich substrate for the hydrogenation reaction. Remarkably, the combination of the bio-chemical conversion with a traditional chemical catalytic one results strategic to obtain bio-products of higher added value [40], as previously stated.

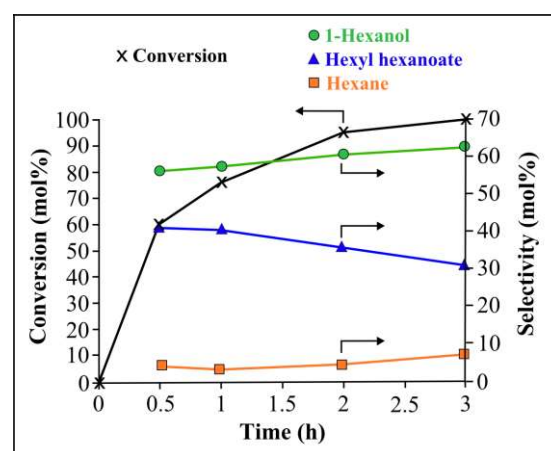
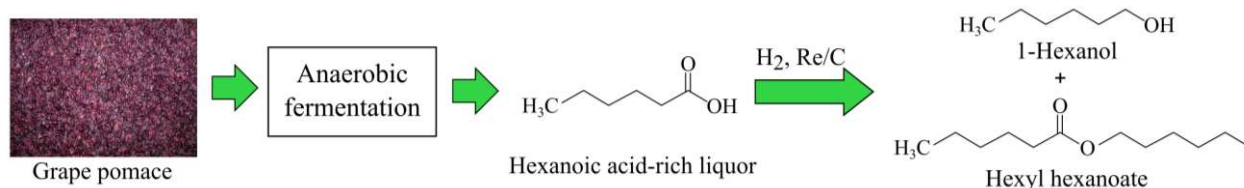


Figure 2: Conversion (mol%) of commercial hexanoic acid and corresponding selectivities (mol%) to 1-hexanol, hexyl hexanoate and hexane adopting 5 wt% Re/C as catalyst. Hydrogenation reaction has been carried out at 220 °C, with H₂ pressure of 115 bar employing 5 wt% Re/C with a substrate/Re ratio of 270 mol mol⁻¹.

On this basis, deepening this cascade approach, the catalytic hydrogenation of the hexanoic acid-rich liquor obtained by fermentation of red grape pomace has been investigated, aimed at the co-production of 1-hexanol and hexyl hexanoate, to jointly use as bio-fuels and/or bio-solvents. For this purpose, the same pre-reduced 5 wt% Re/C catalyst has been proposed, claiming the low price of rhenium (respect to traditional noble metals) and its good resistance to poisoning [41]. The cascade approach is shown in Scheme 1:



Scheme 1: Cascade process for the production of 1-hexanol and hexyl hexanoate from grape pomace.

In Fig. 3, data related to the hydrogenation of hexanoic acid-rich liquor at 220 °C and 115 bar H₂ are reported, and compared with the corresponding ones obtained from the commercial hexanoic acid, working under the same reaction conditions.

