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# Electrocatalytic transformation of biosourced organic molecules

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## Abstract

Lignocellulosic biomass represents a very huge renewable carbon reservoir to generate derivatives of paramount interest for producing biofuels or value-added chemicals. The main problem to achieve high conversion rate, selectivity and yield from electrooxidation or electro-hydrogenation/hydrogenolysis of the raw biopolymers constituting lignocellulosic biomass (lignin, cellulose, and hemicellulose) into monomers and oligomers (aromatics, sugars, polyols, acids, furans, etc.) is their low solubility and accessibility to catalysts. The search for alternative bio-sourced media represents an important research axis. Derivatives of these biopolymers are interesting building blocks. But these molecules are very complex in structure and possess different chemical functions making their selective electroconversion difficult. The development of nanostructured catalytic materials adapted for the selective activation/conversion of a given chemical bond/function at low overpotentials is a very huge challenge for the future, as well as the design of reactors allowing the conversion of highly concentrated solutions, in order to integrate these electrochemical processes in biorefinery.

**Keywords.** Lignocellulosic biomass, Electro-hydrogenation/hydrogenolysis, Electrooxidation, (Non)-Kolbe electrolysis, Biofuels, Biobased chemicals.

## 1. Introduction

Electrochemical methods are non-thermal activation processes allowing performing different organic reactions (oxidation/reduction, formation of C-C, C-O, C-N, C-F bonds, etc.) under mild conditions (close to room temperature and pressure) and replacing strong, dangerous, and toxic oxidant/reductive/nucleophilic/electrophilic chemicals by electrons and electrolyte as reactants [1]. Moreover, the catalyst formulation, electrode potential, electrolyte composition, reactant concentrations and flow rate are levers allowing precisely tuning activity and selectivity towards a given product [2]. Organic electrosynthesis has received paramount attention at both laboratory and industrial scales for different applications such as pollutant treatment [3], synthesis of chemicals [4], and energy/hydrogen production [5]. Table 1 gives some examples of organic electrosynthesis processes developed at the industrial scale [1].

Now, the substitution of fossil carbon with renewable carbon is necessary to decrease our impact on the environment and climate change [6]. Amongst the renewable carbon reservoirs, non-edible lignocellulosic biomass from agricultural residues, grass, and forests, is composed of 30-45 % cellulose, 20-50 % hemicellulose and ca. 20 % lignin according to the feedstock [7], which represent very abundant raw materials to produce biofuels and chemicals [8]. Electrochemical activation and conversion of these biopolymers are difficult owing to low solubility in common solvents, complexity, and variability in structure, which hamper catalyst activity. But their derived monomers and oligomers (aromatics, sugars, polyols, acids, furans, etc.) constitute some of the key building blocks for further conversion into biobased chemicals [9]. The present contribution is focused on recent developments and trends concerning the electro-conversion of complex biomass compounds into

chemicals of industrial interest. Owing to their high importance for both raw biomass depolymerization and upgrading, electro-hydrogenation/hydrogenolysis (ECH) [10] and electrooxidation (ECO) [11] will be particularly discussed, but other kinds of reactions, such as Kolbe/(non-Kolbe) electrolysis [9], will also be presented.

## **2. Electroconversion of raw biopolymers**

Although ECH can be performed, ECO represents the most important way to upgrade raw biopolymers, particularly towards carbonyls and carboxylic derivatives [11].

Electrochemical degradation of lignin (non-crystalline three-dimensional biopolymer of mainly phenyl propane units held together by different linkages (Fig. 1)) is expected to give value-added products, such as vanillinic, phenolic, benzaldehyde, acid derivatives, etc. [12]. The activity and selectivity on both noble and non-noble transition metals were studied (Pt, Ni, Co, NiCo, etc. in aqueous alkaline media [13,14], PbO<sub>2</sub> [15] and Ir-based electrode either in aqueous medium [16] or in ionic liquids [17], etc.). The assistance of electron-transfer mediators or of nitroaromatic oxidant can help to decrease the oxidation potential by improving the reaction rate of the cleavage of  $\beta$ -O-4 linkages. But the direct electrochemical conversion of recalcitrant raw lignin still involves different competitive reactions; poor selectivity and yields in value-added products generally lower than 10 wt% are obtained [12,18]. The design of new catalytic systems adapted to the chemical structures of lignin is necessary, but generalization is difficult due to the different kinds of bonds to activate (Fig. 1) and the inherent variability of lignin according to the feedstock.

