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CATALYTIC WET OXIDATION OF BLACK LIQUOR

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Abstract

The major aspects of wet air oxidation and catalytic wet air oxidation have been reviewed in this work paying special attention to the reaction mechanisms, kinetics and the industrial process. In the experimental section a set of heterogeneous catalysts have been tested in the wet oxidation of non-wood black liquor. The oxidation runs were performed batchwise in a laboratory-scale mechanically stirred slurry reactor for 1 h at a temperature of 170°C and total pressure of 12 bar. Pure oxygen was used as oxidant agent. Results showed that Fe/AC, AC and CuO promote the formation of acids, whereas CeO₂ was found to be effective for the complete oxidation of black liquor. It was also observed that highly concentrated streams cause catalyst deactivation due to active sites blockage.

Keywords black liquor, wet oxidation, catalytic wet oxidation, partial wet oxidation

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Nomenclature

| | |
|---------------------|--|
| a | Gas-liquid interfacial area (m^{-1}) |
| A | Pre-exponential factor ($\text{mol}^{1-m-n} \cdot \text{m}^{-3m+n+1} \cdot \text{s}^{-1}$) |
| C_{org} | Organics concentration ($\text{mol} \cdot \text{m}^{-3}$) |
| $C_{O_2}^*$ | Saturation oxygen concentration ($\text{mol} \cdot \text{m}^{-3}$) |
| $C_{O_2,L}, C_{2R}$ | Oxygen concentration in the bulk liquid ($\text{mol} \cdot \text{m}^{-3}$) |
| C_{1R} | Oxygen concentration in the gas-liquid interface ($\text{mol} \cdot \text{m}^{-3}$) |
| C_{3R} | Oxygen concentration in the catalyst ($\text{mol} \cdot \text{m}^{-3}$) |
| d_{vs} | Mean bubble diameter (m) |
| D_e | Effective diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$) |
| E | Activation energy ($\text{J} \cdot \text{mol}^{-1}$) |
| k_L | Liquid mass-transfer coefficient ($\text{m} \cdot \text{s}^{-1}$) |
| k_1 | Heterogeneous reaction rate constant for the LHHW model (*) |
| \tilde{k} | Embedded rate constant ($\text{mol} \cdot \text{kg}_{cat}^{-1} \cdot \text{min}^{-1}$) |
| K | Adsorption equilibrium constant ($\text{m}^3 \cdot \text{mol}^{-1}$) |
| m, n | Orders of reaction (-) |
| m_{cat} | Catalyst loading (kg) |
| r_H | Heterogeneous contribution to reaction rate (*) |
| r_m | Rate of oxygen mass transfer ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) |
| r_r | Reaction rate ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) |
| P_R | Oxygen pressure in the bulk gas (Pa) |
| P_{1R} | Oxygen pressure in the gas-liquid interface (Pa) |
| R | Universal gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) |

* Units vary according to the order of reaction

| | |
|-------|--|
| T | Temperature (K) |
| v | Molar volume ($\text{m}^3 \cdot \text{mol}^{-1}$) |
| X_0 | Initial active site concentration ($\text{mol} \cdot \text{kg}_{\text{cat}}^{-1}$) |

Greek letters

| | |
|--------------------|-------------------------------------|
| ε_{LD} | Dynamic liquid hold up |
| ε_{LS} | Static liquid hold up |
| ε_P | Intra-particle porosity |
| γ | Ratio of maximum fluxes of reactant |
| η_D | Dynamic wetting efficiency |
| η_E | Total wetting efficiency |
| η_S | Static wetting efficiency |
| ξ | Gas hold up |
| τ | Residence time (h) |

Abbreviations

| | |
|-------|---|
| AC | Activated Carbon |
| AOSC | Average Oxidation State of Carbon |
| COD | Chemical Oxygen Demand (mg O ₂ /L) |
| CPWAO | Catalytic Partial Wet Air Oxidation |
| CWAO | Catalytic Wet Air Oxidation |
| DF | Dilution Factor |
| ELKM | Extended Lumped Kinetic Model |
| ESR | Electron Spin Resonance |
| GLKM | General Lumped Kinetic Model |
| LHHW | Langmuir-Hinshelwood-Hougen-Watson |
| LHSV | Liquid Hourly Space Velocity (h ⁻¹) |
| PBC | Packed Bed Column |
| SE | Stoichiometric Excess |
| STP | Standard Temperature and Pressure |
| TBR | Trickle Bed Reactor |
| TIC | Total Inorganic Carbon (mg C/L) |
| TOC | Total Organic Carbon (mg C/L) |
| VIS | Visible |
| WAO | Wet Air Oxidation |

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Chapter 1

Introduction

1.1. General introduction

The pulp and paper industry wastewaters are highly polluted streams that represent a serious threat to the environment. The composition of these wastewaters is extremely complex and includes compounds such as lignin, organic acids, unsaturated fatty acids, resin acids, and sulfur and phenolic compounds. As a result of the complex composition, the treatment of these high-organic-content effluents is viewed as a concern for the feasibility and economy of the entire pulping process [1,2].

Non-wood pulp mills are considered to be an attractive alternative to typical Kraft mills for those countries with limited forest resources. The use of non-wood fibers such as straw materials, bagasse, and bamboo not only provides an easy-to-pulp feedstock, but also an interesting alternative for agricultural residues disposal. However, these mills, which are mostly small scale, do not have the required technology for the wastewater recovery. In some cases, this lack of technology has led to the discharge of highly contaminated streams directly to the environment, with the consequent contamination of water and soil. To sum up, the high capital investment required to recover black liquor and thus meet the pollution standards represent an economic burden for the small mills, while its discharge is a serious threat for the environment. Therefore, alternative methods for black liquor treatment are required in order to settle these problems and hence

guarantee the economic feasibility of small soda mills in an environmentally-responsible way [3,4].

The Wet Air Oxidation (WAO) has been reported as a promising process for organic pollutants removal in industrial effluents due to its simplicity, and the fact that no chemicals are involved in the process. The high heat of reaction (usually sufficient to sustain the desired temperature without the need to supply additional heat) and the energy generation through the gaseous products expansion in a turbine result in low operation costs for the process. However, the severe temperature and pressure conditions required to completely oxidize the refractory carboxylic acids involve high structure capital costs [5-10].

The use of metal based catalysts in the WAO of industrial wastewaters has been shown as an effective alternative to overcome the high energy requirements of non-catalytic WAO. Nevertheless, the high prices and the unavoidable deactivation problems of catalysts may partly offset the catalyst effect [5-7,11].

A number of valuable chemicals including acetic acid, formic acid, and lactic acid have been found to be common intermediates in the oxidation pathways of the most common organics in industrial wastewaters. It has been suggested that some of these intermediates could be recovered if the oxidation was stopped at a certain point instead of completely oxidizing the organic compounds to end products. This process is the partial wet air oxidation and is usually performed in the presence of a catalyst. Besides the improvement of the oxidation rates, catalysts can also increase the selectivity towards the desired intermediates [12].

1.2. The soda process

The soda process is a sulphur-free pulping method that is usually performed in continuous digesters at temperatures between 130-160°C for 10-30 min in presence of anthraquinone. The absence of sulphurs in the white liquor, and thereby the lower delignification capability limits the application of the soda process to low lignin content compounds i.e. non-wood fibers [3,4].

The soda mills overtake Kraft mills in terms of operational cost due to the lower price of non-wood feedstock and the cost saving in chemicals (only sodium hydroxide is required). However, the yield of chemicals and energy recovering is significantly lower than in Kraft pulp mills [3,4,13].

Black liquor is the byproduct obtained when the lignocellulosic feedstock is cooked in the digester in presence of the pulping chemicals. It contains approximately half of the organics in the feedstock and its composition is affected by a wide range of factors. These factors include digester conditions, feedstock, yield of the pulping stage, pulping chemicals properties, chemicals-to-wood ratio, and brownstock washing efficiency [14-16].

The complex composition and the high ash and silica content of non-wood black liquor are the source of most of the troubles related to the black liquor recovery in soda pulp mills. The reaction between silica and hydroxide leads to the formation of water-soluble silicate ions, resulting in scaling problems and an increase in black liquor viscosity. It has been suggested that the silicate could be precipitated and filtrated either prior to the pulping by adding calcium hydroxide to the pulping liquor, or afterwards by lowering the pH of black liquor through the addition of process carbon dioxide [4,13].

