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Hydrotreating Catalytic Processes for Oxygen Removal in the Upgrading of Bio-Oils and Bio-Chemicals

Iñaki Gandarias and Pedro Luis Arias

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<http://dx.doi.org/10.5772/52581>

1. Introduction

In a future sustainable scenario a progressive transition by the chemical and energy industries towards renewable feedstock will become compulsory. Energy demand is expected to grow by more than 50% by 2035 [1], with most of this increase in demand emerging from developing nations. Clearly, increasing demand from finite petroleum resources cannot be a satisfactory policy for the long term. The transition to a more renewable production system is now underway; however, this transition needs more research and investment in new technologies to be feasible.

Biomass appears as the only renewable source for liquid fuels and most commodity chemicals [2]. This is the reason why, in the near future, bio-refineries in which biomass is catalytically converted to pharmaceuticals, agricultural chemicals, plastics and transportation fuels will take the place of petrochemical plants [3]. Indeed, biomass represents 77.4% of global renewable energy supply [4]. Current technologies to produce liquid fuels from biomass are typically multistep and energy-intensive processes, including the production of ethanol by fermentation of biomass derived glucose [5], bio-oils by fast pyrolysis or high pressure liquefaction of biomass [6,7], polyols and alkanes from hydrogenolysis of biomass derived sorbitol [8], and biodiesel from vegetable oils [9]. Biomass can also be gasified to produce CO and H₂ (synthesis gas), which can be further processed to produce methanol or liquid alkanes through Fischer–Tropsch synthesis [10].

The so-called “First Generation” biofuels, such as sugarcane ethanol in Brazil, corn ethanol in US, oilseed rape biodiesel in Germany, and palm oil biodiesel in Malaysia, already present mature commercial markets and well developed technologies. Nonetheless, there is a worldwide increasing awareness against the use of edible oils and seeds to generate transportation fuels, and critical voices have aroused questioning the actual sustainability of these

“First Generation” biofuels. In fact, nowadays 95 % of biodiesel is made from edible oil [9]. This means that possible food resources are being used as automotive fuels when some part of the World’s population is suffering from hunger. Therefore, large-scale production of biodiesel from edible oils may bring about a global imbalance in the food supply market. Another significant concern of using “First Generation” technologies is the deforestation and the destruction of ecosystems. Indeed, the expansion of oil-crop plantations for biofuel production on a large scale has caused deforestation in countries such as Malaysia, Indonesia and Brazil because more and more forest has been cleared for plantation purposes. In addition to this, in developing countries energy crops are powerful competitors for scarce water resources [11].

Being the non-edible portion of the plant and the most abundant source of biomass, lignocellulosic biomass materials are attracting growing attention as sustainable and renewable energy sources. The so-called “Second Generation” technologies for the production of fuels and chemicals can use a wide range of lignocellulosic biomass residues such as agricultural, industrial, and forest wastes, and also energy crops (willow, switchgrass) that do not compete with food crops for available land. The average composition of lignocellulosic material is as follows: 50% cellulose, 25% hemicellulose, and 20% lignin [12]. Cellulose is a linear polysaccharide with β -1,4 linkages of D-glucopyranose monomers (Figure 1). Hemicellulose is a more complex polymer containing five different sugar monomers: five carbon sugars (xylose and arabinose) and six carbon sugars (galactose, glucose, and mannose). Lignin is a highly branched aromatic polymer, that consists of an irregular array of variously bonded “hydroxy-” and “methoxy-” substituted phenylpropane units. Lignin is mainly found in woody biomass. Lignocellulosic materials can be converted into liquid fuels by three primary routes, including (i) syngas production by gasification, (ii) bio-oil production by pyrolysis or liquefaction, and (iii) acid hydrolysis reactions [13].

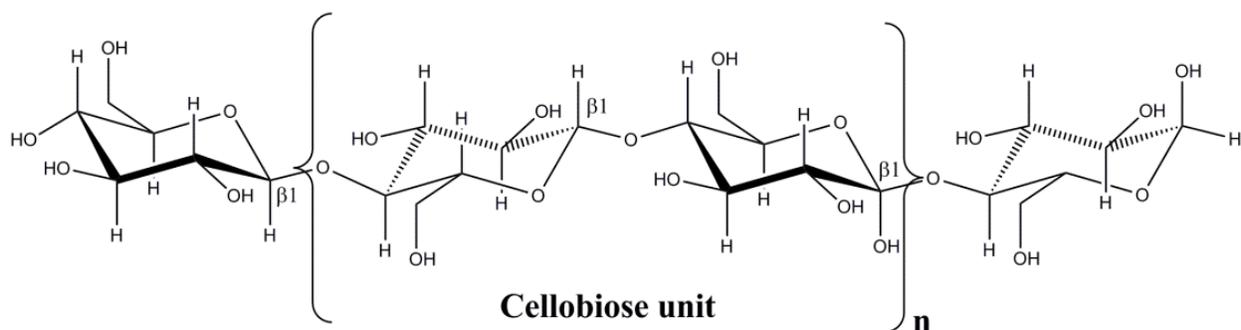


Figure 1. Chemical structure of cellulose.

In the pyrolysis process, biomass feedstock is heated in the absence of oxygen, forming a gaseous product, which after cooling condenses. Depending on the operating conditions that are used, pyrolysis processes are known as slow or fast pyrolysis. Fast pyrolysis processes are characterized by high rates of particle heating (heating rate $> 1000^{\circ}\text{C}/\text{min}$) to temperatures around 500°C , and rapid cooling of the produced vapors to condense them (vapor

residence time 0.5-5s). In order to obtain that fast heating rates, it is essential to use reactors that provide high external heat transfer (such as fluidized bed reactors) and to guarantee an efficient heat transfer through the biomass particle, using biomass particle size of less than 5 mm [7]. Fast pyrolysis produce 60-75 wt% of liquid bio-oil, 15-25 wt% of solid char, and 10-20 wt% of non condensable gases, depending on the feedstock. In slow pyrolysis biomass is heated to around 500°C at much lower heating rates than those used in fast pyrolysis. The vapor residence times are much longer; they vary from 5 min to 30 min. As a consequence of the lower heating rate and of the longer vapor residence time, lower yields to pyrolysis oils and higher yields to char and gas products are obtained (Figure 2). As a result of all this, for bio-oil production from biomass, fast pyrolysis processes are preferred.

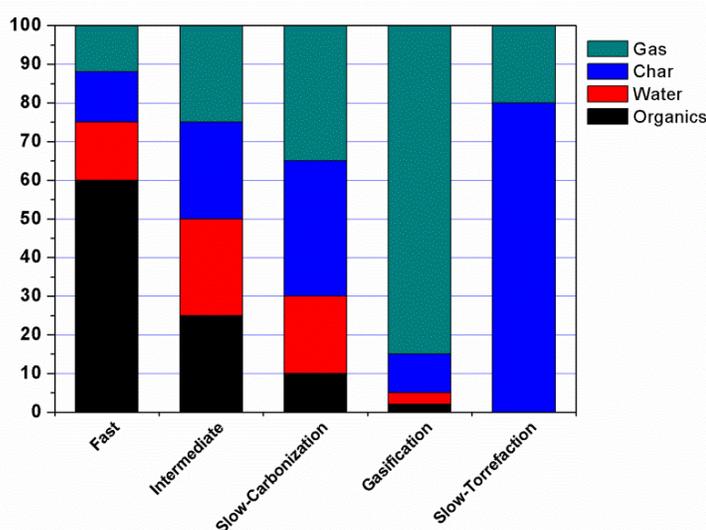


Figure 2. Product spectrum from pyrolysis. Data from [14].

Bio-oils are dark-red brown color liquids. They are also known as pyrolysis oils, bio-crude oil, wood oil or liquid wood. Bio-oils usually have higher density, viscosity and oxygen content compared to fuel-oil. While the sulfur and nitrogen content is usually smaller (Table 1). The high oxygen content of bio-oils generates some negative characteristics like low heating value (HV), immiscibility with conventional fuels and high viscosity. A serious problem of bio-oils is their instability during storage, as their viscosity, HV and density are affected. This is because some of the organic compounds present in bio-oils are highly reactive. For instance, ketones, aldehydes and organic acids react to form ethers, acetals and hemiacetals respectively [15]. Therefore, bio-oils need to be upgraded to reduce their oxygen content in order to increase their stability, to be miscible with conventional oil, and to increase their H/C ratio. This upgrading can be carried out through three different routes: (i) catalytic hydrotreating, usually known as hydrodeoxygenation (HDO), which consists mainly on decarboxylation, hydrocracking, hydrogenolysis and hydrogenation reactions, (ii) zeolite upgrading or (iii) through esterification reactions. Zeolite upgrading is carried out without external hydrogen sources, and therefore the resulting oil has lower HV and H/C than conventional fuels. Esterification can significantly increase the chemical and physical properties

of bio-oil, however it requires using high amounts of alcohols, which are highly demanded. Catalytic hydrotreating appears to have the greatest potential to obtain high grade oils which are compatible with the already available infrastructure for fossil fuels.

Property	Pyrolysis Oil	Heavy Oil
Moisture Content, wt %	15-30	0.1
pH	2.5	
Elemental Composition, wt %		
Carbon	54-58	85
Hydrogen	5.5-7.0	11
Oxygen	35-40	1.0
Nitrogen	0-0.2	0.3
Ash	0-0.2	0.1
Higher Heating Value, MJ/kg	16-19	40
Viscosity (50°C), cP	40-100	180
Solids (wt%)	0.2-1.0	1

Table 1. Typical Properties of Wood Pyrolysis Bio-Oil, and Heavy Fuel Oil [13].

