CHEMISTRY

# Kinetic modelling of wet oxidation treated debarking water

Merit Kindsigo[a*], Marjaana Hautaniemi[a], and Juha Kallas[a,b]

[a] Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, 53851 Lappeenranta, Finland
[b] Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

**Abstract.** The objective of the research was to compare the behaviour of two kinetic models in parameter estimation with lignin containing waters, based on experiments of wet oxidation of debarking water. When comparing the results of the models, the model with lignin included (M2) was found to be more suitable for describing the kinetics of wet oxidation of debarking water. Lignin degraded first to other chemically oxidizable compounds rather than straight to biodegradable products. The activation energies for the degradation reactions fell with a change in the pH from 5 to 12 from 51 to 21 kJ/mol and from 84 to 12 kJ/mol, respectively. This supports the experimental finding that lignin degradation is faster in basic conditions. The model could predict the degradation of lignin as well as the important wastewater parameters COD and BOD.

**Key words:** wet oxidation, lignin, parameter estimation, reaction kinetics.

**List of symbols**

| | |
|---|---|
| $c_A$ | Concentration of lignin (COD that corresponds to lignin), mg L$^{-1}$ |
| $c_{A,0}$ | Initial concentration of lignin in the solution, mg L$^{-1}$ |
| $c_E$ | Concentration of chemically oxidizable compounds (COD), mg L$^{-1}$ |
| $c_{E,0}$ | Initial concentration of chemically oxidizable compounds in the solution, mg L$^{-1}$ |
| $c_B$ | Concentration of biodegradable compounds (BOD), mg L$^{-1}$ |
| $c_{B,0}$ | Initial concentration of biodegradable compounds in the solution, mg L$^{-1}$ |
| $c_C$ | Concentration of compounds other than lignin (COD–COD$_{lignin}$), mg L$^{-1}$ |
| $c_{C,0}$ | Initial concentration of compounds other than lignin in the solution, mg L$^{-1}$ |
| $c_D$ | Concentration of CO$_2$, mg L$^{-1}$ |
| $c_{D,0}$ | Initial concentration of CO$_2$, mg L$^{-1}$ |
| $c_{O2}$ | Liquid phase oxygen concentration, mg L$^{-1}$ |
| $E_a$ | Activation energy, kJ mol$^{-1}$ |
| $k$ | Reaction rate constant, min$^{-1}$ |
| $k^0$ | Frequency factor, min$^{-1}$ |
| $K^0$ | Frequency factor defined in Eq. 7, min$^{-1}$ |
| $K^0_{mean}$ | Frequency factor defined in Eq. 9, min$^{-1}$ |
| $R$ | Gas constant, 8.314 J mol$^{-1}$ K$^{-1}$ |
| $t$ | Reaction time, min |
| $T$ | Temperature, °C |
| $T_{mean}$ | Mean temperature between the lowest and the highest temperatures used in the estimation, °C |
| *Subscripts* | |
| $i$ | Reaction pathway, 1, 2, 3, or 4 |
| *Superscripts* | |
| $n$ | Oxygen reaction order for the reaction pathways 1, 2, 3, or 4 |

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* Corresponding author, merit.kindsigo@gmail.com

# 1. INTRODUCTION

Papermaking is a branch of industry that requires large amounts of water and effective wastewater treatment is essential. Because of its chemical properties, effluent from paper mills can cause environmental damage and must be treated before disposal (Elvers et al., 1991: 547–557) – the effluent produced is currently one of the most toxic wastewaters in the papermaking industry. Wastewaters from the debarking process are heavily contaminated by fatty and resin acids, tannins, and lignins and their derivatives. The presence of lignins and their derivatives, as well as polymerized tannins, causes these wastewaters to be highly coloured (Field et al., 1988).

Lignin is an amorphous polymer with a high content of functional groups, which allows a wide range of linkages between the lignin and some carbohydrates. Although it is evident that physical and chemical inter-actions occur between lignin and carbohydrates, it has been difficult to verify the precise type and amount of chemical linkages. Lignin, however, not only interacts with some carbohydrates but also with cationic chemicals used in paper making, causing a negative effect on the brightness and strength of the paper (Elvers et al., 1991: 547–557; Gullichen and Paulapuro, 2000: 28–65).

Oxidative polymerization is a way of neutralizing the toxicity of the debarking effluent constituents; however, it does not eliminate the pollutants from the aqueous solution. Wet oxidation involves liquid phase oxidation of organic or oxidizable inorganic components at elevated temperatures and pressures using a gaseous source of oxygen. This process has a very limited interaction with the environment; if the oxidation is not complete, it can be coupled with biological treatment to eliminate or to treat any remaining waste (Debellefontaine and Foussard, 2000). In WO processes, the organic contaminants dissolved in the water are either partially degraded into biodegradable intermediates by means of an oxidizing agent or mineralized into innocuous inorganic compounds such as $CO_2$, $H_2O$, and inorganic salts, which remain in the aqueous phase (Luck, 1999). Advanced Oxidation Processes (AOP) are suited for destroying dissolved organic contaminants such as halogenated hydrocarbons, aromatic compounds, pentachlorophenol (PCP), nitrophenols, detergents, pesticides, etc. AOPs can also be used to oxidize inorganic contaminants such as cyanide, sulphide, and nitrite (Munter, 2001).

The non-complete oxidation can be explained by taking into account the fact that the oxidation rate increases with the increase in the molecular weight/ carbon number (Mishira et al., 1995). As a result, low molecular weight acids, which are the last organic intermediates formed prior to the formation of carbon dioxide, are the most recalcitrant compounds for the oxidation process and remain in the solution. The formation of carboxylic acids causes a decrease in the pH over the duration of the process and also an increase in the biodegradability of the wastewater.