One interesting strategy could be to first electrochemically modify the biopolymer to introduce new functionalities along the polymer backbone. The selective electrooxidation of lignin primary alcohols into carboxylic acids has been performed in

a H<sub>2</sub>O/CH<sub>3</sub>CN (70/30), NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> electrolyte with TEMPO as a mediator [19]. The water-soluble oxidized lignin could further undergo an acid treatment leading to aromatic monomers with a yield of ca. 30%.

ECO of cellulose [20,21] (linear crystalline polymer of glucose units [22]) and hemicellulose [23] (branched polymers of mainly xyloses and glucoses [24]) on Au electrode in 1.3 M NaOH aqueous solution leads to water-soluble derivatives bearing carboxylic groups and water-insoluble hybrid materials composed of cellulose or xylans and Au nanoparticles. No indication of the structure/composition of products was provided. The recalcitrant nature of biopolymers makes them difficult to depolymerize and selectively form interesting oligomers for further (electro)chemical modifications.

The low solubility of raw biopolymers in aqueous media and their low accessibility to catalysts make difficult the electrocatalytic processes. The search for bio-sourced solvents capable of dissolving biomass or decreasing its recalcitrance is therefore needed [18,25]. For instance, the solubility of cellulose and its accessibility to catalysts was improved using mixtures of levulinate alkyl ammonium ionic liquids,  $\gamma$ -valerolactone and water [26]. These new solvents should have an electrochemical window wide enough to remain stable at high potentials, provide extra-oxygen atoms for lignin oxidation and limit overoxidation into CO<sub>2</sub>. The design of more efficient catalyst compositions/structures [18] must also consider their adaptation to the new chemical environments.

Another strategy consists in previously converting lignin by (physico)chemical or biological treatments into monomers, dimers and oligomers [27] that could be further more facily electrochemically modified.

### **3. Electroconversion of derived oligomers**

### 3.1. Electroconversion of lignin derivatives

Amongst the lignin depolymerization products, phenols, methoxyphenol monomers, and lignol dimers possess the most abundant structures and chemical functions in compounds from lignin pretreatments (Fig. 2) and are of great interest as model molecules in electrocatalytic studies aimed at lignin upgrading [28,29].

ECH of lignin monomers and dimers aims at producing mainly liquid fuels (phenols, hydrocarbon, cyclohexanol, etc.) with yields depending on the catalyst and the molecule structure. At 75 °C on a Raney nickel in 30% NaOH, mixtures of guaiacol and related lignin model monomers produced mainly cyclohexanol derivatives through aryl ether bond cleavage followed by aromatic group hydrogenation, with yields up to 93% and current efficiency between 18 and 26% [30], mainly due to the competitive hydrogen evolution reaction (HER). At 80°C in 0.1 M NaOH aqueous solution, lignin model dimers (3-phenoxyphenol, 4-phenoxyphenol and 3-phenoxyanisole) yielded on Ru/activated carbon cloth catalysts 87% cyclohexanol for 100% conversion with a faradic efficiency reaching 96% [31], through cleavage of 4-O-5 bonds and hydrogenation of aromatic groups. Studies at skeletal nickel showed that the substituent on the carbon atom adjacent to the  $\beta$ -O-4 ether bond ( $C_\alpha$ ), alcohol or ketone, involves steric and electronic perturbations that create a hierarchy of cleavage rates. It is then proposed that selection of experimental conditions, as for example the use of cosolvents, could help to orient the selectivity of the reaction [32].

