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## **The Rise of Lignin Biorefinery**

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Lignocellulosic biomasses, lignin-first biorefinery, reductive catalytic fractionation, heterogeneous catalysts, hydrogenation, liquid-phase reforming, transfer hydrogenolysis, biofuels, biobased polymer, active pharmaceutical ingredients.

## **Abstract**

Lignocellulosic biomasses, ranging from softwood to agriculture and forestry wastes, represent the most abundant resource for modern biorefinery. In the course of the last years, we have witnessed the rise of “reductive catalytic fractionation” processes of lignocellulosics in which priority attention is given to lignin that is “firstly” converted into aromatic feedstocks. This opinion outlines recent advances in the reductive valorization of lignocellulosic biomasses *via* lignin-first biorefinery approach with particular emphasis on the fundamental catalytic reactions involved in the extraction and depolymerization of lignin as well as in the stabilization of the obtained phenolic units. Finally, a brief overview on the further transformations of lignin derived monolignols and phenolics into added value chemicals, fuels, polymeric materials and active pharmaceutical ingredients is presented.

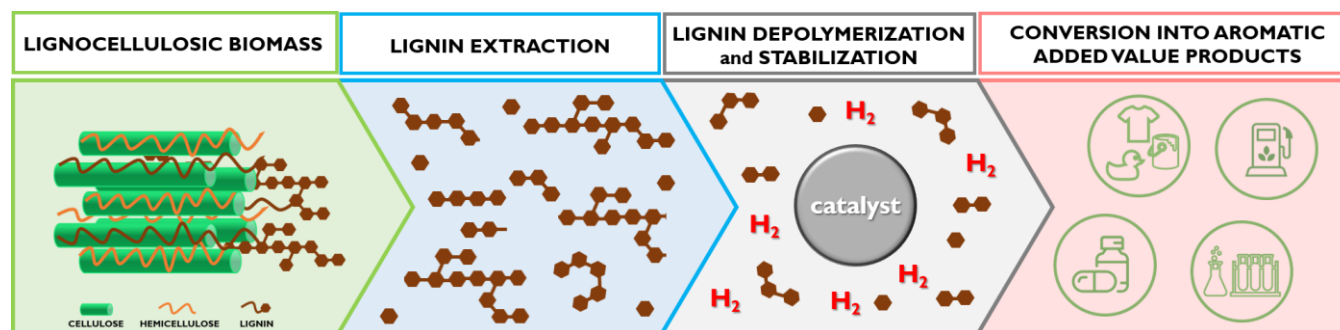
## **The global sustainability context of modern biorefinery**

Industrial chemistry is in the midst of changing its fossil nature by using renewable biomasses and agro-industrial/urban wastes as feedstocks thus reducing, at the same time, its energy and environmental impact [1]. The driving force behind this scenario needs to be found both on new green economy strategies launched by several countries in the world [2] as well as thanks to social movements that are actually strengthening the public awareness of the environmental crisis [3]. In 2019, the Global Climate Strike promoted by the Swedish teenager activist Greta Thunberg has captured the world's attention on the climate change and on the achievement of the Paris goals [4]. In this context, United Nations undersigned the 2030 Agenda for Sustainable Development, an action program where 17 ambitious goals (SDGs) and 169 targets have been implemented to eradicate poverty, to protect the planet and to ensure prosperity for all [5].

Residual and non-edible lignocellulosic biomasses represent key feedstocks for a modern biorefinery for their relative low-price and high quantity availability [6]. Lignocellulosics present a complex chemical architecture characterized by three major constituents such as cellulose (35-50%), hemicellulose (25-30%) and lignin (15-30%) that allow to obtain different and innovative platform molecules [7]. In the course of the years, several biorefinery technologies have been proposed, many of which require physico-chemical pretreatments [8] in order to allow the valorization of holocellulosic (cellulose+hemicellulose) components of biomasses into fuels and chemicals [9] relegating lignin to the role of “ugly duckling”. The native structure of lignin, in fact, was irreparably altered during biorefinery processes thus strongly limiting its chemical upgrading into added value chemicals [10]. However, the native phenolic constituents of lignin are of particular interest for a lignocellulosic biorefinery aimed to the sustainable production of green aromatic compounds. For this reason, the biorefinery approach of the Reductive Catalytic Fractionation (RCF) - where a priority attention is given to the depolymerization of lignin (the so called “lignin-first” biorefinery) - has raised a lot of attention in the last years [11-14].

## The Revolution of “Lignin-first” approach in the catalytic valorization of lignocellulosics

The lignin-first approach is a heterogeneous catalyst-dependent process that involves three elementary steps: solvolysis, fractionalization/depolymerization and reductive stabilization. The obtained monolignol and phenolic units can be subsequently used as feedstocks for the preparation of aromatic chemicals, bio-based fuels, polymers and drugs (Figure1).