Not only fuels, but also commodity chemicals are nowadays derived from petroleum-based resources. Commodity chemicals are involved in the production of a wide variety of products and thus are an essential and integral part of the modern societies. Hence, in the search for a sustainable scenario, it is crucial to also look towards alternative biorenewable sources for these chemicals. In the case of platform chemicals coming from biomass, such as glucose, levulinic acid, 5-(hydroxyl-methyl furfural), sorbitol, or glycerol, they usually have higher O/C ratio than most commodity chemicals. Therefore, the conversion of these platform chemicals into value-added chemicals usually requires O removal reactions.

This book chapter summarizes the main aspects involved in the catalytic hydrotreating processes for the oxygen removal from bio-oils and from biomass based platform chemicals.

2. Hydrotreating catalytic processes in bio-oil upgrading

As it has been stated in the introduction, a general characteristic of bio-oils coming from the pyrolysis of biomass is their high oxygen content (35-40 wt%). More than 300 compounds have been identified in bio-oil, most of them containing oxygen atoms. The exact composition of the bio-oil depends on the type of biomass fed. These compounds can be classified in five broad categories: (i) hydroxyaldehydes, (ii) hydroxyketones, (iii) sugars and dehydrosugars, (iv) carboxylic acids, and (v) phenolic compounds [16]. Hydroprocessing of biomass-

derived oils differs from processing petroleum because of the importance of deoxygenation as compared to nitrogen or sulfur removal. Bio-oil hydrodeoxygenation (HDO) process implies complex reaction networks that includes cracking, decarbonylation, decarboxylation, hydrocracking, hydrogenolysis, hydrogenation and polymerization. The upgrading process should yield a product with lower amount of water and oxygen, decreased acidity and viscosity, and higher HV. The complexity of the reactions and the high variety of oxygenated compounds make the evaluation of bio-oil upgrading difficult and has brought the use of model compounds such as phenol, guaicol, 2-ethylphenol, methyl heptanoate or benzofuran to test different catalysts and to understand the main characteristics of the HDO process. Elliot [17] has reported the HDO reactivity of different organic compounds that are typically present in bio-oils (see Figure 3). Olefins, aldehydes and ketones can easily be reduced by H₂ at temperatures as low as 150–200 °C. Alcohols react at 250–300 °C by hydrogenation and thermal dehydration to form olefins. Carboxylic and phenolic ethers react at around 300 °C. Regarding the operating pressures, due to the low solubility of hydrogen in organic and aqueous solutions, high pressures are required to guarantee high availability of hydrogen in the vicinity of the catalyst (80–300 bar of H₂ pressure) [15].

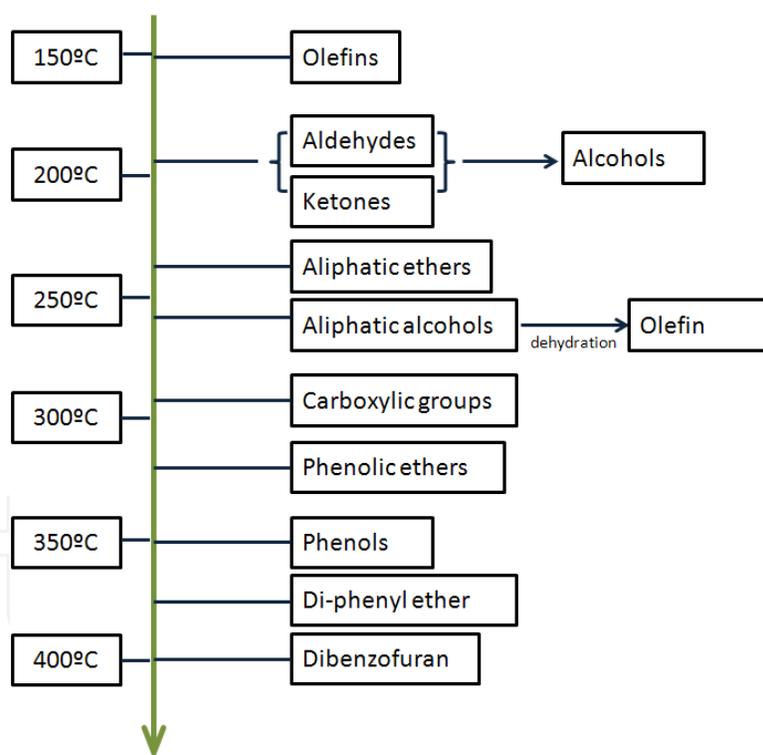


Figure 3. Reactivity scale of organic components under HDO conditions. Adapted from [17].

2.1. Catalysts and reaction mechanisms

HDO is a process closely related to hydrodesulphurization (HDS), which is highly developed in the oil-refinery industry. In both processes, hydrogen is used to remove the heteroa-

tom in the form of H_2O and H_2S respectively. This is the reason why several works on bio-oil HDO use catalytic systems already used in HDS processes, such as Co-Mo or Ni-Mo based catalysts. These catalysts are active in their sulphide form, so they need to be pretreated with H_2S before operation to obtain Co-MoS₂ or Ni-MoS₂ active sites. Romero et al. [18] using Co-MoS₂ type catalysts for the HDO of 2-ethylphenol at 340°C and 7 MPa of hydrogen pressure proposed the reaction mechanism described in Figure 4. It is suggested that the oxygen from the molecule adsorbs on a vacancy of a MoS₂ matrix. At the same time, the H_2 from the feed dissociatively adsorbs on the catalyst surface forming S-H species. The addition of a proton to the adsorbed oxygenated molecule leads to an adsorbed carbocation. This intermediate can directly undergo a C–O bond cleavage and the aromatic ring is regenerated leading to ethylbenzene. The vacancy is afterwards recovered by elimination of water.

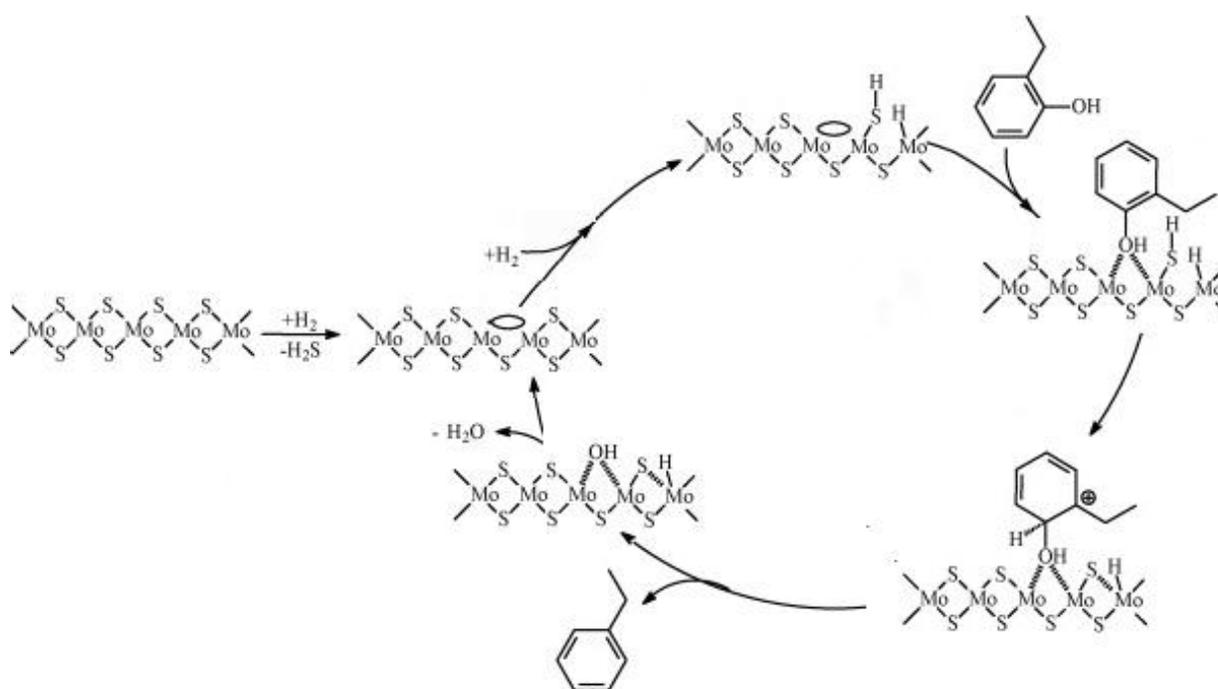


Figure 4. Proposed mechanism of HDO of 2-ethylphenol over a schematic Co-MoS₂ catalyst Adapted from [18].

The problem of using MoS₂ type catalysts for HDO of bio-oils is that during prolonged operation sulfur stripping and oxidation of the surface of the catalyst occurs, causing deactivation of the catalyst. The reason is that as compared to conventional oil, the sulfur content of bio-oil is very low (less than 0.1 wt % [19]). One alternative to avoid this problem is the co-feeding of H_2S to the system, in order to regenerate the sulfide sites. For instance, in the HDO of aliphatic esters over a CoMoS₂/Al₂O₃ and NiMoS₂/Al₂O₃ catalysts a promoting effect was observed in the activity of the catalyst when co-feeding H_2S , however this co-feeding did not prevent from catalyst deactivation. This promoting effect was related to the increase in Brønsted acidity in the presence of H_2S [20]. Nonetheless, the use of H_2S has also some drawbacks. In the HDO of phenol over a Ni-MoS₂-Al₂O₃ catalyst, it was observed an

inhibitory effect of H_2S , leading to a decrease in phenol conversion and not preventing catalyst deactivation. This was ascribed to the competitive adsorption between phenol and H_2S [21]. Moreover, the formation of sulfur-containing compounds such as dimethyl sulfide, diheptyl sulfide, hexanethiol and heptanethiol was observed in the HDO of aliphatic oxygenates over Co-MoS₂ catalysts, even in the absence of sulfiding agents [22]. Therefore, the use of MoS₂ type catalysts in bio-oil HDO seems challenging, because sulfur free bio-oil can be contaminated by sulfur, and because wood-based bio-oils contain high amounts of phenolic compounds that would compete with H_2S for the active sites of the catalyst.