Many kinetic models for multi-compound solutions have been suggested in the literature. One of the first ones was the General Lumped Kinetic Model (GLKM), proposed by Li et al. in 1991. Other models found in the literature are, for instance, the Lumped Kinetic Model (LKM) by Zhang and Chuang (1999), the Extended Kinetic Model (ELKM) by Belkacemi et al. (2000), the Multi-Component Kinetic Model by Escalas et al. (1997), the Lumped Kinetic Model for Oil Wastes (LKM-OW) by Lopez Bernal et al. (1999), and the Lumped Kinetic Model for Wastewater Biodegradability Prediction by Verenich and Kallas (2002).

The present study focuses on the modelling of wet oxidation of debarking water and compares the results, effectiveness, and reliability of two models. The first model (M1) is an application of the model for wet air oxidization (WAO) proposed by Li et al. (1991) and the second model (M2) is a modification of the model proposed by Verenich and Kallas (2002).

# 2. KINETIC MODELLING

Most kinetic models suggested in the literature for multi-compound solutions follow the evolution of the reaction by controlling general parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total oxygen demand (TOD), or total organic carbon (TOC). These models are especially useful because when properly applied they are capable of predicting the evolution of these parameters throughout the reactions. A model of special interest because it allows prediction of not only COD but also BOD is the Lumped Kinetic Model for Wastewater Organic Burden Biodegradability proposed by Verenich and Kallas in 2002. The models used in the present paper, M1 and M2, are based on those proposed by Li et al. (1991) and Verenich and Kallas (2002), respectively. The differences of M2 are addition of a TOC parameter, which gives the opportunity to estimate the amount of emerging inorganic substances, not only the decrease of COD; stoichiometric constant m; lignin degradation (calculated to $COD_{lignin}$); and oxygen partial pressure.

The first kinetic model (M1), shown in Fig. 1, is based on a three-reaction scheme, the principles of which follow the generalized model for the WAO of organic compounds proposed by Li et al. (1991). In this model three groups of organic substances are defined to exist in the liquid and gaseous effluents: initial compounds and other relatively unstable organic compounds (lump E); refractory intermediates, i.e. acetic acid (lump B); and oxidation end products (lump D); $k_1$, $k_2$, and $k_3$ are the reaction rate constants in the scheme.
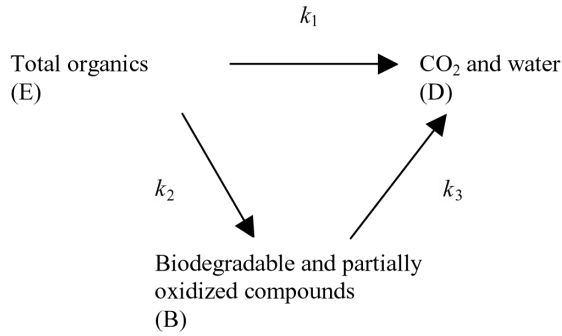
**Fig. 1.** Reaction pathways for wet oxidation of lignin (Li et al., 1991), model M1.



**Fig. 2.** Reaction pathways for wet oxidation of lignin (Kindsigo et al., 2009), model M2.

According to this reaction pathway, oxidation of the total organics (lump E, measured via COD) and bio-degradable compounds (lump B, described by BOD) is assumed to proceed in two parallel ways: in the first one, compounds are oxidized to the end products of the reaction; and in the second one, the matter contained in the waste stream is partially oxidized and becomes biodegradable. The biodegradable compounds are further oxidized to the end products, i.e. carbon dioxide and water.

The reaction system is expressed mathematically as follows:

$$\frac{dc_E}{dt} = -k_1 c_E - k_2 c_E, \tag{1}$$

$$\frac{dc_B}{dt} = k_2 c_E - k_3 c_B, \tag{2}$$

$$\frac{dc_D}{dt} = m_1 k_1 c_E + m_2 k_3 c_B, \tag{3}$$
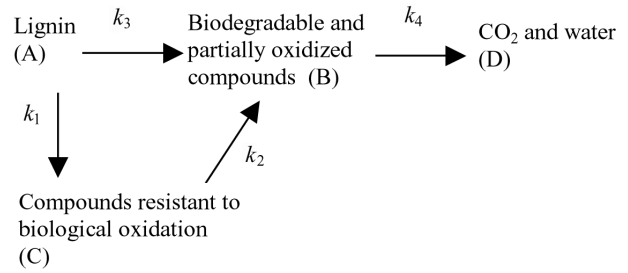
where $m_1$ and $m_2$ are stoichiometric constants and

$$k_i = k_i^0 \exp\left(-\frac{E_{ai}}{RT}\right) c_{O2}^{ni}. \tag{4}$$

At 'zero' time, the concentrations of lumps E, B, and D are the concentrations of $c_{E,0} = (COD)_0$, $c_{B,0} = (BOD_7)_0$, $c_{D,0} = 0$. In the calculations, the formation of the end products, $CO_2$ and water, was evaluated through the change in TOC.

The activation energies $E_{ai}$ and frequency factors $K_i^0$ were estimated from the Arrhenius equation (10), where $k_i^0$ was merged with $c_{O2}^{ni}$ to give $K_i^0$. Other basic equations (Eqs 10–13) are the same as for the second model (M2).