ECO in aqueous media was historically less studied because reaction products tend to polymerize. The electrooxidation of guaiacol in  $6 \cdot 10^{-3}$  M  $H_2SO_4$  aqueous solution on a  $PbO_2/Nb$  electrode at 70 °C led after 45 min to 94 % conversion; an important quantity of insoluble polymers and low amounts of catechol, methoxyhydroquinone, 3-methoxycatechol, formic, oxalic and maleic acids were obtained [33]. ECO of non-

phenolic lignin model dimers on a Ni anode led also to polymerization as main reaction, and low amounts of aldehydes and corresponding carboxylic acids [34]. But recently, Zhou et al. [35] developed a manganese-doped cobalt oxyhydroxide (MnCoOOH) catalyst allowing via a base-catalyzed mechanism the selective upgrading of lignin derivatives with C(OH)-C or C(O)-C units to benzoate and cyclohexanone/cyclohexanol oil to adipate with 91.5 % and 64.2 % yields, respectively. The study of mineralization of guaiacol into CO<sub>2</sub> and H<sub>2</sub>O in Na<sub>2</sub>SO<sub>4</sub> and NaCl aqueous solutions on Ti/Sb-SnO<sub>2</sub> and Ti/Pb<sub>3</sub>O<sub>4</sub> anodes interestingly showed that maleic acid acted as intermediate in the degradation mechanism. Maleic acid belongs to the top-12 value-added chemicals from biomass [36] and stopping the reaction at this stage represents an interesting challenge.

To overcome the problems of solubility of lignin model compounds, stability of reaction products and high degradation level in aqueous media, ECO of lignin model oligomers is often performed in organic media, with the aim at breaking β-O-4 bonds to yield valuable aromatic molecules. ECO of model dimers containing β-O-4 bonds in 0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN at room temperature leads generally mainly to alcohol-containing molecules, except when the C<sub>α</sub> bears a hydroxyl group, which allows the selective formation of aldehyde derivatives [37]. Often, the reactions are performed in the presence of redox mediators, such as triarylamine, laccase, iodine ion, etc., to improve selectivity [38].

Here again, the search for bio-sourced solvents capable of dissolving lignin derivatives and orienting the selectivity of their reaction is paramount importance, instead of using acetonitrile or other problematic solvents [39]. Design of dedicated nanostructured plurimetallic catalysts optimized for specifically activate a kind of chemical bond are also mandatory.

### 3.2. Electroconversion of cellulose/hemicellulose derivatives

Glucose and xylose are the main sugars from cellulose and hemicellulose hydrolysates [40]. Their acid treatments lead to furfural and 5-hydroxymethylfurfural, respectively, both considered as versatile biobased top-platform molecules for chemicals and fuels [41].

Although xylitol and sorbitol, the main reaction products from xylose and glucose ECH [42], are very important biobased building blocks, relatively few recent literatures are devoted to the study and development of this reaction. Liang et al. [43] studied the ECH of dihydroxyacetone and glyceraldehyde, the simplest monosaccharides, at different pH on platinum and palladium electrodes, and showed that dihydroxyacetone was first reduced into acetol and then into acetone, while glyceraldehyde was first reduced into 3-hydroxypropionaldehyde, then hydrogenated into 1,3-propanediol. In contrast, ECH of furfural and 5-hydroxymethylfurfural in aqueous medium is extensively studied over numerous catalysts at different pH, leading mainly to furfuryl alcohol [44,45], furoin [45] and 2-methylfuran [44] from furfural (FF), and 2,5-dihydroxymethylfuran (DHMF) and 2,5-dimethyl-2,3-dihydrofuran (DMDHF) from 5-hydroxymethylfurfural (HMF) [44]. Monometallic catalysts have different behavior towards HMF hydrogenation according to the pH (Table 2) [44], and the relationship reaction onset potential/overpotential for HER was considered. The development of modified catalysts (nanostructuring and/or formation of binary and ternary alloys) with controlled HER overpotential to improve faradaic efficiency and reactant surface adsorption strength to improve HMF or FF ECH rate/selectivity towards DHMF and furfuryl alcohol, respectively, appears of paramount importance. However, ECH in 0.2 M sulfate buffer (pH 2.0) at -1.2 V vs

Ag/AgCl on Zn electrodes allowed converting 5-hydroxymethylfurfural into 2,5-hexanedione with 81.6% selectivity and 72.4% faradic efficiency [46].

