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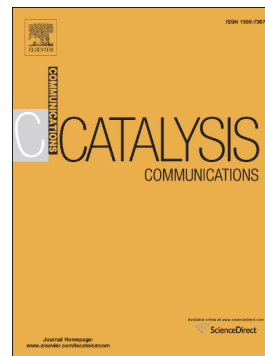
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Oxidative conversion of lignin over cobalt-iron mixed oxides prepared *via* the alginate gelation

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Abstract

The depolymerization of polymer lignin model to low molecular weight products was studied in water, at 200°C under 100 MPa of 10% O₂ using cobalt-iron mixed oxides as catalysts. These nanostructured oxides with different Co/Fe ratios were prepared *via* alginate gelation. X-ray diffraction, scanning electron microscope, and size exclusion chromatography were used to study the influence of the Fe/Co ratios on the structure and the properties of the oxides as well as the morphology, the structure, and the composition of the obtained degraded products. The results showed that the oxides used in this study were versatile catalysts with a high catalytic activity for lignin depolymerization. Furthermore, these oxides demonstrated high yield and high selectivity towards aromatic compounds.

Keywords. Heterogeneous catalysis, Biomass, lignin, Catalytic processes, Catalyst preparation

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1. INTRODUCTION

The development of environmentally friendly processes for the production of biofuels and bioproducts based on renewable resources are rapidly increasing the availability of different types of lignin. Therefore, while the fossil resources are declining, this natural polymer has been seeing as a major renewable source for energy, materials and chemicals [1]. It can be converted to commercial products via biological, chemical or thermo-chemical processes. However, its valorization is still in the early stage due to the diversity of its botanical sources (softwood, hardwood, eucalyptus, annual plants), the type of pulping processes from which it is generated (kraft, soda, organosolv, etc...), the complexity of its structure and variability of its p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, and the diversity of its functional groups, etc.) (Fig.S1). Among several lignin fragmentation approaches studied in the literature, the oxidative depolymerization has been viewed as a promising method for the conversion of lignin to small phenolic compounds such as vanillin, syringaldehyde and p-hydroxybenzaldehyde [1-6]. Many homogeneous and heterogeneous catalysts have been used for the oxidation of both lignin and lignin model compounds. The studies were performed in ionic liquids, acidic, alkaline or organic media. For example, vanillin was produced from lignin in concentrated alkaline medium, under oxygen pressure, in the presence of a transition metal [2, 3]. Das *et al.* [7] studied the depolymerization of alkaline lignin in aqueous 1-ethyl-3-methylimidazolium acetate $C_2C1Im][OAc]$ under oxidizing conditions using several transition metal salts. The major degradation products obtained in this study were guaiacol, syringol, vanillin, acetovanillone, and vanillic acid. To control the production of guaiacol and phenols after lignin depolymerization, Shu *et al.*[8] tested Pd/C catalysts with metal chloride [8]. They

showed that the addition of ZnCl_2 and CrCl_3 to Pd/C promoted the production of high amounts of guaiacol and phenols, respectively. More recently, Lyu *et al.*[9] used alkaline oxidation with molecular oxygen to depolymerize lignin to aromatics and organic acids. They found that using oxygen under high temperature and long time, more vanillin and organic acids were produced, while under oxygen deficient condition, the primary product was p-coumaric acid [9]. One of the major drawbacks of most of the lignin depolymerization processes is the char formation which has a negative impact on the yield of the obtained low molecular weight fragments. To overcome this problem, Okuda *et al.*[10] suggested the use of phenol in supercritical water. Chen *et al.*[11] tested mesoporous catalysts SBA-15 and a series of other modified mesoporous catalysts. They prevented char formation after the depolymerization of hydrolyzed lignin in ethanol solvent at 300 °C for 4 h using Ni/Al-SBA-15 catalyst. Other scientists suggested the use of metal oxides [12]. Recently, Tricobalt tetroxide (Co_3O_4) and Hematite ($\alpha\text{-Fe}_2\text{O}_3$) have attracted more attention as stable metal oxides. They have been used in toluene oxidation [13] as well as carbon monoxide and methane oxidation [14]. Several methods have been suggested for their synthesis. Unfortunately, most of them are based on nonrenewable sources. Therefore, due to the growing interest for the protection of the environment and the stricter regulations against toxic substances, researchers have been looking for green alternatives with regards to raw materials [15], reaction media, and mediators used in such synthesis paths. In this context, polysaccharides have been considered as a promising candidate that controls the size and the morphology of metal oxides. Among several polysaccharides, alginate has been considered as one of the most investigated anionic biological polysaccharide due to its functional groups content (carboxyl, hydroxyl). It is isolated mainly from brown algae and has a cation exchange capacity of $5.6 \text{ mmol} \cdot \text{g}^{-1}$. Its annual production is estimated to be around 36,000 tonnes per year [16].

