

Degradation of lignins by wet oxidation: model water solutions

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Abstract. Nowadays many paper industries are faced with the problem of wastewaters being badly biodegradable because of tannins, lignins, etc. Wet oxidation (WO) is an appropriate method for the destruction of very complex, multi-dimensional, and permanent compounds. This paper studies the WO of lignin water as a model case with the aim of degrading lignin and enhancing water biodegradability. The experiments were performed at various temperatures (110–190 °C), partial oxygen pressures (0.5–1.5 MPa), and pH values (5, 9, and 12) in a batch stainless steel high pressure reactor. The experiments showed that increasing the temperature improved the processes efficiency. At the lowest temperature tested 75% lignin reduction was detected and a temperature increase improved the lignin removal to 100% at 190 °C. The effect of temperature on the COD removal rate was lower, but detectable: 20% of organics was oxidized at 110 °C, but 53% at 190 °C. Oxygen partial pressure changes affected the process results modestly. Lignin removal increased by about 10% and COD removal by 4% with an oxygen partial pressure increase from 0.5 to 1.5 MPa. The effect of pH occurred mostly on lignin removal. Increasing the pH enhanced the lignin removal efficiency from 60% to nearly 100%. In all cases, a good biodegradability (BOD/COD ratio over 0.5) was achieved starting at a temperature of 150 °C, pH 9, irrespective of the experimented pressures. The biodegradability (BOD/COD) of the remaining organic matter increased during WO and approached almost 1 at the highest temperature of 190 °C.

Key words: lignin, wet oxidation, COD, biodegradability.

INTRODUCTION

Growing concern about increasing global pollution has forced many researchers to find more environmentally friendly methods for waste elimination. Industrial wastewaters cause many problems: they are highly concentrated, toxic,

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and frequently resistant to biological treatment. In these cases conventional wastewater treatment methods (for instance, biological treatment) need not give satisfactory results.

Wet oxidation (WO) or wet air oxidation (WAO) is an attractive treatment for waste streams that are too dilute to incinerate and too concentrated for biological treatment [1]. It has successfully found an industrial application for the treatment of hazardous, toxic and non-biodegradable waste streams [2].

Wet oxidation is a liquid-phase reaction between organic material and dissolved oxygen. It is used around the world to treat industrial wastewaters and sludges (organics over 10–20 g/L) at moderate temperatures (110–320°C) and at pressures from 0.5 to 25 MPa. Under these conditions, complex organic compounds are mostly oxidized into carbon dioxide and water along with simpler forms, which are biodegradable. Unlike other thermal processes, WO produces no NO_x, SO₂, HCl, dioxins, furans, and fly ash. The residence times of WO may range from 15 to 120 min [1–4].

The WO temperatures and pressures depend on the nature of the feed and the process objectives. For example, WO in the temperature range of 165–200°C improves the dewatering ability of the sludge. Temperatures of 200 to 280°C are used in such applications as spent activated carbon regeneration and conversion of refractory compounds to biodegradable substances. Higher temperatures (280–320°C) provide essentially complete oxidation [4–6].

Most organic compounds are stoichiometrically oxidized: hydrogen is converted to water; organic nitrogen to NH₃, NO₃, or elementary nitrogen; halogen and sulphur are converted to inorganic halides and sulphates; phosphorus to phosphate. Metals are generally converted to their highest oxidation state [4, 6].

It has been observed that the effectiveness of WO is limited by the rate of oxidation of the low molecular weight carboxylic acids [7]. Use of catalysts during the WO process is an option for process improvement. Many catalysts (precious metals, metal oxides and salts, and their complexes) have been used to enhance the efficiency of the process and improve the characteristics of the water.

An advantage of the WO process is that it creates minimal air pollution problems since the contaminants tend to stay in the aqueous phase [3] and it is one of the few processes that do not turn pollution from one to another form, but make it disappear [4].

Historically, pulp and paper production has been recognized as a significant point source of pollution [8]. The paper industry effluents can cause considerable damage to the receiving waters if discharged untreated, since they have high concentrations of chlorinated compounds, suspended solids, fatty acids, tannins, resin acids, lignins and their derivatives, sulphur and sulphur compounds, etc. [9].