Another alternative is the use of bi-functional catalysts formed by the combination of transition metals and oxophilic metals, such as MoO₃, Cr₂O₃, WO₃ or ZrO₂. In this case, the oxophilic metal acts as a Lewis acid site. The oxygen ion pair of the target molecule is attracted by the unsaturated oxophilic metal. The second step of the mechanism is hydrogen donation. In this case, the hydrogen molecule is dissociatively adsorbed and activated on the transition metal. Finally, the activated hydrogen is transferred to the adsorbed molecule.

Regarding the support, γ -Al₂O₃ is the most commonly used one. Nonetheless, it has to be taken into account the structural changes that γ -Al₂O₃ might suffer under the typical operating conditions in HDO. In contact with hot water ($T > 350^\circ\text{C}$), γ -Al₂O₃ is converted into a hydrated boehmite (AlOOH) phase with a significant decrease in the acidity and surface area [23]. Moreover, the relatively high surface acidity of Al₂O₃ is thought to promote the formation of coke precursors. In fact, coke formation is one of the main factors affecting the stability of the catalyst. Therefore, the use of less acidic or neutral support like active carbon or SiO₂ is an interesting alternative [24]. For instance, Echeandia et al. [25] using Ni-WO₃ on active carbon for the HDO of 1 wt% phenol in n-octane at 150-300°C and 15 bar observed lower coke formation on the surface of the active carbon with respect to alumina support. Based on product analysis, they also concluded that HDO of phenol occurs via two separate pathways: one leading to aromatics through a direct hydrogenolysis route, and the other one to cyclohexane, through a hydrogenation-hydrogenolysis route (see Figure 5). In terms of obtaining a final product with high octane number and reducing the consumption of hydrogen, direct hydrogenolysis reaction is preferred. Nonetheless, aromatics are harmful to human health and its content in transportation fuels is limited by legislation. Therefore, it is important to understand which sites are responsible of each route, in order to obtain an upgraded product with the desired aromatic content. CeO₂ and ZrO₂ supports have also shown to give good results in the HDO of different molecules. ZrO₂-supported noble metal catalysts (Rh, Pd and Pt) [26] were compared with the conventional sulfided CoMo/Al₂O₃ catalyst in the HDO of Guaiacol in the presence of H₂ at 300 °C. Sulfided CoMo/Al₂O₃ deactivated due to carbon deposition, and the products were contaminated with sulfur, however, neither problem was observed with the ZrO₂-supported noble metal catalysts. As a conclusion, a good support for HDO should provide high affinity for the oxygen-containing molecule while presenting moderate acidity in order to minimize the formation of coke deposits.

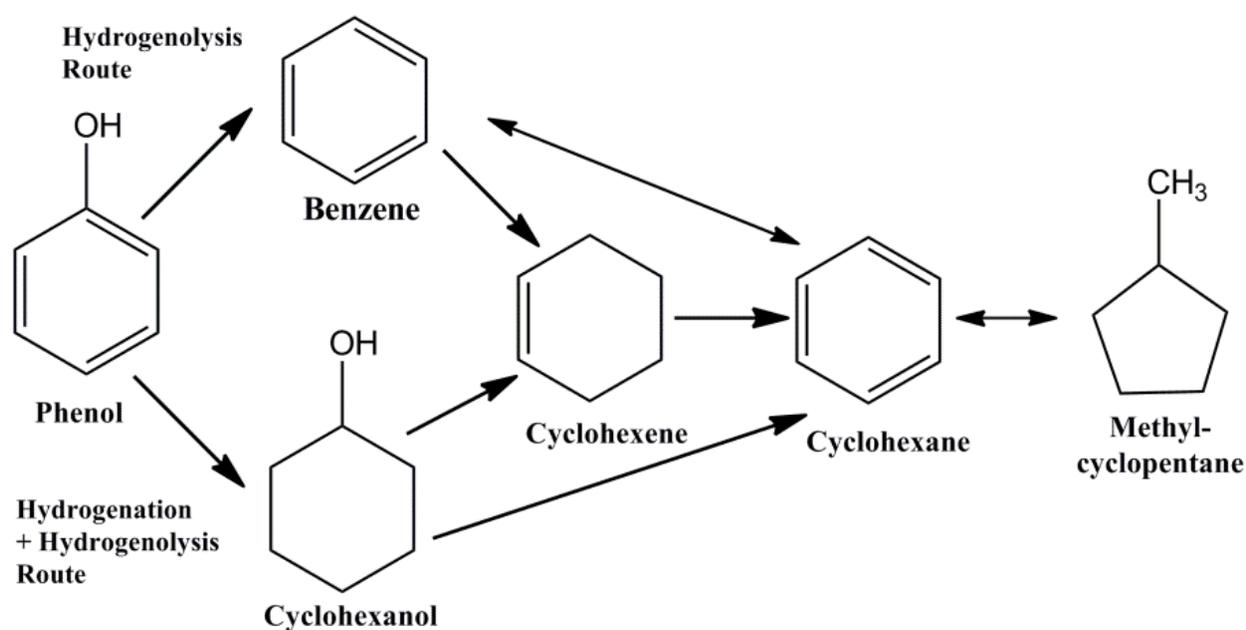


Figure 5. Scheme of phenol HDO. Adapted from [25].

2.2. Upgrading of real bio-oils

An important aspect in the HDO of bio-oils is the required degree of deoxygenation. It is assumed that the upgraded oil should contain less than 5 wt% oxygen so that the viscosity is decreased to that required for fuel applications [17]. However, during the hydrotreating, not only the oxygen is removed in the form of water, but also the saturation of double bonds occurs. This saturation has two significant negative effects. The first one is related to the quality of the upgraded oil, because the saturation of the aromatic components has a highly detrimental effect in the octane number. For instance, the octane number of toluene (119) decreases to 73 when the aromatic ring is hydrogenated [10]. The second negative effect is related to the consumption of hydrogen. According to Venderbosh et al. [27] in order to achieve 50% of deoxygenation 16 g H₂/Kg of bio-oil is required, which is close to the expected stoichiometry value. Nonetheless, if the aim is to obtain the total removal of oxygen, the H₂ consumption increases to 50 g H₂/Kg of bio-oil; which means that the H₂ consumption is 56% higher than the stoichiometry value. Some other studies suggest even higher H₂ consumption requirements, 62 g H₂/Kg of bio-oil [28]. This deviation of the H₂ consumption from the stoichiometry value is explained on the basis of the different reactivity of the oxygenated compounds present in the bio-oil. High reactive compounds, such as ketones, are easily converted with low hydrogen consumption. However, more complex molecules, such as phenols, might suffer the hydrogenation/saturation of the molecule and therefore the hydrogen consumption exceeds the stoichiometric prediction at the high degree of deoxygenation.

In order to obtain high degrees of HDO but minimizing the hydrogenation of aromatics in bio-oil, two step hydrogenating processes have been developed. In the first stage, high reac-

tive and unstable compounds are transformed into more stable ones at low temperature (270°C, 136 atm H₂) and without a catalyst. In the second step, a deeper HDO is carried out at higher temperatures (400°C, 136 atm H₂) and using hydrotreating catalysts. The two-step hydrotreatment allows 13% reduction in hydrogen consumption for equivalent oil yield. Nonetheless, the reported octane number of the upgraded bio-oil, 72, is still lower than that of gasoline [17].

Environmental aspects should also be taken into account. Aromatic compounds have on one hand high octane number; however, they are also harmful to health. Indeed, environmental standards for aromatics in transportation fuels are becoming more restrictive. Thus, it seems challenging to achieve an agreement between obtaining oils with high octane number while fulfilling aromatic content policies.

3. Hydrogenolysis reactions in the valorization of platform chemicals

Biomass components have a great potential as building block intermediates. Indeed, sugars, vegetable oils and terpenes can be employed for synthesizing products with a high added value, such as chemicals and fine chemicals. There are hundreds of different processes to obtain chemicals from biomass origin building blocks. This chapter deals with those processes involving hydrotreating for the removal of oxygen. In the first part of this section, some examples of significant hydrogenolysis reactions in the valorization of platform chemicals will be given, while the last part will be focused on one of the most studied hydrogenolysis processes; the conversion of glycerol into propanediols (PDO).

As it has been previously stated, platform chemicals coming from biomass usually contain higher O/C ratio than most commodity chemicals; thus main valorization processes require the removal of oxygen. One widely used process to remove oxygen is hydrogenolysis. Hydrogenolysis is a type of reduction that involves chemical bond dissociation in an organic substrate and simultaneous addition of hydrogen to the resulting molecular fragments [33]. Therefore, reaction for oxygen removal involves the cleavage of the C-O bond and the addition of hydrogen (oxygen is removed in the form of H₂O). This is a significant aspect, because, in those processes where the starting and target molecule have the same number of carbons it is important to use catalytic systems that present high activity in C-O bond hydrogenolysis while low activity in C-C bond hydrogenolysis.