The second kinetic model (M2), shown in Fig. 2, was developed in order to predict not only the changes in COD and BOD but also lignin degradation. The same model has been applied earlier to model solutions of wet oxidation of lignin (Kindsigo et al., 2009). In this model, the reaction system is divided into lumps with respect to the biodegradability of the organic substances (see Fig. 2). The first lump, A, is lignin described as COD that corresponds to lignin. As illustrated in Fig. 2, the oxidation of lignin, A, leads to the formation of biodegradable compounds, B, and to other compounds that are difficult to oxidize biologically (COD–$COD_{lignin}$), lump C. Lump B is characterized via BOD analysis and incorporates the products of partial oxidation, such as carboxylic acids, aldehydes, alcohols, or other substances that can be utilized by microorganisms. Lump C undergoes further oxidation into lump B. Lump B is oxidized further into the final products, that is the compounds containing inorganic carbon, i.e. carbon dioxide and water (lump D).

This reaction system is expressed mathematically as follows:

$$\frac{dc_A}{dt} = -k_1 c_A - k_3 c_A, \tag{5}$$

$$\frac{dc_B}{dt} = -k_3 c_A + k_2 c_C - k_4 c_B, \tag{6}$$

$$\frac{dc_C}{dt} = k_1 c_A - k_2 c_C, \tag{7}$$

$$\frac{dc_D}{dt} = m k_4 c_B, \tag{8}$$

where $m$ is a stoichiometric constant and

$$k_i = k_i^0 \exp\left(-\frac{E_{ai}}{RT}\right) c_{O2}^{ni}. \tag{9}$$

At 'zero' time, the concentrations of lumps A, B, C, and D are the concentrations of $c_{A,0} = (COD_{lignin})_0$, $c_{B,0} = (BOD_5)_0$, $c_{C,0} = (COD-COD_{lignin})_0$, $c_{D,0} = 0$. The COD corresponding to lignin is calculated as $COD_{lignin} = a \cdot c_{lignin}$ ($a = 1.28$, the calculated average), where $a$ is the ratio of COD and lignin concentrations in the solution before oxidation ($a = COD_{-30}/c_{lignin-30}$; –30 marks the 30 minutes before the outset of the oxida-

tion process) based on lignin model-solution experiments carried out earlier (Kindsigo and Kallas, 2006). The COD corresponding to the other compounds is calculated as $c_C = COD_{others} = COD - COD_{lignin}$. In the calculations, the formation of end products, that is of the compounds containing inorganic carbon and water, is evaluated through the change in TOC.

The activation energies, $E_{ai}$, and frequency factors, $K_i^0$, are estimated from the Arrhenius equation (10), where $k_i^0$ is merged with $c_{O2}^{ni}$ to give $K_i^0$:

$$k_i = K_i^0 \exp\left(-\frac{E_{ai}}{RT}\right). \tag{10}$$

The Arrhenius equation, in its traditional form (Eq. 10), has two strongly correlating parameters, $E_{ai}$ and $K_i^0$. By suitably increasing the values of both $K_i^0$ and $E_{ai}$, $k_i$ could remain virtually unchanging. Therefore, a new parameterization of Eq. (10) should be performed. The parameterization can be written in the following form (Haario, 1994):

$$k_i = K_{imean} \exp\left(-\frac{E_{ai}}{R}\left(\frac{1}{T} - \frac{1}{T_{mean}}\right)\right), \tag{11}$$

where

$$K_{imean} = K_i^0 \exp\left(-\frac{E_{ai}}{RT_{mean}}\right) \tag{12}$$

and $T_{mean}$ is the mean temperature between the lowest and the highest temperatures used in the estimation. The values of the original frequency factors $K_i^0$ have to be recalculated from Eq. (12).

For the cases where $c_{O2}^{ni}$ cannot be assumed to be a constant ($n_i \neq 0$), a 'scaled' liquid phase oxygen concentration was introduced

$$k_i = k_i^0 \exp\left(-\frac{E_{ai}}{RT}\right)\left[\frac{c_{O2}}{c_{O2,mean}}\right]^{ni}, \tag{13}$$

where $c_{O2,mean}$ refers to the liquid phase oxygen concentration at the mean temperature of the experiments. The oxygen concentration in the liquid phase was calculated as suggested by Tromans (1998). Scaled concentration was chosen instead of unscaled $c_{O2}$ to allow easier comparison of the results as the units of the parameters remain unchanged.

The activation energies and frequency factors for the models above were obtained using parameter estimation. The computations were performed with the MODEST software package (Haario, 1994), resulting in the same method and calculations as used by Kindsigo et al. (2009). When the model parameters had been estimated, the reliability of the estimated values and their interdependence were studied.

## 3. EXPERIMENTAL PROTOCOLS

Wet oxidation reactions were tested to degrade wastewaters coming from pulp and paper mills or lignin containing waters as a model case (synthetic water). In one case, lignin containing water was oxidized by wet oxidation under certain conditions; in the other case, wastewater from the debarking process was oxidized by wet oxidation partially under the same conditions (Table 1).

### 3.1. Materials

The wastewater used in the present research was debarking water, supplied by a Finnish pulp and paper mill, taken from the first main paper mill process, wood debarking. In the paper mill the debarking water effluent was conducted to evaporation units in order to separate clean water as the condensate and a concentrated solution. The evaporation concentrate had a dark brown colour and the dry solid content was between 20% and 25% (Verenich et al., 2005). The original debarking water had the following characteristics: 250–280 $gO_2/L$ of COD; 80–120 gC/L of soluble TOC; 170–185 g/L of soluble tannins/lignin; 20–40% of biodegradability; $1 \times 10^6$–$1.2 \times 10^6$ Pt–Co of colour; 0.75–0.85 g/L of aldehydes, and pH ~8.

