

Oil shale ash as a catalyst in wastewater treatment in the pulp and paper industry

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Abstract

The pulp and paper industry is one of the largest and most polluting industries in the world, mainly due to coloration and toxicity problems in wastewaters. Wood debarking, a primary wood treatment process, produces an aqueous effluent that is currently considered as one of the most toxic wastewaters in the papermaking industry. Due to the biological toxicity of the stream debarking wastewater, which contains hardly any biodegradable lignin, is the unsolved problem for wastewater biological treatment. Wet oxidation (WO), water treatment in elevated temperatures and pressures, is an effective process for lignin destruction in debarking water. The main problems in process realization are temperature that is too high (close to 200°C), pressure that is too high and the long duration time of treatment (1.5-2 hours) for lignin degradation. The way to decrease the process temperature and pressure is to use catalytic wet oxidation (CWO).

The catalytic effect of an Estonian oil shale alkaline ash (waste material of multicomponent composition forming in high quantities at heat and power production based on firing of local low-grade carbonaceous fossil fuel) in WO of lignin containing waters has been established. The composition of ash is presented. The results of CWO are compared with WO results without ash. Catalytic wet oxidation of lignin water using platinum (Pt) as the catalyst is also briefly presented. It is demonstrated that a certain amount of ash accelerates the oxidation process of organics in water; it degrades the lignins content more quickly, as well as the values of COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) in lower reaction temperatures and pressures, such as those in WO.

Keywords: catalytic wet oxidation, lignin degradation, oil shale ash.



1 Introduction

Advanced oxidation processes (AOPs) are suitable for lower concentrations and rather small waste streams. They can be used in combination with biological treatment methods or separately. Many competing technologies are suitable for these kinds of effluents. Concentrated, toxic and biologically resistant waste streams cause much bigger problems. Incineration should be considered for highly concentrated waste streams. Various oxidation technologies are, however, suited for the elimination of concentrated organic aqueous wastes; because of the environmental disadvantages of incineration, liquid phase oxidation can be considered an appropriate approach.

Wet oxidation (*also known as hydrothermal treatment*) is one of the processes that have successfully found industrial application in the treatment of hazardous, toxic and non-biodegradable waste streams at rather high concentration. Wet oxidation is a promising technology for the treatment of such liquid wastes, and can also be used when various catalysts, for example, iron, cadmium, or hydrogen peroxide, are included to enhance the process efficiency or to use lower temperatures and pressures.

Typical conditions for WO range from 100°C to 372°C at elevated pressures (1–20 MPa) to maintain water in the liquid phase and ensure that oxidation reactions take place in the liquid phase. Residence times may range from 15 to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75–90%. Insoluble organic matter is converted to simpler soluble organic compounds, which are in turn oxidised and eventually converted to carbon dioxide and water, etc.

Catalytic wet oxidation (CWO) is the same process as conventional wet oxidation except that a catalyst is added to the waste stream. The introduction of catalysts to the wet oxidation system accelerates complete destruction of organic compounds and allows the use of less severe operating conditions; resulting in a substantial decrease in processing costs.

According to Peng et al. [1] an optimal catalyst should be inexpensive, efficient and environmentally benign. To maintain the catalyst activity in dynamic process conditions, the pelletized catalyst should possess mechanical strength (Wang et al. [2]) and the active compounds should not crush or leach into the reaction medium. The demanding conditions in industrial wastewater streams impose additional demands on the catalyst (Bhargava et al. [3]). As Levec and Pintar [4] have stated, the major problem is that the most efficient and stable catalysts are very expensive, and thus not suitable for wastewater treatment or end-of-the-pipe treatment processes.

A number of different waters, such as dyeing and printing WW, Lei et al. [5]; Donlagic and Levec [6], caustic WW, Yang et al. [7], phenolic WW, Lin and Chuang [8], perfume WW, Zhao et al. [9], oily WW, Zerva et al. [10] and lignin containing pulp and paper mill WW, Kindsigo and Kallas [11] that have been treated by WO have demonstrated a tendency for improvement in their biodegradability, i.e. the ratio of BOD to COD.



According to Zhang and Chuang [12] commonly used metal oxides such as MnO_2 , CuO and Fe_2O_3 are not suitable as catalysts of CWO for the treatment of pulp and paper mill effluents. In addition to the fact that these catalysts do not provide sufficient efficiency, they are dissolved in acidic streams, and due to the leaching of catalyst, an extra process step is thus required to remove the harmful dissolved metals from the effluent. Santos et al. [13] have studied catalytic wet oxidation of phenol on active carbon (AC) and Quintanilla et al. [14] WO with a Fe/activated carbon (Fe/AC) catalyst.