3.1. Hydrogenolysis of sugars

Two types of sugars are present in biomass: hexoses (six-carbon sugars), of which glucose is the most common one, and pentoses (five-carbon sugars), of which xylose is the most common one. Glucose and xylose can be easily hydrogenated to yield sorbitol [29] and xylitol [30] respectively. These two molecules can undergo C-C and C-O hydrogenolysis in the presence of hydrogenation catalysts, leading mainly to a mixture of ethyleneglycol, glycerol, and 1,2-propanediol. Other products such as butanediols, lactic acid, methanol, ethanol, and propanol can also be formed (Figure 6). Ni is known to show high hydrogenolysis activity

towards C-C and C-O bond hydrogenolysis, this is the reason why, the use of Ni on different acid supports seems an interesting alternative for this process. For instance, Ni supported on NaY zeolite gave 68% sorbitol conversion with 75% combined selectivity to 1,2-PDO and glycerol at 220°C and 60 bar H₂ pressure after 6 h [8]. The addition of Pt to the catalyst did not influence its activity and selectivity significantly. However, in the case of 20 wt% Ni/Al₂O₃ prepared by coprecipitation, the addition of 0.5 wt% of Ce significantly increased sorbitol conversion (from 41% to 91%) and the stability of the catalyst [31]. It seems that the addition of Ce considerably reduces Ni leaching, and hence improves the stability of the catalyst. Other catalytic systems have also been reported besides the Ni acid-support ones. For instance, Ru supported on carbon nanofiber and graphite felt composite catalysts gave 68% sorbitol conversion and 79% propylene glycol selectivity at 220°C and 8.0 MPa hydrogen pressure [32].

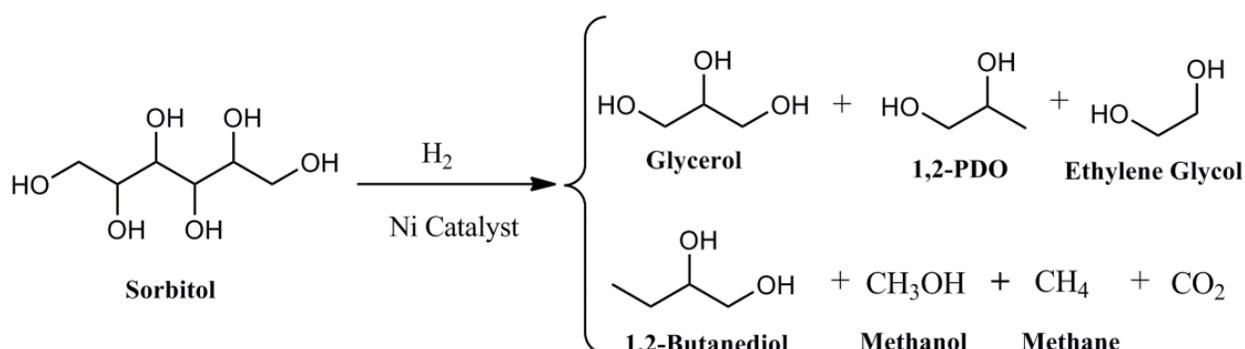


Figure 6. Reaction products of catalytic hydrogenolysis of sorbitol over supported Ni catalyst in the aqueous phase. Adapted from [31].

3.2. Hydrogenolysis of 5-Hydroxymethyl-Furfural (HMF)

5-Hydroxymethyl-furfural (HMF) can be obtained in a biphasic reactor from the acid-catalyzed dehydration of hexoses [33]. HMF by itself cannot be used as motor fuel due to its high boiling point (283°C). However, it can be transformed to 2,5-dimethylfuran (DMF) through a two consecutive hydrogenolysis reactions (see Figure 7). DMF not only decreases the boiling point to a value suitable for liquid fuels, but also attains the lowest water solubility and the highest octane number (RON) of the mono-oxygenated C₆ compounds, while preserving a high energy density 30 kJ cm⁻³, which is 40% higher than the energy density of bio-ethanol and comparable to the one of gasoline (35 KJ cm⁻³) [34]. Roman-Leshkov et al. [34] used CuRu/C catalysts (prepared by incipient wetness impregnation) in a flow reactor using 5 wt % HMF in a 1-butanol solution at 220 °C and 6.8 bar H₂ pressure. Yields to DMF of 71% were measured. An important aspect in their process is that the catalyst should be chloride-resistant, because, NaCl was used in the dehydration step of hexoses to HMF to increase their solubility in water. Very recently, Luijckx et al. [35] reported the production of 2,5-DMF by the hydrogenolysis of 5-HMF over a Pd/C catalyst in 1-propanol. Due to simultaneous alcoholysis, significant amount of ethers products were formed.

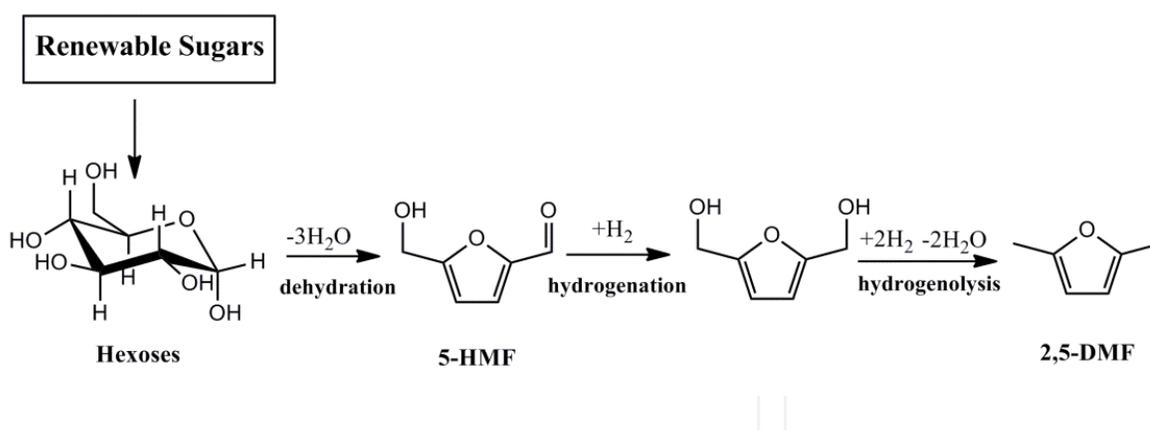


Figure 7. Reaction scheme for the conversion of sugars into 2,5-dimethylfuran. Adapted from [36]

3.3. Hydrotreating of vegetable oils and hydrogenolysis of fatty acids

Biodiesel is currently obtained from the transesterification reaction of vegetable oils. A possible drawback of this technology is that large investment is required to build up new biodiesel plants. An interesting alternative is to directly feed the vegetable oil into the hydrotreating unit of a petroleum refinery, for instance, vegetable oil can be co-fed with heavy vacuum oil HVO. Under typical hydrotreating conditions (300-450°C, 50 bar H₂ pressure, sulfidedNiMo/Al₂O₃ catalyst), vegetable oils are transformed into alkanes through three different pathways: decarboxylation, decarbonylation and HDO. The straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes (Figure 8) [37]. It was reported that mixing the sunflower oil with HVO does not decrease the rate of desulfurization. Moreover, the rate of vegetable oil hydrotreating is faster than the rate of HVO desulfurization. For industrial application, corrosion problems should be taken into account and the formation of waxes should be minimized, as they can plug the reactor.

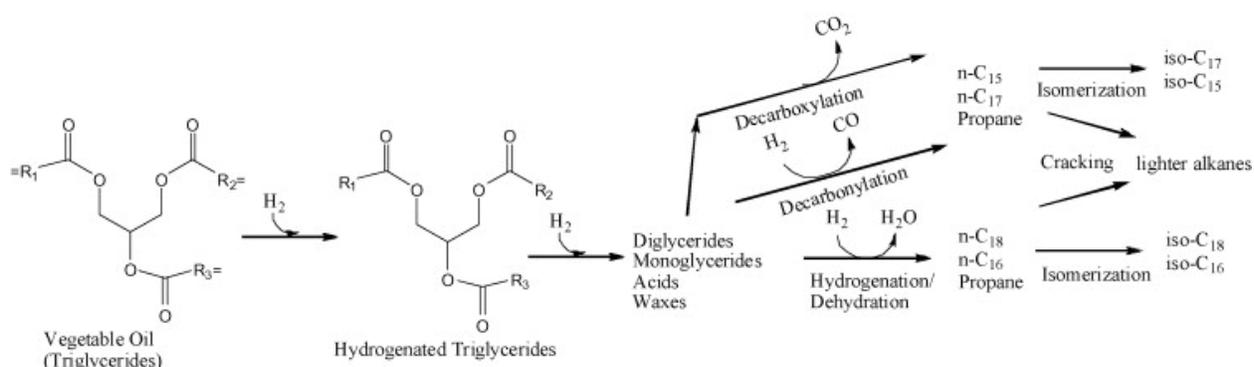
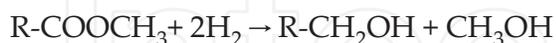


Figure 8. Reaction pathway for conversion of tri-glycerides to alkanes [37].