The current study focuses on the preparation of cobalt and iron oxides using the alginate gelation process and their use, separately or as a mixture, in a new aqueous catalytic system for the depolymerization of lignin polymer models (Fig. 1).

2. MATERIALS AND METHODS

2.1. Synthesis of coniferyl alcohol: 4-hydroxy-3-methoxy cinnamyl alcohol

Coniferyl alcohol was obtained according to the procedure described by Ludley and Ralph [17]. Briefly, coniferaldehyde (4 g, 22 mmol) was dissolved in ethyl acetate (250 ml) and then in sodium borohydride (1.67 g, 44 mmol). The reaction mixture was stirred overnight. A yellow precipitate was formed and poured in water (250 ml). This new mixture was stirred for 1h, followed by three successive liquid-liquid extractions. The organic fractions were combined and dried over magnesium sulphate. Finally, the solvent was removed by rotary evaporation and the solid residue was recrystallized in dichloromethane/hexane mixture, giving a pure coniferyl alcohol at 82 % yield (Fig.S2a).

2.2. Synthesis of Sinapyl alcohol: 4-hydroxy-3,5-methoxy cinnamyl alcohol

Sinapyl alcohol was obtained as follows according to the procedure described by Ludley and Ralph [17], Quideau et al. [18] and Barakat et al [19]: 4-acetyl-sinapylaldehyde (b) was prepared at 90% yield by acetylation of Sinapylaldehyde (Fig.S2b) with acetic anhydride/pyridine (1/1). The 4-acetyl-sinapylaldehyde was dissolved in dichloromethane to which borane/tert-butylamine complex (1.5 eq) was added. The mixture was stirred at room temperature for about 4h. The reaction was stopped when the starting material had completely disappeared. The solvent was evaporated under reduced pressure. The residue was hydrolyzed with 0.5M sulfuric acid in ethanol/water (1/1) for 2 h. Ethanol was removed by evaporation, and the product was extracted

with ethyl acetate. The ethyl acetate solution was washed with saturated ammonium chloride and dried over magnesium sulphate. The solvent was removed by rotary evaporation and the solid residue was recrystallized in dichloromethane/hexane mixture, giving a pure 4-acetyl-sinapyl alcohol (Fig. S2b) at 70 % yield. 4-acetyl-sinapyl alcohol (400 mg) was dissolved in pyrrolidine (5 mL). Once the dissolution was complete, the obtained solution was diluted with 100 mL of ethyl acetate and washed with 1M sulfuric acid (3 x 50mL) and saturated with ammonium chloride (3x 50mL). After drying over magnesium sulphate and evaporation, the solid residue was recrystallized in dichloromethane/hexane mixture, giving a pure sinapyl alcohol (d) at 60 % yield (Fig.S2).

2.3. Synthesis of lignin model polymers

Lignin model polymers are synthetic analogues of lignin. They are polymerized by peroxidase from lignin monomers (Fig.S2). Two bulk lignin model polymers were prepared using Zulaufverfahren method (ZL) [20]: Guaiacyl-syringyl (GS) based lignin polymer, which is an angiosperm lignin model (composed of G and S units), and Guaiacyl (G) based lignin polymer which is a gymnosperm lignin model (consists almost entirely of G units). The polymerization reaction of G and GS lignin monomers in the presence of peroxidase/hydrogen peroxide was run under a gentle stirring for 4 h at 25°C. The mixture was left to react overnight. Lignin models were collected by centrifugation, washed with dichloromethane and water, and then freeze dried.