A model solution of lignin was prepared using alkali lignin (Aldrich Co.). The alkali lignin was dissolved in 300 mL of distilled water. As a result, a solution with the following properties was obtained: 750–780 $mgO_2/L$ COD and 250–270 mgC/L of soluble TOC; 600 mg/L of soluble tannins/lignin; 35–100% of biodegradability; 2917–3683 Pt–Co of colour; and pH 5–12. A solution of sodium hydroxide (NaOH) was used to increase the pH and sulphuric acid ($H_2SO_4$) was used to decrease the pH at the beginning of the experiments. During wet oxidation the pH value was recorded but not controlled (Kindsigo and Kallas, 2006).

**Table 1.** Operating conditions of wet oxidation experiments

| | Feed | |
|---|---|---|
| | Evaporation concentrate of debarking water | Recalcitrant lignin model water solution |
| Partial pressure of $O_2$, MPa | 0.3, 0.6, 1.0, 1.5 | 0.5, 1.0, 1.5 |
| Temperature, °C | 130, 150, 170, 190, 200 | 110, 130, 150, 170, 190 |
| Dilution degree, times | 10, 14.3, 25, 50, 100 | No dilution rate |
| Initial pH | 5, original pH (~8), 10, 12 | 12 |

## 4. RESULTS AND DISCUSSION

The wet oxidation experiments (experimental procedure, analytical methods) with the above-mentioned waters and their results are given in previous papers (Kindsigo and Kallas, 2006, 2009). For this reason this paper does not present experimental results in detail.

### 4.1. Modelling of reaction kinetics

The kinetic parameters in models were evaluated for the wet oxidation of debarking water in the temperature range of 130–200 °C and oxygen partial pressure of 1.0 MPa at the initial pH values of 5, 8 (original pH), 10, and 12 (Table 1). The original frequency factors $K_i^0$ were obtained by recalculating $K_{i\,\text{mean}}$ values from Eq. (12).

Dissimilarity analysis to stoichiometric constants was done and is briefly presented in Fig. 3, which gives an example of the performance of the model (M1) in the wet oxidation of lignin at certain chosen conditions ($T = 170$ °C, pH 8). The influence of stoichiometric constant can clearly be seen in the figure.

In model M1, given in Fig. 1, two factors were not included – oxygen partial pressure (it was assumed to be constant and with a very small effect) and the possible importance of the effect of lignin degradation on non-biodegradable and biodegradable compounds simultaneously by different pathways. The model was not modified to account for changes in lignin concentration in addition to COD and BOD. Addition of these factors into the model gave the second model (M2), which turned out to be more suitable for our purposes.

When applying model M2, given in Fig. 2, the oxygen reaction order for each reaction, $n_i$, was first determined from Eq. (13) from the experiments carried out at 190 °C and pH 5 with oxygen partial pressures of 0.3, 0.6, 1.0, and 1.5 MPa. The values obtained were $n_1 = 1.1$, $n_2 = 0.0002$, $n_3 = 1.1$, and $n_4 = 0.35$. These values were assumed to be valid also for the other experimental conditions (pHs, temperatures). The results show that oxidation depends to some extent on oxygen partial pressure; a zero value assumption is valid only for reaction 2, where the chemically oxidizable compounds other than lignin degrade to biodegradable products (Fig. 2).

Table 2 gives a comparison of the evaluated kinetic parameters for model M2, presenting the changes first without the possible influence of oxygen concentration ($n_i = 0$) and then including oxygen concentration (in the temperature range of 150–190 °C and oxygen partial pressure of 1.0 MPa at the initial pHs of 5, 8, 10, and 12). Generally, the obtained results were remarkably similar, which supports the assumption that the changes in the oxygen concentration can be excluded from the model estimation parameters. The oxygen partial pressure was constant, 1.0 MPa, in these experiments,
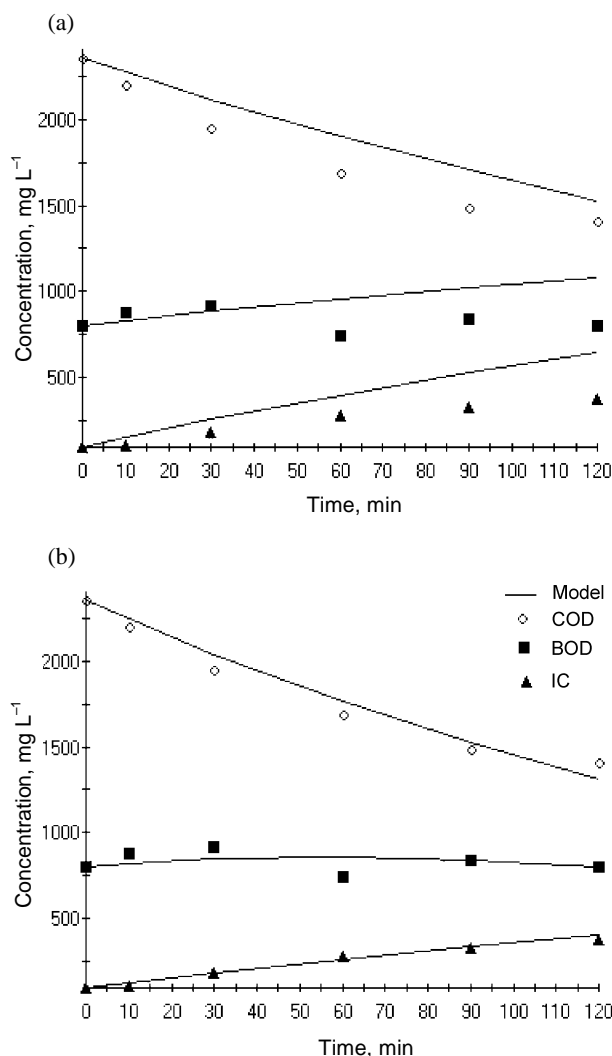