1.3. Objectives

The main objective of this work is to find suitable heterogeneous catalysts for the partial WAO of industrial wastewaters. The most suitable catalysts are those capable to improve the oxidation rates of organic pollutants while maximizing the formation of valuable chemicals. The catalysts price and resistance to deactivation are of utmost importance in the evaluation criteria. The analysis of the catalysts performance is used to check the convenience of the use of catalysts in the wet oxidation processes.

The secondary aim is the outlining of the new research stage on Catalytic Partial Wet Air Oxidation (CPWAO), namely, the study of CPWAO in laboratory-scale continuous reactor. The outlining of the following stage of the research primarily consists of the proposal of proper reactor configurations, operational conditions and catalysts.

1.4. Structure of the work

In order to achieve the above-mentioned objectives, an extensive literature survey on the wet oxidation and an experimental research on the catalyst performance were carried out. The work structure can then be divided in two big parts; the theoretical part (chapter 2) and the empirical part (chapters 3, 4, 5).

In chapter 2, the wet air oxidation and the catalytic wet air oxidation processes are presented paying special attention to the kinetics, the reaction mechanisms and pathways and how they are affected by the conditions of the reaction. A selection of the most reported catalysts in the WAO of organic pollutants is also presented in this chapter. Finally, an approach to the industrial WAO process is presented. In this approach the most used reactor configuration and the parameters affecting the big-scale reaction as well as the scaling problems are discussed.

An extensive description of the experimental research can be found in chapter 3. The chapter is centered in the equipment used, the experimental procedure, the materials (paying special attention to the catalysts preparation), and the experimental plan. The parameters that were analyzed and the analysis techniques are also detailed in chapter 3.

All the results and important data of the experimental research are presented and briefly described in chapter 4.

Finally, the discussion of the results and the conclusions of the work can be found in chapter 5. The discussion section includes an educated analysis of the results and of their consistency in comparison with the literature data. The conclusions and recommendations for further studies draw the end point to the work.

Chapter 2

Background and literature review

2.1. Wet air oxidation

The wet air oxidation process is a simple and clean alternative to deal with high-organic-matter effluents such as sewage sludge or wastewaters from dyeing, chemical, or pulping industries. During this process organic compounds in the liquid phase are ideally completely oxidized to carbon dioxide and steam. A gaseous source of oxygen (either air or pure oxygen) is used as oxidant under elevated conditions of temperature (125-315°C) and pressure (2-21 bar). These high energy conditions are required to ensure the complete oxidation of the stable intermediates i.e. low-molecular-weight carboxylic acids [5,6,11].

The WAO process has been reviewed as a very promising alternative process to wastewater treatment. This industrial interest in WAO is primarily due to (i) the simplicity of the process, (ii) the low operating cost, and (iii) the fact that no harmful species are involved in the process [5,8-10].

The explanation for the low operating cost lies mainly in three aspects. Firstly, the autothermal nature of the process, which means that the heat of oxidation is sufficient to sustain the required temperature inside the reactor. Secondly, the fact that the unique reactant required is oxygen (i.e. no expensive chemicals are needed). And finally, the possibility to generate energy through the gas expansion in a turbine [5,8-10].

WAO has also been considered an effective alternative to biological wastewater treatment due to its capability of oxidizing non-biodegradable compounds [2,11].

2.1.1. Physical stage of wet air oxidation

The WAO of organic compounds can be divided in two stages. In the first stage, called physical stage, the oxygen is transferred from the bulk gas to the bulk of the liquid. In the second one, the chemical stage, the transferred oxygen reacts with the organic compounds [5].

Although most of the literature is focused on the chemical stage, the physical stage of the WAO also plays an important role in the overall reaction rate.

Vaidya et al. [12] described the oxygen transfer from the bulk gas to the bulk of the liquid as a three-step stage consisting of the (i) transfer of oxygen from the bulk gas phase to the gas-liquid interface, (ii) instantaneous saturation of the interface with oxygen, and (iii) transfer of the dissolved oxygen from the gas-liquid interface to the bulk of the liquid.

It is well known that the gas phase mass transfer resistance can be neglected under high oxygen partial pressure due to the high diffusivity of oxygen in the gas phase and its low solubility in water. As a result, the liquid phase mass transfer is considered to be the unique controlling resistance [8,12,17-19]. The oxygen mass transfer rate can then be presented as

$$r_m = k_L a (C_{O_2}^* - C_{O_2,L}) \quad (2.1)$$

where r_m is the rate of oxygen mass transfer, k_L the liquid mass-transfer coefficient, a the gas-liquid interfacial area, $C_{O_2}^*$ the saturation oxygen concentration, and $C_{O_2,L}$ the concentration of oxygen in the bulk liquid [5].

It can be observed from eq. 2.1 that the rate of oxygen mass transfer can be enhanced by increasing either the liquid mass-transfer coefficient or the oxygen solubility in the liquid phase. The liquid mass-transfer coefficient is significantly affected by the intensity of

turbulence in the liquid phase, and therefore it can be enhanced by increasing the stirring speed [5].

A number of authors [12,16,20,21] studied the effect of the operating conditions on the liquid mass-transfer resistance. They demonstrated that above a certain stirring intensity, the rate of oxidation was not affected by the speed of agitation, indicating the absence of liquid film resistance and thereby the kinetically-controlled character of the reaction.

The effect of temperature on saturation oxygen concentration depends on the working temperature. The solubility decreases with the increase of temperature for temperature values below 93.3°C and increases with the increase of temperature for higher temperatures [22]. The behavior of oxygen solubility in the range of interest for normal WAO operation is presented in fig. 1

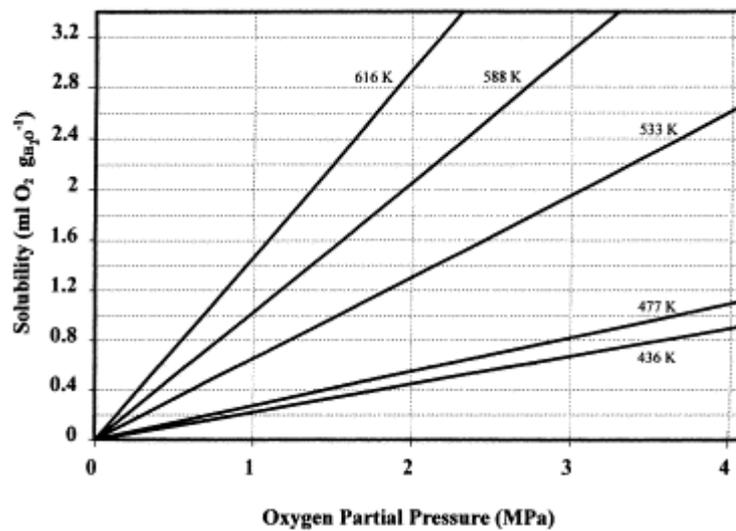


Figure 1. Solubility of oxygen in water [8].

As it can be seen from figure 1, the oxygen solubility in water is linear function of pressure for constant temperature; thereby it can be predicted with Henry's law [23].

The oxygen solubility in water is also affected by the presence of sodium. The effect of sodium on the oxygen solubility is relevant in the WAO of black liquor due to its high sodium content. Broden et al. [24] observed that the solubility of oxygen in aqueous salt solutions is less than in pure water. The oxygen solubility in NaOH and NaHCO₃ solutions at different pressures is compared with the solubility in pure water in fig. 2.