2.4. Characterization of lignin polymer model

The initial lignin models and the residue (after catalysis reaction) were characterized using size-exclusion chromatography (SEC) [20]. The samples were acetylated in a mixture of acetic anhydride/pyridine (1:1) for 24 h at 40°C. The reaction products were then poured into ice water

and extracted with dichloromethane (3x30 mL). Organic layers were washed with dilute hydrochloric acid (2x20 mL), saturated sodium bicarbonate solutions (2x20 mL), and finally water (3x20 mL). The organic fractions were dried over magnesium sulphate and concentrated under reduced pressure to recover the acetylated lignin model. The SEC analyses were performed using a multi-detection system consisting of a pump (model 510, Waters), autosampler (U6K injector, Waters), two Polymer Laboratories columns (PLgel Mixed D, 5 μ) and refractive index (RI) detector (model 920, Waters). THF was used as an eluent. 100 μ L of 0.1 % of acetylated samples were injected into thermostatically controlled PLgel columns (40°C). The flow rate was 1ml/min. Determination of the average molar mass was done based on the elution of polystyrene standards. Synthetic lignin polymers were also analyzed by thioacidolysis to estimate the content of β -O-4 linked structures according to Jacquet et al. [21]. The main degradation products were analyzed by GC as TMSi derivatives using a J&W Scientific column (DB 1, 30m x 0.25 mm x 0.25 μ m film), FID detection and tetracosane as an internal standard.

2.5. Preparation and characterization Cobalt-Iron oxide

In continuation with our previous works [22, 23], cobalt-iron oxides with different Co/Fe ratios were prepared using the alginate gelling method. 2wt% aqueous solution of sodium alginate was prepared under a gentle stirring for 3h at room temperature. 60 ml of the obtained solution was added dropwise into a 100 ml of homogeneous metal solution containing Co²⁺, Fe³⁺, Fe²⁺ or a mixture of Co²⁺/Fe²⁺/ Fe³⁺ with a total concentration of 0.15M. The obtained hydrogel beads were left in the metal solution overnight under a gentle stirring. The beads were then removed from the solution, filtered, washed and dried in an oven at 40°C. To convert the hydrogel beads to the desired oxide, the beads were calcinated during 4h at 600°C. The phase of the products

was determined by a powder X-ray diffraction, using a Bruker D2 PHASER diffractometer, with the Bragg–Brentano geometry, CuK α radiation ($\lambda=1.5418$ Å) with 30KV and 10 mA. The pattern was scanned through steps of 0.010142° (2 θ), between 10 and 80°. The morphology and the size of the products were observed by scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM/EDS).

3.2. Oxidative catalytic depolymerization of lignin model polymers

The whole catalytic depolymerization process is shown in Fig.1. Experiments were conducted in a reactor of 500 cm³ (Parr 5500, USA). The reactor was loaded with 50 mg polymer lignin, 10 mg of catalyst, 30 mL of distilled water and 100 MPa of 10% O₂ in N₂. The mixture was heated for 2h at 200°C, and then the mixture was extracted with CH₂Cl₂. The organic solution was dried over MgSO₄ and evaporated under reduced pressure. The residues were dissolved in 1mL of CH₂Cl₂ in the presence of internal standard. The analysis of the organic phase was performed on a system GC/MS-QP 2010 Shimadzu, equipped with a SLB-5MS capillary column (30 m x 0.25 mm x 0.25 μ m), using helium as a carrier gas. The temperature was ramped at 10 °C/min from 80 to 250 °C, where it was kept for 10 min. The residue after CH₂Cl₂ extraction was dissolved in dioxane/water (90:10) and filtered to eliminate the catalyst. The dioxane was evaporated under reduced pressure at 50°C and the residues were dissolved in dioxane (3 mL) and freeze dried and analyzed by SEC.

3. RESULTS AND DISCUSSION

Two bulk synthetic lignin polymers (GS-based polymer: a model of an angiosperm (mixture of G and S units), and G-based lignin polymer: a model of a gymnosperm lignin (composed mainly of G units)) were prepared and characterized after thioacidolysis using size-exclusion

chromatography (SEC). The results show that G-based lignin model has a molecular weight of 2380 g/mol and a β -O-4 of 467 $\mu\text{mol/g}$ lignin while GS-based lignin model has a molecular weight of 2050g/mol and a β -O-4 of 662 $\mu\text{mol/g}$ lignin (Table S1). The obtained results are in good agreement with reported data from literature [20, 24]. The content in β -O-4 bonds in G-based lignin model is lower as compared to that in GS-based lignin model, which is in agreement with previously published data [21]. The molecular weight of the G-based lignin model is higher than that of GS-based lignin model, and is close to that of organosolv lignin. The polydispersity index (PI) was 2.3 and 2.7, respectively for G-based lignin model and GS-based lignin model, indicating a wide range of molecular weight distribution. However, the obtained polydispersity index remains closer to that of many polymers that are currently used in the polymer industry (PI around 2). Therefore, these polymers can be considered as good models for industrial lignins. In summary, the composition of the obtained product in terms of G, S units and level of β -O-4 bonds gives an idea about the dependence of the catalytic process on the substrate's molecular structure.