Lignin has remained one of the most difficult biopolymers to characterize [10]. Lignin characteristically differentiates wood from other cellulosic materials found in the plant kingdom. In its natural state as it occurs in woody cells, it is an amorphous indefinitely large polymer known as *native lignin* or *protolignin*. Its most important property is rigidity and the increased stiffness it gives to cell

walls. It is present in the fine cavities within the cell wall, where it acts as a bulking agent. Owing to its low hygroscopicity, it improves the dimensional stability of the cell wall [11].

Lignin is a very complex and a quite insoluble three dimensional network polymer [12]. Its basic structural unit consists of phenylpropane with a phenol ring that is substituted by zero, one, or two methoxyl groups. The addition of one methoxyl group to the phenol ring produces a *guaiacyl unit*; the addition of two methoxyl groups results in a *syringyl unit* [13]. It is widely accepted that the biosynthesis of lignin stems from the polymerization of three types of phenylpropane units (monolignols) [13, 14]. These units are coniferyl, sinapyl, and *p*-coumaryl alcohol [10, 13, 14].

In recent years, the enzymatic degradation of lignin by laccase has received increasing attention because of its potential application in the pulp and paper industry [15] as well as studies with different microorganisms [16–19], but only a few with WO [20–22].

The present work was carried out to investigate the effects of different parameters on lignin-containing water by WO (as a model case). Lignin was chosen as a model compound having high polydispersity, which inhibits seriously the treatment of wastewaters.

EXPERIMENTAL

Materials

For the present research, a model solution of lignin was prepared using alkali lignin. The alkali lignin (Aldrich Co.) was dissolved in 300 mL of distilled water. As a result, a solution with the following properties was obtained: 600 mg/L lignin, 0–20 mgO₂/L biological oxygen demand (BOD), 750–780 mgO₂/L chemical oxygen demand (COD), and 250–270 ppm of soluble total organic carbon (TOC).

A solution of sodium hydroxide (NaOH) was used to increase the pH and sulphuric acid (H₂SO₄) was used to decrease the pH at the beginning of the experiments. During WO the pH value was recorded but not controlled.

Experimental procedure

The WO experiments were carried out in a 0.3-L stainless-steel high-pressure batch reactor (Parr Instrumental Co, USA). The reactor was equipped with a 4-bladed turbine-type impeller stirrer, an electric heating jacket, a cooling system, a gas inlet, a liquid sampling tube, and a gas release valve. A thermal sensor and external heating element were provided to control the reaction temperature. In all cases pure oxygen was used as the oxidizing agent. The impeller was operated at 700 rpm. During the experiments variable temperatures, pressures, and pH values were used.

For all runs, the cold reactor was loaded with 300 mL of feed. After pre-heating to the desired temperature, pure oxygen was introduced into the vessel up to the desired oxygen partial pressure and this was fixed as the starting point of the oxidation reaction. The preheating period lasted 20–40 min (average 30 min), depending on the desired temperature. Liquid samples were taken periodically during the whole reaction time. After a 2-h period, the reaction was stopped by rapidly cooling the reactor with cold water. When a sufficiently low temperature was reached, the reactor was depressurized and the treated water solution was removed.

The reaction samples were analysed for lignin content, BOD, COD, TOC, pH, aldehydes, colour, biodegradability (in the present paper BOD/COD), and the average oxidation state of carbon atoms (AOSC). The AOSC indicates the oxidation state of the organics in the mixture [23–25].

Analytical methods

The lignin concentration was measured with a photometric method of the Hach Company using relevant solutions of the Hach Co. Sodium carbonate solution and Hach Co. tannin-lignin reagent react with lignin forming blue-coloured intermediates. After 25 min of reaction time the colour intensity was measured.

The lignin content, colour, and aldehydes were measured by a direct-read HACH DR/2000 spectrophotometer at wavelengths of 700, 455, and 630 nm, respectively. COD was analysed by the closed reflux dichromate method [26], using a COD reactor (Hach Company, USA) and spectrophotometer DR/2000 (Hach Company, USA). BOD was assessed by standard BOD₅ tests [26], carried out by Dr Lange & Co (Germany). TOC was measured with a Shimadzu 5050 TOC Analyzer.

RESULTS AND DISCUSSION

The experimental conditions tested in the WO process are listed in Table 1.

In all cases the initial pH was 5, 9, and 12, which decreased modestly during the WO process. At the end of the WO the pH was about 2–4 units smaller than at the beginning.

