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Study of liquid-phase catalytic oxidation of natural renewable raw materials in alkaline media

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Abstract. The present study is devoted to liquid-phase catalytic oxidation of natural raw materials (polysaccharides, lignin) with the aim of their utilization, obtaining valuable chemical products and development of environmentally friendly intumescent flame retardants for wood. For this purpose, a method of oxidation of raw materials: polysaccharides and lignin, by oxygen in the presence of catalyst is proposed. The main oxidation products of catalytic oxidation (salts of polyoxy- and polyphenoxy acids) are analyzed using the data acquired with the aid of GC-MS experiments.

Oxidation of organic substances is one of the most widespread methods of preparative chemistry, and organic synthesis [1]. Molecular oxygen (O₂), and the other oxidizers, such as H₂O₂, NaOCl, KIO₃, etc. and metal oxides (Cr₂O₃, Na₂Cr₂O₇, KMnO₄, etc.) are widely used for this purpose. Some compounds of transition metals allows obtaining the high rate of oxidation and products yield. However, such oxidizers do not satisfy the environmental safety of oxidation leading to formation of the toxicants and produce the heavy metals' ions.

The most environmentally friendly and cheap oxidizer is the molecular oxygen. At the same time under soft conditions (up to 150 °C) it is a very weak oxidizer and being in the nature generally in triplet state, is not capable to interact directly with the molecules of the organic substances (in singlet state). In this regard, liquid-phase oxidation by gaseous oxygen demands preliminary activation of reagents (substrate or molecular oxygen). In the most cases for non-catalytic processes, and in the presence of homogeneous and heterogeneous catalysts of liquid-phase oxidation key stage of process is oxidation substrate activation due to its transfer to free radical form. Oxygen reduction in such processes occurs via the series of consecutive one-electron stages [2].

The use of homogeneous catalysts allows to reduce the temperature of oxidation and to change the ratio of reaction products due to possible interaction of transition metals compounds with peroxides, free radicals and other oxidation products. Processes of oxidation of organic compounds by oxygen in the presence of copper and the can be widely used in the processing of vegetable raw materials [2]. In 1995 Skibida and Sakharov [3] published the information of the new process describing the liquid-phase catalytic oxidation of starch-containing raw materials by oxygen (Figure 1).



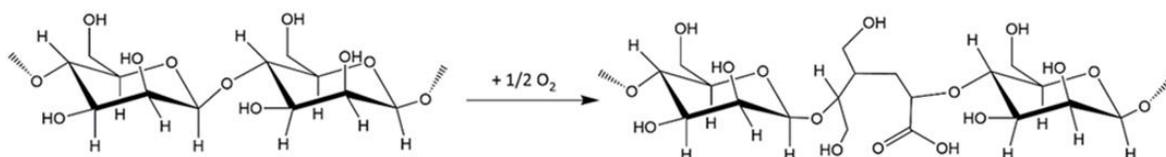


Figure 1. Scheme of oxidation of starch-containing raw materials by oxygen.

The oxidative modification of polysaccharides, leading to polyacids as main products, is widely applied in practice due to the availability of raw materials and high consumer-attractive properties of oxidized polysaccharides. Salts of polyacids are used as water-soluble glues in the production of paper and cardboard, as components of drilling agents, etc. the oxidizing agent, used until recently for the oxidation of polysaccharides, was hydrogen peroxide since gaseous oxygen presents low activity in such procedures [4, 5]. However, when copper complexes and bases are present, not only the simple in structure alcohols and ketones, but also polysaccharides (e.g. starches, dextrans, cellulose) can be oxidized by oxygen, achieving high rates. These high rates of oxidation by oxygen, exceeding the ones achieved by oxidation with hypochlorites, are reached at temperatures 40-90°C [6]. The oxidation of polysaccharides proceeds with the greatest efficiency in the presence of copper and alkali salts. On the contrary, the molecular weight of an initial polysaccharide exhibits a slight decrease during the first minutes [7].