3.1. Characterization of cobalt-iron mixed-oxides

The reaction between Co^{2+} , Fe^{3+} , Fe^{2+} and the alginate functional groups such as hydroxyl and carboxylic acid groups enable the nucleation and the growth of nano-oxides nuclei that, after the calcination step, get converted to metal oxides nanoparticles. The obtained oxide phases depend essentially on the ratio of metal cations. The results of the XRD analysis of the obtained oxides were summarized in Fig.S3. After consecutive thermal treatment of Co–alginate and Fe–alginate xerogels, pure cubic spinel Co_3O_4 (Fig.S3-a) and hematite $\alpha\text{-Fe}_2\text{O}_3$ were produced (Fig.S3-c). The peaks shown in Fig.S3-a at 2θ values of 18.96, 31.23, 36.71, 38.43, 44.76, 55.61, 59.16, 65.07 correspond to the diffraction planes (111), (220), (311), (222), (400), (422), (511), (440).

This phase is assigned to Co_3O_4 face-centered cubic structure belonging to Fd-3m space group. When the iron concentration reached 50% of the total solution concentration, a transition zone was observed. Both $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4$ and $\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$ co-exist (with abbreviation of CoFeO) (Fig.S3-b). The textural analysis of the as-synthesized mixed-oxides was achieved by determining specific surface area (S_{BET}) and pore volume. $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$, (CoFeO) mixed oxide has greater porosity and specific surface area compared to $\alpha\text{-Fe}_2\text{O}_3$ and Co_3O_4 oxides. More precisely, the CoFeO mixed oxide comprised a total pore volume ($0.045 \text{ cm}^3/\text{g}$) that was lower than that of the $\alpha\text{-Fe}_2\text{O}_3$ ($0.07 \text{ cm}^3/\text{g}$), which is similar of Co_3O_4 ($0.07 \text{ cm}^3/\text{g}$). The S_{BET} for the CoFeO was $42.7 \text{ m}^2/\text{g}$ compared to only $31.3 \text{ m}^2/\text{g}$ for Co_3O_4 and $24.4 \text{ m}^2/\text{g}$ for $\alpha\text{-Fe}_2\text{O}_3$. The SEM was used to characterize the surface topography and the morphology of the as-synthesized oxides (Fig.S4). Each material showed a particular morphology. Alginate biopolymer acts as a sacrificial bio-temple [25], and a nanoreactor [26] that controls the nucleation and the growth of the nanoparticles [13]. $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$ (CoFeO) oxides showed a flake/spherical-like morphology following the same shape of hematite and spinel nano-oxide (Fig.S4-B). Polyhedral with octahedral-like morphology was formed for $\alpha\text{-Fe}_2\text{O}_3$ (Fig.S4-C). Fig.S4-D shows a spherical-like particle with an average diameter of about 39 nm for Co_3O_4 . The cubic spinel structure must give a cubic morphology owing to the privileged growth along the axes (100). However, this shape exhibits an isotropic evolution providing spherical particles which is in concordance with the result reported by Givanneli *et al.* [27].