Since biological treatment is generally considered to be the most environmentally friendly and cheapest method for the removal of organic material, many types of WW are treated biologically, although this form of treatment is not suited for all types of waste. Waste which is contaminated by large molecules such as polymers, or toxins that are hazardous to biological agents has to be pre-treated prior to biological treatment. The use of WO leads to the breakdown of large molecules and also has a destructive effect on toxic substances. Consequently, the oxidation process significantly improves the biodegradable characteristics of WW.

Wood obtained from forest trees is the most important source of cellulosic material (fibre) for the pulp and paper industry. Wood meets over 90% of the world's fibre requirement. The three main structural wood constituents are cellulose, hemicellulose and lignin.

The lignin content of softwoods is typically in the range of 25% - 30% of the wood dry solids, whereas the common lignin content of temperate-zone hardwoods varies between 20% and 25% of the wood dry solids.

Lignin is a highly amorphous phenolic polymer of indeterminate molecular weight (Hill [15]). It is also characteristic that, unlike wood carbohydrates, the chemical structure of lignin is irregular in the sense that different structural elements (phenylpropane units) are not linked to each other in any systematic order.

The chemistry of lignin is extremely complex; it has three-dimensional molecules. The molecules are all large, having a molecular weight of several thousand. In general, lignin is characterized by having hydroxyl (OH) or methoxyl (OCH_3) groups attached to the benzene carbon atoms (Clark [16]).

As lignin is recalcitrant to common purification methods, it needs special treatment. Wet oxidation has been effective for lignin degradation, but the process itself is rather slow and, therefore, may not be economically reasonable in today's world energy situation.

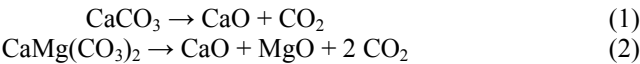
A good alternative to WO of lignin waters is catalytic wet oxidation (CWO) - it removes organics efficiently from an industrial stream obtaining better oxidation rates at lower temperatures and pressures. Catalysts are a good possibility to enhance also the lignin degradation but commercial catalysts are usually expensive. At the same time, there are many industrial residues, including from power plants, which could be used effectively in wastewater treatment or in other waste elimination technologies.

Residual ash of Estonian oil shale is a mostly unused waste substance containing a remarkable amount of Ca oxides and various other metal oxides and

salts. In the light of its composition, this ash has been estimated as a potential catalyst in wet oxidation processes.

2 Residual ash of power plants

For fuels that contain carbonate minerals, such as Estonian oil shale, the thermal decomposition of these minerals during incineration has to be considered. The most frequent carbonate minerals in Estonian oil shale are limestone (CaCO₃), dolomite (CaMg(CO₃)₂), and also, to some extent, siderite (FeCO₃). Carbonate minerals decompose during fuel combustion, the solid phase formed (e.g. CaO and MgO) is transferred to ash residue, and the gaseous phase evolves as carbon dioxide (CO₂), called “mineral carbon dioxide” (Ots [17]). General thermal decomposition of calcium carbonate and dolomite is given as follows:



The formed lime (CaO) takes part in solid state reactions with sandy-clay minerals resulting in formation of different secondary silicates and aluminates of complicated composition (Kuusik et al. [18]). As a result, the content of free lime will be lower as compared to theoretic one, but being enough high to give in aqueous suspensions the high alkali reaction (pH = 12-13).

The ash samples used are formed in boilers operating with different combustion technologies. The ashes and ash-mixes had been collected from pulverized firing or fluidized bed combustion boilers at Estonian power plant. The pulverized firing (PF) ashes are of the type: BA – bottom ash, and CA – cyclone ash. The fluidized bed combustion (FBC) ash types are: INT – intrex ash, and MIX – a mix of ashes taken from different sections of electrostatic precipitators (ESP1 ESP4).

The content of main oxides and of the basic elements are given in tables 1 and 2. Solid material composition was determined by IRIS Intrepid II Inductive Coupled Plasma Spectrometer (Thermo Electron Corporation, software: TEVA: thermo elemental validated analysis) (Velts et al. [19]; Kuusik et al. [18]).