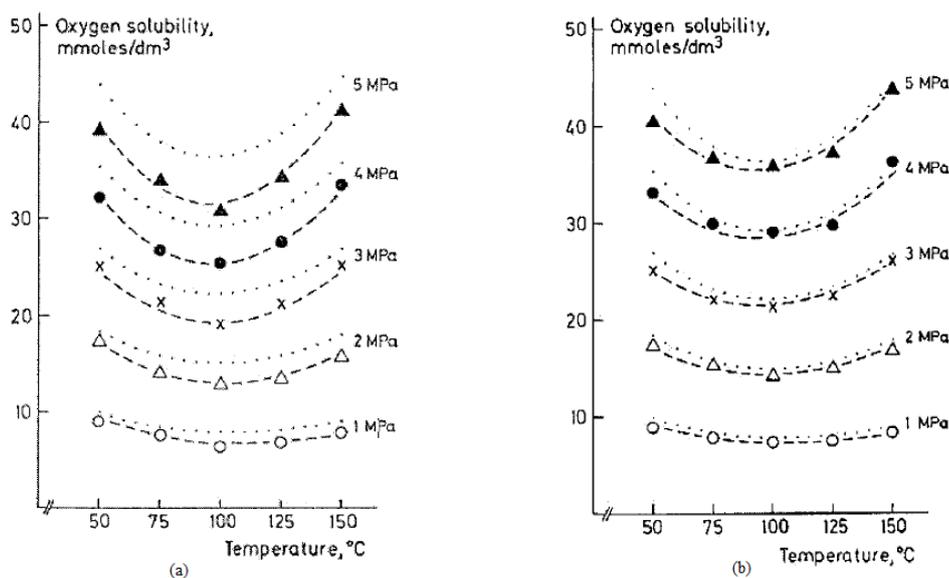


Figure 2. Oxygen solubility in (a) 0.1 M NaOH (b) 0.1 M NaHCO3 [24]

2.1.2. Reaction mechanisms

The WAO of organic compounds follows an extremely complicated pathway that involves the formation of several intermediates. Among them, the most common are the low molecular weight carboxylic acids and especially acetic acid. Several studies on the WAO of a wide range of organic pollutants and refractory intermediates have been carried out in order to understand the parameters influencing the WAO of organic compounds. A better understanding of the wet oxidation reaction would help to enhance reaction rates and predict the intermediates formation and their behavior under certain oxidation conditions [5].

Even though the exact reaction pathway of the WAO of organic compounds has not been established even for a single compound, it is well known that the WAO of organic matter occurs mostly via free-radical chemical reactions. Some authors indirectly evidenced the free-radical mechanism through co-oxidation, or using free-radical inhibitors or promoters [12,25]. However, only Robert et al. [26] have provided direct evidence of the presence of free-radicals during the WAO of organic compounds. In their study they used the spin trapping technique coupled to ESR spectroscopy to successfully identify the hydroxyl radical (HO \cdot) in the WAO of cellulose.

The oxidation of organic compounds is usually preceded by an initial induction period where the oxidation rate is slow. The length of the induction period represents the time required to reach the minimum free radical concentration [8].

Besides the free-radical reactions, which account for most of the WAO reactions, there are various other reaction types such as thermal degradation, hydrolysis, and decarboxylation that can occur in the WAO of organic compounds [5].

Parameters such as temperature, oxygen partial pressure, solution pH, composition of the reactor walls, and nature of the organic compounds undergoing WAO have a significant influence on the type of free-radical reactions that take place during the WAO and on the stability of the free-radical intermediates [5].

Hamoudi et al. [27] studied the effect of temperature and oxygen partial pressure on the WAO of phenol. In their study, phenol was oxidized for 2 h at 130°C and oxygen partial pressure of 0.5 MPa, and at 220°C and oxygen partial pressure of 3 MPa achieving a TOC conversion of 5% and 88% respectively. The phenol concentration was not revealed.

The effect of pH on the WAO of organic compounds strongly depends on the compound undergoing oxidation and it can be rather complex [12]. The influence of pH can be attributed to the pH-dependent oxygen solubility, the chemical structure of the organic compounds under a certain pH, and the promotion of scavenging of free-radical species with changing pH [5].

Vaidya et al. [12] studied the role of metal walls with a reactor with a pyrex liner. They observed that in absence of the pyrex liner the metal walls rapidly destroy the free radicals, resulting in a significant decrease of phenol destruction.

Regarding the nature of the compounds undergoing WAO, it is significant that not only the compounds themselves define the WAO mechanism, but also the interaction with other compounds in mixtures has a strong effect on the overall reaction pathway. Jin et al. [28] observed that the lignin content affects the acetic acid production in the WAO of a lignocellulosic mixture. In their study they compared the yield of acetic acid formation in the wet oxidation of four different feedstock: cellulose, lignin, rice hulls, and sawdust, being the lignin content in sawdust higher than in rice hulls. They reported the highest acetic acid yield for rice hulls (11.7%) followed by sawdust (9.7%), cellulose (9.0%) and lignin (6.3%). These results indicate that (i) the acetic acid production in presence of

lignin was higher than in its absence, and that (ii) the yield of acetic acid production was indirectly proportional to the lignin content. Jin et al. suggested that the effect of phenol (formed in the lignin breakdown) as an oxidation retarding leads to the formation of hydroxymethylfurfural (HMF) and 2-furaldehyde (2-FA). These two intermediates are known for their high acetic acid oxidation yield. The oxidation retarding effect of phenol may also help retard the oxidation of acetic acid, which also leads to an increase in acetic acid yield to some extent.

2.1.3. Kinetics

The high number of reactions and intermediates involved in the WAO of organic matter make it unrealistic to develop a kinetic model based on the reaction mechanism for a complex organic mixture. Therefore, the oxidation rate laws have to be expressed by means of lumped parameters representative of the organics concentration like TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) [16,29,30].

The WAO rate law can be represented by the power-law kinetic rate

$$r_r = A \cdot e^{-E/RT} \cdot (C_{org})^m \cdot (C_{O_2,L})^n \quad (2.2)$$

where r_r is the reaction rate, A the pre-exponential factor, E the activation energy, R the universal gas constant, T the reaction temperature, C_{org} the concentration of organics (in terms of lumped parameters), and $C_{O_2,L}$ the oxygen concentration in the bulk liquid. The superscripts m and n are the orders of reaction and their typical values are 1 and ~ 0.4 respectively [8]. Unfortunately, this approach is often too simple to adequately describe the WAO of organic mixtures [30].

Li et al. [31] proposed a simplified lumped concentration model based on the two step reaction concept for the non-catalytic WAO of organic mixtures, the General Lumped Kinetic Model (GLKM). This model, also named the triangular scheme (fig. 3), is based on the division of all the organic compounds involved in the WAO in three lumps:

- Lump A: Parent compounds and unstable intermediates except acetic acid
- Lump B: Refractory intermediates (acetic acid being a typical representative)
- Lump C: Oxidation products

In the GLKM model it is assumed that some of the organic compounds are directly oxidized to carbon dioxide and water, whereas the rest are first oxidized to stable intermediates.

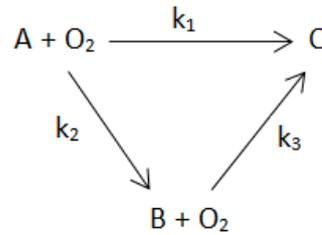


Figure 3. General lumped kinetic model (GLKM) [28].

Assuming first order for the reactants and order zero for the oxygen, the rate equations for the three lumps can be represented as follows [31].

$$\frac{dC_A}{dt} = -(k_1 + k_2)C_A \quad (2.3)$$

$$\frac{dC_B}{dt} = k_2C_A - k_3C_B \quad (2.4)$$

$$\frac{dC_C}{dt} = k_1C_A + k_3C_B \quad (2.5)$$

2.1.4. Chemistry of wet oxidation of a non-wood black liquor

As it has been mentioned in the previous sections, the pathway followed during the wet oxidation of a stream containing a mixture of organic compounds is unknown. Nevertheless, a schematic outline of the most significant steps of the oxidation of these streams can be useful to better understand the whole process.

A diagram of the chemical stage in the wet oxidation of a non-wood black liquor is presented in fig. 4. It can be observed that part of the carbon dioxide generated during the oxidation reacts with sodium hydroxide producing sodium carbonate and sodium hydrogen carbonate. These compounds react with the acids (M-COOH) in the neutralization reaction. Once the oxidation has started, the pH starts to drop immediately due to the acids formation and the consumption of sodium hydroxide. The pH drop becomes faster when NaHCO_3 and Na_2CO_3 are consumed (i.e. the acids generated in the oxidation are no longer neutralized). The acidic pH reduces the solubility of lignin degradation products in the medium, causing the precipitation of high-molecular-weight phenolic compounds.