ECO is one of the main studied reactions for polyols and aldoses transformation into value-added compounds. Glycerol, a byproduct of different raw biomass treatment processes, has been studied in aqueous acidic and alkaline media, using platinum-group metals or non-noble metals as catalysts [2]. Main oxidation products on p group-modified platinum catalysts are dihydroxyacetone in acidic media and glyceraldehyde in alkaline media at low potentials, glyceric acid/glycerate at middle potentials and degradation products at high potentials [2]. On Ni-based catalysts, the onset potential of glycerol electrooxidation being higher than 1.1 V vs. the reversible hydrogen electrode, the selectivity is relatively poor and the main products are formate, glycolate and other carboxylates [2,47]. Few articles have been published in recent years on sorbitol electrooxidation. In alkaline aqueous media at Pt/C, Au/C, Pd/C, and Au–Pd/C, the main reaction products are glucose and gluconate [48]. Glucose, xylose and cellobiose possess all an anomeric reductive function in C1 position that is preferably oxidized in alkaline media (glucose oxidation reaction rate is at least 10-fold higher under alkaline in comparison to acidic conditions [49]) on platinum group metals into gluconate, xylonate and cellobionate [42,50]. However, it would be very interesting to oxidize glucose into its di-carboxylate derivative, glucarate, which is an open door for the development of bio-based nylons [49]. This reaction implies oxidation of both the anomeric function (C1) and the primary alcohol (C6). But (electro)oxidation of primary alcohols remains an important challenge in organic chemistry, at least without protecting the anomeric function. Indeed, the electrooxidation of methyl glucoside on Pt<sub>9</sub>Bi<sub>1</sub>/C catalyst led to 100 % selectivity towards methylglucuronate at 40% conversion [51]. However, non-PGM-based

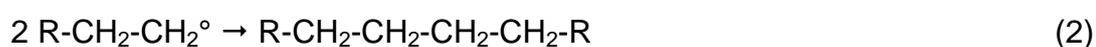
catalysts ( $\text{Ni}_x\text{Fe}_y$  oxide or nitride alloys with flower-like nanostructures) manifest promising activity and selectivity towards the ECO of glucose into glucarate [52]. ECO of HMF into furandicarboxylic acid (FDCA, a precursor of green polymers) is also an interesting reaction and high-profile topic. On Au/C, the oxidation of the primary alcohol is more difficult than that of the aldehyde function, conversely to Pd/C. The formation of FDCA involves then different intermediates at low potentials, 5-hydroxymethyl-2-furancarboxylic acid on Au/C and 2,5-Diformylfuran on Pd/C, then formylfurancarboxylic acid at higher potential and FDCA. In an Anion Exchange Membrane Electrolysis Cell, a  $\text{PdAu}_2/\text{C}$  Alloy yielded 83% FDCA with 100% HMF conversion at the electrode potential of 0.9 V, but other oxidative products were formed involving difficult and uneconomical purification step [53]. Non-noble Ni/NiOOH electrodes gave outstanding performance with yield of up to 90% and faradaic efficiencies up to 80% for the direct electrochemical conversion of 10 wt% HMF at pH 12 in a flow cell [54], but at a cell voltage of ca. 2.0 V (i.e. higher consumption of electrical energy).

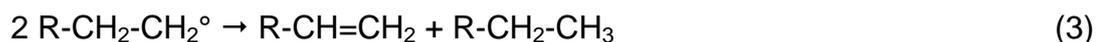
#### 4. Electroconversion of organic acids

Carboxylic acids/esters can be produced from ECO of biomass compounds, biotechnological methods, and transesterification of vegetable oils [9]. They then constitute a large accessible variety of compounds from biomass to produce value-added chemicals or biofuels. The anodic decarboxylation of organic acids into  $\text{CO}_2$  at potentials higher than that of water oxidation forms two  $\text{R-CH}_2\text{-CH}_2^\circ$  radicals.



These radicals can react together and either dimerize forming R-R molecules (Kolbe electrolysis) [55] or undergo disproportionation reaction.

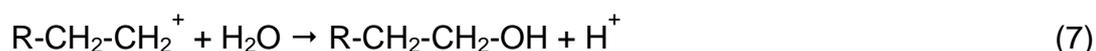
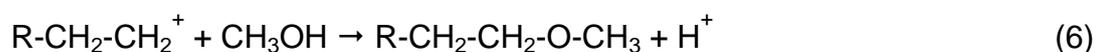




Radicals can also undergo a second electron loss, leading to the formation of carbocations that can react differently according to the environment (non-Kolbe reactions [56]).