Table 1. Experimental conditions of WO for the removal of lignin from an aqueous solution

Parameter	Value
Lignin concentration	100–600 mg/L
Experimental time	120 min
Oxygen partial pressure	0.5–1.5 MPa
Temperature range	110–190 °C
pH	5–12

The effect of temperature

Increasing the reaction temperature increased the oxidation rate of the process. After 2 h about 75% lignin reduction was detected at the lowest temperature tested. A gradual temperature increase improved lignin removal to 100% as shown in Table 2. The effect of temperature on the COD removal rate was lower, but detectable (Table 3). By the end of the reaction 20% of the organics was oxidized at 110°C, but 53% of the organics was oxidized at 190°C.

The influence of temperature on lignin removal and biodegradability is illustrated in Fig. 1. It is of interest to note that in the lignin removal process greater changes occurred during the first 30 min, and at 190°C almost 100% removal was obtained in 60 min.

The BOD/COD ratio shows the biodegradable organic matter contained in the water with respect to the total organic matter. As can be seen, biodegradability depends quite much on temperature. Biodegradability enhanced with increased temperature. The highest temperature showed the best results. The BOD/COD ratio was improved mostly because of increasing BOD values. Biodegradability was 0.03 at the beginning of the process in all cases (before the preheating period), 0.22–0.27 at zero time, and 0.47 at the end of the WO process (120 min) at a temperature of 110°C. However, the ratio increased to 1 at 190°C. It is widely accepted that biodegradability (BOD/COD) over 0.5 is a good ratio

Table 2. Effect of temperature on lignin reduction during a 120-min oxidation process

Time, min	Lignin reduction, %				
	110°C	130°C	150°C	170°C	190°C
–30*	0	0	0	0	0
0	6	9	17	8	20
10	30	51	68	71	78
30	54	74	85	88	92
60	64	82	91	94	99
90	70	86	94	97	100
120	75	88	97	99	100

* The average preheating period.

Table 3. Effect of temperature on biodegradability and COD removal at the end of a 120-min oxidation process

Temperature, °C	Biodegradability, BOD/COD	Total COD removal, %
110	0.47	20
130	0.44	30
150	0.56	39
170	0.63	48
190	1.00	53

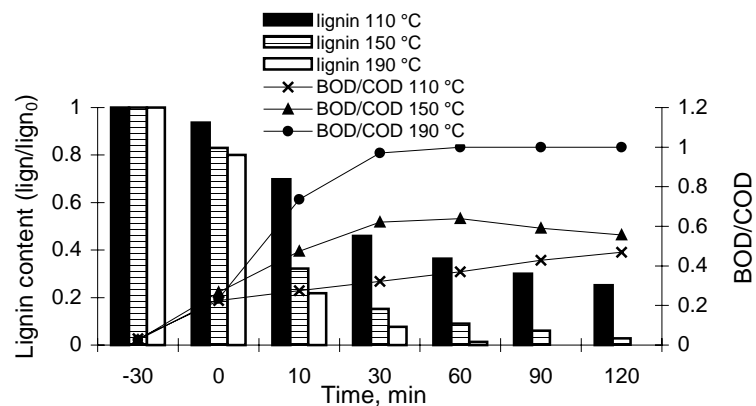


Fig. 1. Effect of temperature on alkali lignin removal and biodegradability (BOD/COD) at pH 12 and pressure 1 MPa.

value [27] and appropriate for further biological treatment – it implies that the wastewater is readily biodegradable.

Figure 2 depicts the dependence of COD removal on temperature and comparison of lignin removal with earlier research [20].

In [20] the initial pH value was 12.4, lignin concentration 300 mg/L, and 1.5 g/L sodium hydroxide (NaOH) was added to the solution. Nevertheless, as can be seen, the lignin removal is quite similar. Significant changes happen in the first 30 min: during this time 77% and 85% of lignin was removed from the water solution (according to [8] and experimental, respectively). At the end of the experiment 90% and 97% of lignin was removed.