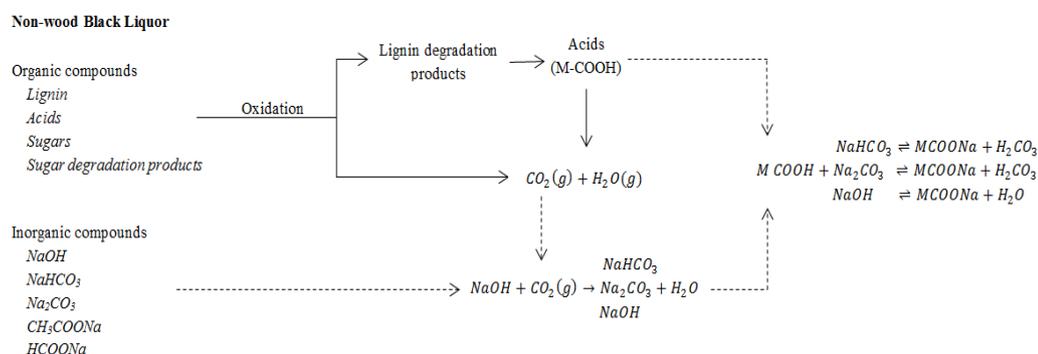


Figure 4. Chemistry of wet oxidation

2.2. Catalytic wet air oxidation

A considerable amount of research has been done on Catalytic Wet Air Oxidation (CWAO) of the most common organic pollutants in order to find the optimal conditions that allow complete oxidation of organic wastewaters in a reasonable time avoiding energy-intensive conditions [5,11].

The CWAO process can be performed either by using homogeneous or heterogeneous catalysts. Homogeneous catalysts, e.g. dissolved copper salts, have been shown to be effective in WAO processes. The presence of the homogeneous catalyst in the same liquid phase as the reactant simplifies reactor operation. However, an additional separation step is required to remove the toxic metal ions which in turn represent an increase in the operational costs [11]. Therefore heterogeneous catalysts are preferred even though they are bounded to suffer deactivation due to leaching and formation of carbonaceous deposits [5,8,11,32].

2.2.1. Physical stage of catalytic wet air oxidation

Besides the steps mentioned in the non-catalytic WAO physical stage, the presence of a solid catalyst involves the competitive or parallel adsorption of the dissolved oxygen and reactant on the catalyst active sites prior to the surface chemical reactions [5].

The path of the gaseous reactants towards the catalyst surface are presented in fig. 5,

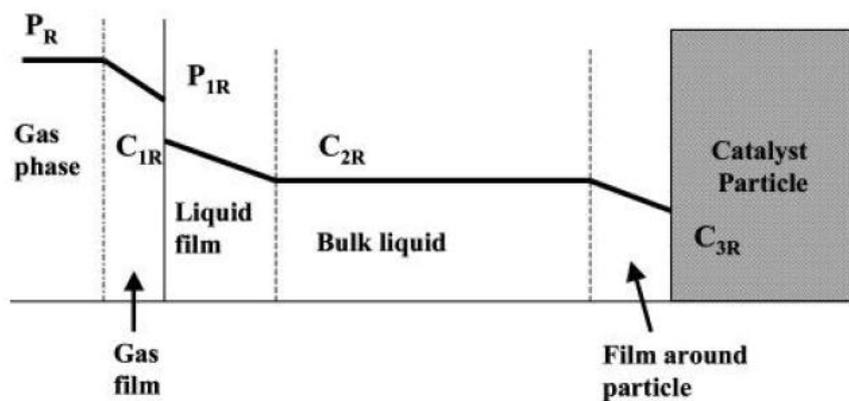


Figure 5. Path of gaseous reactants to catalyst surface in slurry reactor [5].

where P_R , and P_{IR} is the oxygen pressure in the bulk gas and in the gas-liquid interface respectively, and C_{IR} , C_{2R} , and C_{3R} are the oxygen concentration in the interface, in the bulk liquid and in the catalyst.

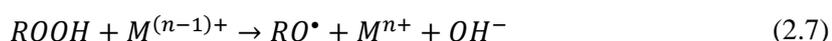
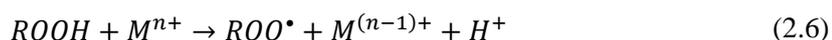
The catalyst particle size has a strong influence both in the hydrodynamic behavior and in the reaction rates of the oxidation. Stüber et al. [33] studied the internal mass transfer limitations of activated carbon catalysts having different particle sizes. They observed that effect of the internal mass transfer is negligible for particle size below 0.3-0.4 mm.

2.2.2. Reaction mechanisms

In the same way as the non-catalytic WAO, the CWAO of organic compounds has been widely proposed to proceed via a free-radical chain reaction mechanism [34-37].

In order to clarify the role of the metal-based catalysts, a number of free radical (homolytic) and ionic (heterolytic) mechanisms have been proposed for the CWAO of organic pollutants. Among them, the most typical are listed below [5].

- a. **Homolytic catalysis.** In the homolytic reaction mechanism, free-radical reactions are promoted via homogeneous mechanisms. This mechanism involves the introduction of a catalytic cycle through the homolytic redox reactions of hydroperoxides:



In eq. 2.6 the free radical propagation is enhanced by the formation of alkyl peroxy radicals, whereas in eq. 2.7 what enhances the free radical propagation is the decomposition of hydroperoxides. The redox potential of the $M^{n+}/M^{(n-1)+}$ couple is a main factor in the oxidation promotion [5,38].

- b. **Coordination catalysis.** Involves the oxidation of a coordinated substrate by a metal ion, which is subsequently regenerated by reaction with oxygen. This mechanism can be either homogeneous or heterogeneous.
- c. **Mars-Van Krevelen adsorption model.** In this redox mechanism, which involves lattice oxygen, the substrate is oxidized by an oxometal specie and subsequently reoxidized by oxygen, completing the redox cycle.

- d. **Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption model.** The LHHW model is a surface catalysis model that involves the adsorption of all the reactants on the catalyst surface. In the LHHW model each reaction is assumed to be an elemental and reversible step.

Besides these mechanisms, Cavani et al. [39] suggested that during the CWAO, catalysts may also involve an oxygen-transfer mechanism in which the role of catalyst is to transfer an oxygen atom to aqueous reactant molecules through complexation and activation.

Sadana et al. [40] proposed a heterogeneous-homogeneous free radical mechanism for CWAO consisting of the initiation on catalyst surface (either by oxygen or reactant molecules activation), homogeneous propagation, and either homogeneous or heterogeneous termination.

Chang et al. [41] reported that exists an optimal catalyst loading for each system due to the catalyst dual role of initiator and terminator of free radicals. They observed that the rate of free radical formation and the rate of free radical destruction increase with catalyst loading until a critical point where the free radical formation dominates. If the catalyst loading is further increased, the free radical destruction dominates, lowering the catalyst activity.

2.2.3. Kinetics

Besides the power law kinetic model, some other models based on the adsorption-desorption mechanisms (i.e. LHHW) have been proposed for the heterogeneous CWAO of organic pollutants. Guo et al. [21] suggested three different kinetic models for the heterogeneous contribution based on the assumption that the adsorption and desorption steps are instantaneous compared to the surface reaction [11]. The rate equations for each model are presented in table 1.

Table 1. Kinetic models proposed for heterogeneous CWAO [21]

| Kinetic model | Equation | Mechanism |
|---------------|---|--|
| M1 | $r_H = k_1[A]^p[O_2]^q$ | Empirical approach |
| M2 | $r_H = \frac{k_1 K_A K_{O_2} [A][O_2]}{(1 + K_A[A] + K_{O_2}[O_2])^2}$ | Single site, $O_2 + * \leftrightarrow O_2^*$ |
| M3 | $r_H = \frac{k_1 K_A K_{O_2}^{0.5} [A][O_2]^{0.5}}{(1 + K_A[A] + K_{O_2}^{0.5}[O_2]^{0.5})^2}$ | Single site, $O_2 + 2* \leftrightarrow 2O^*$ |
| M4 | $r_H = \frac{k_1 K_A K_{O_2}^{0.5} [A][O_2]^{0.5}}{(1 + K_A[A])(1 + K_{O_2}^{0.5}[O_2]^{0.5})}$ | Dual site, $O_2 + 2* \leftrightarrow 2O^*$ |

Where r_H is the heterogeneous contribution to the reaction rate, k_1 is the rate constant for surface reaction step, K_A and K_{O_2} the adsorption equilibrium constants for model compound and oxygen respectively, $[A]$ the concentration of organics (in terms of lumped parameters) and $[O_2]$ the oxygen in the bulk liquid.