3.2. Oxidative catalytic depolymerization of lignin model polymers

The whole catalytic depolymerization process is shown in Fig.1. For both polymers G and GS-based lignin models, the effect of two separated catalysts and that of a combination of two catalysts were tested (Co_3O_4 or $\alpha\text{-Fe}_2\text{O}_3$, and $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$). More than thirty

molecules were identified during the catalytic fragmentation of the lignin polymers. Their structures were summarized in Fig.2. As expected, most of the detected molecules were phenyl derivatives having different level of oxidation. Some alkylbenzene derivatives were also found. The presence of the two different monomers G and S make very hard and very complex the control of the lignin depolymerization. Nonetheless, the three types of catalysts used in our study demonstrated good conversion and relatively high selectivity for some compounds (Fig.3 and Table 1). The mixed-oxide $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$ showed the highest conversion rate for both G and GS-based lignin models (67.4% and 69.6%, respectively) (Table 1). As it is shown in Fig.2 & 3, the obtained products belong to the families of aromatic alcohols, alkylbenzene, aromatics aldehydes/ketones and aromatic acids. Fig.3 and Table 1 show the selectivity of each catalyst for both types of lignin models (G and GS-based lignin models). As shown in Fig.3, the selectivity of the catalysts was different with respect to the type of the substrate. In the case of GS-based lignin model, mixed oxide (CoFeO) showed the highest selectivity for acids followed by alkylbenzenes. However, Fe_2O_3 showed the highest selectivity for aldehydes (48%) with 30% yield and 64% conversion, followed by alkylbenzenes, alcohols and acids, respectively. Using the same substrate (GS-based lignin model), the selectivity of Co_3O_4 was different from that of the other two catalysts. The highest selectivity was obtained for alcohols, followed by aldehydes, alkylbenzenes, and acids, respectively. In the case of G-based lignin model, it was clear that the three catalysts were more selective for alkylbenzenes. The highest selectivity was obtained by using mixed-oxide followed by Fe_2O_3 and then Co_3O_4 . In the case of mixed oxide (CoFeO), Fe_2O_3 and Co_3O_4 , the yield was, respectively, 39%, 30% and 27%, at 60% conversion. For the same order of catalysts, the selectivity was 56%, 48%, and 45%, respectively. Furthermore, mixed oxide and Co_3O_4 had similar order of selectivity: alkylbenzenes followed by aldehydes,

acids, and then alcohols. Using, this substrate (G-based lignin model), Co_3O_4 produced aromatic alcohols at 24% yield and 40% selectivity. However, the order of selectivity of the Fe_2O_3 towards the four families of compounds was different as compared to that of the two other catalysts: alkylbenzenes followed by alcohols, acids, and then aldehydes, respectively. The selectivity of Fe_2O_3 and mixed oxide (CoFeO) for alcohols was lower compared to that of Co_3O_4 . It was 19.15% at 62% conversion rate for Fe_2O_3 and 2.36% at 67.37% conversion rate for mixed oxide. These results showed that the selectivity for alkylbenzenes, aldehydes, alcohols or acids depends on the type of the catalysts and the nature of the substrate. Since the determination of the molecular weight of any raw material including lignin is important for the manufacturing of several high value-added products such as bio-composites and biopolymers, the size exclusion chromatography (SEC) was used to determine the average molecular weight (M_w) of fractionated lignin models. The results are presented in Fig.4 and Table 2. As it is shown in this figure, a good separation was obtained for both substrates. GS and G-based lignin models had a multimodal molecular distribution with an average molecular weight (M_w) of 2250 and 2030, respectively (Table 2). The fragments obtained from G-based lignin model had a M_w of 340, 360, and 320 Da using Co_3O_4 , Fe_2O_3 and CoFeO mixed oxide ($\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$), respectively. In the case of GS-based lignin model, the obtained fragments had an M_w of 370, 430, and 340 Da using Co_3O_4 , Fe_2O_3 and CoFeO oxide, respectively. The decrease in M_w demonstrated the oxidative depolymerization effect of the three catalysts on the lignin polymer models.

It is worth well mentioning here that the current solid-based catalytic system has several advantages as compared to other types of lignin hydrolysis systems such as the base-catalyzed liquid-phase systems. The major advantage is the recyclability of the solid catalyst. Q. Song et al.

[28] reported that their Nickel-based catalysts could be recycled by magnetic separation and reused for four times without losing activity. The second big advantage of such heterogenous catalytic system is the possibility of obtaining high yield of low molecular weight products. In the base-catalyzed liquid-phase system, the highly reactive products get polymerized quickly, thereby, limiting the amount of the final product containing low-molecular-weight phenolic compounds [29]. This difference in the yield of low molecular weight products could be related to the porosity and the high specific area of the porous solid-based catalytic systems.