Different accompanying elements, a wide spectrum of ions (Ca, K, Na, Al, Si, Fe, Mg, Mn, S²⁻, SO₃²⁻ and SO₄²⁻) and several heavy metals (Co, Cr, Cu, Ni, Pb, V, Zn, Cd) are present in the ash in small concentrations. Table 2 gives an overview of some basic elements in oil shale ash.

Table 1: Main oxides in the ash samples.

Substance (%)	PF/BA	PF/CA	FBC/MIX	FBC/INT
CaO _{general}	57.19	49.39	33.28	47.59
CaO _{free}	30.0	22.52	10.33	18.87
MgO	8.07	14.19	9.50	13.65



Table 2: Average content of basic elements present in oil shale ash (per g of ash).

<i>Ash type</i>	<i>Ca</i>	<i>Mg</i>	<i>Fe</i>	<i>Al</i>	<i>S</i>	<i>K</i>
<i>PF, g/g</i>	0.425	0.038	0.03	0.015	0.018	0.007
<i>FBC, g/g</i>	0.215	0.033	0.02	0.034	0.024	0.017
	<i>Mn</i>	<i>Na</i>	<i>Zn</i>	<i>Si</i>	<i>Cr</i>	<i>Cu</i>
<i>PFm, µg/g</i>	545	540	155	70-100	25	20*
<i>FBC, µg/g</i>	385	890	≈30	100-150	45	10

*In some samples ≈100 µg/g.

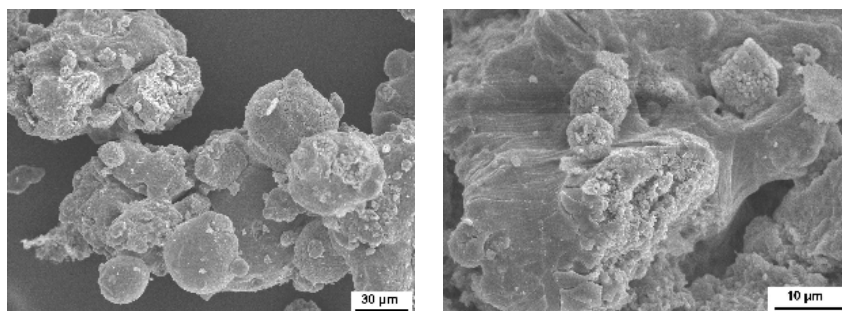


Figure 1: Bottom ash of PF/BA. Zoom 500x (in left) and 2000x (in right). SEM images performed by Dr. V. Mikli from the Centre of Materials Research of Tallinn University of Technology.

2.1 Surface analysis and particle size

The results of SEM analysis – surface observations of ash particles of samples PF/BA and CFB/MIX are presented in Figure 1. Comparison of PF and FBC ash particles shows that a distinctive feature of FBC ashes is that the particles formed are porous not smooth, PF ashes particles, on the other hand, are round and with a smooth surface characteristic for glassy phase.

SEM analysis gives good images of ash particle surfaces, particle sizes, and melting phase genesis during combustion using different combustion technologies and methods.

Particle size analysis results are given in Figure 2. As can be seen, the diameter of the particles is mostly in the size range of 100–500 µm.

When comparing PF and FBC ash, it can be seen that the mean diameter of PF ash particles is much bigger (250 µm) than that of FBC ash particles (mean diameter 28 µm). This may be of significance in the use of ash as a catalyst in the WO process. It is not known how particle size affects chemical reactions in WO; a question worth further research.

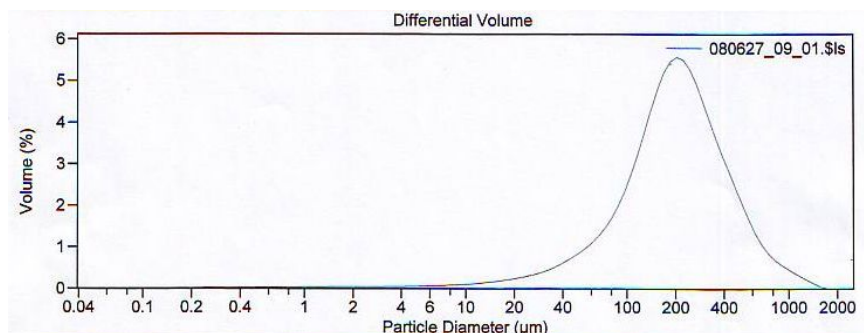


Figure 2: Particle diameter of PF/BA ash.