M1 is the simplest approach and is equivalent to the power law equation. M2, M3, and M4 are based on the LHHW rate laws. M2 consists of a reversible adsorption of reactant and oxygen molecules on the same active site of the catalyst, with the subsequent rate determining irreversible surface reaction. M3 is also based on the single site adsorption model but considers that the oxygen molecule is dissociated into oxygen atoms. Finally M4 assumes that the dissociated oxygen and the reactant molecules are adsorbed on different active sites.

These models have proved to be reasonably effective in different studies [21,42-45]. However, they are not accurate enough for wastewaters containing a mixture of organic compounds.

Since kinetic rate equations for heterogeneous catalyzed reactions are based on the same laws of chemical kinetics as those applied to homogeneous processes, attempts were made to use the GLKM in the context of CWAO [16,46]. Unfortunately, the GLKM does not consider the reactant adsorption nor the product desorption. This results in kinetic constants violating Arrhenius equation, and negative activation energies [11,30].

Belkacemi et al. [30] extended the GLKM to solid-catalyzed wet oxidation by including physical and chemical steps to describe the reactant adsorption, the surface reactions, and

the product desorption. This new model (fig. 6), called Extended Lumped Kinetic Model (ELKM) is based on the LHHW approach.

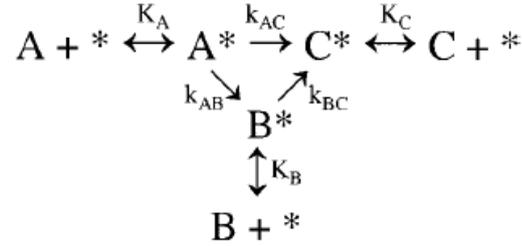


Figure 6. Network reaction pathway for heterogeneously catalyzed wet oxidation [30]

where the three lumps are defined as follows:

- Lump A: Parent water-dissolved compounds
- Lump B: Soluble intermediates, including the stable ones
- Lump C: Gaseous and solid end products

Belkacemi et al. suggested the following set of rate equations either for a perfectly stirred liquid-batch transient reactor or a steady-state liquid-plug flow continuous fixed-bed reactor with a constant fluid streamwise velocity

$$\frac{dC_A}{dt(\text{or } d\tau)} = -\frac{m_{cat}(\tilde{k}_{AB} + \tilde{k}_{AC})K_A C_A}{1 + K_A C_A + K_B C_B + K_C C_C} \quad (2.8)$$

$$\frac{dC_B}{dt(\text{or } d\tau)} = \frac{m_{cat}(\tilde{k}_{AB}K_A C_A - \tilde{k}_{BC}K_B C_B)}{1 + K_A C_A + K_B C_B + K_C C_C} \quad (2.9)$$

$$\frac{dC_C}{dt(\text{or } d\tau)} = \frac{m_{cat}(\tilde{k}_{AC}K_A C_A + \tilde{k}_{BC}K_B C_B)}{1 + K_A C_A + K_B C_B + K_C C_C} \quad (2.10)$$

where m_{cat} is the catalyst loading, τ the residence time, and \tilde{k} the embedded rate constant, which can be represented as

$$\tilde{k}_{AB} = k_{AB} \cdot X_0; \quad \tilde{k}_{AC} = k_{AC} \cdot X_0; \quad \tilde{k}_{BC} = k_{BC} \cdot X_0$$

being X_0 the concentration of initial active sites.

The following assumptions were made in the elaboration of the ELKM rate equations

- i. Surface reactions are rate controlling compared to the adsorption/desorption steps
- ii. All the active sites are identical
- iii. All elementary steps involve partial first order relative to their respective reactants
- iv. Dissolved oxygen concentration is considered constant
- v. Mass transfer interfacial limitations and intraparticle resistance are neglected
- vi. No irreversible loss of active sites occurs

The model was successfully tested using literature data dealing with a large variety of pollutants and a wide range of conditions [30].

2.2.4. Previous work

The catalytic partial wet air oxidation (CPWAO) for the production of valuable chemicals has not been as extensively studied as the complete CWAO for environmental purposes (organics removal).

The unique study specifically focused on the chemicals production from the CWAO was carried out by McGinnis et al. [47]. In their work, they reported the production of formic acid, acetic acid, methanol, and a mixture of hydroxylated organic acids as a result of the WAO of different kind of woods. In their work, formic acid and acetic acid were the major acids produced, accounting for 80-95% of the total acidity. When milder conditions were employed, the yield of hydroxylated acids, such as glycolic and lactic acid was higher. Regarding the methanol formation, they observed that the conditions which maximized the yield of acids minimized the yield of methanol.

Based on the enhanced formation of acids of CWAO using ferric sulfate, cupric sulfate, and aluminum sulfate as a catalysts in their previous experience [48], the acids formation in presence of ferric sulfate was studied. They observed that the addition of ferric sulfate decreased the yield of acetic acid whereas the yield of formic acid was increased [47].

Despite the opposite purposes of the complete and the partial CWAO of organics, the analysis of the previous studies on complete CWAO can provide an idea of the catalysts

performance that can be useful to predict their suitability for the valuable intermediates production.

The noble metal based catalysts have been reported to have higher catalytic activities and higher resistance to leaching than transition metal based catalysts (TOC removal of 78.8% after 200 min using Mn/Pd oxide in black liquor CWAO, in front of 57.8% using Mn/Cu oxide) [6,11]. Nevertheless, the high cost and the vulnerability to deactivation make them inappropriate for the industrial CWAO process.

Garg et al. [2] studied the CWAO of a diluted Kraft black liquor over a CuO/CeO₂ (60/40 wt%) catalyst (8 g/L) in a temperature range of 115-150°C and a total air pressure of 0.6 MPa. The experiment was carried out in a 500 mL autoclave where the black liquor and the catalyst were mixed using a magnetic stirrer. They reported maximum COD reduction of 71.4% after 5 h of reaction for extremely acid pH. However, no conclusions can be deduced from this study because most of the COD removal was due to the precipitation of dissolved solids from the synthetic pulp due to the low pH and thus not because of the oxidation process.

Dhakhwa et al. [1] also studied the performance of the CuO/CeO₂ catalyst, but in their study they used non-wood black liquor as a substrate and pure oxygen as oxidizing product (0.8 MPa). Experiments were carried out in a mechanically stirred (1000 rpm) 700 mL stainless steel batch reactor in the presence of 300 mL of black liquor and a catalyst load of 3 g/L during 4 h. Maximum COD removal (51%) was obtained at 170°C and initial pH of 7.5.

The CWAO of black liquor over unsupported CuO catalyst was studied by Akolekar et al. [6]. In their work they used a nickel autoclave (1.2 L) and a pure oxygen pressure of 500 kPa. CWAO after 200 min at 190°C, catalyst loading of 5.05 g/L and stirring speed of 1000 rpm resulted in 38.4% TOC removal.

The fact that phenol is considered to be an intermediate in the oxidation pathway of higher molecular weight aromatic compounds has led to a number of studies on CWAO of phenol [5,11].

Kim et al. [49,50] studied the phenol CWAO over different alumina supported metal oxides (Cu, Ni, Co, Fe, and Mn). Among them copper oxide showed the highest catalytic activity, probably due to its highest surface reducibility, whereas Fe, Co, and Ni oxides

hardly showed catalytic activity. On the other hand, manganese oxide had the highest amount of carbonaceous deposits.

Chen et al. [41,51] investigated the effectiveness of the supported CeO_2 catalyst on phenol CWAO, reporting $\gamma\text{-Al}_2\text{O}_3$ as the most suitable support, with a cerium optimal content of 20 wt%. CeO_2 supported catalyst are less effective than pure CeO_2 oxides, however, the fewer content of ceria reduces the price of the catalyst. Experiments were carried out at 180°C , oxygen partial pressure of 1.5 MPa and catalyst loading of 3 g/L during 4 h (most of conversion within the two first hours), achieving 70% of TOC removal. The authors reported high resistivity to leaching.