4. CONCLUSION

The development of new approaches for lignin depolymerization is quite challenging due to the complexity of its structure. While simplified model compounds often lack relevance to the real chemistry of lignin, the use of industrial lignins poses significant analytical challenges due to the complexity of the lignin structure and the lack of reproducibility in terms of the lignin chemical and physical properties. Ideally, new methods and processes should be tested on model compounds that are complex enough to mirror the structural diversity of lignin, but still of sufficiently low molecular weight to enable a facile analysis. In this study, two synthesized lignin models were depolymerized using three types of catalysts that were synthesized using alginate gelling method: Co_3O_4 , Fe_2O_3 and $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$ mixed oxide. The three catalysts demonstrated a high catalytic activity during lignin depolymerization. Molecular weights of the final products were lower than that of the original lignin polymer models indicating depolymerization of lignins to small aromatic products via **catalytic** oxidation.

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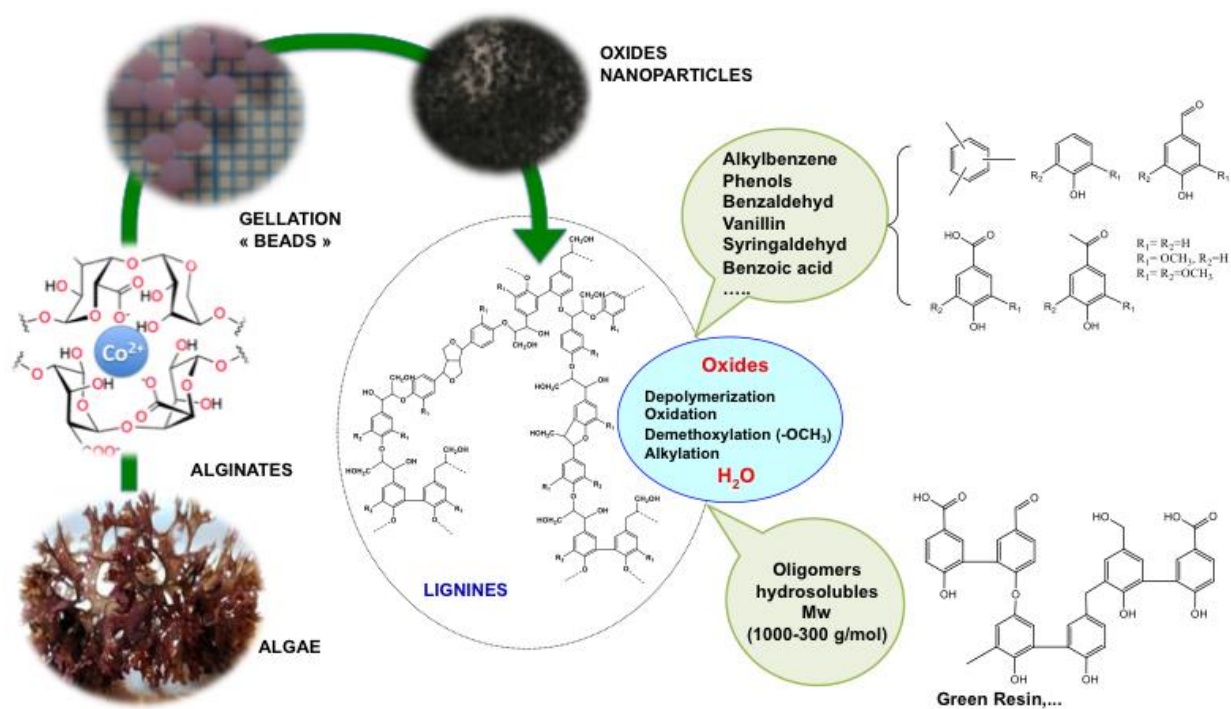


Fig.1. Catalytic depolymerization of lignin in water using cobalt-iron mixed-oxides