3 Materials and methods

Wet oxidation experiments were carried out in a high-pressure stainless steel (T316SS) batch reactor (Parr Instrumental Co., U.S.A.), which is a cylindrical vessel with a volume of 450 mL and with a capacity to work in up to 5 MPa of pressure and at a temperature of 350°C. Pure oxygen was used as the oxidizing agent in all cases. The impeller was operated at 700 rpm.

Experimental and operating conditions of the CWO process were chosen similar to earlier research experiments: lignin concentration 600 mg/L, oxygen partial pressure 1 MPa; temperatures 150° and 170°C, experiment duration 120 minutes, see: Kindsigo and Kallas [20]; Kindsigo and Kallas [11].

The initial pH of the lignin water model solution was approximately 7. Adding the ashes increased this pH remarkably and in most cases it reached the range 11–12. The pH was measured during the experiments but not controlled. The reaction samples were analyzed for lignin content, COD, TOC, pH and colour.

Two extremely different catalysts were used when studying the catalytic wet oxidation of the lignin water model solution, - a pure platinum catalyst (TU 13405 TN, 1 wt% on activated carbon from Aldrich Chemical Company Inc.) and the previously described Estonian power plant ashes.

4 CWO of lignin water model solution

The aim in using the ashes was to establish the effects of the amount of ash, previous mixing, the content of the ash (origin of the ash), different temperatures of the WO process, and the pH of the solutions (ash *versus* pure NaOH), using also the Pt catalyst for comparison. In the experimental results, COD and lignin reduction have been taken under consideration as the main factors having greatest importance for making conclusions about process efficiency.

When researching the influence of the amount of ash on lignin degradation, three amounts were selected for trials – 0.25, 0.5 and 1 g ash per litre. Increasing the amount of ash increased the lignin removal efficiency (Fig. 3) from 52% to 86%.

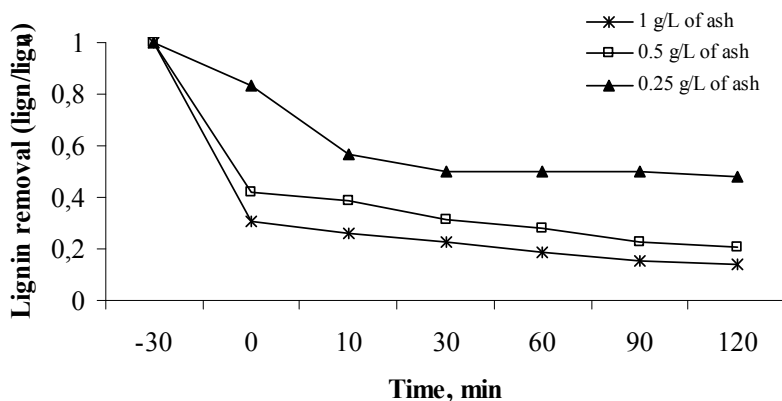


Figure 3: Effect of the amount of ash on lignin degradation at a temperature of 150°C and pressure of 1 MPa.

Table 3: Influence of mixing on lignin degradation ($\text{lignin}/\text{lignin}_0$).

Time	FBC/MIX				PF/BA	
	T= 150°C		T= 170°C		T= 150°C	
	mixing	no mixing	mixing	no mixing	mixing	no mixing
-30	1	1	1	1	1	1
0	0.42	0.70	0.45	0.81	0.66	0.69
10	0.38	0.46	0.35	0.43	0.39	0.45
30	0.31	0.38	0.32	0.35	0.29	0.37
60	0.28	0.35	0.26	0.30	0.22	0.31
90	0.23	0.30	0.22	0.27	0.22	0.28
120	0.21	0.27	0.19	0.25	0.21	0.26

Adding the ash to the studied water always caused an increase in pH. The addition of 0.5 and 1 g/L of ash resulted in pH of 12, adding 0.25 g/L of ash gave pH of 11.2. The pH always decreased during the WO process (as in earlier WO studies without a catalyst). Since the initial pH was quite similar, so was the final pH (at the end of process) – in most cases 7–8. With smaller ash amounts (0.25 g/L) a bigger decrease of pH (down to 6.8) was obtained at higher temperatures (170°C). With bigger ash amounts (0.5 and 1 g/L) pH followed the same trends at different temperatures. The explanation of pH decrease is the formation of organic acids during WO.