Fatty alcohols can be obtained by catalytic hydrogenolysis of fatty acid methyl esters. Small-chain fatty alcohols are used in cosmetics and food and as industrial solvents or plasticizers, while the large-chain fatty alcohols are important as biofuels and as nonionic surfactants or

emulsifiers. Fatty alcohols are produced by hydrogenolysis, in the presence of Cu based heterogeneous hydrogenation catalysts, operating under H₂ pressures between 20 and 30 bar and temperatures in the range of 97-197°C [38]. High hydrogen pressures are required to increase the solubility of hydrogen in the reaction mixture, in order to boost the availability of H₂ at the catalyst surface and to reduce mass transport limitations [39]. The stoichiometry of the reaction is presented below:



3.4. Hydrogenolysis of glycerol

In the last years, much attention has been devoted to the valorization of glycerol. Glycerol is obtained as byproduct in the transesterification reaction of fatty acids to produce biodiesel. With the significant increase of worldwide biodiesel production, there is also an important increase in glycerol availability. Due to the increments in biodiesel manufacture, important amounts of glycerol have been placed in the market, and glycerol has become a waste difficult to handle. The volumes of glycerol remaining unsold in recent years are a clear example of wasted energy and material resources. This is the reason why intense research activity has started worldwide in order to find an exit to the big amounts of glycerol produced. Glycerol price has experimented constant reduction during the last years. Low glycerol prices allow new interesting applications like the production of high added value chemicals. Effective valorization of glycerol will enable to make more cost effective biodiesel production and to replace fossil fuels as the raw material for the production of commodity chemicals.

Among the different possible transformations of glycerol, the hydrogenolysis to propanediols (PDO) presents special interest due to the big number of applications of both 1,2 and 1,3-propanediol (PDO). 1,3-PDO has traditionally been considered a specialty chemical; it has been used in the synthesis of polymers and other organic chemicals, but its market has been quite small. However, over the past years this situation has changed significantly. 1,3-PDO is a starting material in the production of polyesters. It is used together with terephthalic acid to produce polytrimethylene terephthalate (PTT), which is in turn used for the manufacture of fibers and resins. This polymer is currently manufactured by Shell Chemical (Corterra polymers) and DuPont (Sorona 3GT). 1,2-PDO is a major commodity chemical traditionally derived from propylene oxide, and hence also based on fossil feedstock. It is a widely used commodity chemical that plays a significant role in the manufacture of a broad array of industrial and consumer products, including unsaturated polyester resins, plasticizers and thermoset plastics, antifreeze products, heat-transfer and coolant fluids, aircraft and runway deicing products, solvents, hydraulic fluids, liquid detergents, paints, lubricants, cosmetics and other personal care products. Today, the industry estimates a global demand for 1,2-PDO between 2.6 and 3.5 billion lb/yr [48]. One of the future main markets for 1,2-PDO shall be the substitution of ethylene glycol (EG) in cooling water systems to prevent freezing, as ethylene glycol is harmful to health.

3.4.1. Reaction mechanisms

Glycerol hydrogenolysis to PDOs consists of hydrogen addition and removal of one oxygen atom in the form of H₂O. In order to design efficient catalysts, it is fundamental to understand the mechanism of this reaction. Three main reaction mechanisms have been proposed in the literature, depending on whether the reaction runs on acid or basic catalytic sites and with or without the formation of intermediate compounds:

- i. dehydrogenation – dehydration – hydrogenation (glyceraldehyde route),
- ii. dehydration–hydrogenation,
- iii. direct glycerol hydrogenolysis.

Below, the main features of each mechanism will be discussed

i. Glyceraldehyde route

One of the first studies related to glycerol hydrogenolysis was developed by Montassier et al. [40] in the late 1980s. They suggested that over Ru/C catalyst glycerol is first dehydrogenated to glyceraldehyde on the metal sites. Next, a dehydroxylation reaction takes place by a nucleophilic reaction of glyceraldehyde with water or with adsorbed -OH species. Finally, hydrogenation of the intermediate yields 1,2-PDO (Figure 9). The main controversial point of this mechanism is the initial dehydrogenation step, which is thermodynamically unfavored due to the high hydrogen pressures used [41]. Therefore, in order to shift the equilibrium, glyceraldehyde dehydration should be faster than glycerol dehydrogenation. Otherwise glyceraldehyde would be hydrogenated back to glycerol on the metal sites. Several authors observed that the addition of a base notably increased glycerol conversion, and this was related to the fact that bases enhance glyceraldehyde dehydration [42-44]. It is interesting to point out that when glycerol hydrogenolysis is carried out under alkaline conditions, marginal 1,3-PDO selectivities are measured.

Apart from 1,2-PDO, other products stemming from C-C bond cleavage were also reported when glycerol hydrogenolysis is conducted under alkaline conditions; mainly, ethylene glycol (EG), methanol and methane. It is suggested that glyceraldehyde can either undergo dehydration or retro-aldolization reactions. The so formed intermediates are hydrogenated in the last step to yield the products of C-C bond cleavage. Because both the glyceraldehyde dehydration and glyceraldehyde retro-aldol reaction are catalyzed by OH⁻, the addition of a base increases the glycerol reaction rate but does not improve the selectivity to 1,2-PDO [45].

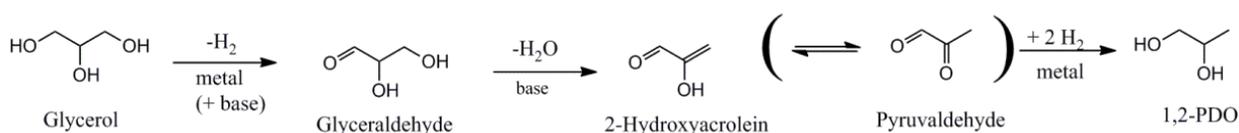


Figure 9. PDO formation from glycerol under alkaline conditions.

ii. Dehydration-hydrogenation route

Dasari et al. [46] observed the formation of acetol (hydroxyacetone) together with 1,2-PDO using copper-chromite catalyst at 473 K and 15 bar hydrogen pressure. Moreover, glycerol hydrogenolysis to 1,2-PDO occurred even in the absence of water. Since the copper-chromite catalyst was reduced in a stream of hydrogen prior to the reaction, no surface hydroxyl species were present to take part in the reaction. Therefore, the mechanism suggested by Montassier et al. (Figure 9) was not able to explain these results. Dasari et al. proposed a new mechanism in which glycerol is first dehydrated to acetol, which is further hydrogenated to 1,2-PDO (Figure 10). Based on their findings, a two step process was developed [47]. In the first step, acetol is generated from glycerol dehydration by a reactive distillation process, operating at 513 K, slight vacuum and using copper-chromite catalyst. The acetol obtained is then hydrogenated at 15 bar H_2 pressure using the same catalyst. The process was patented in the USA in 2005 [48].

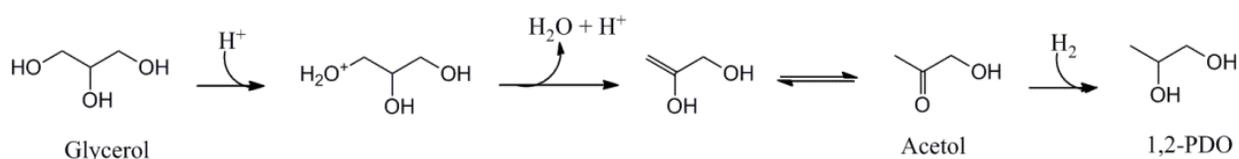


Figure 10. PDO formation via the dehydration-hydrogenation route.

According to Schlaf, acid-catalyzed hydrogenolytic cleavage of -OH group occurs through an initial protonation of the hydroxyl group that leads to the formation of a carbocation and water [49]. Thermodynamically, the formation of a secondary carbocation is more favored than the formation of a primary carbocation. Therefore, operating under acid conditions should bring about higher selectivity to 1,3-PDO. The fact that product distribution is usually shifted towards 1,2-PDO seems to be a complex function of operating conditions, catalyst and starting materials. Ethylene glycol, ethanol, methanol and methane are usually reported as degradation products. Ethylene glycol and methanol are formed from the C-C bond cleavage reaction of glycerol, while ethanol stems from the further hydrogenolysis of ethylene glycol.

iii. Direct glycerol hydrogenolysis

A direct glycerol hydrogenolysis mechanism was recently proposed by Yoshinao et al. [50]. The experiments were carried out using $Rh-ReO_x/SiO_2$ and $Ir-ReO_x/SiO_2$ catalysts at 393 K and 80 bar H_2 pressure. The low reaction temperature implies that the dehydration-hydrogenation route was not further possible, due to the endothermic character of glycerol dehydration and the required activation energy, and suggests the energetically more favored direct hydrogenolysis reaction [51]. They suggested a direct hydride-proton mechanism. The selected catalysts are able to activate hydrogen easily and to form hydride species. It is proposed that glycerol is adsorbed on the surface of ReO_x clusters to form alkoxide species. Glycerol can form two adsorbed alkoxides: 2,3-dihydroxypropoxide and 1,3-dihydroxyiso-

propoxide; it is suggested that the formation of 2,3-dihydroxypropoxide is preferred as it requires a smaller adsorption cross-section than 1,3-dihydroxyisopropoxide [52]. Next, the hydride attack to the 2-position of 2,3-dihydroxypropoxide gives 1,3-PDO, while the hydride attack to the 3-position of 2,3-dihydroxyisopropoxide yields 1,2-PDO. The higher selectivity to 1,3-PDO obtained (1,3-PDO/1,2-PDO ratio = 2.7) is explained on the basis of the higher stability of the six membered-ring transition state that leads to the formation of 1,3-PDO as compared to the stability of the seven membered-ring transition state that leads to the formation of 1,2-PDO (Figure 11).

(a) Glycerol hydrogenolysis to 1,3-PDO (b) Glycerol hydrogenolysis to 1,2-PDO



Figure 11. Model structures of the transition states of the hydride attack to the adsorbed substrate in the glycerol hydrogenolysis [52].

