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Obtaining Aromatic Aldehydes from Biobutanol Production Wastes

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Abstract

A catalytic process of the oxygen-driven oxidation of aspen wood and enzymatic lignin as a waste of processing aspen wood into biobutanol was investigated in a static reactor using a rotating magnetic stirrer in an alkaline medium. The effect of temperature and of a mode of alkali feeding into reactor on the yield of syringaldehyde and vanillin was studied. It has been established that the fermentation lignin is close to the native lignin being much more efficient as compared with lignosulphonates for using as a feedstock for the preparation of vanillin and syringaldehyde. Separation is experimentally realized concerning the stages of lignin oxidation by oxygen, on the one hand, and the retro-aldol cleavage of oxidation products into vanillin and syringaldehyde, on the other hand.

Key words: vanillin, syringaldehyde, wood, aspen, biobutanol enzymatic lignin, wastes, technology, catalytic oxidation, mechanism

INTRODUCTION

For the last 20 years, the biotechnologies are becoming more and more demanded in the world production of motor fuel. The biobutanol production of the second generation represents an intensely developing process aimed primarily at the production of fuel from non-food renewable carbohydrates, wood and waste wood industry [1, 2]. At the Corporation Biotechnology JSC there was developed a novel technology for producing enzymatic butanol from cellulose-containing raw material [2]. At the first stage of the production the wood ground to a micron size is subjected to enzymatic hydrolysis. The solutions of sugars are fed to the further processing into butanol, acetone and ethanol. Lignin formed at the stage of enzymatic cellulose hydrolysis is proposed to use for the production of fuel pellets [3].

The lignin content in the wood of different tree species ranges from 20 to 40 % [4]. By

means of catalytic oxidation the lignin can be converted into aromatic hydroxy aldehydes, vanillin and syringaldehyde; the lignins of softwood are converted into vanillin, whereas hardwood species yield a mixture of vanillin and syringaldehyde [58]. The yields of aromatic aldehydes from native lignins, *i. e.*, in the processes of wood oxidation exceeds 20 mass % for softwood to amount up to 40 % as calculated for lignin obtained from the oxidation of hardwood species [9]. In the course of wood chemical processing at pulp-and-paper mills, the native lignin undergoes significant changes, including the changes of the condensation character. Such lignin species produce under oxidation a significantly lower (2–3 times) yield of aromatic aldehydes as compared to the native lignin [10].

Earlier it was demonstrated that the oxidation of wood brown rot, *i.e.* the lignins formed in the course of wood decay under the action of cellulolytic fungi under naturally

occurring conditions (enzymatic lignin, EL) results in the production of aromatic aldehydes with high yields. The oxidation of white wood (fir) EL resulted in the formation of 13.9 mass % of vanillin [11], that of pine gave 19 mass % of vanillin [12], whereas the oxidation of birch EL resulted in obtaining 3.75 mass % of vanillin and 11.15 mass % of syringaldehyde [12]. These values correspond to 80–90 % of aldehyde yields in similar processes of wood oxidation. Only the authors of [13] observed 8% vanillin yield in the course of oxidizing the brown rot of the Douglas fir by copper oxide, as compared with 20 % of vanillin in the oxidation of appropriate wood [14]. Such a significant difference could be, to all appearance, caused by too deep destruction of the wood and, therefore, of lignin by brown rot fungi [13]: the Klason lignin content in the brown rot of Douglas fir wood was equal to 89.5 %, whereas the same value for the brown rot of pine wood amounted to 66 % [12].

The two to three-fold excess in the aromatic aldehydes yields resulting from EL as compared with the technical grade raw materials (including lignosulphonates those were applied on the industrial scale before the 1970s) indicates the attractiveness of the EL as a raw material for the production of vanillin and syringaldehyde [10]. The resources of brown rot in the nature are huge, but scattered and therefore they are futile for using as an industrial feedstock.

In the course of biobutanol production at the stage enzymatic hydrolysis on the industrial scale there is a substrate formed similar to the brown rot wood lignin in the properties and the structure [15, 16]. Consequently, the EL as the biobutanol production waste could appear a promising raw material for in order to obtain vanillin and syringaldehyde.