Solvolysis in non-Kolbe reaction allows forming esters, ethers, olefins, amides, alcohols (Hofer-Moest reaction), etc.



Kolbe electrolysis is mainly devoted to the synthesis of linear alkanes to produce extremely high-grade biodiesel and biokerosene [57]. The choice of the electrode material and experimental conditions (pressure, co-reactants, organic or biphasic solvents, additives, electrode potential or applied current, etc.) can orient the reaction towards either (non)-Kolbe or Kolbe electrolysis reactions [56], and allow decreasing the competition with the water oxidation reaction occurring at the high electrode potentials needed for those reactions.

## 5. Conclusion and outlooks

Owing to the complex structures of compounds from biomass, which exhibit different chemical functions that can be reduced or oxidized, the development of adapted electrocatalysts is of course of paramount importance to achieve acceptable activity and high selectivity towards the desired product. The catalytic activity is often improved using surface engineering methods, but still, electrocatalyzed biomass conversion leads to the formation of many intermediates and side-products in

addition to the desired one. Therefore, additional purification steps involving use of water or other solvents and consumption of energy are necessary, which increase the cost of the process. However, to integrate electrochemical methods in biorefinery, it is mandatory to demonstrate their advantages over classical biomass treatment methods: high activity and total selectivity are prerequisites, high concentrations of reactants must be used and of products achieved, and electrical energy consumption must be lowered to decrease the OPEX.

Modeling/experiment interactions could help to improve catalytic activity and selectivity by determining the redox potential of given reactant/product couple and developing active sites with the convenient electronic structure for the reaction.

Engineering of electrochemical reactors is another domain that can make electrochemical methods more attractive for biorefinery. Generally, electroconversion of organics is performed in an undivided cell or a divided cell with an ionic conductor separator, under batch or flow configuration [1,12]. Because biomass molecules produced in biorefinery can be either reduced or oxidized into valuable compounds, paired-electrochemical processes can be developed, allowing decreasing the electrical energy cost as value-added compounds are formed at both electrodes. Process intensification can be achieved by the development of microreactors [45]. The coupling of electrochemistry with physical activation techniques, for example ultrasounds (sonoelectrochemistry) [58], light (photoelectrochemistry) [59], etc., can also allow improving selective conversion of biomass.

The selectivity can be controlled by the chemical environment, then the electroconversion of biomass biopolymers or derivatives in ionic liquids or deep eutectic solvents attracts great attention owing to high catalytic efficiency, high solubility of biomass molecules, unique molecular structure, and recyclable property

[17,28]. The use of bio-sourced aprotic solvents, such as  $\gamma$ -valerolactone, also allowed performing electrocarboxylation of furfural to give 2-furyl(hydroxy)acetic acid with a yield of 82% [60].

### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Table 1. A few examples of typical industrial processes based on organic electrosynthesis.<sup>1</sup>**

Chemical function	Reactant	Product	Companies
<b>Anodic oxidation</b>			
C=C	Butene	Methylene ketone	Exxon
C-OH	Propargylic alcohol	Propiolic acid	BASF
Ar-CH <sub>3</sub>	p-methoxytoluene	p-methoxybenzaldehyde	BASF
Arenes	Naphtalene	Naphtaquinone	Holliday
<b>Anodic dimerization</b>			
R-CO <sub>2</sub> H	Adipic acid monoester	Sebacic diester	BASF, Asahi Chemical
	Suberic acid monoester	Tetradecanonic diester	Soda Aromatics
<b>Cathodic hydrogenation</b>			
C=C	Maleic acid	Succinic acid	CERCI
C=N	2-methylindene	2-methylindolin	BASF
C=O	Glucose	Sorbitol/mannitol	CERCI
	Oxalic acid	Naphtaquinone	Holliday
<b>Cathodic dimerization</b>			
C=C	Acrylonitrile	Adiponitrile	Monsanto