**Fig. 3.** Performance of the model without a stoichiometric constant (a) and with a stoichiometric constant (b) for the experimental data observed at $T = 170$ °C, pH = 8.

so changes in solubility, if any, were only due to changes in temperature. The stoichiometric constant $m$ evaluated for reaction 4 (see Fig. 2) was $0.24 \pm 0.15$ within 95% confidence at each pH value in both cases.

Figure 4 presents the activation energies of lignin degradation reactions 1 and 3, where lignin was assumed to degrade to other chemically oxidizable compounds and biodegradable compounds, respectively. It is seen that in both cases, based on the experiments carried out with the debarking water, the activation energy, which indicates the rate of lignin degradation, decreases as a function of pH. The same observation was made in the lignin model-solution experiments (Kindsigo and Kallas, 2006). The activation energies estimated from the model-solution and debarking water experiments (Kindsigo et al., 2009) behave differently. The different behaviour is especially evident in the case

**Table 2.** Evaluated frequency factors $K_i^0$ and activation energies $E_a$ with their 95% confidence intervals for wet oxidation of debarking evaporate concentrate at 130–200 °C and oxygen partial pressure of 1.0 MPa (using model M2). Comparison of the models with liquid phase oxygen concentration included and not included

| Initial PH | Reaction | $c_{O2}$ not included in the model ($n_i = 0$) | | | $c_{O2}$ included in the model | | |
|---|---|---|---|---|---|---|---|
| | | $K_i^0$, min$^{-1}$ | $E_a$, kJ mol$^{-1}$ | Regression coefficient $R^2$, % | $K_i^0$, min$^{-1}$ | $E_a$, kJ mol$^{-1}$ | Regression coefficient $R^2$, % |
| 5 | 1 | $(3.2 \pm 0.4) \times 10^4$ | $51 \pm 12$ | 84.4 | $389 \pm 55$ | $35 \pm 11$ | 84.3 |
| | 2 | $0.017 \pm 0.005$ | $3 \pm 28$ | | $0.0078 \pm 0.0022$ | $0.3 \pm 26$ | |
| | 3 | $(7.6 \pm 3) \times 10^7$ | $84 \pm 33$ | | $(4.9 \pm 1.8) \times 10^7$ | $74 \pm 34$ | |
| | 4 | $539 \pm 82$ | $38 \pm 14$ | | $166 \pm 25$ | $34 \pm 14$ | |
| 8 | 1 | $1150 \pm 150$ | $39 \pm 11$ | 88.9 | $36 \pm 5$ | $26 \pm 10$ | 88.9 |
| | 2 | $0.058 \pm 0.017$ | $9 \pm 26$ | | $0.029 \pm 0.008$ | $6.5 \pm 2$ | |
| | 3 | $(1.6 \pm 0.6) \times 10^7$ | $78 \pm 36$ | | $(2.2 \pm 0.9) \times 10^7$ | $71 \pm 39$ | |
| | 4 | $4.6 \pm 0.7$ | $22 \pm 13$ | | $1.4 \pm 0.2$ | $17 \pm 13$ | |
| 10 | 1 | $(2.6 \pm 0.8) \times 10^4$ | $51 \pm 12$ | 86.7 | $31 \pm 5$ | $25 \pm 13$ | 84.5 |
| | 2 | $55 \pm 21$ | $35 \pm 34$ | | $0.044 \pm 0.014$ | $8 \pm 29$ | |
| | 3 | $(1.5 \pm 0.4) \times 10^4$ | $51 \pm 25$ | | $(1.4 \pm 0.6) \times 10^4$ | $52 \pm 39$ | |
| | 4 | $34 \pm 2$ | $26 \pm 14$ | | $1.1 \pm 0.2$ | $16 \pm 16$ | |
| 12 | 1 | $18 \pm 3$ | $21 \pm 11$ | 90.3 | $0.99 \pm 0.18$ | $10 \pm 12$ | 90.2 |
| | 2 | $98 \pm 72$ | $39 \pm 51$ | | $23 \pm 16$ | $33 \pm 48$ | |
| | 3 | $0.53 \pm 0.23$ | $12 \pm 25$ | | $0.04 \pm 0.02$ | $3 \pm 26$ | |
| | 4 | $88 \pm 32$ | $34 \pm 25$ | | $28 \pm 9$ | $30 \pm 25$ | |
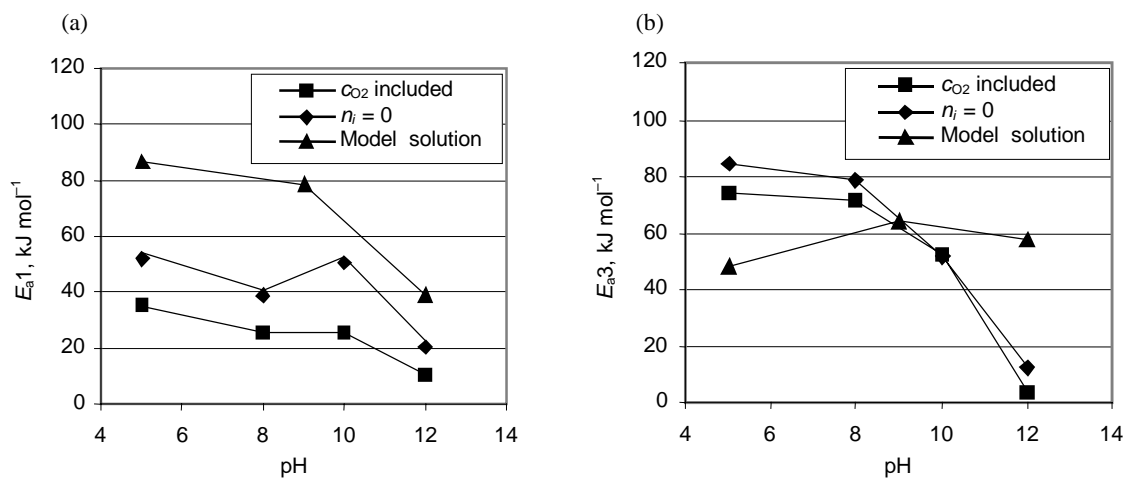