A different direct glycerol hydrogenolysis mechanism was established by Chia et al. [53] trying to explain the hydrogenolysis of different polyols and cyclic ethers over a Rh-ReO_x/C catalyst. They concluded from DFT calculations that the -OH groups on Re associated with Rh are acidic. The acidic nature of ReO_x was also reported before [54]. Such acidic Re sites can donate a proton to the reactant molecule and form carbenium ion transition states. In the case of glycerol hydrogenolysis, the first step involves the formation of a carbocation by protonation-dehydration reaction. This carbocation is stabilized by the formation of a more stable oxocarbenium ion intermediate resulting from the hydride transfer from the primary -CH₂OH group. Final hydride transfer step leads to 1,2-PDO or 1,3-PDO [53]. The authors also reported that the secondary carbocation is more stable than the primary carbocation. Nevertheless, higher selectivity to 1,2-PDO was obtained (1,3-PDO/1,2-PDO ratio = 0.65).

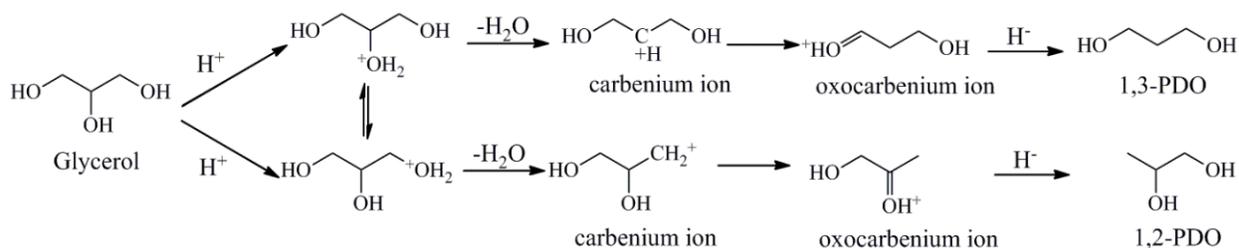


Figure 12. Reaction mechanism for direct glycerol dehydrogenation. Adapted from[55].

3.4.2. Catalytic systems

i. Noble metals

Hydrogenolysis reactions involve the addition of hydrogen to an organic molecule. Therefore, hydrogenolysis catalysts must be able to activate hydrogen molecules. Noble metals are known to be active for the dissociation of hydrogen molecules and are widely used in hydrogenation reactions. The first studies on glycerol hydrogenolysis were carried out using Ru based catalysts [56]. Feng et al. [57] studied the effect of different supports (TiO_2 , SiO_2 , NaY , $\gamma\text{-Al}_2\text{O}_3$) on Ru based catalysts. The TiO_2 supported catalyst exhibited the highest activity giving a glycerol conversion of 90.1%; however, it also favored the production of ethylene glycol over 1,2-PDO. In contrast, Ru/SiO_2 showed the lowest activity, but resulted in much higher selectivity to 1,2-PDO. They also performed blank reactions with the supports, achieving no significant conversions; which indicated that the supports cannot catalyze the reaction independently. Ru particle size was affected by the type of support, and a correlation was established between the size of the Ru particle and the activity of the catalyst, being higher with decreasing Ru particle size.

Apart from Ru, other noble metals have also been studied. For instance, Furikado et al. [58] compared the activity of various supported noble-metal catalysts (Rh, Ru, Pt and Pd over C, SiO_2 and Al_2O_3). Among all the catalysts, the best results in terms of 1,2-PDO selectivity were achieved with Rh/SiO_2 at low reacting temperature and low glycerol conversions (7.2). Nevertheless, the selectivities to 1,2-PDO obtained were rather low, due to the over-hydrogenolysis of 1,2- and 1,3-PDO to 1 and 2-PO.

The use of noble metal-base bifunctional catalytic systems has also been reported. As it was previously described in the glyceraldehyde based mechanism, the dehydration of glycerol to glyceraldehyde, and further dehydration of glyceraldehyde to pyruvaldehyde are both thought to be catalyzed by adsorbed hydroxyls. The effect of different base additives on the performance of Ru/TiO_2 was reported [45]. The addition of Li or Na hydroxides dramatically increased the glycerol hydrogenolysis activity of Ru/TiO_2 and the selectivity to 1,2-PDO. The highest conversion of glycerol (89.6%) and the highest selectivity to 1,2-PDO (86.8%) were observed with LiOH . The selectivity to 1,2-PDO was similar with all the bases added, which showed that the selectivity to 1,2-PDO is independent of base concentration within a certain range. However, the selectivity to ethylene glycol decreased no matter which base was added. Almost no reaction was observed in the absence of Ru/TiO_2 , indicating that the presence of metal is required in order to take place glycerol hydrogenolysis. The lower selectivity to ethylene glycol with increasing base addition to the reacting solution was explained by the fact that ethylene glycol presented higher affinity to adsorb in the surface of the catalyst and to suffer the attack of hydroxyl groups, whose concentration was higher at elevated pH values [59].

Noble metal-acid catalytic systems have also been used. According to the mechanism in Figure 10, glycerol is firstly dehydrated to acetol, which is then hydrogenated to 1,2-PDO. The first dehydration step is supposed to be catalyzed by acid sites while the second one by metal sites. Therefore, one interesting option to increase the selectivity to target product, 1,2-

PDO, is the use of bifunctional noble metal-acid catalysts. Different Bronsted acids like sulfonated zirconia, zeolites, homogeneous H₂SO₄ and Amberlyst 15 were tested together with Ru/C [60,61]. Acid-type cation-exchange resin Amberlyst 15 was the most effective co-catalyst. Nevertheless, a weak point in the system of Ru/C with Amberlyst 15 is that the reaction temperature is limited to 393 K. At higher temperatures sulfur compounds such as SO₂ and H₂S, which are formed by the thermal decomposition of the sulphonic groups of the resins, poison the catalyst. Using Amberlyst 70 the reacting temperature can be increased to 453 K before observing thermal decomposition [62].

Catalyst	H ₂ (bar)	Temp. (°C)	Glyc. Conc. (wt.%)	mg _{cat} /g _{glyc}	Time (h)	Conv. (%)	Product Selectivity (%)	Ref
Ru/TiO ₂ , 5wt%	50	180	20	96	12	90.1	1,2-PDO (21), EG (41)	[57]
Pt/C, 3wt% + CaO 0.8 M	40	200	1	233	5	40	1,2-PDO (71), lactic acid (19), EG (9)	[42]
Ru/C, 5wt% + Amberlyst 15	80	120	20	112.5	10	79.3	1,2-PDO (75), 1-PO(8), 2-PO (2), EG (7)	[63]
Ru/C, 5wt% + Amberlyst 70	80	180	20	12.2	10	48.8	1,2-PDO (70), 1,3-PDO (1.3), 1-PO (7.1), EG (8.3)	[62]
Cu/Al ₂ O ₃ , 60wt%	1	120 -200	30	-	0.066 h ^{-1 a}	100	1,2-PDO (96.9), acetol (1.4)	[64]
Cu/SiO ₂ , 30wt%	90	180	80	62.5	12	32.7	1,2-PDO (98), EG (1)	[65]
Cu _{0.4} /Mg _{5.6} Al ₂ O ₉ + NaOH	30	180	75	166	20	91	1,2-PDO (96), EG (3)	[44]
Pd _{0.04} Cu _{0.4} Mg _{5.6} Al ₂ (OH)	20	180	75	166	10	77	1,2-PDO (98), EG (1.6)	[66]
Ir-ReO _x /SiO ₂ , 4wt% (Re/Ir = 1)	80	120	20	37.5	36	81.0	1,2-PDO (4.2), 1,3-PDO (46.3), 1-PO (41.2)	[72]

^a WHSV (weight hour space velocity)

Table 2. Selected examples of hydrogenolysis of aqueous glycerol over heterogeneous catalysts. PDO: Propanediol, PO: Propanol, EG: Ethylene Glycol.

The use of more stable inorganic salts can avoid the temperature problems related to ion-exchange resins. Balaraju et al. [67] used the combination of Ru/C catalyst with different inorganic salts such as niobia, zirconia-supported 12-tungstophosphoric acid or acid caesium 12-tungstophosphate in glycerol hydrogenolysis at 453 K. The best results were achieved with those co-catalysts presenting a high number of medium strength acid sites. Particularly, with niobia as co-catalyst 62.8% glycerol conversion and 66.5% 1,2-PDO selectivity were reported. Another option is the use of a noble metal on acid supports. Vasiliadou et al. [68] investigated glycerol hydrogenolysis on Ru-based (γ -Al₂O₃, SiO₂, ZrO₂) catalysts at 513 K and 80 bar. The nature of the oxidic support was found to influence the ability of the catalyst to both activate the glycerol substrate and selectively convert it to propanediol. The characterization of the catalytic materials revealed a correlation between catalytic activity for the

hydrogenolysis reaction and total acidity, as the yield to hydrogenolysis products increased with the concentration of the acid sites. However, increased acidity was also responsible for the promotion of the excessive hydrogenolysis of the desired 1,2-propanediol to propanols.

ii. Cu based catalysts

Cu has been extensively investigated in the glycerol hydrogenolysis reactions. Although its hydrogenation activity is generally lower than that of noble metals, its much lower price and its ability to catalyze C-O bond but not C-C bond hydrogenolysis make Cu catalysts attractive for this process. There are some works in the literature that report the use of other transition metals like Ni or Co, however, Cu based catalysts are predominant. Vapor phase glycerol dehydration reaction was studied by Sato et al. [69] over different copper catalysts at 513 K and atmospheric N₂ pressure. They observed that basic MgO, CeO₂, and ZnO supports showed low acetol selectivity, while acidic supports, such as Al₂O₃, ZrO₂, Fe₂O₃, and SiO₂, effectively promoted acetol formation. The best results were obtained with Cu/Al₂O₃ catalyst. Increments in copper content lead to increments in acetol selectivity. Moreover, the activity of the Al₂O₃ support alone was rather low, which indicates that copper metal sites play a significant role in glycerol dehydration. Continuing with vapor phase processes, Akiyama et al. [64,70] studied glycerol hydrogenolysis in a fixed-bed down-flow glass reactor at temperatures between 340 and 473 K, atmospheric hydrogen pressure, and using Cu/Al₂O₃ catalysts. In the two step reaction they observed that glycerol dehydration to acetol was favored at relatively high temperatures. However, acetol hydrogenation to 1,2-PDO was favored at lower temperatures, because it is an exothermic reaction and the dehydrogenation of 1,2-PDO occurs preferentially at high temperatures. Based on these findings, they developed a reactor with gradient temperatures, at the top of the reactor glycerol dehydration reaction occurred at 453 K while at the bottom of the reactor acetol was hydrogenated to 1,2-PDO at 418 K. Really high 1,2-PDO yields (94.9%) were reported.