To characterize the state of organics in a mixture, AOSC is applied [23–25]. Using molar concentrations for TOC and COD it can be calculated according to

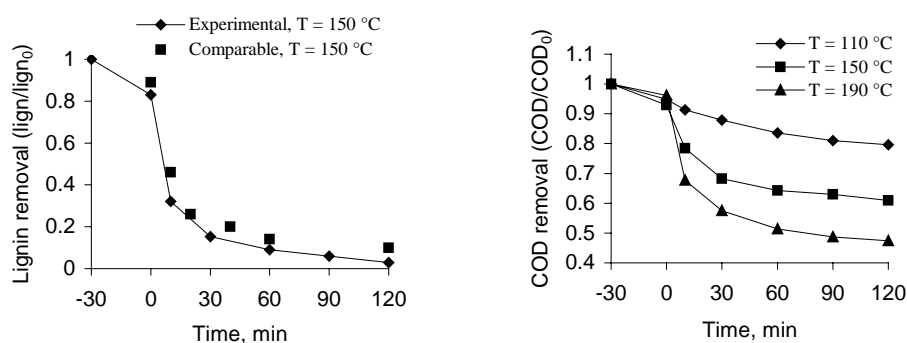


Fig. 2. Effect of temperature on alkali lignin (experimental and ref. [20]) and COD removal at pH 12, pressure 1 MPa for 120 min.

the following equation:

$$\text{AOSC} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}}$$

The theoretical AOSC is −4 for methane and +4 for carbon dioxide, +2 for formic acid, and 0 for acetic acid. Higher AOSC values consequently indicate a high oxidation state for the organics in the mixture, but cannot indicate how much partial and total oxidation has taken place since the start of reaction [23–25].

The calculation of AOSC showed higher values at higher temperatures (Fig. 3). This indicates that the whole oxidation of the water solution improved with increased temperature. Increasing AOSC may show that evolving intermediates during the oxidation process have been successfully degraded or the process continues.

A clear relationship was observed between the lignin concentration and colour, which had similar trend lines during the oxidation process with respect to temperature (Fig. 4). The correlation line is presented in Fig. 5. Therefore, more

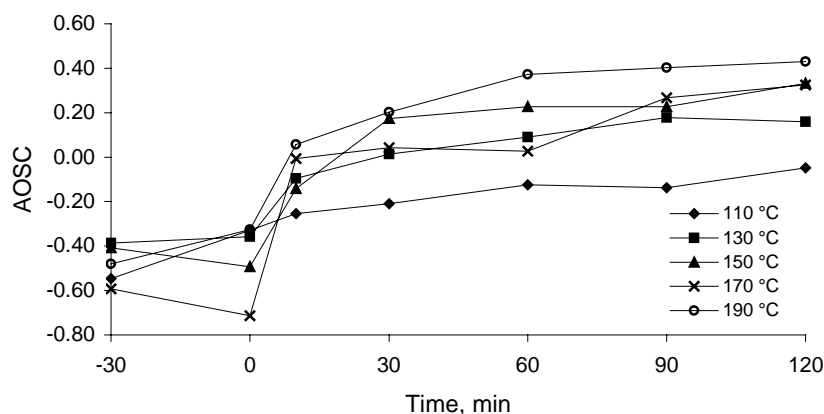


Fig. 3. The oxidation state of carbon atoms (AOSC): comparison at different temperatures at pH 12, pressure 1 MPa.

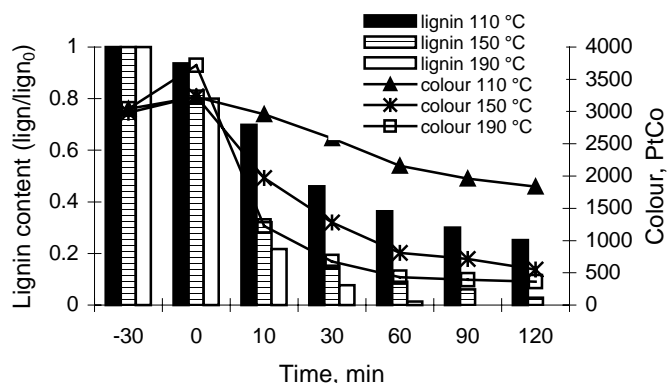


Fig. 4. Relationship of lignin and colour reduction during the oxidation process at pH 12, pressure 1 MPa.