**Fig. 4.** Activation energies for lignin degradation reactions 1 and 3 at different pHs. Comparison of the results obtained with the liquid phase oxygen concentration included in the model, neglecting the oxygen concentration ($n_i = 0$), and earlier results obtained for the model-solution experiments.

of reaction 3, where lignin degrades to biodegradable compounds. The degradation to biodegradable compounds could be explained by the differences in the compositions of lignin in the debarking water and of the model solution, that is, there may be different groups, causing e.g. polymerization, which was not analysed in these studies.

Examination of the activation energy of reaction 2, where the chemically oxidizable compounds other than lignin degrade to biodegradable products, shows that the activation energy rises as a function of pH, indicating

the compounds degrade preferably in acidic media than in basic media. The same observation was made in the experiments carried out with the lignin model solution (Kindsigo and Kallas, 2009) where the highest lignin (and other phenol compounds) removal was achieved at pH 12 while the highest COD removal in general was achieved at pH 5. In the case of reaction 4, where the biodegradable products degrade to the end products, $CO_2$, and water, the lowest activation energies were found at neutral conditions.

The first-order reaction rate constants were calculated for each reaction based on Eq. (10). Analysis of these constants suggests similar conclusions as analysis of the activation energies. The lignin degradation rate is fastest at pH 12, while the other chemically oxidizable compounds degrade fastest at pH 5. Examples are shown in Figs 5 and 6. Note that the models with and without liquid phase oxygen concentration gave quite similar results.

Comparison of the reaction rates of the lignin degradation of reactions 1 and 3 (see the reaction scheme in Fig. 2, calculated from Eq. (10) and based on the results shown in Table 3) shows reaction 1 to be more successful in the degradation of lignin than reaction 3. Similarly to the model-solution experiments, it is seen that lignin decomposes first to other chemically oxidizable compounds rather than straight to biodegradable compounds. Particularly interesting is the fact that the higher the pH, the more important reaction 1 is.
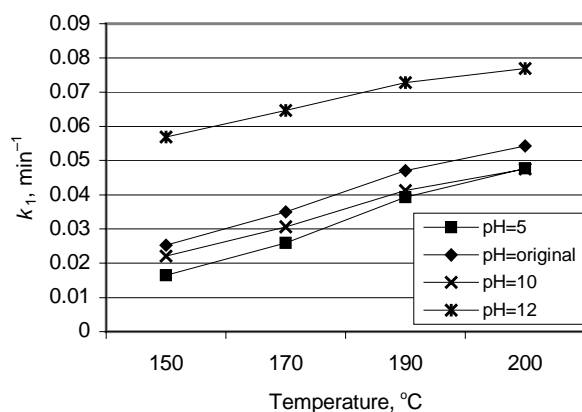
The calculated reaction rates of the lignin degradation in reactions 1 and 3 were compared with the corresponding reaction rates calculated in the lignin model-solution experiments. Especially in the case of reaction 1, which appeared to be the most important pathway in lignin degradation, the reaction rates were very close to each other (Fig. 7).

Figure 8 presents a comparison of the experimental and calculated (estimated in MODEST) results of lignin degradation in the lignin water model solution and debarking water. It can be seen that the trend lines are mostly similar. This similarity supports the authors' assumption that lignin behaviour in different environments does not differ significantly.



**Fig. 7.** Comparison of the calculated reaction rates of lignin degradation (reaction 1) in the model solution and in debarking water.