The aim of this work consisted in studying the catalytic oxidation of EL by oxygen in alkaline medium.

EXPERIMENTAL

In this work we used aspen EL powder obtained by treating the suspension of aspen wood dust (*Pypulus trumula*) in water by a complex of hydrolytic enzymes (cellulase, xylanase, cel-

lobiase) at a ratio of 2.5 g/kg of dust at 55 °C for 12 h [17], as well as air-dry aspen wood (the fraction less than 0.1 mm).

The composition of EL and wood was determined by means of the methods described in [18]. The cellulose content in EL determined by a nitrogen-alcohol technique was equal to 21.8 mass % as calculated for dry solid matter, the content of lignin (determined by means of a sulphuric acid technique) amounted to 55.1 mass %. The moisture content was equal to 3.4 mass %. The lignin content in aspen wood amounted to 21.8 mass %.

The experiments were conducted using a stainless steel autoclave with the volume capacity of 1 L at the temperature ranging within 120–170 °C and the partial oxygen pressure equal to 0.2 MPa. Stirring was carried out using a magnetic stirrer (800–900 L/min, the diameter of the autoclave amounted to 85 mm, magnetic stirrer 10 mm in diameter and 60 mm long, the Reynolds number calculated for the pure water amounted to $Re = (2.9-3.2) \times 10^5$. Oxygen gas was fed into the reactor from the buffer tank *via* a special calibrated valve as the gas absorbed by the reaction mixture while maintaining a constant pressure. The Volume of oxygen absorbed was measured according to lowering the pressure in the buffer tank. The temperature is automatically adjusted within an accuracy of ± 1 °C.

The reaction mixture was prepared by sequentially adding to the reactor of 3.75–7.50 g dry EL or aspen wood, 7.7–15 g of NaOH, 150 mL of H₂O, and 3.2–5 g of a catalyst (CuSO₄ · 5H₂O), under agitation.

Continuous feeding the solution of alkali into the reactor under pressure in corresponding experiments was provided by means of a ND-100-10 metering pump. Loading: 8.75 g of lignin, 3.73 g of the catalyst, 125 mL of water; $T = 160$ °C, oxygen pressure amounting to 2 atm. At the 45th minute, the reactor was purged with argon to terminate oxidation, with further feeding 3.85 M NaOH solution with a flow rate of 50 mL/h for 45 min, then 150 mL/h for 5 min.

In certain time intervals (5, 10, 15 min *etc.*) a part of the reaction mass was taken for sampling. A resulting sample of 13–15 mL in volume was adjusted with 1 M HCl solution to pH 3–4 to be exhaustively extracted with ethyl acetate.

The oxidation of EL by nitrobenzene was carried out in a rocking stainless steel reactor with the volume capacity equal to 100 mL at the temperature of $(170 \pm 4)^\circ\text{C}$ for 3 h. Loading: 1.8 g of lignin, 37.5 mL of 2 M NaOH, 2.1 mL of nitrobenzene [19]. Upon the process completion, the reaction mass was acidified with sulphuric acid solution (1.5 mL of 40 % H_2SO_4) to extract with chloroform.

The aldehyde concentration was determined by GLC (column $30\text{ m} \times 0.32\text{ mm}$, SE-30 as the liquid phase carrier). The column temperature was equal to 170°C . Anthracene was used as the internal standard.

RESULTS AND DISCUSSION

Catalytic oxidation of enzymatic lignin

The technique used allowed us to study the dynamics of the accumulation of aldehydes in the course of the oxidation of EL and whole aspen wood under various conditions.

The yield of aldehydes depending on the time exhibit two maxima those are stably reproduced (Figs. 1 and 2). Such a bimodal distribution could be, to all appearance, caused either by the degradation features of branched and cross-linked polymers [20] or by the presence of two lignin species those exhibit different reactivity level in the oxidation processes [12].