Duarte [23], investigated the activity of a set of metal oxides catalysts in the CWAO of black liquor. In his work, he studied not only the organic pollutants removal but also the acetate and formate production, being possible to analyze which reaction pathways are favored by which catalysts. The catalyst that showed the highest catalytic activity in the COD and TOC reduction were CeO_2 (71.3 % and 70.0 %), CoO (71.5 % and 68.2 %), and CuO (71.6 % and 68.1 %). He also suggested that among these three catalysts, those with higher TOC conversion promoted the complete oxidation to end products, whereas those with lower TOC conversion promoted the intermediates formation. Therefore, CeO_2 was reported as a suitable catalyst for the complete oxidation of organic matter, while CuO and CoO were reported to be adequate for the partial WAO.

Duarte also studied the leaching of the different metals. He observed that CuO was the catalyst with the highest leaching rate. CoO had a lower leaching rate, however, it easily got stuck in the reactor walls.

Activated carbon catalysts have been found to be a promising alternative for the CWAO of organic pollutants due to their low price and the capability to overcome some of the problems related with the use of metals [33,45,52-55]. Although the role of AC in CWAO still remains uncertain, it is believed that its good performance is related to its high adsorption capacity and its potential to generate oxygenated free radicals for the oxidation reaction initiation [33]. The performance of the AC strongly depends on its specific properties meaning that two different kind of AC can have a very different performance in the CWAO [56,57].

Quintanilla et al. [54] prepared Fe/AC catalysts and compared their performances with a commercial AC. They reported that the iron enhanced the activity of AC. And almost no

leaching was observed, maintaining a long term constant activity despite the coke deposition. The low deactivation makes the Fe/AC a very interesting catalyst.

2.2.5. Considerations about the use of catalysts

The use of catalysts is a promising alternative to non-catalytic WAO due to its enhanced oxidation rate even at milder conditions. However, there are different aspects that need to be taken into account in order to guarantee the effectiveness and feasibility of the use of heterogeneous catalysts in the WAO of industrial wastewaters. Besides the catalyst composition, the most significant aspects are [5]:

- Catalyst preparation
- Catalyst stability and deactivation
- Catalyst reuse and regeneration

2.2.5.1. Catalyst preparation

The catalyst preparation methods can be used to manipulate the chemical and physical properties of the catalyst, which in turn, influences its activity. The oxidation state of the metals is a good example of a chemical property that can be altered by the preparation method. Regarding the physical properties, the distribution and mobility of active components, the surface area, the pore size and distribution, and the phase of active components or support can be tailored by using a specific preparation method [5].

2.2.5.2. Catalyst stability and deactivation

The rapid deactivation of heterogeneous catalysts is primarily due to poisoning of active sites, coke deposition, metal leaching, and sintering, and represents a significant burden for the CWAO. Enhancing the catalyst stability while maintaining a high level of activity is a focus key for the researchers. Nevertheless, the high-temperature and the acidic conditions make this purpose challenging [5,11].

Unlike metal oxides, precious metals supported on stable supports have good stability against leaching, however, the formation of carbonaceous deposits is still a problem [11].

Formation of carbonaceous deposits

The formation of carbonaceous deposits limits the access of reactants and dissolved oxygen to the active sites of the catalyst. The adsorption of these partially oxidized intermediates is promoted by low temperatures and low catalyst concentration [11,58-62].

The degree of coke deposition varies depending on the metals compounding the catalysts. Kim et al. [63] reported that among different transition metal oxide catalysts supported on γ -Al₂O₃, the Mn oxide catalyst showed the highest amount of carbonaceous deposits after the CWAO of phenol in a batch reactor. On the other hand, a number of authors [64-67] observed that the metal doping restrained the formation of carbonaceous deposits.

Metal leaching

The formation of low-weight carboxylic acids in addition to the high temperatures typical from the CWAO processes create a harsh environment that can result in the leaching of metal ions out of the catalyst [68-72]. In some cases the leached metal ions represent a threat for the environment, being necessary their recovery [73,74].

Among the different catalysts that have been shown effective in the CWAO of organic compounds, copper catalysts are the most vulnerable to leaching. The concentration of dissolved copper ions above certain levels changes the heterogeneous reaction into homogeneous, positively influencing the rate of oxidation [75]. In order to prevent metal ions leaching, Fenoglio et al. [76,77] proposed a polytetrafluorethylene (PIFE) coated catalyst capable to reduce the direct contact between active species and aqueous reaction medium while allowing the reactants to diffuse and react into the catalyst.

2.2.5.3. Catalyst reuse and regeneration

The effectiveness of the catalytic regeneration is a key factor for the economic viability of the CWAO processes. The types of regeneration methods are highly dependent on the type of deactivation, however, the thermal-based treatments in an oxidizing gas stream are the most common [5].

Massa et al. [78] reported that catalysts deactivated by coke deposition can recover their initial activity after regeneration at 400°C under air stream. Chen et al. [79] proposed catalyst rinsing with an organic solvent as an alternative to remove coke deposits.

2.3. The industrial catalytic wet air oxidation process

The most important industrial heterogeneous CWAO processes are the Nippon Shokubai Process and the Osaka Gas Process. The former is usually carried out with a Pt-Pd/TiO₂/ZrO₂ supported catalyst at temperature ranges of 160-270°C, a pressure of 0.9-8 MPa, and a residence time of ~1 h, achieving >99% conversion of organic pollutants [8,80-82]. On the other hand, the Osaka Gas Process involves the use of an Fe-Co-Ni-Ru-Pd-Pt-Cu-Au-W catalyst supported on TiO₂ and ZrO₂. The operating conditions vary according to the type of waste and the required destruction efficiency [8,22,80].

Despite these two consolidated processes, the heterogeneous CWAO has not achieved such deep penetration as other non-catalyzed wet oxidation processes [83]. This lower industrialization of the CWAO process is primarily due to: (i) the lack of efficient, robust and inexpensive catalysts able to stand the harsh conditions prevailing under industrial conditions, and (ii) the lack of a comprehensive reactor design framework and methodology for scale-up, and reactor selection and operation.

The election of a specific type of reactor has a very strong effect on the hydrodynamics and transport phenomena occurring in the heterogeneous CWAO [84]. The choice of the reactor configuration is dictated by practical considerations, and it must promote performance criteria such as minimization of physical internal and external mass transfer resistances [83]. The multiphase nature of heterogeneous CWAO reactions, the demanding temperature and pressure conditions, and the complex radical reaction mechanism, make the reactor design an extremely challenging process [83-85].

It has been demonstrated that some reactions proceed differently whether they are carried out in different reactor configurations [86], hence the extrapolation of kinetic data collected in one reactor configuration to predict the performance in a different reactor type might lead to erroneous conclusions. These differences are normally due to effects such as mass or heat transfer and different liquid to solid ratios [87].

Different types of reactors have been proposed for three-phase catalytic reactions. Among them, the most typical are [83]:

- Trickle bed reactor
- Packed bubble column
- Three-phase fluidized bed
- Slurry bubble column

Trickle Bed Reactors (TBR) are the most used configuration in the heterogeneous CWAO processes. They consist of vertical columns packed with a catalyst bed. In this type of reactors gas and liquid reactants typically flow co-currently downward [88]. In Packed Bubble Columns (PBC), the fixed bed is flooded at low gas-to-liquid ratio conditions and co-current up-flow streams. Three-phase fluidized beds are interesting alternatives for adiabatic operations and wastewaters with high organic loadings. In this configuration, the batch catalyst particles are re-circulated and back-mixed by co-current up-flow streams. Finally, in the slurry bubble column, the liquid-solid suspension as well as the bubbling gas phase are driven upward through the column. The four configurations are schematically presented in fig. 7 [83,84].