**Figure 1.** The revolution of “Lignin-first” approach: from lignocellulosic biomasses to added value products.

The first step in the RCF permits the extraction of lignin from the lignocellulose with short chain alcohols (C1-C4) or cycle ethers (mainly dioxane) generally used as solvolytic solvents as such or in mixture with water (Table 1) [15-22]. The use of organic solvents or their mixture with water takes inspiration from the well-known organosolv processes that allow an effective solubilization of lignin preserving its native structure [8]. The fractionalization/depolymerization and stabilization steps are redox-active catalyst driven. The fragmentation is thermally dependent (200-250°C for 2-6 h) and it is generally enhanced by increasing the polarity of the reaction media [18, 20]. The most adopted catalytic systems are noble metals on a carbon support or other typical hydrogenation/hydrogenolysis catalysts with Pd/C and Ru/C being the most investigated (Table 1) [32]. The redox catalysts activity is foremost crucial in the reductive stabilization of the lignin fragments suppressing repolymerization reactions and formation of condensed lignin products, thus increasing the overall monomer yield (it was demonstrated

that an excessive degree of unsaturation in phenolic units corresponds to a more extensive repolymerization with formation of stable C-C bonds). [23]

**Table 1.** Selected catalytic processes for the reductive upgrading of lignocellulosic biomasses under lignin-first conditions (PS: Propyl Syringol; PG: Propyl Guaiacol ; PohS: 4-n-Propanolsyringol; PohG: 4-n-Propanolguaiacol; PeneS: n-4-Propenylsyringol; PeneG: n-Propenylguaiacol)

Source	Solvent	Catalyst	Reaction conditions	Products	Ref.
Birch	MeOH	Ni/C	240°C, Ar, 6 h	PS, PG, PeneS, PeneG	[15]
Poplar	MeOH	Pd/C	250°C, 20 bar H <sub>2</sub> , 3 h	PohS, PohG, PS, PG	[16]
Poplar	MeOH	Ru/C	250°C, 40 bar H <sub>2</sub> , 15 h	PohS, PohG, PS, PG	[17]
Poplar	MeOH/H <sub>2</sub> O (7:3)	Pd/C	200°C, 20 bar H <sub>2</sub> , 3 h	PohS, PohG, PS, PG	[18]
Birch	EtOH/H <sub>2</sub> O (1:1)	Pd/C	195°C, Ar, 1h	PeneS, PeneG	[19]
Birch	2-PrOH	Pd/C	200°C, 30 bar H <sub>2</sub> , 3 h	PohS, PohG	[20]
Poplar	2-PrOH/H <sub>2</sub> O (7:3)	RANEY® Ni	220°C, N <sub>2</sub> , 18 h	Alkenes and arenes	[21]
Pine	Dioxane/H <sub>2</sub> O (1:1)	Pd/C	195°C, 35 bar H <sub>2</sub> , 24 h	PohG, PG	[22]

### The basic chemistry beyond the lignin biorefinery

Lignin fractionation/depolymerization involves the cleavage of C-C and C-O bonds in the presence of a redox catalyst and a reducing agent. Over the past decades, aromatic ethers have been used in order to mimic the 4-O-5,  $\alpha$ -O-4 and  $\beta$ -O-4 lignin linkages [24-28] with the latter being the realistic target for the production of phenolics in high yield by means of hydrogenolysis reactions [14]. A direct correlation between the amount of  $\beta$ -O-4 in the lignocellulosic substrates and the monomer yield that generally follows the trend softwoods < herbaceous crops < hardwoods has been demonstrated [29, 30]. It is worth to underline that the lignin content and the structure of repeating monomeric-units strongly differ on passing from softwoods (21-29% wt, almost entirely characterized by the presence of guaiacyl units)

to hardwoods (18-25% wt, composed by guaiacyl and syringyl units) and herbaceous (15-24% wt, containing guaiacyl, syringyl and p-hydroxyphenyl units) [7]. An increasing attention has been paid to the use of agro-industrial wastes and residues for their ready and cheap availability as well as engineering crops opportunely designed in order to maximize the yield to desired phenolic compounds [11]. However, at present, the high cost of pretreatments (in the case of waste and residues) or the presence of alterations of the morpho-physiological plant parameters accompanied by a stunted growth (with respect to engineering crops) prevent their direct use for biorefinery purposes.