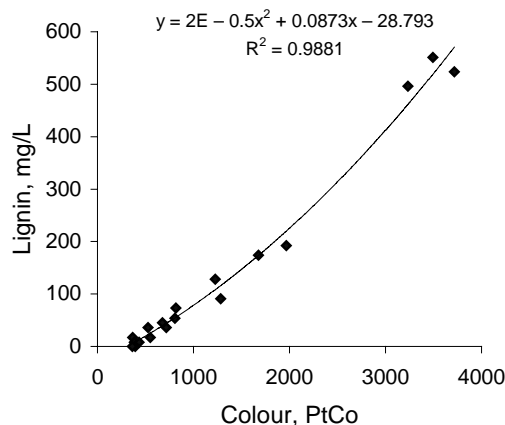


Fig. 5. Trend line of lignin and colour concentration at a temperature range of 150–190 °C.

complicated analysis of lignin can be avoided and the concentration of lignin can be determined using the results of the colour measurements.

The effect of oxygen partial pressure

Three oxygen partial pressures (0.5, 1, and 1.5 MPa) were tested at all temperatures. In general, the effect of pressure was not as significant as that of temperature. Figure 6 depicts the behaviour of the alkali lignin concentration and COD removal during the WO experiments at different oxygen partial pressures. Increasing and decreasing the pressure did not result in large changes in the process compared to the original oxygen partial pressure (1 MPa). The differences were

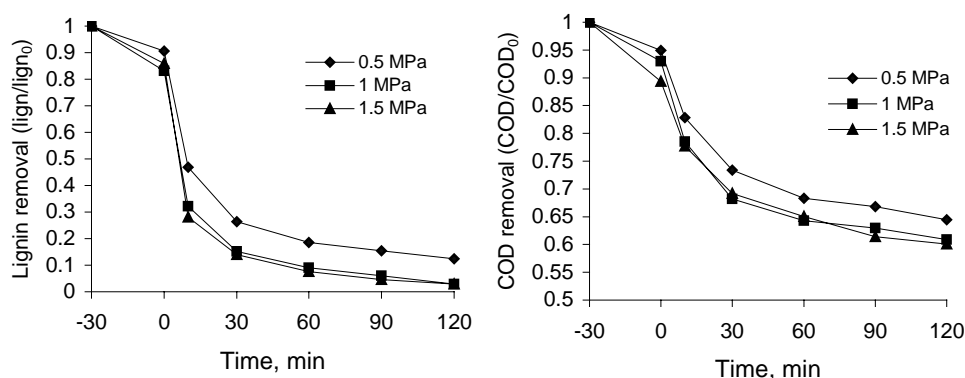


Fig. 6. Effect of oxygen partial pressure on alkali lignin and COD removal at pH 12, temperature 150 °C.

Table 4. Comparison of biodegradability (BOD/COD) at different oxygen partial pressures, temperature 150 °C, pH 12

Time, min	BOD/COD		
	0.5 MPa	1 MPa	1.5 MPa
-30	0.03	0.03	0.03
0	0.18	0.27	0.19
10	0.43	0.47	0.47
30	0.54	0.62	0.64
60	0.58	0.64	0.66
90	0.55	0.59	0.65
120	0.52	0.56	0.67

quite modest. Lignin removal improved by about 10% and COD removal by only 4% at the highest pressure (1.5 MPa) used in the experiments.

Some results concerning biodegradability are presented in Table 4. It can be seen that the effect of pressure on biodegradability was small. Final results differ by about 15% with respect to each other. The higher the oxygen pressure, the higher the BOD/COD. Generally, all pressures were good enough considering the ratio of BOD/COD. A value over 0.5 means that the water is easily biodegradable.

The effect of pH

The effect of pH on lignin removal was clearly observed, but the effect on COD removal was small. Increasing the pH enhanced the lignin removal efficiency by approximately 40% (from 60% to nearly 100%). Earlier studies show that lignin removal gives the best results in alkaline media [20, 21]. Therefore, it is necessary to point out that lignin reduction is sensitive to pH, while removal of organics (COD) is quite independent. At the beginning of the WO at higher pH oxidation starts faster, but the final (after 2 h) COD value was the same, with 38% removal achieved (Fig. 7).