**Fig. 5.** First-order reaction rate constant vs. temperature of lignin degradation (reaction 1).



**Fig. 8.** Comparison of the experimental and calculated results of lignin degradation in the model solution and debarking water.
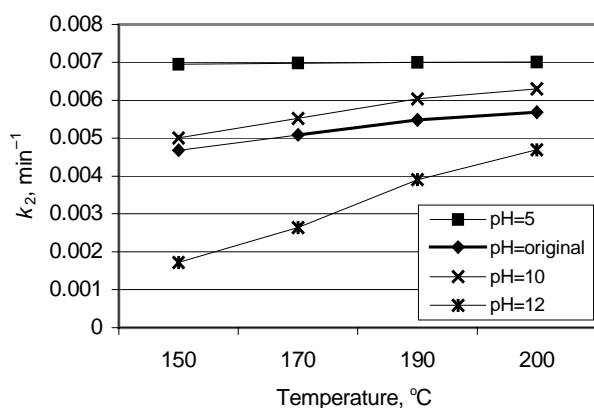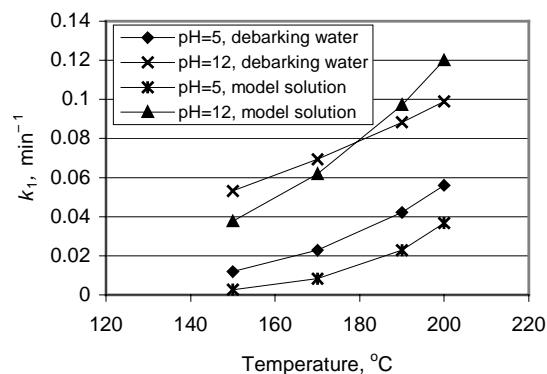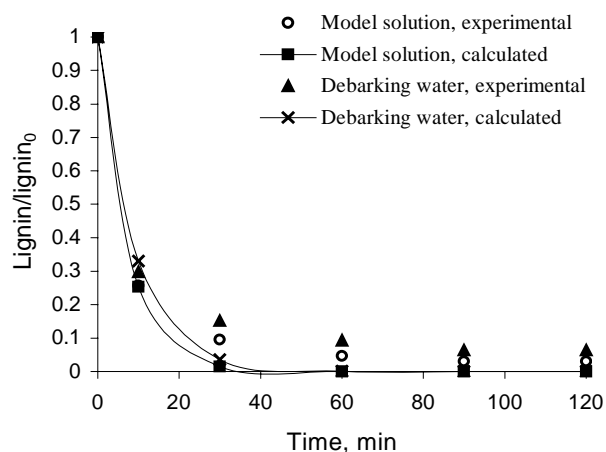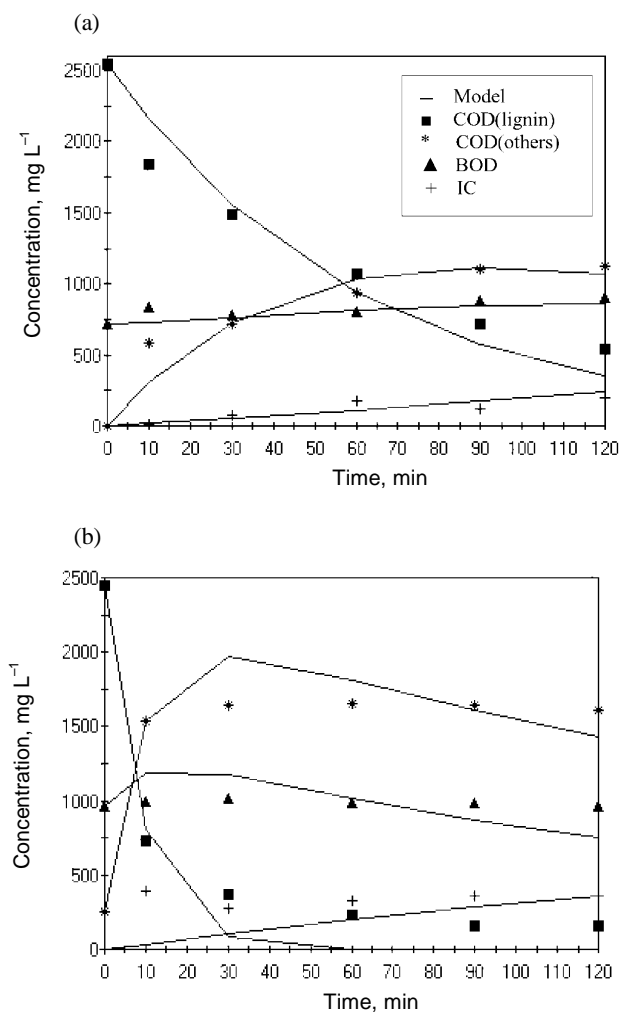


**Fig. 6.** First-order reaction rate constant vs. temperature of reaction 2, where non-biodegradable compounds degrade to biodegradable compounds.
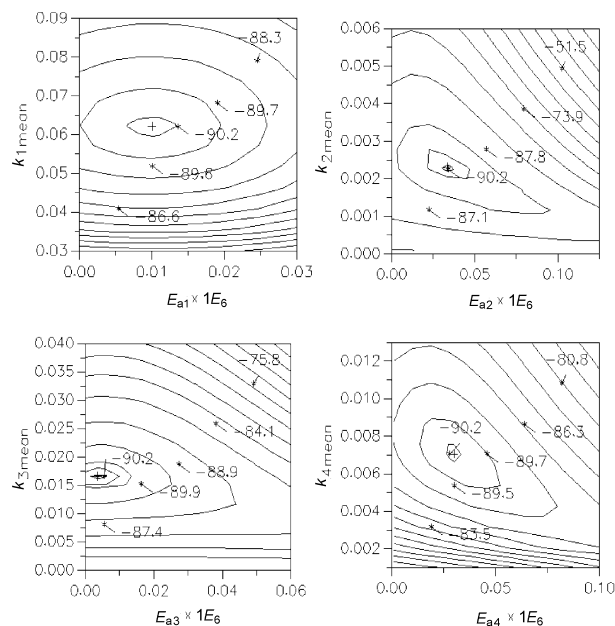
Figure 9 presents an example of the performance of the model in the wet oxidation of lignin under two most extreme conditions of the experiments: at 190 °C and

pH 12 and at 150 °C and pH 5. The previous observation is confirmed: lignin decomposes much more rapidly at pH 12 than at lower pHs. Figure 9 also shows that at lower pH values the ratio of biodegradable products to non-biodegradable products is higher than at pH 12. Generally, the model explains the experimental data reasonably well.