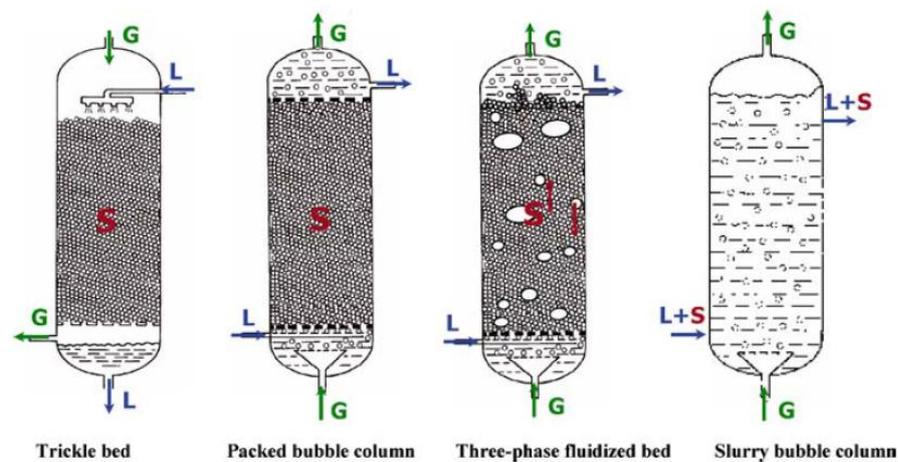


Figure 7. Reactor configurations used in the heterogeneous CWAO processes [83]

The most significant advantages and disadvantages of each configuration are summarized in table 2 [5,89].

Table 2. Advantages and disadvantages of each reactor configuration

| | Advantages | Disadvantages |
|---------------------------|---|--|
| Trickle bed reactor | <ul style="list-style-type: none">• Low liquid holdup• High catalyst loading• Low catalyst deactivation | <ul style="list-style-type: none">• Liquid maldistribution• Incomplete wetting• High intraparticle resistance• Potential for fouling and bed plugging |
| Packed bubble column | <ul style="list-style-type: none">• High wetting efficiency• Good liquid distribution• Good heat and mass transfer | <ul style="list-style-type: none">• Restricted to low gas flow rates• High backmixing and pressure drop |
| Three-phase fluidized bed | <ul style="list-style-type: none">• High external mass transfer• Low intraparticle resistance | <ul style="list-style-type: none">• Low catalyst load |
| Slurry bubble column | <ul style="list-style-type: none">• Excellent heat transfer• Good mass transfer• Ease of catalyst addition and regeneration | <ul style="list-style-type: none">• Requires a catalyst separation process• Uneven catalyst distribution along the column |

Not only the reactor configuration but also the material of construction affects the effectiveness of the whole CWAO process. Emanuel et al. [90] reported that the termination of free radicals is increased by metallic surfaces. However, this effect can be neglected in the full-scale industrial reactors due to the low surface area to volume ratio [12,91].

2.3.1. Considerations about the industrial catalytic wet air oxidation process

There are some parameters that need to be taken into account before discussing the suitability of each reactor configuration for the heterogeneous CWAO of organic compounds.

2.3.1.1. Catalyst wetting

The catalyst wettability in fixed bed reactors operations is an extremely complex phenomenon affecting important reactor design parameters including pressure drop, liquid hold up and wetting efficiency [92]. Wetting is defined as the fraction of the external particle surface covered by liquid [5]. To describe the wetting pattern of catalyst particles, the liquid hold up can be split in dynamic (ϵ_{LD}) and static (ϵ_{LS}). The intra-granular porosity of the catalyst particles (ϵ_p) is assumed to be fully wetted because of the effect of capillary forces [5,83].

Static hold up formation is typical of fixed bed reactors, whereas it is avoided in fluidized beds and slurry reactors due to the circulatory patterns of the catalyst particles. The static hold up limits the reactant access to the catalyst, yielding thereby a passive boundary represented by the static wetting efficiency (η_S). It has been suggested that the undesirable static hold up can be overcome through a forced pulsing flow. The liquid flow induced pulse allows both direct oxygen mass transfer through unwetted catalyst surface and the resupply of other reactant dissolved in the liquid phase [88,92-94].

On the other hand, the dynamic hold up refers to the flowing liquid that covers the catalyst particle surface. The fraction of catalyst covered by dynamic hold up is known as dynamic wetting efficiency (η_D), therefore the total wetting efficiency (η_E) can be expressed as

$$\eta_E = \eta_D + \eta_S \quad (2.11)$$

The total wetting efficiency is an important parameter in fixed bed reactor operations like TBR and PBC as it gives an indication of the extent of catalyst utilization [83,92]. The external total wetting efficiency is a function of flow rates of gas and liquid, operating pressure, physical properties of liquid and diameter of the catalyst particle [92]. The wetting efficiency is improved with the increase of the gas superficial velocity in up-flow configuration or, with the increase of pressure in a down-flow configuration [84].

There might be some cases where the low liquid irrigation rates allow the coexistence of dry spots with wetted zones on the catalyst surface (i.e. trickled bed reactors). The dry spots represent a potential hazard for the system due to their high temperature. The high

temperatures of the dry spots are due to (i) the good mass transfer of gaseous reactants to the catalyst surface in absence of a liquid layer, and (ii) the poor heat transfer between the catalyst and the gaseous medium. The good mass transfer enhances the reaction rate in the dry spots, which in turn represent a higher generation of heat of reaction. The limited heat transfer between the dry spots and the medium causes the overheating of the dry spots. A sketch with the typical wetting structure of the catalyst grains as well as a one-dimensional representation of the particle wetting is presented in fig 8 [83].

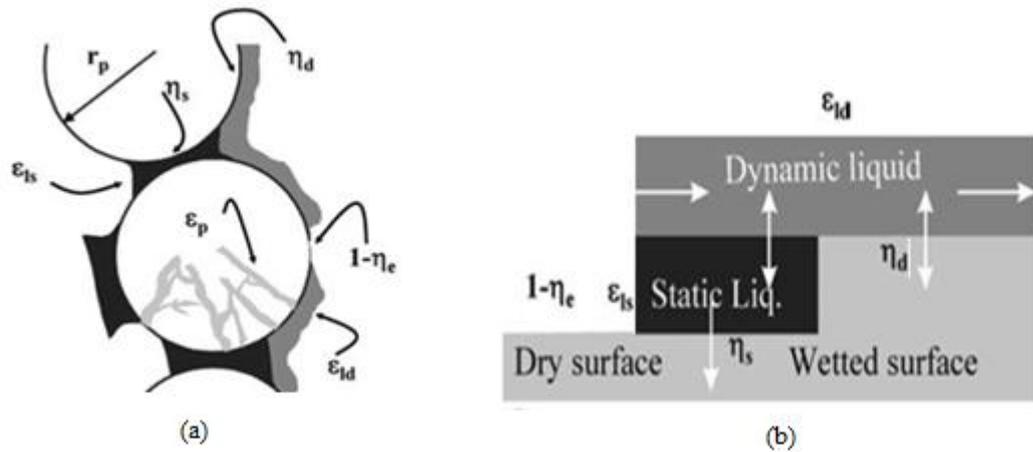


Figure 8. (a) Local wetting structure of the porous catalyst grains. (b) Connectivity model of the gas, liquid, and solid interfaces [83].

To better illustrate the role of catalyst wetting, it is convenient to define a ratio of the maximum fluxes of reactants inside the catalytic grains (γ)

$$\gamma = \frac{D_{eP} \cdot C_p}{D_{eO_2} \cdot C_{O_2}} \quad (2.12)$$

where, D_{eO_2} and D_{eP} represent, respectively, the effective diffusivity of oxygen and organic compounds, and C_{O_2} and C_p their concentration in the liquid phase. The γ -ratio express the relative presence of species in the liquid phase. Therefore, the most suitable reactor configuration will vary according to the value of the γ -ratio [83].

When $\gamma \gg 1$, the dissolved pollutants are in large excess in comparison to the oxidants, meaning that the reaction is gas-limited controlled. In this case, the most appropriated configuration is the one that promotes partial wetting of the catalyst (i.e., trickle bed reactor). On the other hand, when $\gamma \ll 1$, the reaction is liquid-limited controlled, meaning that oxygen becomes in excess with respect to the pollutant. A more appropriate configuration would favor complete wetting of the catalyst to facilitate massive access of the dissolved pollutant to the catalyst external surface. Here packed bubble columns are expected to outperform trickle beds [83].