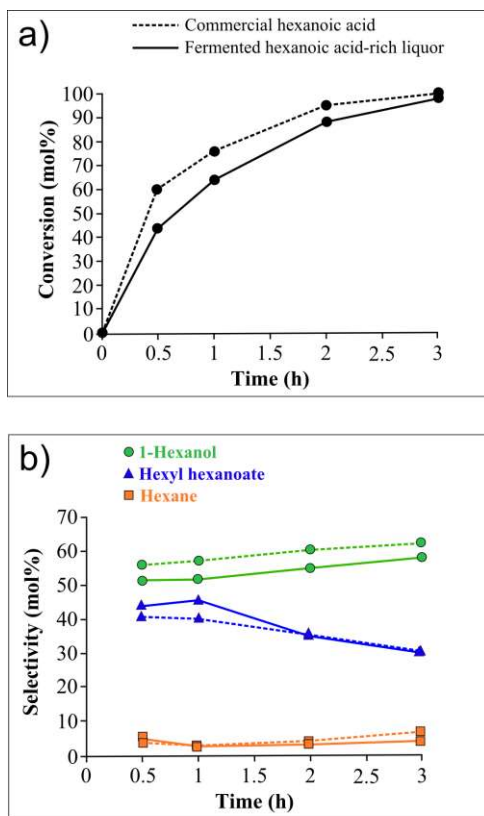


Figure 3: Graph a): Conversion (mol%) of commercial hexanoic acid (---- dashed line) and fermented hexanoic acid-rich liquor (— solid line). Graph b): Selectivity (mol%) to 1-hexanol, hexyl hexanoate and hexane starting from commercial hexanoic acid (dashed line) and hexanoic acid-rich liquor obtained by fermentation of red grape pomace (solid line). Hydrogenation reactions have been carried out at 220 °C, with H₂ pressure of 115 bar employing 5 wt% Re/C with a substrate/Re ratio of 270 mol mol⁻¹.

The results obtained from the hydrogenation of the fermented hexanoic acid-rich liquor are in agreement with those achieved in the hydrogenation of commercial hexanoic acid. In fact, when the fermented hexanoic acid-rich liquor was employed, the conversion was only slightly slower resulting, however, complete after 3 h, as in the case of commercial hexanoic acid. Regarding the selectivities to 1-hexanol and hexyl hexanoate, the trend previously ascertained for the commercial hexanoic acid has been further confirmed. Moreover, the formation of hexane is minimal, as for the hydrogenation of the commercial hexanoic acid.

The 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 sugars [42]. These compositional differences might have repercussions on the chemical composition of the corresponding fermented liquors, as confirmed by the higher hexanoic acid purity of the corresponding fermented white grape pomace (87 wt% vs

93 wt% of red and white grape pomace, respectively). GC-MS analysis of the crude fermented white grape pomace was carried out, to investigate the presence of other minor compounds (Fig. 4).

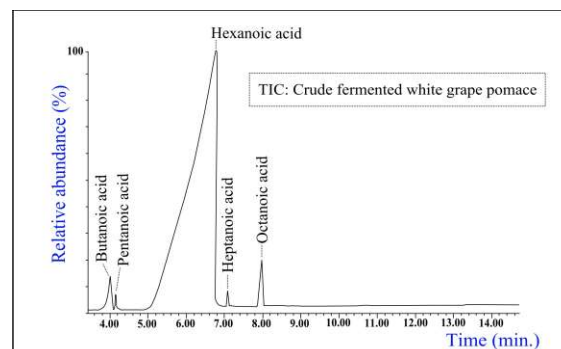


Figure 4: Total Ion Current (TIC) of the crude fermented white grape pomace.

Above chromatogram confirms the presence of C₄-C₈ carboxylic acids in the crude fermented white grape pomace, resulting rich in hexanoic acid, as in the case of the corresponding red one [7]. If compared to this latter, the fermented white grape pomace shows a similar qualitative distribution of the fermentation by-products. Also this new substrate has been hydrogenated under the same reaction conditions already adopted for the conversion of the crude fermented red grape pomace (5 wt% Re/C with a substrate/Re ratio of 270 mol mol⁻¹, T=220 °C, H₂=115 bar), achieving analogous results. In fact, the complete substrate conversion has been reached after 3 hours, with corresponding selectivities of 60, 30 and 5 mol% in 1-hexanol, hexyl hexanoate and hexane, respectively. The catalytic system is not affected by the presence of the minor components, demonstrating its robustness towards both proposed real feedstocks. The similarity between white/red fermented substrates has been further confirmed by the GC-MS analysis of the respective hydrogenated mixtures. In particular, hydrogenated solution deriving from white grape pomace shows the presence of 1-hexanol, butyl butanoate, hexyl hexanoate and hexyl octanoate (Fig. 5), confirming the previous data on the red grape pomace hydrogenated solution [7].