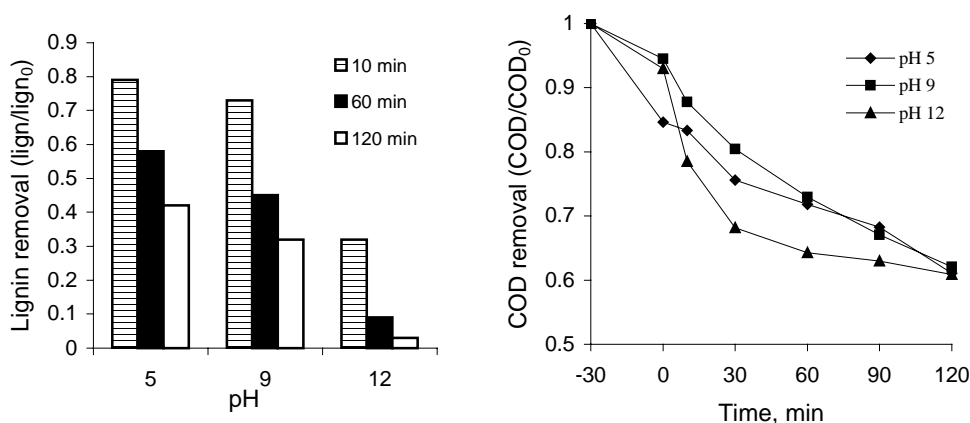


Fig. 7. Effect of pH on alkali lignin and COD removal at a pressure of 1 MPa, temperature 150 °C.

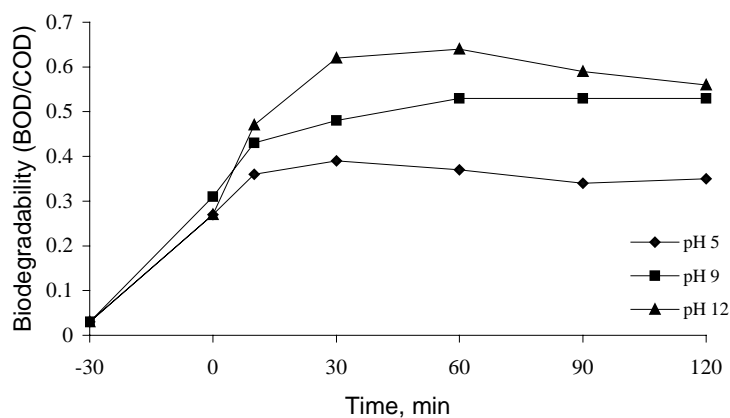


Fig. 8. Effect of pH on biodegradability at a pressure of 1 MPa, temperature 150 °C.

The influence of pH on biodegradability (BOD/COD ratio) is illustrated in Fig. 8. It can be seen (Figs 7 and 8) that the difference of the BOD/COD ratio compared at COD removal is detectable (it means that the BOD is more sensitive to pH than the COD). A relatively low degree of COD removal did not affect the biodegradability (BOD/COD) of the water solution. Increasing the pH increased the BOD/COD ratio as well, which at the end of the process was 0.35, 0.53, and 0.56 at pH values of 5, 9, and 12, respectively. At higher pH values probably the reaction mechanism changes and the formation of OH radicals with high oxidation properties occurs. Faster oxidation of organics at higher pH values is suggested as a possible reason [28]. This is accompanied probably by faster formation of relatively more biodegradable compounds.

In all cases, during the WO process the initial pH decreased modestly. It can be explained by different reactions that occur during the process: aromatic compounds decomposed rapidly, organic substances degraded easily, carboxylic and other acids were formed, which caused the decrease in the pH.

Preheating period and better oxidation conditions

It is of interest to note that certain changes occur already during the preheating period before the WO starts. The preheating period lasts about 20–40 min and has different effects on the various solution parameters, most strongly on the lignin concentration. As can be seen in Table 2, lignin had reduced already 6–20% before oxygen was introduced into the reactor, at “zero” time. During preheating the colour was notably increased (Fig. 4). The higher the temperature, the higher the colour increase is. This indicates that considerable chemical changes happen already in the preheating period, which affect the following WO process.