Selected data of lignin degradation with different ashes are presented in Table 3 (0.5 g/L of ash in every case).

The purpose of mixing experiments was to find out the effect of pre-mixing. Thus, 'mixed' samples were stirred for 3 hours before the WO process, and 'unmixed' samples were introduced straight to the WO reactor. Three hours was

selected for the mixing because earlier ash leaching experiments show that the dissolution equilibrium is reached after 3 hours: pH, conductivity and ions concentrations in water remain unchanged after 3 hours.

As can be seen in Table 3, there is minor difference in WO lignin reduction after 2 hours for either of the versions (mixing-no mixing). Somehow, the ash itself affects the lignin degradation results – there is a remarkable difference in the time-dependence of the results with different ash samples. Pre-mixing of the FBC/MIX ashes give already 30–40% more effective lignin degradation at ‘zero’ time, whereas with PF/BA ashes the pre-mixing makes no difference.

WO, a hot advanced oxidation process, is based on reactions of OH-radicals with organics. One source of these radicals is OH-ions, so it is possible to influence the reaction rate by pH regulation. CaO in the ash is a source of OH-ions through Ca(OH)_2 formation. A key question is whether the WO result is the same if the initial pH of the water solution is fixed by ash or by NaOH, i.e., whether ash has any additional catalytic influence.

The results show (Fig. 4) that there is a difference in COD and lignins removal efficiency between ash and NaOH usage: lignin and COD removal rates clearly show that ash is more effective (about 20% in all cases). It can thus be assumed that ash itself has certain additional catalytic properties, probably caused by metals (metal oxides) in the ash composition (Tables 1 and 2). A remarkable removal rate in lignin degradation was also detected within the pre-heating time – for ‘zero’ time, 58% of lignin was removed with ash, while only 3% was removed with NaOH. It means that ash is working as coagulant.

For comparison, some experiments were done with a Pt catalyst. The same amounts of Pt catalyst were used (0.25, 0.5 and 1 g/L) as in the ash experiments.

A surprising finding was COD behaviour compared to lignin behaviour when using Pt as a catalyst (Fig. 5). In the figure, it can be seen that for ‘zero’ time (during preheating) 78% of COD was removed (with 1 g/L Pt). At the same time,

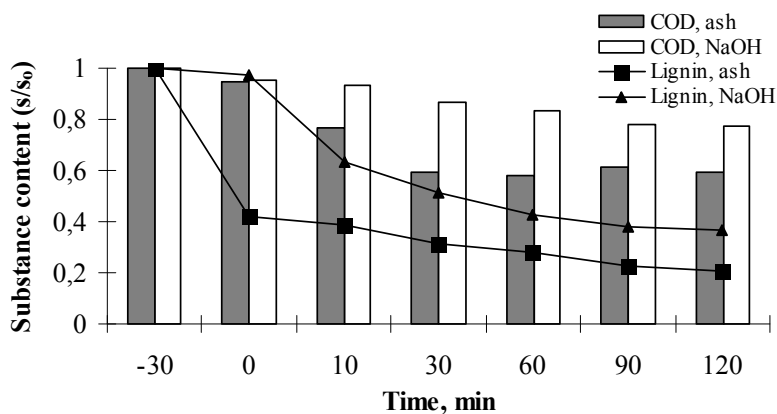


Figure 4: Comparison of influence of ash and NaOH on COD and lignin removal at a temperature of 150°C and pressure of 1 MPa.

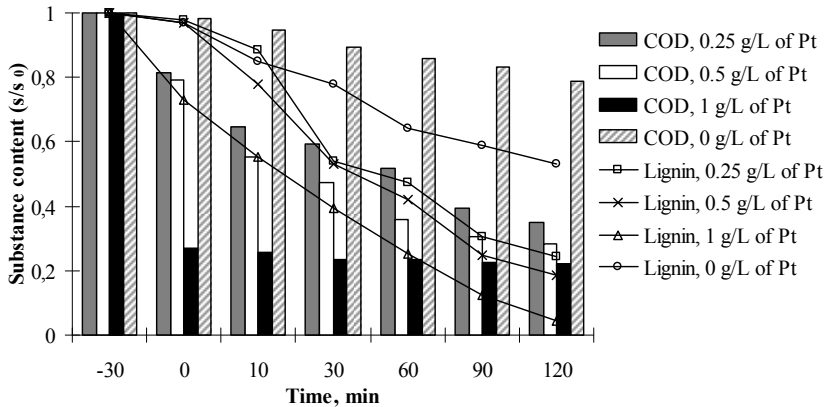


Figure 5: Effect of the amount of Pt-catalyst on COD and lignin removal at a temperature of 150°C and pressure of 1 MPa.