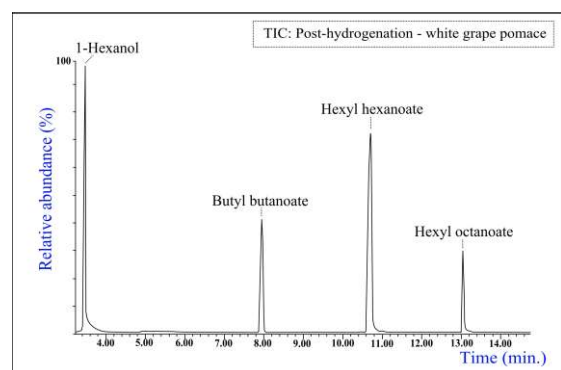


Figure 5: Total Ion Current (TIC) of the hydrogenated final mixture from crude fermented white grape pomace. Hydrogenation reaction has been carried out at 220 °C, with H₂ pressure of 115 bar employing 5 wt% Re/C with a substrate/Re ratio of 270 mol mol⁻¹.

After having investigated the preferential production of 1-hexanol, the possibility of exploiting also the acidity of the catalyst support was considered, in order to address the reaction towards the selective hexyl hexanoate formation, considering that also this compound is an interesting bio-fuel [23]. For this purpose, for the first time, 5 wt% Re/ γ -Al₂O₃ (with a substrate/Re ratio of 270 mol mol⁻¹) was tested towards the hydrogenation reaction of commercial hexanoic acid (Fig.6).

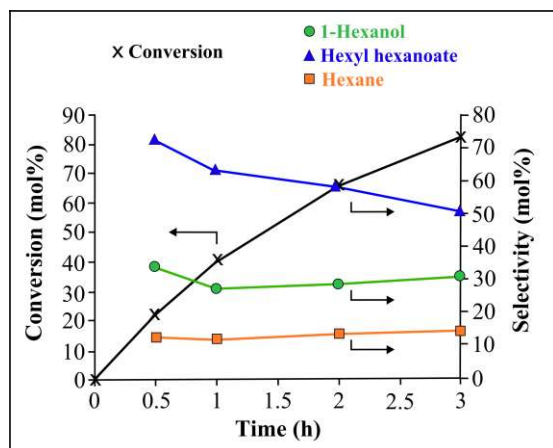


Figure 6: Conversion (mol%) of commercial hexanoic acid and corresponding selectivities (mol%) to 1-hexanol, hexyl hexanoate and hexane adopting 5 wt% Re/Al₂O₃ as catalyst. Hydrogenation reaction has been carried out at 220 °C, with H₂ pressure of 115 bar employing 5 wt% Re/Al₂O₃ with a substrate/Re ratio of 270 mol mol⁻¹.

The obtained results highlight that ester formation is prevailing over that of alcohol, as desired. In particular, hexanoic acid conversion in the presence of 5 wt% Re/ γ -Al₂O₃ is slower than that achieved with 5 wt% Re/C (Fig. 2). Remarkably, the slower kinetics given by 5 wt% Re/ γ -Al₂O₃ is the real responsible for the prevailing formation of the hexyl hexanoate. As a further comparison, after 3 hours of hydrogenation, 5 wt% Re/C led to complete substrate conversion with selectivities to 1-hexanol and hexyl hexanoate of about 60 and 30 mol%, respectively (Fig. 2). Instead, under the same reaction conditions, 5 wt% Re/ γ -Al₂O₃ gave the hexanoic acid conversion of about 80 mol% with selectivities to 1-hexanol and hexyl hexanoate of about 30 and 51 mol%, respectively (Fig. 6). As for 5 wt% Re/C catalyst, a low selectivity to hexane was achieved after 3 h with 5 wt% Re/Al₂O₃. Furthermore, to better tune the acidity, several physical mixtures of 5 wt% Re/C together with different amounts (up to 3 grams) of niobium phosphate (NbPO) as the acid co-catalyst, have been tested for the hydrogenation of commercial hexanoic acid. The corresponding catalytic data are reported in Fig. 7. The data show that the addition of NbPO led to a moderate slowdown of the hexanoic acid conversion, which is offset by a relevant improvement of the hexyl hexanoate selectivity, as in the case of 5 wt% Re/ γ -Al₂O₃. The highest hexyl hexanoate selectivity of about 70 mol% was achieved using the physical mixture composed of [1.1 g of 5 wt% Re/C + 2 g of NbPO]. Further increase of NbPO amount does not lead to corresponding gain on the ester selectivity, rather enabling the formation of the hexane by-product (Fig. 7). Based on these data, the selective synthesis of hexyl hexanoate can be achieved either i) by working with a