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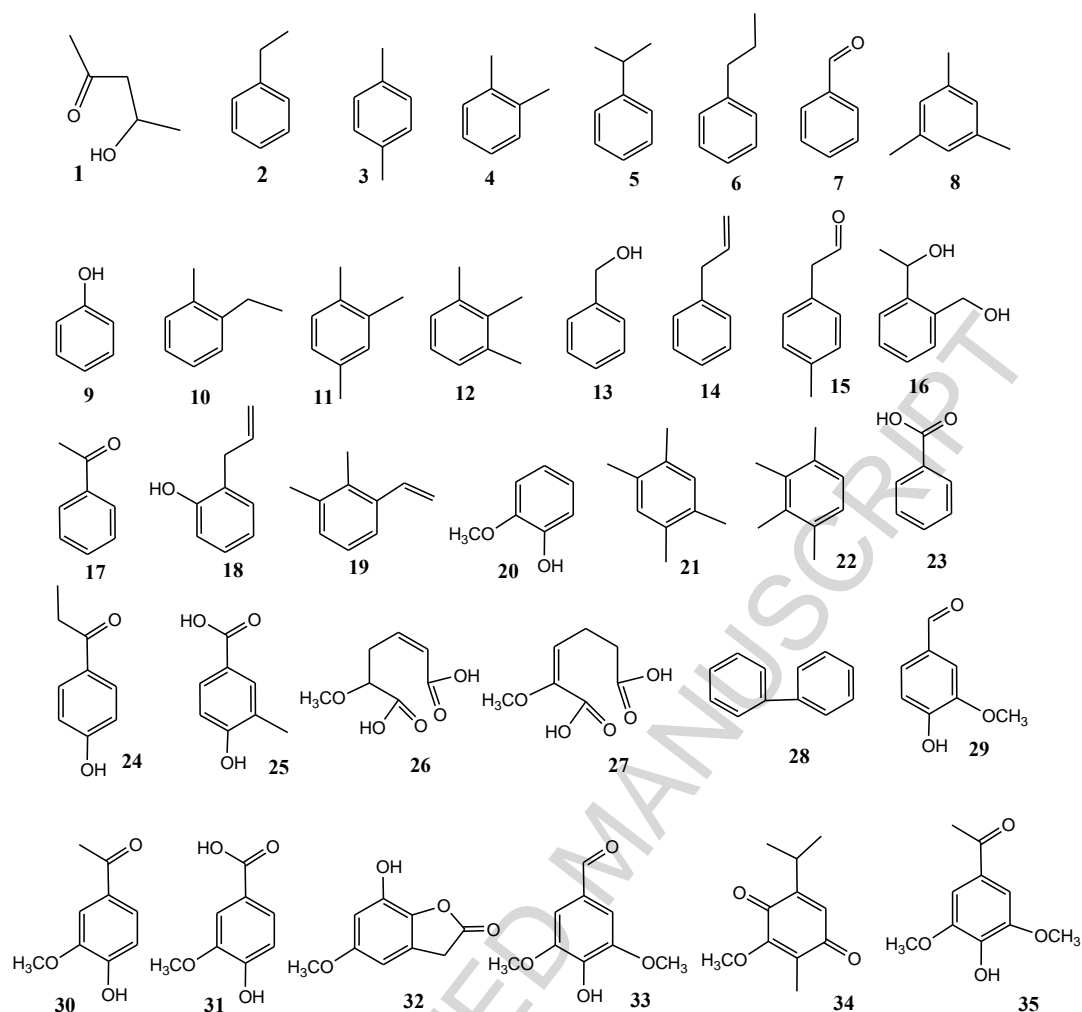


Fig.2. Molecular structure of different products revealed by **GC-MS**, and obtained via depolymerization of lignin model polymers by the catalytic oxidative action.