Together with classical reductive processes (that imply the use of high-pressure  $H_2$ ), indirect hydrogen sources have been used thus allowing, *inter alia*, milder reaction conditions and increased safety processes [31, 32]. For instance, triflic acid [33], formic acid (also generated in-situ) [34] or silanes [35] were efficiently adopted as H-donor additives. Since the pioneering studies of Ford and coworkers, supercritical methanol was utilized to generate the hydrogen necessary through reforming or when used in mixture with  $H_2O$  *via* sequential reforming and water gas-shift reactions (liquid-phase reforming conditions). [36] Instead, when 2-propanol is used as reaction medium, tandem dehydrogenation/hydrogenolysis processes allow the depolymerization of lignin (transfer hydrogenolysis conditions) [21, 37].

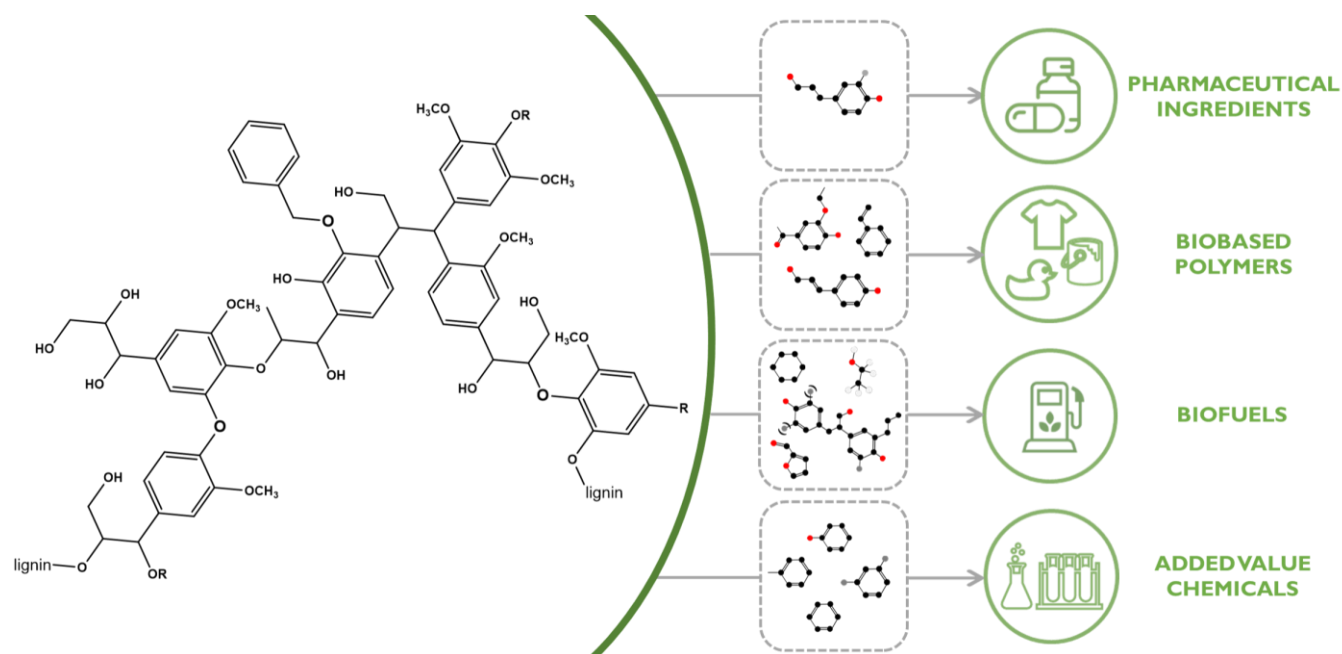
Among all alternatives to the use of molecular hydrogen, the possibility to obtain hydrogen directly from lignocellulose itself is definitively attractive [38]. Even if recent studies demonstrated the self-hydrogen transfer hydrogenolysis of  $\beta$ -O-4 linkages in lignin model molecules [28], the hemicellulose fraction appears to be the best H-donor substrate for the reductive upgrading of lignocellulose without the addition of hydrogen (or H-donor) to the reaction mixture [38]. Hemicellulose was used as internal H-donor source in one of the first contribution of the RCF process under flow conditions in the presence of the Pd/C catalyst by Samec and co-workers [38]. The reductive upgrading of lignocellulose with flow-through systems, if compared with classic batch reactors, offers several advantages including a better control of reaction conditions (that can be opportunely tuned in the course of the RCF process) an



easier catalyst recover/reuse and a catalyst-free pulp that can be directly valorised into other added value products [38-40].

### From phenolic units to added value products

The depolymerization products of lignocellulosics lead to a variety of compounds that can be rightfully considered bio-derived building blocks for the sustainable production of added value chemicals, fuels, polymers and pharmaceuticals (Figure 2) [41-43].