neutral support (such as 5 wt% Re/C), working at lower temperatures and longer reaction times, or ii) by exploiting the acidity of the catalytic system (such as 5 wt% Re/Al₂O₃ or a physical mixture of [5 wt% Re/C + NbPO]), working at higher temperatures and shorter reaction times. Hydrogenation tests on crude fermented grape pomace in the presence of the above acid catalytic systems are in progress and preliminary results agree with those obtained from the hydrogenation of commercial hexanoic acid.

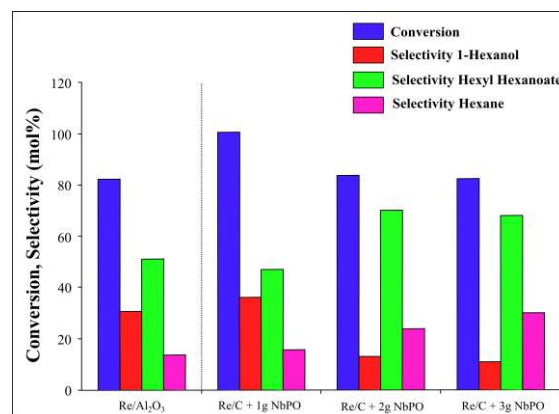


Figure 7: Effect of the acidity of the proposed catalytic systems towards the hydrogenation of commercial hexanoic acid. Hydrogenation reactions have been carried out at 220 °C, with H₂ pressure of 115 bar for 3 h employing 5 wt% Re/C with a substrate/Re ratio of 270 mol mol⁻¹.

4 CONCLUSIONS

In this work, the hydrogenation of commercial hexanoic acid has been investigated, adopting 5 wt% Re/C as the main heterogeneous catalyst, which is more selective towards hexyl hexanoate formation at low reaction temperature, or towards 1-hexanol at high one. Moving from model compounds to real waste biomass, the co-production of 1-hexanol and hexyl hexanoate by catalytic hydrogenation of hexanoic acid-rich liquor, deriving from acidogenic fermentation of the red/white grape pomaces, has been proposed. In the developed bio-refinery scheme, red/white grape pomaces have been preliminary upgraded into a hexanoic acid-rich liquor by direct anaerobic fermentation. Catalytic hydrogenation of the crude fermented white or red grape pomace with 5 wt% Re/C gave similar results to the commercial hexanoic acid, highlighting negligible matrix effect towards the reaction of our interest. From this perspective, it is noteworthy that the fermented hexanoic acid-rich liquor has been hydrogenated without having carried out any preliminary purification treatment, making the integrated proposed cascade process simple and sustainable. Moreover, the use of rhenium-based acid catalytic systems, in particular 5 wt% Re/Al₂O₃, significantly shifted the selectivity towards hexyl hexanoate production, and this is even more evident using niobium phosphate as the acid co-catalyst (within the system [5 wt% Re/C + niobium phosphate]). An appropriate control of selectivity is strategic to modulate the composition of the final hydrogenated mixture, which affects its subsequent use as biofuel, requiring limited

work-up procedures. According to these promising data, the exploitation of exhausted red/white grape pomaces for the development of a new combined bio-chemical process opens the way to different applications of these waste biomasses.

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7 LOGO SPACE