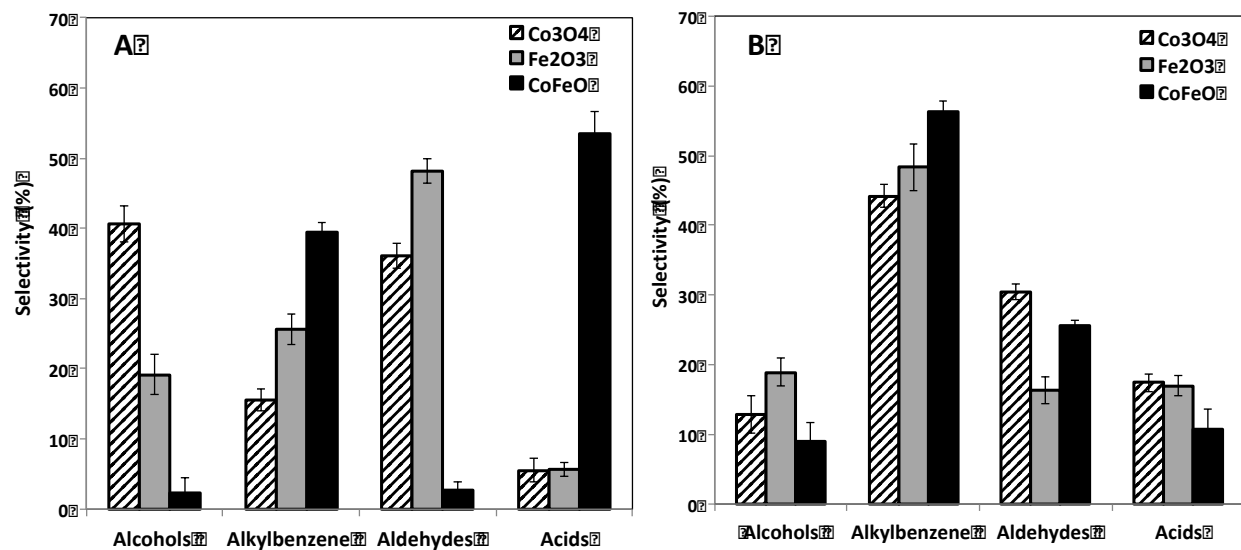


Fig.3. Selectivity of the three catalysts (only major products were considered): (A) GS-based lignin model and (B) G-based lignin model, (CoFeO: the mixed oxide $\text{Co}_{1.8}\text{Fe}_{1.2}\text{O}_4/\text{Co}_{0.8}\text{Fe}_{1.2}\text{O}_3$).

Table 1. Depolymerization yields for Lignin-G and lignin-GS

Yield (mg/g lignin model)	G-based lignin model			GS-based lignin model					
	Co ₃ O ₄	Fe ₂ O ₃	CoFeO	Co ₃ O ₄	Fe ₂ O ₃	CoFeO (Run1)	Run 2	Run 3	Run 4
		60.6	62.7	67.4	62.2	63.7	69.6	67.4	73.1
2*	0.38	0.00	0.00	2.83	3.70	0.96	0.87	0.91	0.98
3	0,35	0.07	0.07	10.51	10.75	3.50	3.60	3.78	3.40
4	0.50	0.13	0.08	8.38	8.75	2.75	2.35	2.87	2.66
7	13.17	9.21	1.45	10.49	4.31	14.03	14.22	14.44	13.89
9	0.59	0.00	0.14	4.02	6.60	1.16	1.11	1.17	1.25
11	0.27	7.59	20.83	0.87	0.92	18.40	18.12	17.89	18.55
13	20.45	10.58	0.61	1.95	1.54	0.79	0.71	0.84	0.67
17	0.23	1.17	0.00	3.58	2.03	0.35	0.34	0.37	0.41
20	0.00	0.05	0.09	3.58	5.86	2.23	2.15	1.92	2.33
23	2.78	2.55	28.15	0.79	1.48	1.80	1.66	1.87	2.04
29	8.69	15.35	0.34	4.17	4.69	1.53	1.66	1.59	1.46
30	0.40	0.34	0.75	2.49	2.12	1.01	1.11	1.24	0.87
33	0.00	0.00	0.00	4.24	1.38	1.77	1.89	1.57	1.93

*Number of products in Fig.2

Run 1 was performed using CoFeO mixed oxide (Co_{1.8}Fe_{1.2}O₄/Co_{0.8}Fe_{1.2}O₃)

Runs 2, 3 and 4 were repeated using CoFeO mixed oxide (Co_{1.8}Fe_{1.2}O₄/Co_{0.8}Fe_{1.2}O₃) in the case of **GS-based lignin model only**

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Table 2. Average molecular weight of lignin models before and after catalytic oxidation over Co_3O_3 , Fe_2O_3 and CoFeO oxides.

Samples	Mw (g/mol)	
	G-based lignin model	GS-based lignin model
Initial	2250	2030
Co_3O_4	340	370
Fe_2O_3	360	430
CoFeO	320	340

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Highlights

- Catalytic conversion of polymer lignin model to high value-added products
- Lignin model polymer is analogue of extracted and natural lignin
- Nanostructured oxides with different Co/Fe ratios were prepared *via* alginate
- Iron-Cobalt oxide a high-performance catalytic activity for lignin depolymerization
- Molecular weights of oligomers were lower than that of the original lignin polymer

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