Sensitivity analysis using a contour plot of $R^2$ for the pairs $E_{ai}$ and $K_{imean}$ was performed to obtain information on the reliability and identifiability of the estimated parameters. Figure 10 shows an example of the typical contour lines observed in the parameter estimation. In Fig. 10, the length of the parameter axis was chosen to be five times the estimated standard error of the parameter (with the lower boundary of zero). The $R^2$ contour plots in Fig. 10 reveal that the global minimum point is found in all cases. The * sign in the plots represents the estimated parameter values. The



**Fig. 10.** Sensitivity contour plots of $R^2$ for the pairs $E_{ai}$ and $K_{imean}$ of the kinetic model (M2) at pH 12.

true values of $E_{ai}$ and $K_{imean}$ are within a high probability in the immediate neighbourhood of the computed minimum. Generally, the more centred the lines are around the most probable point, the better the identification of the parameters.

In some cases, however, the value of the activation energy tended to fall to a very low level. For example, in Fig. 10 this occurred with the estimation of $E_{a3}$. The behaviour could relate to the earlier observation that at pH 12, reaction 3 did not seem to have much importance in lignin degradation compared with reaction 1, which makes it more difficult to determine the kinetic parameters for this reaction. Nevertheless, a minimum was found in this case, too. Similarly, the one-dimensional objective functions could be printed for each parameter showing the minimum points.

## 5. CONCLUSIONS

Two models were developed to describe the kinetics of wet oxidation of debarking solutions. The first model (M1) was based on the scheme proposed earlier by Li et al. (1991) and allows the prediction of COD and BOD and thus also biodegradability. The second model (M2) was based on the scheme proposed by Verenich and Kallas (2002) and modified to take into account changes in lignin concentration in addition to COD and BOD. Both models assume that compounds containing inorganic carbon, e.g. $CO_2$, are formed as a final product, estimated through the change in TOC in the models.

(a)



(b)



**Fig. 9.** Performance of the model ($c_{O2}$ included) for the experimental data observed under (a) 150 °C and pH 5 and (b) 190 °C and pH 12. IC, inorganic carbon.

In the first model (M1), the main focus was on finding the effect of stoichiometric constants. Results showed that stoichiometric constants $m_1$ and $m_2$ had a detectable effect, but the model generally remained poor considering all numbers.

The second model (M2) was found to be more suitable for describing the kinetics of wet oxidation of debarking water than M1. Therefore, more detailed analysis of modelling was carried out for this model. The importance of the different reaction pathways was studied. Lignin was found to degrade first to other non-biodegradable compounds rather than straight to bio-degradable products. The activation energies for the reactions reduced from 51 to 21 kJ/mol and from 84 to 12 kJ/mol, respectively, with a change in the pH from 5 to 12. This supports the experimental finding that lignin degradation is faster in basic conditions. In contrast to lignin, degradation of other non-biodegradable com-pounds was faster at lower pH. The lowest activation energies for the degradation of biodegradable com-pounds to end-products were obtained in neutral conditions, yet the highest reaction rates were calculated at pH 5.

Oxygen concentration was both included and omitted from the model. However, it did not seem to influence the results greatly.

The obtained correlation constants were not very high, although they were found reasonable. The reaction system is rather complicated and many parameters have to be estimated at the same time. The reliability and identifiability of the estimated parameters was studied in detail and 95% confidence intervals were given to the parameters. Most of the parameters were well identified, in some cases slight interdependence of the parameters could be observed.

The results given by model M2 agreed with the experimental data and also with earlier results obtained for the wet oxidation of lignin in model solutions. The model could predict the degradation of lignin as well as the important wastewater characteristics COD and BOD.

In general, model M2 can be used for describing wet oxidation and other industrial oxidation processes to predict the demineralization, changes of biodegrad-ability, and degradation of the target compound in any multi-compound solution.

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# Paberitööstuse koorevee lagundamine märgoksüdatsiooniga: reaktsioonide kineetika ja modelleerimine

## Merit Kindsigo, Marjaana Hautaniemi ja Juha Kallas

Paberitööstus on üheks suurimaks veetarbe ja heitvee tekkega tööstusharuks. Nimetatud heitvesi on tugevalt saastunud ja ülimalt toksiline, sisaldades rasvhappeid, tanniine, ligniine ning nende ühendeid. Märgoksüdatsioon on sobilikuks meetodiks komplekssete, mitmetasandiliste ja inertsete reoainete lagundamiseks, nagu ligniinid ning tanniinid.

Käesoleva töö eesmärgiks oli võrrelda kahe kineetilise mudeli sobivust ligniine sisaldava vee lagunemis-reaktsioonide ja nende kiiruse kirjeldamiseks. Kasutatavad katseandmed saadi paberitööstuse kooreveega. Võrdluses selgus, et teine mudel (M2) on koorevee märghapenduse kineetika kirjeldamiseks sobivam. Tulemuste kohaselt lagunes ligniin esmaselt pigem keemiliselt oksüdeeruvateks ühenditeks kui otse biolagunevateks ühenditeks. Aktivatsioonienergia vähenes pH 5 puhul 51-lt 21-le kJ/mol ja pH 12 puhul 84-lt 12-le kJ/mol. See omakorda toetab varasemate katsete tulemusi, et ligniin laguneb kiiremini aluselises keskkonnas.

Antud mudeliga saab ennustada ligniini lagunemist samuti kui teiste heitvee oluliste näitajate (KHT ja BHT) muutusi.