Some of the best results in terms of glycerol conversion and 1,2-PDO selectivity were recently reported using Cu on base supports. For instance, Yuan et al. [44] developed a Cu based solid catalyst (Cu_{0.4}/Mg_{5.6}Al₂O_{8.6}) via thermal decomposition of the as-synthesized Cu_{0.4}Mg_{5.6}Al₂(OH)₁₆CO₃ layered double hydroxides. This bifunctional highly dispersed Cu-solid base catalyst was effective for hydrogenolysis of aqueous glycerol. The measured conversion of glycerol reached 80.0% with a 98.2% selectivity of 1,2-propanediol at 180 °C, 30 bar H₂ and 20 h. The addition of Pd to the same catalytic system notably increased the activity of the catalyst [71]. It was suggested that the hydrogen spill over from Pd to Cu favored glycerol hydrogenolysis to 1,2-PDO.

iii. Metal oxide modified-noble metal

As stated above, the use of acid or base as a co-catalyst gives 1,2-PDO as a main product. To obtain more valuable 1,3-PDO, the most effective approach has shown to be the use of noble metal (Ir, Rh or Pt) combined with oxophilic metals. Shinmi et al. [52] modified Rh/SiO₂ catalyst with Re, W and Mo. Re addition showed the largest enhancing effect on catalytic activity and also increased the selectivity to 1,3-PDO. The Rh-ReOx/SiO₂ (Re/Rh = 0.5) exhibited 22 times higher glycerol conversion (79%) and 37 times higher 1,3-PD yield (11%) than

Rh/SiO₂. In a more recent work, an Ir–ReO_x/SiO₂ (Re/Ir = 1) catalyst prepared by a similar method to that for Rh–ReO_x/SiO₂, catalyzed the hydrogenolysis of glycerol to 1,3-PDO in a more effectively way (1,3-PDO/1,2-PDO ratio = 11) [72]. Based on characterization results, the authors suggested that oxidized low-valence Re clusters are attached to the Ir or Rh metal particles. Glycerol is adsorbed on the surface of MO_x species (M = Mo, Re and W) at the OH group to form alkoxide. Hydrogen is activated on the noble-metal (Rh or Ir) surface. The alkoxide located on the interface between MO_x and the noble-metal surface is attacked by the activated hydrogen species, and the C–O bond neighboring to the C–O–M group is dissociated. The hydrolysis of the resulting alkoxide releases the product (see Figure 11). One of the weak point of these catalytic systems is that they are also active in the further hydrogenolysis of both 1,2 and 1,3-PDO to 1-PO.

In summary, Cu based catalysts are active and selective for the production of 1,2-PDO from glycerol. However, if the aim is to produce the more valuable 1,3-PDO, different approaches are required. The used of noble metals combined with low-valence metal oxide seems to be a promising alternative. Nonetheless, there is still room for improvement; both in catalyst design and in process engineering, as PDOs further hydrogenolysis significantly affect the final yields to target products.

4. Main alternatives to the use of molecular hydrogen

In the previous sections the significance that hydrogenolysis reactions have and will have in the future bio-refineries has been highlighted. In fact, they will be essential in fuel and chemical manufacturing. Hydrogenolysis involves chemical bond dissociation in an organic substrate and simultaneous addition of hydrogen. Therefore, hydrogen is required as reactant in all hydrogenolysis reactions. This is the reason why, most of the literature works referred to hydrogenolysis report experiments conducted under molecular hydrogen (H₂) atmosphere. Nevertheless, the use of molecular hydrogen has some important drawbacks:

- i. Liquid phase processes are preferred to gas phase processes as they are more energy efficient. However, H₂ presents really low solubility on aqueous or organic solutions. As a consequence, when operating in liquid phase it is necessary to operate at elevated hydrogen pressures to obtain significant hydrogen concentrations near the catalysts. This, on one hand, notably increases the cost of design and building of the future plants, and on the other hand, increases the operating cost related to safety measures, as hydrogen is easily ignited and shows high diffusivity.
- ii. Most of the nowadays available hydrogen gas is produced from fossil fuels by energy intensive processes. Therefore, if sustainability is the goal it is a contradiction that the main reactant in most of the biorefinery processes is based on fossil resources.
- iii. The low density and high diffusivity of hydrogen make problematic and expensive its transportation and storage. This problem is more relevant for small size biomass conversion facilities.

Hydrogen from non fossil origin will surely be a reality in the oncoming years, as reforming processes from various renewable compounds (like biomethane, glycerol or ethanol) and water splitting processes using solar light are being intensively developed. Nonetheless, the problems of transportation, storage and low solubility in liquid solutions will remain. One interesting option that could solve the problems associated to the use of molecular hydrogen is to directly generate the required hydrogen in the active sites of the catalyst.

4.1. Bio-oil upgrading using hydrogen donating solvents

One interesting approach to reduce the consumption of molecular hydrogen during the HDO of bio-oils is to use hydrogen donating solvents. For instance, Elliott has reported that when the bio-oil upgrading is carried out in the presence of a hydrogen donor solvent (tetralin, 1-1 ratio with bio-oil feedstock) the oxygen removal increases from 70 to 85% and less deactivation of the catalyst was observed. Some of the components already present in the bio-oil, such as alcohols or acids, may also provide hydrogen for the deoxygenation reactions [10]. Traditional catalysts active in hydrogen transfer reactions, such as Pd, Ni or Cu should be used in this process [73].

Another attractive option is to use hydrogen donating solvents during the hydrotreating of biomass. The idea is to obtain a bio-oil with a lower oxygen content, and therefore, easier to upgrade. This concept has been mainly applied in the pyrolysis of lignin. If a hydrogen donor molecule is added during the pyrolysis, both depolymerization and hydrogenation occur simultaneously. Remarkable results have been obtained using hydrogen-donating solvents, such as tetralin or 9,10-dihydroanthracene [74]. However, a major drawback is the need for large quantities of these solvents. At this point, formic acid appears to be a promising donor molecule, as it can be obtained together with levulinic acid from the hydrolysis of biomass. On heating, formic acid decomposes completely into CO_2 and two active hydrogen atoms, which are efficient scavengers of any radical species formed in the lignin. By successive homolytic cleavage of the covalent linkages of the lignin, including aromatic rings, most of the oxygen is removed as water and hydrocarbons are formed (Figure 13). When pyrolysis is carried out with formic acid, lignin can be converted into hydrogen-rich, oxygen depleted products with no added catalyst [75].

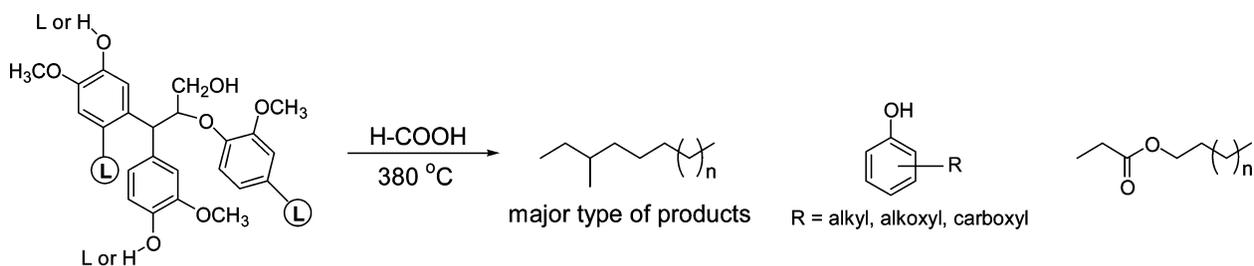


Figure 13. Schematic picture of the products formed upon the pyrolysis of lignin in the presence of formic acid [75].

4.2. Hydrogenolysis with in-situ generation of hydrogen

4.2.1. Aqueous Phase Reforming (APR)

One interesting option to in situ generate the required hydrogen for hydrogenolysis reactions is through aqueous phase reforming (APR). APR is a quite well known process in which a polyol is converted to hydrogen and CO₂ in the presence of water. The hydrogen generated can be further used in the hydrogenolysis reaction. The specific case for combined glycerol APR and hydrogenolysis to 1,2-PDO is shown in Figure 14. If the process is perfectly balanced, glycerol is fully converted into 1,2-PDO, being CO₂ and H₂O the only byproduct. Tailored metal-acid bifunctional catalysts or combination of catalysts are required to obtain high yields to 1,2-PDO. Indeed, there must be a proper balance between the C-C bond cleavage reactions that lead to the production of hydrogen, and the C-O bond cleavage reactions that lead to the formation of PDOs [76]. While Pt is known to be active in C-C bond cleavage, its combination with other metals active in C-O bond hydrogenolysis, like Ni, Sn or Ru, over acidic supports appears as promising formulations to obtain high yields to 1,2-PDO [77]. However, glycerol APR itself runs at elevated pressure and therefore the advantage over conventional hydrogenolysis at high hydrogen pressure is marginal with regard to equipment and safety costs.