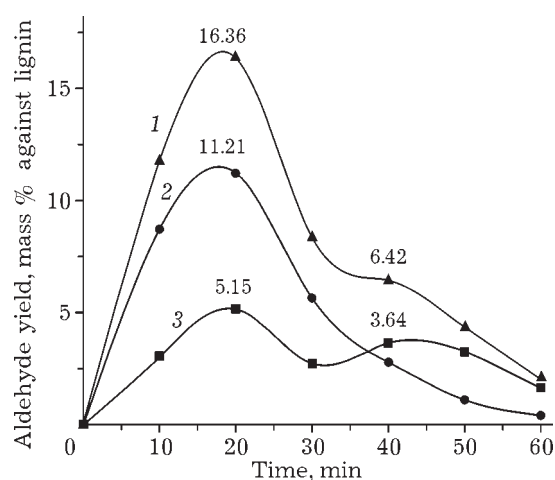


Fig. 1. Enzymatic lignin oxidation ($T = 160^\circ\text{C}$, substrate 7.5 g, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 3.2 g, NaOH 9.6 g, H_2O 150 mL, $p_{\text{O}_2} = 0.2\text{ MPa}$): 1 – total product yield, 2 – syringaldehyde, 3 – vanillin.

For the reactor used, the time of appearing the peaks that could be used in order to evaluate the reaction rate, remains almost unchanged when the temperature decreases from 170 to 130°C . Only at 120°C there is an abrupt increase observed for the time of appearing the first maximum, whereas the second peak cannot be registered (Table 1). This demonstrates the fact that at the temperature values above 130°C , despite relatively high stirring intensity (800–900 L/min), the oxidation process in the reactor with a rotating magnetic stirrer takes place within the diffusion region.

It is known that the oxidation of lignins in the diffusion mode gives low yields of vanillin and syringaldehyde [9, 21–23]. Thus, the oxidation rate and selectivity for lignin-containing substrates increases with decreasing in the concentration thereof in the solution and with increasing the intensity of mass exchange [9, 21–23]. Both of these effects are connected with the transition from the diffusion region to the kinetic region of the process.

High yields of the aldehydes in the process of heterogeneous catalytic oxidation with gaseous oxygen were obtained in a rocking reactor of intense stirring, wherein the oxidation mode is similar to the kinetic one, until the temperature being equal to 160°C [14, 23]. Under such conditions, the yield of aromatic aldehydes in the course of aspen wood powder oxidation at 160°C reaches 31 mass % [14, 23]. In the

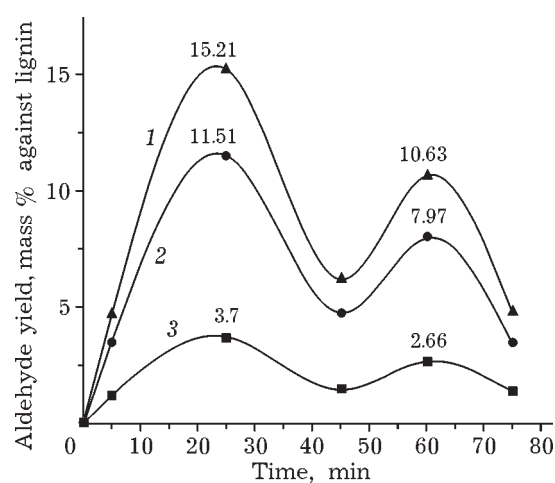


Fig. 2. Oxidation of whole aspen wood ($T = 160^\circ\text{C}$, wood 15 g, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 3.2 g, NaOH 7.7 g, H_2O 150 mL, $p_{\text{O}_2} = 0.2\text{ MPa}$): 1 – total product yield, 2 – syringaldehyde, 3 – vanillin.