Copper salts are the most effective catalysts of oxidation of polysaccharides in the presence of alkali. In the absence of the catalyst, starch and cellulose practically cannot be oxidized at temperatures below 100°C. However, lignin, which contains many of high reactive phenolic groups (under high rates), can be oxidized by oxygen at measurable rates, even without the catalyst. The role of the catalyst (Cu^{2+} ions) is to activate the deprotonated forms of substrate to react with oxygen. In other words, the role of bivalent copper ions is supposed to be the facilitation of the oxidation of anion forms of substrate (interaction of intermediate radicals or anion radicals with O_2). However, high-molecular polysaccharides with a low content of end aldehyde groups are redox inactive in anaerobic medium and the rate of reduction of Cu^{2+} to Cu^+ ions (due to electron transfer from substrate anion form to Cu^{2+}) is one hundred times lower than the rate of oxygen adsorption during the process of polysaccharides oxidation in alkaline mediums. Therefore, it seems that direct interaction of oxygen with anions A^- in coordination sphere of copper ion that leads to the formation of hydroxycarboxylates (as the main primary products of oxidation). Absorption of oxygen, on the other hand, is completely stagnated after neutralization of introduced alkali by the polyoxyacids, formed during the oxidation process. Thus, by varying of the amount of introduced alkali the degree of polysaccharides oxidation into polyacids can be altered, giving the possibility to tailor the properties of the final product (such as viscosity, bonding ability, solubility in water, etc.).

Starch can be used as initial raw material for receiving salts of polyoxyacids, as well as any of other starch-containing raw materials (like corns of maize, oats, rice, etc.), including ill-conditioned raw materials (such as grain-crops affected by various fungus diseases, waste of rice slashing, waste of mill houses, etc.). In so doing, the prime cost of the final product can be decreased significantly. Moreover, similar to the polysaccharides behavior, under oxidation in alkali media with or without the catalyst, has been found to be exhibited by lignin. Lignin is amongst the most abundant biopolymers on earth. It is estimated that the planet currently contains 3×10^{11} metric tons of lignin with an annual biosynthetic rate of approximately 2×10^{10} tons [8]. Lignin constitutes approximately by 30% (of the dry weight) of softwoods and by about 20% of hardwoods [9]. It is absent from primitive plants such as algae, and fungi which lack a vascular system and mechanical reinforcement. The presence of lignin within the cellulosic fibre wall, mixed with hemicelluloses, creates a naturally occurring composite material that imparts strength and rigidity to trees and plants. Lignin, moreover, is one of the most important bio-resources for obtaining raw materials needed for the synthesis of environmentally compatible polymers, since it is non-toxic and extremely versatile in performance. Lignins are derived from renewable resources such as trees, grasses, and agricultural crops. About

30% of wood constituents are lignin. Furthermore, the production of lignin as a by-product of pulping process is worldwide over 30 million tons per year [9]. Lignin is a random copolymer consisting of phenyl propane units having characteristic side chains. Lignin slightly crosslinks and takes an amorphous structure in the solid state. The molecular motion is observed as glass transition by thermal, viscoelastic and spectroscopic measurements. The hydroxyl group of lignin plays a crucial role during its interaction with water. Lignin is usually considered as a polyphenolic material having an amorphous structure, which arises from an enzyme-initiated dehydrogenative polymerization of *p*-coumaryl, coniferyl and sinapyl alcohols [10]. The basic lignin structure consists of two components; one is the aromatic part and the other is the C₃ chain. The only usable reaction site in lignin is the OH group, which is the case for both phenolic and alcoholic hydroxyl groups. In the process of radical-based biosynthesis, the types of reactants employed to produce the lignin polymer are three: 4-hydroxyphenyl (1), guaiacyl (2), and syringyl (3) structures (Figure 2).