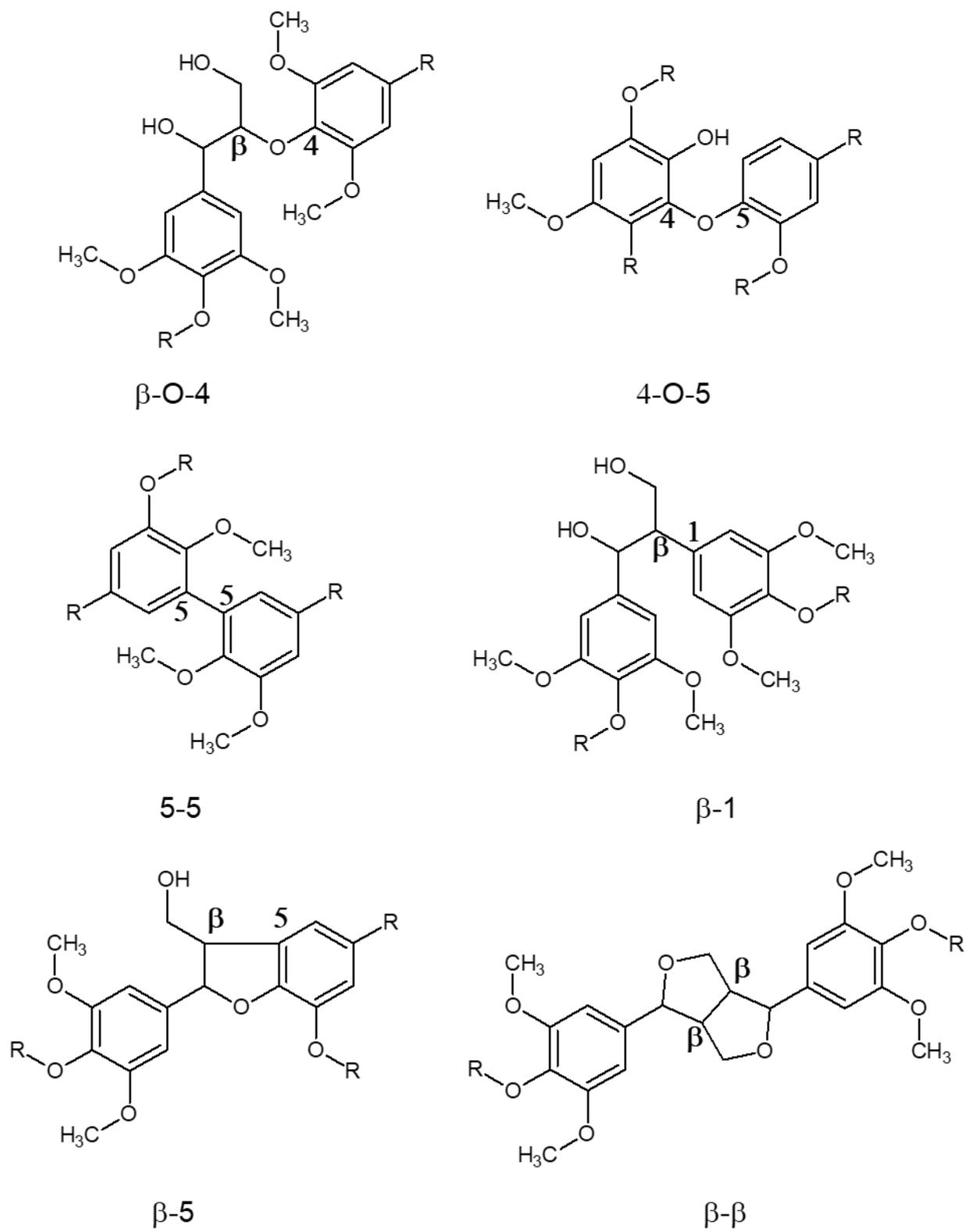
**Table 2. Main products formed on different monometallic catalysts in neutral and acidic environments.**

Neutral medium (0.1 M Na <sub>2</sub> SO <sub>4</sub> )	DHMF	Fe, Ni, Ag, Zn, Cd, In
	DHMF + hydrolysis products	Pd, Al, Bi, Pb
	hydrolysis products	Co, Au, Cu, Sn, Sb
Acidic medium (0.5 M H <sub>2</sub> SO <sub>4</sub> )	DHMF	Fe, Ni, Cu, and Pb
	DHMF + DMDHF	Co, Ag, Au, Cd, Sb, Bi
	DMDHF	Pd, Pt, Al, Zn, In