**Figure 2.** A schematic overview of potential added value products of lignin biorefinery.

Since the lignin is strongly linked with holocellulosic fractions, the simultaneous partial degradation of hemicellulose often takes place leading to RCF processes thus affording a variety of C5 derived polyols and furanics. At the same time, once the solid carbohydrate cellulose pulp (intrinsically rich of C5-C6 sugars) is separated from the reaction medium it can be either valorised by enzymatic hydrolysis [44] or via a heterogeneous catalysed hydrogenation/hydrogenolysis process into biofuels [45-49]. Sels and co-workers demonstrated, for the first time, a proof-of-concept valorization of the RFC carbohydrate pulp for the enzymatic production of bio-ethanol [23]. Rinaldi and coworkers recently

presented a “lignin-centered convergent approach” for the reductive conversion of poplar or spruce wood into aliphatic and aromatic bio-hydrocarbons over a phosphidated Ni/SiO<sub>2</sub> catalyst [46]. In these regards, recent reports proposed the use of lignocellulosics for the direct production of jet fuels [47] or bio-derived fuel additives [48].

The increased importance of the use of bio-based products, arisen in consumer attitudes and perceptions, has pushed companies (Avantium, BASF SE, Covestro, DuPont de Nemours, Novamont, Neste and many others) to the production of plastics and materials from renewable monomers. Furthermore, the central role of lignin - as natural source of aromatics for the modern polymer industry - is absolutely clear. Phenolic units obtained as such from lignin deconstruction (e.g. phenylpropanols and propylphenols) have, so far, a limited direct market application [10]. They can be further converted into bio-BTX aromatics (benzene, toluene and xylene) but final sales costs are still too high if compared with those of analogous petrol-derived compounds. However, their impact in the next years can be colossal considering, for example, that the combination of the lignin-derived benzene with bio-ethylene (obtainable from bio-ethanol) could provide a biorefinery route for the production of styrene (global market of \$49 billion in 2018 with a forecast CAGR of 4.5% in 2019-2025) [50].

In a very interesting contribution, it was demonstrated that the lignin oil can be directly used, after reaction with epichlorohydrin, in the production of biobased epoxy resins [51]. Several monolignols and phenolics have been successfully used for the production of biopolymers [52-57]. P-coumaric acid can be used as precursor of polyesters, while epoxy resins can be successfully produced starting either from 4-propylguaiacol and vanillin [58]. Vanillin is a key intermediate of biobased polymers since it can be used, also *via* its oxidative dimer – divanillin, for the preparation of polyacetals, polyaldimines (Schiff base polymers), methacrylates, polyurethans, polybenzoxazines and other conjugated polymers [59]. Bisphenols (obtained via coupling of two phenolic units) and their derived precursors can be used as starting monomers for polycarbonates, polyesters, epoxy resins as well as liquid crystals and optoelectronic conjugated polymers [59].

Phenols and lignans already represent an important class of natural products with pharmacological and nutraceutical properties: it has been reported the use of polyphenols against ischaemic heart disease and the potential application of ligno-phenols in the attenuation of vascular oxidative stress and/or inflammation as well as the anti-inflammatory and antinociceptive properties of the sinapyl alcohol have been reported [60].

Aromatic compounds obtainable from the reductive upgrading of lignocellulose have found also applications as precursors for the production of active pharmaceutical ingredients (API) and other biobased drugs. The research group of Katalin Barta has successfully developed a new synthetic strategy, called “cleave and couple”, in which lignocellosic deriving aromatic and aliphatic compounds undergo transformation through the formation of C-C and C-N bonds [61]. In particular, the authors proposed the use of functionalized phenolic monomers for the preparation of several pharmaceutical active compounds and, very recently, they presented a synthetic protocol for the production of a series of 2-benzazepine derivatives (commonly used as antidepressants) from phenylpropanol [62] opening new frontiers for lignin-biorefinery.

### **Future challenges**

The reductive catalytic fractionation of lignocellulosic biomasses breaks a new ground for a green and sustainable biorefinery. By now, we have all the necessary background to push the production of aromatics from the native lignocellulose under classic batch conditions, however, many scientific and technological challenges are ahead of us. In particular, the use of agro-industrial and domestic wastes as feedstocks, more sustainable hydrogen sources (e.g.  $H_2O$  as in-situ hydrogen donor medium or photo-driven water splitting) and the development of innovative one-pot multistep continuous flow processes for the direct conversion of lignin fractions into pharmaceutical drugs will further increase the overall efficiency and sustainability of the next generation of biorefineries.

## Conflict of interest statement

Authors declare no conflict of interests.

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