TABLE 1

Effect of the oxidation conditions of enzymatic lignin and aspen wood on the formation of aromatic aldehydes

Exp. No.	Temperature, °C	Concentration, g/L		Yield*, mass % with respect to lignin (min)		
		Catalyst	Alkali	Vanillin	Syringaldehyde	Total amount of aldehydes
1	120	9.41	45.29	1.60 (95)	1.76 (75)	3.31 (75)
2	130	9.41	45.29	0.98 (30)	4.66 (30)	5.64 (30)
				1.64 (100)	2.09 (70)	3.11 (80)
3	140	9.41	45.29	2.33 (35)	3.60 (35)	5.93 (35)
				3.36 (85)	2.54 (85)	6.14 (85)
4	150	6.02	56.47	2.78 (30)	6.50 (30)	9.28 (30)
				1.43 (50)	0.74 (50)	2.17 (50)
5	160	6.02	56.47	5.15 (20)	11.21 (20)	16.36 (20)
				3.64 (40)		6.42 (40)
6	170	6.02	56.47	2.86 (20)	8.18 (20)	11.04 (20)
				4.87 (70)	2.00 (70)	6.87 (70)
7	160	6.02	45.29	3.70 (25)	11.51 (25)	15.21 (25)
				2.66 (60)	7.97 (60)	10.63 (60)

Note. Substrate concentration in the experiments Nos. 1–6 was equal to 44.12 g/L, in the experiment No. 7 (aspen wood) being of 88.24 g/L.

*In parentheses, there is the time of reaching the maximum concentration of aromatic aldehydes presented.

reactor we used with a rotating magnetic stirrer, the mass exchange is less intense, and this mode could result with relatively high probability in a fast and deep, non-selective oxidation in the near-surface region of the gas-liquid interface.

In accordance with these patterns the maximum yields of aldehydes in the course of the oxidation of aspen wood and EL amounted to 15–16 mass %, as calculated with respect to lignin, including 11 % for syringaldehyde (see Figs. 1, 2, exp. Nos. 5 and 7 presented in Table 1), which is twice lower than the maximum results obtained from the oxidation of aspen wood with oxygen. Nevertheless, the same yields of aromatic aldehydes from the EL and timber indicates that the EL of aspen can be oxidized into syringaldehyde and vanillin just as efficiently as wood.

It should be noted that the yields obtained almost coincide with the best results of the oxidation of lignosulphonates by oxygen and nitrobenzene [25, 26]; these values could be increased in the process transition from the diffusion region to the kinetic one. The nitrobenzene oxidation of the aspen EL under investigation we performed gives twice the yield of aromatic aldehydes as compared to the results

of the catalytic oxidation (see Fig. 1) and demonstrates a maximum possible production of aromatic aldehydes from such raw materials (vanillin – 8.0 %, syringaldehyde – 26.4 %).

Consequently, the EL under consideration, just as the lignins of brown rot, would require less consumption of reagents (alkali, oxygen) in the course of using as a substrate for the production of aromatic aldehydes as to compare with, for example, sulphite liquors and lignosulphonates.

It is known that oxidation of lignins at low (less than 160 °C) temperature values is accompanied by low yields of vanillin and syringaldehyde [9, 21–23]. The systematic 3- to 5-fold decrease observed for the yields of aromatic aldehydes with decreasing the temperature from 160 to 120 °C (see Table 1) corresponds to the mentioned patterns.

Mechanism of aromatic aldehyde formation

Earlier, we proposed a mechanism for the formation of vanillin in the course of lignin oxidation, which mechanism comprises the stages of the oxidation of ionized phenolic groups in lignins and a subsequent retro-aldol cleav-

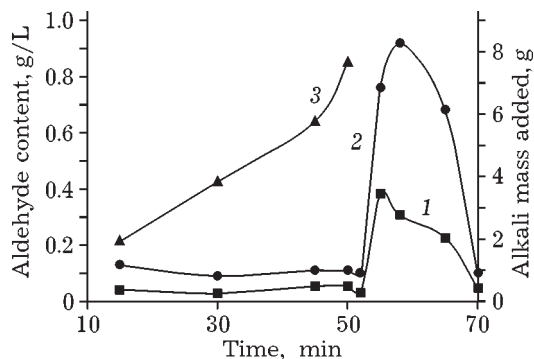


Fig. 3. Yield of aromatic aldehydes in the course of enzymatic lignin oxidation under the conditions of continuous feeding the alkali to the reactor: 1 - vanillin, 2 - syringaldehyde, 3 - alkali.

age of the phenolpropene aldehyde fragment formed *via* oxidation [26, 27].