**Figure caption.**

**Fig. 1.** Commonly proposed linkages in lignin.

**Fig. 2.** Example of chemical structures of molecules issued from depolymerization of lignin.



**Fig. 1**

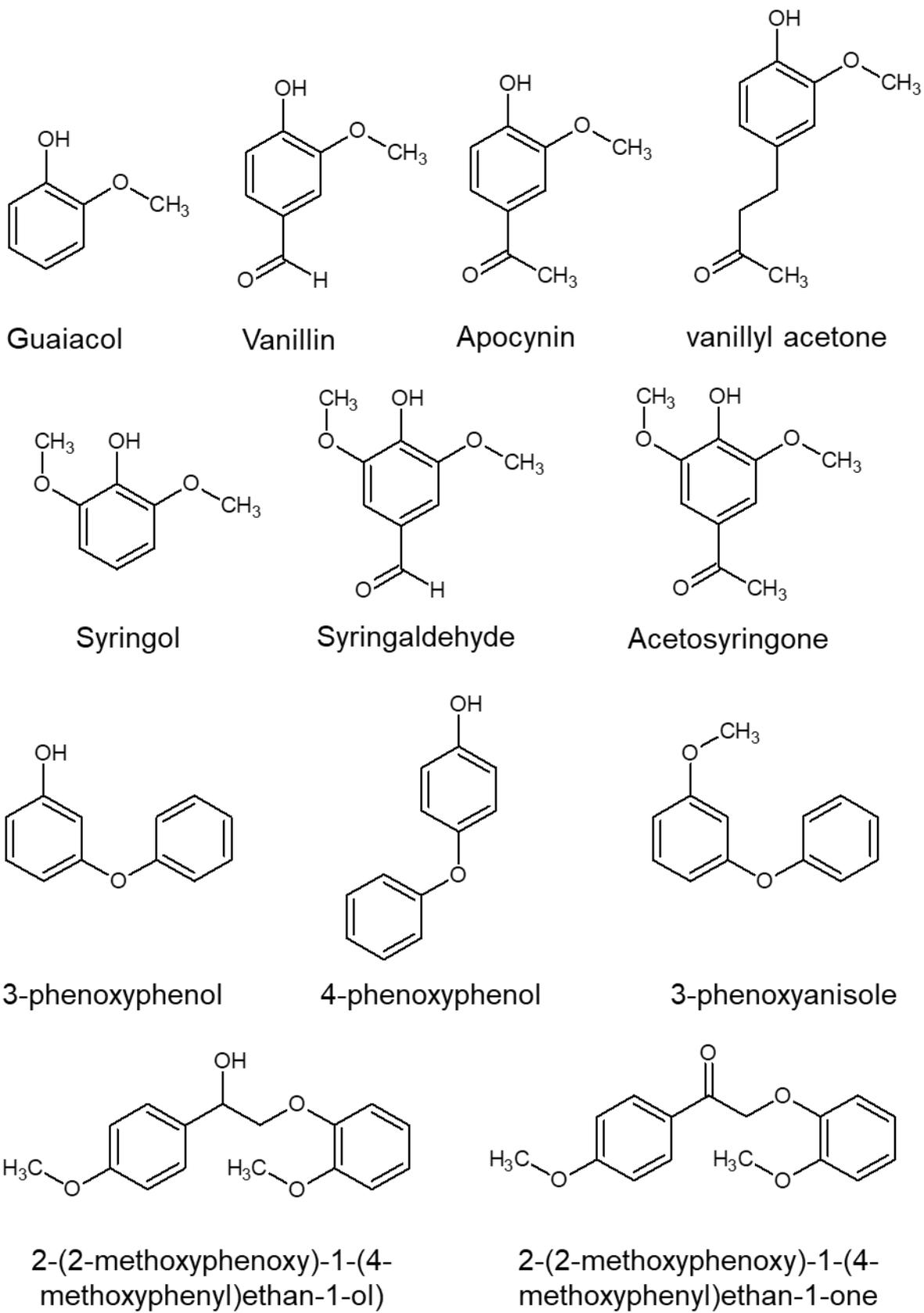


Fig. 2