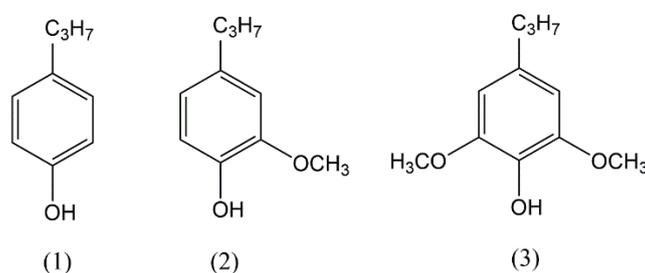


Figure 2. Chemical formula of 4-hydroxyphenyl (1), guaiacyl (2), and syringyl (3) molecules.

In the present study, we have focused on the study of catalytic oxidative modification of lignin and simple natural saccharides (glucose and sucrose), as model systems, by the chromatography mass spectrometry (GC-MS) method.

GC-MS measurements were performed on a gas chromatograph Trace-1310 and Single Quadrupole MS ISQ Detector. The pyrolysis products were injected into the GC capillary quartz column 15 m × 320 μm i.d. and 0.25 μm film (TG-SQC, Thermo Scientific Phase) under the temperature-programmed conditions in the range of 40 – 290°C with gradient 15°/min. MS-spectra of degradation components were identified and interpreted by matching the results with NIST Mass Spectral.

The GC-MS analysis of hexane solutions of silanated products of initial sucrose (the top chromatogram) and the oxidized sucrose after receiving acids from salts (the lower chromatogram) presented on Figure 3.

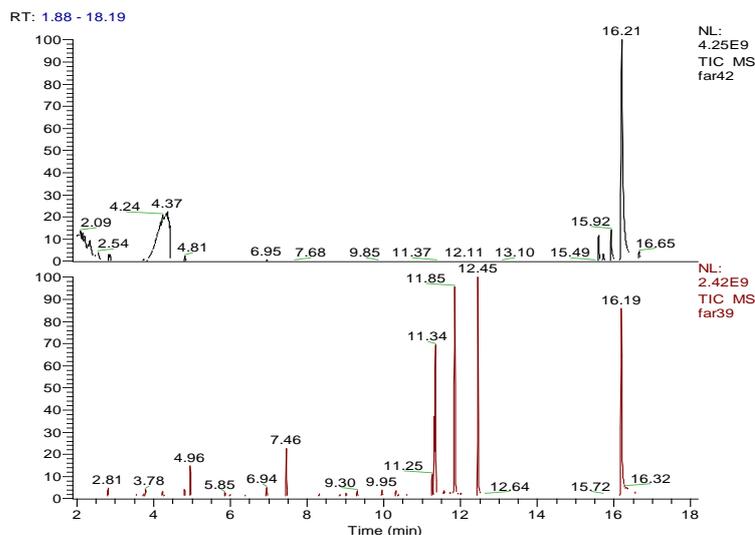


Figure 3. Gas chromatograms of the hexane solutions of silanated products of initial sucrose (the top chromatogram) and the oxidized sucrose after receiving acids from salts (the lower chromatogram).

Gas chromatograms of the hexane solutions of silanated products of oxidized glucose presented on Figure 4.

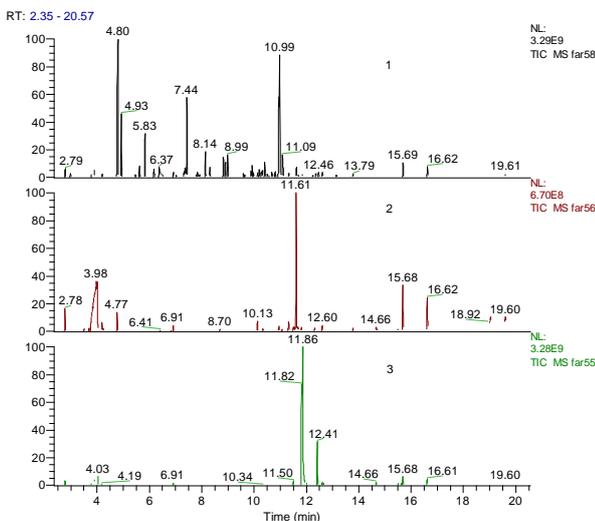


Figure 4. Gas chromatograms of the hexane solutions of silanated products of oxidized glucose: 1 – the oxidized dried-up glucose after receiving acids from salts; 2 - the oxidized dried-up glucose without receiving acids from salts; 3 – initial glucose.