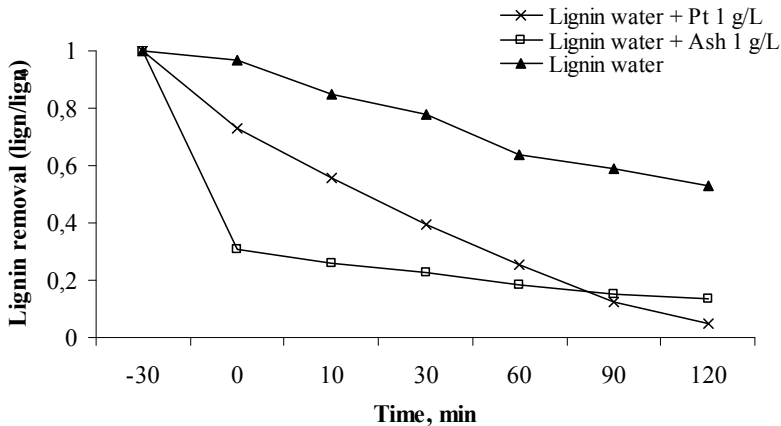


Figure 6: Lignin degradation at 150°C, pressure 1 MPa.

only 27% of lignin was removed. Nevertheless, the effect of Pt on lignin removal is dependent on catalyst amount. It was clearly seen that a larger catalyst amount gives higher lignin removal: After 120 minutes, 76% of lignin was removed with 0.25 g/L Pt, and 95% of lignin was removed with 1 g/L Pt.

Figure 6 presents a comparison of the results for the three experimental conditions studied. The figure clearly explains the behaviour of the runs. The best result for lignin removal was obtained using a Pt catalyst (removal 95%). A lignin water and ash combination gave a slightly lower but still quite effective result (lignin removal 86%). Ash causes quick lignin degradation during the pre-heating time, which permits remarkable shortening of the process duration (if the aim of the process is only lignin degradation). Under the selected conditions, lignin removal without a catalyst in pure lignin water was quite modest (47%).

It is necessary to point out that initial pH in these waters before addition of the catalysts was 6.3 to 6.8. Addition of Pt did not change the pH of the solution; addition of ash increased pH to 12. Lignin water without a catalyst (ash or Pt) had too low pH and also too low temperature for effective lignin degradation.

Comparison between different ashes gave fewer differences than expected. The decrease trend lines were quite similar for lignin and COD removal for all ashes. The results after 2 h process differed only 6% with COD and 10% with lignin. It can be concluded that the effect of the specific origin of the ash (same power plant but different technologies) and the particle size is insignificant compared to the amount of or absence of ash.

It can be stated that the main active agent in the ash is probably the CaO, which dissolves, and leaches to the solution, and hence increases the water pH. The catalytic influence of ash itself was also noticed but it was smaller than the effect of pH. The Pt catalyst is more effective than the ash but also much more expensive. Consequently, the power plant ash used in current study is worth to be considered use as a catalyst in certain waters. It can be concluded that the kind of ash used and the particle size is insignificant as compared to the amount of ash. It means that the content of free lime in samples was enough high to receive the results described and the difference in ashes composition was insignificant.

5 Conclusions

Catalytic wet oxidation of lignin-containing waters has been under investigation in this research. CWO using a Pt-catalyst and residual ash from an Estonian oil shale was tested to determine its efficiency in treating lignin-containing waters compared to common WO.

Catalytic WO showed good performance – using 1 g/L of residual ash gave lignin removal of 86% and COD removal of 39% at 150° C (a lower temperature and pressure than with WO). It was noted that the ash catalyst caused a remarkable removal rate for lignin degradation already during the pre-heating – for ‘zero’ time, 58% of lignin was degraded. The Pt catalyst was found to be more effective than ash but it is also much more expensive. For this reason, it is worth considering the use of alkali oil shale ash used as a catalyst for WO of lignin-containing waters. Much research remains to be done in the area of CWO of lignin-containing waters: what really happens during pre-heating; how to separate effectively the used catalyst and treated water; considerations related to aging of the Pt-catalyst; and could a Pt-catalyst be used in packed bed columns in view of the speed of the reactions.