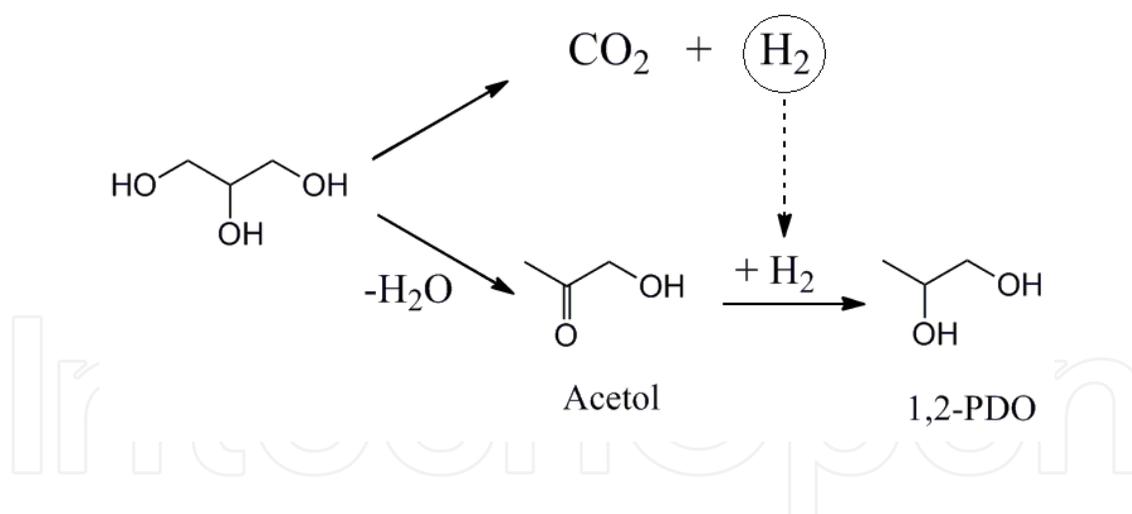


Figure 14. Combined glycerol APR and hydrogenolysis to 1,2-PDO.

The same benefits that have been previously addressed for the use of *in situ* generated hydrogen in glycerol hydrogenolysis can be applied to the conversion of other higher polyols, like sorbitol or xylitol. However, the considerable research effort that has been directed to the conversion of glycerol yet has not been paid to other biomass based polyols. Therefore, the amount of works related to high polyol hydrogenolysis with *in situ* generation of the required hydrogen is quite scarce. As a consequence of this, it is a really interesting and open research field.

Huber et al. [78] studied the production of renewable alkanes (C1-C6) from the aqueous phase reforming of sorbitol using a Pt/SiO₂-Al₂O₃ catalyst. They suggested a multistep bifunctional reaction pathway. The first step involves the formation of CO₂ and H₂ on the Pt sites, and the dehydration of sorbitol on the acid sites of the silica-alumina support. These initial steps are followed by hydrogenation of the dehydrated reaction intermediates on the metal catalyst (Scheme 9). 64 % alkane selectivity at 92% sorbitol conversion were recorded at 498 K and 39.6 bar. When hydrogen was co-fed, alkane selectivity significantly increased up to 91%. Glucose showed to be less active than sorbitol over a Pt/Al₂O₃ catalyst at 538 K and 52.4 bar of N₂ pressure, achieving moderate alkane selectivities (49.5%) [79]. Therefore, it seems that initial hydrogenation of glucose to sorbitol and subsequent aqueous phase reforming of the sugar is more effective than direct aqueous phase reforming of glucose.

4.2.2. Catalytic Transfer Hydrogenation

Catalytic transfer hydrogenation (CTH) is a process in which hydrogen is transferred from a hydrogen donor molecule to an acceptor [80]. CTH reactions can be of industrial importance as the renewable production, transportation and storage of hydrogen donors can be cheaper than those for molecular hydrogen. For CTH, it has been reported that adjacent sites may be necessary for donor and acceptor molecules [73]. Therefore, the first criterion to be fulfilled by the selected hydrogen donor molecules is to be soluble in the compound to be hydro-treated. Moreover, in order to improve the yield of desired products, reactions other than dehydrogenation of the donor should be minimized under the operating conditions. The best hydrogen donors for heterogeneous CTH include simple molecules like cyclohexene, hydrazine, formic acid and formates [81]. Alcohols like 2-propanol (2-PO) or methanol can also be used as hydrogen donors; primary alcohols are generally less active than the corresponding secondary alcohols due to the smaller electron-releasing inductive effect of one alkyl group as against two [82]. The most active catalysts for heterogeneous transfer reduction are based on palladium metal. Other noble metals such as Pt and Rh are also widely utilized. Sometimes, other transition metals such as Ni and Cu have also been reported but for operation at higher temperature [73].

In this area, the most studied process has been the conversion of glycerol into 1,2-PDO. Musolino et al. [83] studied glycerol hydrogenolysis by transfer hydrogenation under 5 bar inert atmosphere, using ethanol and 2-PO as solvents and hydrogen donor molecules over 10PdFe₂O₃ catalyst at 453 K. They observed that complete glycerol conversion and high selectivities to 1,2-PDO could be obtained when the hydrogen came from the dehydrogenation of the solvent. Formic acid has also been used as a hydrogen donor molecule in the glycerol hydrogenolysis process using Ni-Cu/Al₂O₃ catalysts [84]. Under the operating conditions used, formic acid was readily converted into CO₂ and H₂, therefore, a semi-continuous set-up was used to continuously pump formic acid to the glycerol water solution, in order to ensure a constant supply of hydrogen at an appropriate rate [85]. For a constant metal content of 35 wt-% (Ni+Cu), increasing Ni proportion caused an increase in glycerol conversion but also an increase in C-C bond cleavage reactions. Cu is known to be active in the C-O bond cleavage but not in the C-C bond cleavage. The presence of Cu and the creation of a

Ni-Cu alloy notably reduced formation of products $<C_3$. This was related to the fact that C-C bond cleavage reactions are ensemble size sensitive and that the formation of a Cu-Ni alloy causes a decrease in the Ni ensemble size. Therefore, the presence of both metals is required for obtaining high 1,2-PDO yields: Ni to provide high hydrogenolysis activity and Cu to shift the selectivity towards C-O bond cleavage. It was also observed that above a certain metal content, further increments led to a decrease in glycerol conversion. This was correlated to the total acidity of the catalyst that also decreased with increasing metal content. A direct glycerol hydrogenolysis mechanism was also proposed (Figure 15).

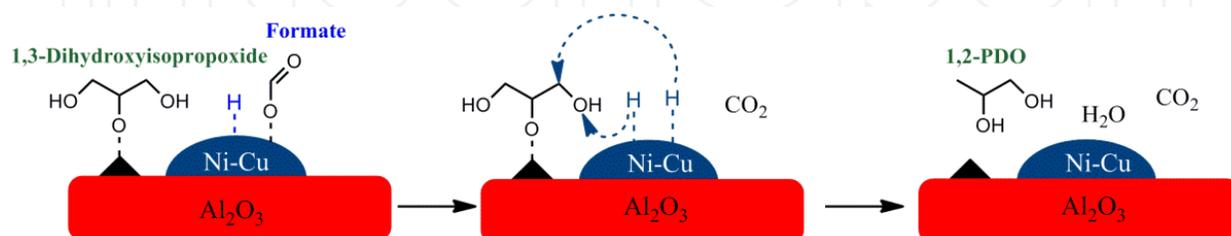


Figure 15. Proposed mechanism for glycerol hydrogenolysis by CTH using formic acid as hydrogen donor molecule [84].

5. Conclusions

Bio-oils coming from the pyrolysis of biomass feedstocks and biomass based platform chemicals present a common limiting feature: their high oxygen content. This oxygen can be removed by catalytic hydrotreating in the form of H_2O . Intensive research is required in this field in order to develop catalytic systems active and stable under the hard operating conditions used: high temperatures and pressures, and high concentrations of sub-critical water. The required bifunctional catalysts must have Brönsted acidity to catalyze dehydration reactions or/and Lewis acid sites to attract the oxygen ion pair of the target molecule; but also metal sites that show the ability to activate hydrogen molecules. In this sense, the combination of oxophilic metals (Re, Mo or W) with Ni or noble metals has shown to be a promising approach. In the case of bio-oil upgrading, the developed catalysts should promote hydrodeoxygenation reactions against hydrogenation reactions that lead to higher hydrogen consumption and reduction in the octane number of the oil. In order to avoid coke formation under the hard operating conditions used, neutral supports appear as an interesting option. In the case of catalysts for platform chemical valorization, C-C bond cleavage reactions should be avoided. Therefore, for some applications, like glycerol hydrogenolysis to 1,2-PDO, Cu based catalysts have to be considered due to the high selectivity of Cu for C-O bond cleavage reactions.

Hydrogenolysis processes for oxygen removal require the use of large amounts of hydrogen, which is commonly supply by operating under high molecular hydrogen pressures. Nonetheless, this might be a problem because nowadays, most technologies to obtain hydrogen are energy intensive and non-renewable. An interesting alternative might be to in-situ

generate the required hydrogen. Among all the alternatives, the use of hydrogen donor molecules that can be obtained from biomass in a renewable way, such as formic acid, appears as a promising approach.

Author details

Iñaki Gandarias* and Pedro Luis Arias

*Address all correspondence to: inaki_gandarias@ehu.es

Department of Chemical and Environmental Engineering, University of the Basque Country (UPV/EHU) Alameda Urquijo s/n, Bilbao, Spain

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