Chromatograms of sucrose are similar except for intensity of peaks. The proposed mechanism of sucrose oxidation leads to formation of pentapyranoses (78.5%), pentafuranoses (11.7%) and acids (8.8%) (Figure 5).

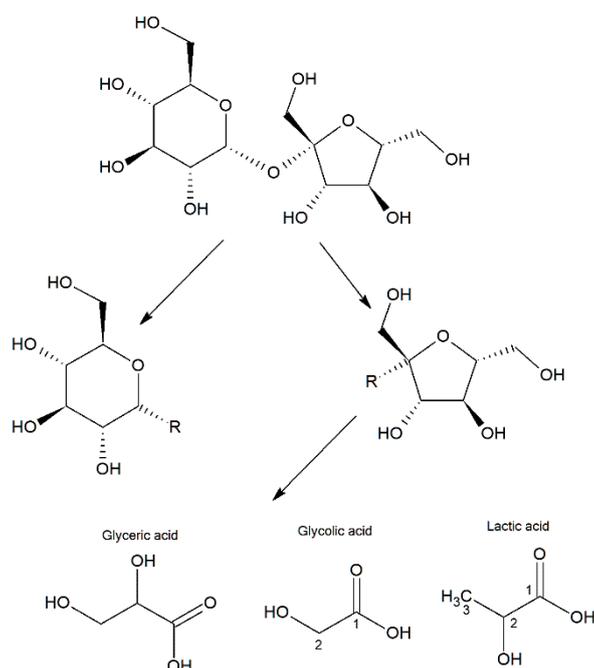


Figure 5. Scheme of proposed mechanism of sucrose oxidation.

The obtained organic acids can be widely used in medicine and food industry.

In this work the way of liquid-phase catalytic oxidation of the lignin oxygen in the presence of salts of transition metals leading to formation of soluble fraction of polyaromatic acids and their derivatives is developed. This way differs from selective pyrolysis in the fact that he answers with the principles of "green" chemistry and represents environmentally friendly single-stage and waste-free process. In addition, main products of processing of lignin in the form of aqueous solutions and emulsions can be received without the big power expenses connected with pyrolysis of lignin containing raw materials. Now homogeneous catalysts allow conducting process in much softer conditions, than classical heterogeneous catalysts, at the same time higher activity and selectivity is peculiar to them.

The oxidized lignin offered for research consisted of viscous, tarry deposit of black color and opaque solution.

Products of lignin oxidation were extracted from obtained solution with use of methylene chloride. The lignin hydrolysates extracted from acidified liquids by methylene chloride are given in Table 1.

The oxidized lignin offered for research consisted of viscous, tarry deposit of black color and opaque solution.

According to provided GC–MS measurements of lignin oxidation products we assume that liquid-phase catalytic oxidation of the lignin by oxygen in the presence of salts of transition metals provides the formation of valuable polyaromatic derivatives (e.g. vanillin).

The process of homogeneous oxidative catalysts in alkaline media allows providing the utilization of lignin, obtaining valuable chemical products and development of environmentally friendly intumescent flame retardants for wood [11].

Table 1. Composition of lignin oxidation products obtained via extraction by methylene chloride.

№	Connection	contents, %
1	Methylbenzaldehyde	3.10
2	2-methyl-5-hydroxycoumarine	10.41
3	2.5-dihydroxy-2.5-dimethoxy furan	7.34
4	Furan carboxylic acid	4.91
5	Propoxybenzene	2.96
6	Methylbenzoic acid	2.43
7	Vanillin	15.03
8	Acetovanilon	3.52
9	Vanillic acid	8.54
10	Isovanillin	4.21
11	Ethers of benzene dicarboxylic acids	28.09
12	Not identified products	9.46

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