References

- [1] Peng, Y., Fu, D., Liu, R., Zhang, F., Liang, X., $\text{NaNO}_2/\text{FeCl}_3$ catalyzed wet oxidation of the azo dye Acid Orange 7. *Chemosphere*, DOI:10.1016/j.chemosphere.2007.10.065, 2007.



- [2] Wang, J., Zhu, W., Yang, S., Wang, W. and Zhou, Y., Catalytic wet air oxidation of phenol with pelletized ruthenium catalysts. *Applied Catalysis B: Environmental* 78, 30–37, 2008.
- [3] Bhargava, S. K., Tardio, J., Jani, H., Akolekar, D.B., Föger, K. and Hoang, M., Catalytic wet air oxidation of industrial aqueous streams. *Catal. Surv. Asia*, 11, 70–86, 2007.
- [4] Levec, J. and Pintar, A., Catalytic wet-air oxidation processes: A review. *Catalysis Today* 124, 172–184, 2007.
- [5] Lei, L., Hu, X., Chu, H. P. and Yue, P. L., Catalytic wet air oxidation of dyeing and printing wastewater, *Wat. Sci. Tech.*, 35(4), 311-319, 1997.
- [6] Donlagic, J. and Levec, J., Oxidation of an azo dye in subcritical aqueous solutions. *Ind. Eng. Chem. Res.*, 36, 3480-3486, 1997.
- [7] Yang, M., Du, S., Wang, X., Yang, X., Du, H. and Wu, M., Catalytic wet air oxidation of spent caustic wastewater. *Huanjing Gongcheng*, 19, 13, 2001.
- [8] Lin, S. H. and Chuang, T. S., Wet air oxidation and activation sludge treatment of phenolic wastewater. *J. Environ. Sci. Health*, A29(3), 547-564, 1994.
- [9] Zhao, J., Gu, G. and Xu, D., Catalytic wet oxidation of perfume wastewater. *Tongji Daxue Xuebao, Zhan Kexueban*, 23(4), 4647, 1995.
- [10] Zerva, C., Peschos, Z., Pouloupoulos, S. G. and Philippoulos, C. J., Treatment of industrial oily wastewaters by wet oxidation. *J. of Hazard. Mat.*, 97(1-3), 257-265, 2003.
- [11] Kindsigo, M., Kallas, J., Wet oxidation of debarking water: changes in lignin content and biodegradability. *Environmental Chemistry Letters*, 7: 121-126, 2009.
- [12] Zhang, Q. and Chuang, K.T., Treatment of combined bleach plant effluents via wet oxidation over a Pd-Pt-Ce/alumina catalyst. *Environ. Sci. Technol.*, 33, 3641–3544, 1999.
- [13] Santos, A., Yustos, P., Gomis, S., Ruiz, G. and Garcia-Ochoa, F., Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon. *Chem. Eng. Sci.*, 61(8), 2457-2467, 2006.
- [14] Quintanilla, A., Casas, J. A., Zazo, J. A., Mohedano, A. F. and Rodríguez, J. J., Wet air oxidation of phenol at mild conditions with Fe/activated carbon catalyst. *Applied Catalysis B: Environ.*, 62(1-2), 115-120, 2006.
- [15] Hill, C. A. S., *Wood modification, Chemical, Thermal and Other Processes*. Wiley Series in Renewable Resources. John Wiley & Sons Ltd., West Sussex, England, 2006.
- [16] Clark, J. d'A., *Pulp Technology and Treatment for Paper*. 2nd edition, Miller Freeman Publications, Inc., San Francisco, USA, 1985.
- [17] Ots, A., *Oil Shale Fuel Combustion*. Tallinna Raamatutrükikoda, Tallin, Estonia, 2005.
- [18] Kuusik, R., Uibu, M. and Kirsimäe, K., Characterization of oil shale ashes formed at industrial-scale CFBC boilers. *Oil Shale*, 22(4), 407-419, 2005.



- [19] Velts, O. Uibu, M., Rudjak, I., Kallas, J. and Kuusik, R., Utilization of oil shale ash to prepare PCC: Leachability dynamics and equilibrium in the ash-water system. *Energy Procedia*, 1, 4843-4850, 2009.
- [20] Kindsigo, M., Kallas, J., Degradation of lignins by wet oxidation: model water solutions. *Proc. Estonian Acad. Sci. Chem.*, 55, 132-144, 2006.