A way to improve the process efficiency is to combine simultaneously all process conditions and shorten the process duration. As a result, the most optimal conditions would be a temperature of 190 °C, oxygen partial pressure 1 MPa,

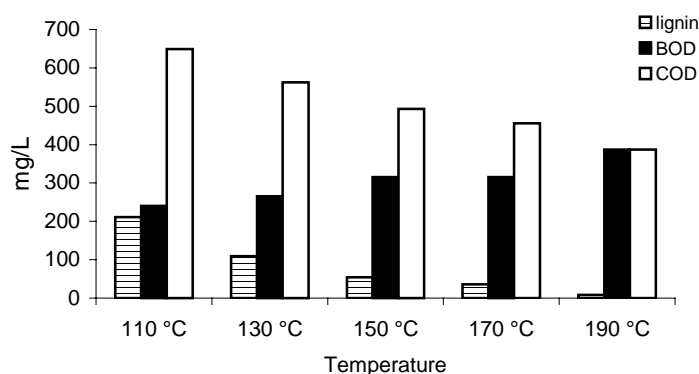


Fig. 9. Lignin concentration, BOD, and COD at different temperatures in 60 min.

pH 12. Under these conditions 99% of lignin was removed in 60 min. Figure 9 shows lignin concentration, and COD and BOD values at different WO temperatures.

It can be seen that at 190°C the maximum biodegradability is achieved: BOD/COD = 1. This means that at this time all more complicated organics are degraded. Good results can be also achieved at a temperature of 150°C, pH 12 with a process duration of 120 min. During this time 97% of the lignin was removed (biodegradability increased to 0.56). Nevertheless, the wet oxidized water should be further treated to remove the remaining organics. Since the BOD/COD ratio was generally over 50%, the appropriate treatment method is biological treatment.

CONCLUSIONS

Degradation of lignin by wet oxidation showed good results – 100% of lignin and 53% of COD were removed at 190°C and at pH 12 from WO treated water. The jar experiments demonstrated that the optimum pH range for the lignin degradation process is 12–13 (strongly alkaline). The relatively short process reaction time, 120 min, showed good results; moreover, during the jar experiments it was observed that most of the reactions occurred within the first 30–60 min. The greatest effect on the process was detected by increasing the temperature. A significant effect was observed at different pH values. The changes in oxygen partial pressure showed a modest effect on the WO process. In all cases, a good biodegradability (BOD/COD ratio over 0.5) was achieved starting at temperature 150°C, pH 9, irrespective of the experimented pressures. The remaining organic matter can be easily removed biologically.

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Ligniiniide lagundamine märgoksüdatsiooniga: ligniini veelahus kui mudelsüsteem

Merit Kindsigo ja Juha Kallas

Tänapäeval on paljud tööstused silmitsi reovetega, mis sisaldavad halvasti lagunevaid või bioloogilistele puhastusprotsessidele inertseid ühendeid nagu näiteks tanniinid, ligniiniid jms. Märgoksüdatsioon on sobilikuks meetodiks komplekssete, mitmetasandiliste ja inertsete reoainete lagundamiseks. Artiklis on uuritud ligniinilahuse kui mudelsüsteemi töötlemist märgoksüdatsiooniga, mille eesmärgiks on lagundada ligniini ja suurendada lahuse biodegradeeruvust. Eksperimentaalne osa viidi läbi erinevate temperatuuride (110–190°C), rõhkude (0,5–1,5 MPa) ja pH-dega (pH 5, 9 ja 12) roostevabast terasest reaktoris. Katsete põhitulemuseks võib lugeda meetodi efektiivsuse tõusu võrdeliselt temperatuuri tõusuga. Kui 110°C juures lagunes 75% ligniinist, siis 190°C juures juba 100%. KHT (keemiline hapnikutarve) ärastusaste oli väiksem, kuid siiski märgatav: 110°C juures oli ärastus 10%, 190°C juures 53%. Olulist mõju protsessile näitas pH tõus: tõusuga 5-lt 12-le paranes ligniini lagundamise efektiivsus 60%-lt peaaegu 100%-ni. Kõige väiksemat mõju protsessile näitas hapniku osarõhu muutus reaktoris (0,5–1,5 MPa): rõhu muutuste puhul oli protsessi efektiivsuse erinevus ligniini lagundamisel 10%, KHT ärastuse puhul 4%. Häid tulemusi sai kõigil juhtudel, kus temperatuur oli vähemalt 150°C ja pH vähemalt 9: nendel tingimustel saavutati biolagundatavuse aste (BHT (bioloogiline hapnikutarve)/KHT) üle 0,5.