In accordance with the proposed mechanism, the formation of process aldehydes could be divided into two stages such as the oxidation of phenolate anions having the structure of lignin that can occur in a slightly alkaline medium, and the retro-aldol cleavage of phenolpropene aldehyde fragments occurring in a strongly alkaline medium with no oxidant. This kind separation of stages performed in an experimental way, could reduce the consumption of alkali in the process, because the oxidation at low pH values could result in the only oxidation of the phenolate ions, *i. e.*, to provide the selectivity as high as possible.

The separation of the process into the two stages of oxidation and retro-aldol cleavage under consideration is experimentally realized by continuously feeding the alkali in the reactor in the course of the oxidation process. Oxygen was fed to the reactor within 45 min, whereafter the reactor was purged with argon gas to stop the oxidation and the residual amount of alkali was added in order to increase the pH value up to the level necessary for the retro-aldol cleavage. The total amount of alkali added in this experiment was the same that was used in previous experiments (see Fig. 1).

Figure 3 presents the results of EL oxidation under the conditions of continuous feeding the alkali to the reactor. Under these conditions, during 45 min under oxygen pressure, and 7 min after displacing the oxygen with argon, vanillin is almost not formed. This could

be caused by a low alkalinity of the solution, which is sufficient for the ionization and oxidation of phenolic groups, but insufficient for retro-aldol cleavage of the oxidation products into vanillin and syringaldehyde. With increasing the alkalinity of the solution after passing 52 min, there starts a retro-aldol cleavage of phenolpropene aldehyde fragments accumulated in the course of oxidation accompanied by a rapid formation of aldehydes.

It can be assumed that the approach with a continuous feed of alkali to the reactor would provide an increase in the process selectivity level due to milder oxidation conditions at a low alkalinity level with the process transition to the kinetic region due to the slowing thereof at a low pH value. However, the total yield of aromatic aldehydes in the course of continuous feeding the alkali appeared two to three times less as to compare with the results of the main set of the experiments wherein the alkali was loaded in the beginning of the experiment. Despite the separation of the stages of oxidation and retro-aldol cleavage, as well as the approximation to the kinetic region of the process, this approach does not allow increasing the selectivity of the process. To all appearance, this could be connected with a high oxidation rate of the phenolpropene aldehyde fragment into by-products in a weakly alkaline medium.

CONCLUSION

Thus, the present work demonstrates the possibility of obtaining vanillin and syringaldehyde *via* catalytic oxidation of enzymatic lignin, the wastes of biobutanol production process. The oxidation of enzymatic lignin and aspen wood in the diffusion mode results in the yield value up to 15–16 mass % of the aromatic aldehyde with respect to lignin. These yields are almost in coincidence with the best results lignosulphonates oxidation by nitrobenzene and oxygen (15–16 mass % with respect to lignin); these values could be increased by transferring the process from the diffusion region to the kinetic one. The results of EL oxidation with nitrobenzene confirm this assumption: the yield of aldehydes amounted to 34.4 mass % with respect to the Klason lignin.

It has been established that the enzymatic lignin represents a concentrated, non-condensed promising technological raw material for the preparation of vanillin and syringaldehyde that exceeds lignosulphonates in the yield of the target products and, therefore, in the consumption of reagents with respect to vanillin obtained.

Separation is experimentally realized concerning the stages of lignin oxidation with oxygen occurring at pH 9–10, and the subsequent retro-aldol cleavage of substituted phenolpropene aldehyde, the latter taking place in a strongly alkaline medium with releasing vanillin and syringaldehyde. Under the conditions of continuous supplying the alkali solution into the oxidation reactor, almost no aromatic aldehydes are formed in the presence of oxygen, but these substances can accumulate after stopping the oxygen supply with increasing the alkalinity of the medium. These facts confirm the mechanism proposed earlier for the formation of vanillin via a plurality of oxidation stages followed by the retroaldol cleavage of oxidation products.

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