2.3.1.2. Interfacial gas-liquid area

In bubble systems, the overall mass-transfer coefficient is strongly affected by the gas-liquid interfacial area, which can be defined as

$$a = \frac{6\xi}{d_{vs}} \quad (2.13)$$

where d_{vs} is the mean bubble diameter and ξ is the gas hold up [95,96]. Gas hold up determines the extent of interfacial area available (the higher the gas hold up, the greater the gas-liquid interface). Gas hold up is directly influenced by the gas flow rate and pressure, and indirectly influenced by the bubble size. Factors including the type of sparger, the flow regime, the fluid properties, and the operating conditions are responsible for the bubble size [8].

2.3.1.3. Pressure and pressure drop in the reactor

The oxygen partial pressure is the critical driving force for mass transfer of oxygen from the gas phase to the liquid phase. A certain oxygen pressure level is required in order to keep the mass transfer resistance at a minimum. There are some factors that can affect the oxygen pressure and thus need to be carefully analyzed.

The pressure drop across the catalyst bed is view as a concern in all those processes that involve a fixed bed. The pressure drop primarily depends on the catalyst pellets size,

increasing with the decrease in pellets size. The presence of suspended solid materials in the waste stream can result in the clogging of the catalyst bed, resulting in an increase in pressure drop across the bed. To protect the catalyst against solid loading, a two stage process can be utilized where the suspended material is initially dissolved in a non-catalytic reactor before being oxidized in a catalytic reactor [8].

Another factor that needs to be taken into account is the increase of non-oxygen species in the gas phase. The formation of carbon dioxide as a product of the organics oxidation can dilute the oxygen content in the gas phase. The water evaporation due to the energy released in the oxidation can also reduce the oxygen partial pressure. The amount of water that is evaporated needs to be effectively controlled in order to maintain an adequate proportion of water in the liquid state. The total operating pressure is used to control the level of water in the reactor [5,8].

2.3.1.4. Catalyst structure

Structured packing with monolithic catalyst has been proposed as an alternative method of incorporating the catalyst into the reactor. Ishii et al. [97] reported that the incorporation of an effective monolithic catalyst increases reaction rate while reducing pressure losses and plugging of the catalyst. They also reported that a thin liquid film is formed between the gas and the monolith wall in the slug flow regime. This film allows high mass transfer rates and keeps the catalyst continuously wetted [98].

2.3.2. Features of reactor configurations

Iliute et al. [84] developed transient 2D axisymmetrical models to simulate the performance of the four above-mentioned reactor configurations (trickle bed reactor, packed bubble column, three-phase fluidized bed, and slurry bubble column). The heterogeneous CWAO of a phenol-contaminated model wastewater over a mixture of CuO, ZnO, and CoO supported on a steam-treated cement was studied.

In their work they compared the performance of TBR and PBC in liquid-limited controlled conditions ($\gamma < 1$). They reported higher rate of phenol conversion for the PBC configuration due to the much faster transport of the liquid reactant to the catalyst

caused by the higher catalyst wetting. They also pointed out that the performance of TBR can be improved by increasing the pressure in the column. The increase in pressure enhances the catalyst wetting and improves the oxygen solubility, which in turn improves its transfer flux to the pellets.

Iliuta et al. also studied the effect of the catalyst size in three-phase fluidized bed. They observed that an increase in the pellet size caused both an increase in the intraparticle mass transfer and an increase in solids holdup. On one hand, the higher intraparticle mass transfer resistance limits the reactants access to the catalyst, worsening the reaction rate. On the other hand, the increase in solids holdup has a positive effect on the mass transfer. As a result of these opposite effects, there is a pellet size that maximizes the organics conversion.

According to their work, phenol conversion is also affected by the liquid flow rate and the liquid Péclet number. They reported that an increase in the liquid superficial velocity or a decrease in the liquid Péclet number negatively affects the phenol conversion. This adverse effect is due to a decrease in solids hold-up and an increase of liquid backmixing [99].

In their study of the slurry bubble column, Iliuta et al. [84] observed that phenol conversion increased with increasing both pellets size and feed concentration. Phenol conversion was also observed to increase with decreasing gas velocity due to the higher solids hold up, resulting in higher liquid-solids mass transfer rates.

Fixed bed reactor configurations provide higher catalyst lifetime and activity in terms of pollutant destruction than fluidized beds and slurry bubble columns. This better performance of fixed-bed reactors is probably due to the different type of deactivation suffered by fixed bed reactors and moving catalyst reactors. In the former configuration deactivation mostly occurs in the first catalytic layers, whereas in the latter particles are more prone to bulk deactivation [83].

2.3.3. Previous work

Among the reactor types presented in the previous section, the trickle bed reactor application on the heterogeneous CWAO of organics in a concurrent downwards mode is the most reviewed in the available literature.

Attempts have been done to perform heterogeneous CWAO using trickle bed reactors in countercurrent mode, however, the higher momentum transfer between gas and liquid phase in countercurrent operation with packed bed having small catalyst particles causes flooding at very low velocities [92].

Pintar et al. [100] studied the CWAO of aqueous solutions of formic acid, acetic acid, and phenol over Ru/TiO₂ catalysts in a trickle bed reactor. All the runs were conducted in a low-interaction trickle-flow regime (superficial liquid flow rate between 0.16-0.50 kg·m⁻²·s⁻¹). This low liquid flow rate resulted in the liquid trickling down the packing in form of droplets, films, and rivulets. The remaining dry pores were occupied by the gas phase. Over 95% TOC reduction was achieved at 230°C, 10 bar of oxygen and residence time of 0.14 min.

Yang et al. [101] compared the performance of a CeO₂/TiO₂ catalyst in a batch slurry reactor and in an up-flow packed bed reactor using phenol as a substrate. While the organics removal decreased in the batch reactor after three time cycles, it stayed stable in the packed bed reactor for 100 h reaction run. This decrease in activity can be attributed to the formation of carbonaceous deposits due to the high ratio of organics to catalyst typical of batch reactors. The formation of these depositions was restricted in the packed bed reactor. Yang et al. reported around 91% COD and 80% TOC removals for 100h reaction at 140°C, air total pressure of 3.5 MPa, gas flow rate of 60 mL/min, and liquid flow rate of 0.5 mL/min.

Stüber et al. [33] also compared the performance of a slurry reactor (batchwise for the liquid and continuous flow for the gas) and a trickle bed reactor at same conditions of pressure and temperature. They reported a better performance of the former, probably due to the incomplete or ineffective catalyst wetting, which in addition to preferential flow at low liquid flow rates and inadequate reactor diameter/particle size ratio can negatively affect the reactor performance [102]. On the other hand, the enhanced homogeneous condensation reactions that lead to catalyst deactivation in slurry batch reactors were not present in the trickle bed reactors [5,43,103].

Eftaxias et al. [45] performed oxidation tests in downflow and upflow mode at three different temperatures (120, 140, and 160°C) and two oxygen partial pressures (0.1 and 0.2 MPa). A commercial activated carbon and phenol were used as catalyst and substrate respectively. The air flow rate was $2.4 \text{ cm}^3\text{s}^{-1}$ (STP) and the liquid flow rates were between $10\text{-}150 \text{ cm}^3 \text{ h}^{-1}$, corresponding to space-times of 0.04-0.6 h. They reported a maximum COD removal of 85% in downflow mode at 160°C and 0.2 MPa.

Mohamed et al. [55] studied the effect of the gas flow rate and the LHSV* in the CWAO of phenolic compounds over activated carbon. They reported that maximum phenol conversion was achieved when Stoichiometric Excess (SE) of oxygen is around 80%. Regarding the liquid flow, they observed that phenol conversion increased as LHSV decreases from 3 to 1 h^{-1} .

A compilation of the TBR operational conditions in the WAO of industrial wastewaters is presented in table 3.

* Liquid hourly space velocity: Volume of liquid feed per hour divided by the volume of the reactor.

Table 3. Operational conditions in trickle bed reactor

| Ref. | Reactor dimensions (mm) | Oxygen source | Catalyst loading (g) | Catalyst particle diameter (mm) | Temperature (°C) | Total pressure (bar) | Oxygen partial pressure (bar) | Gas flow rate (mL/min) | Liquid flow rate (mL/min) | LHSV (h ⁻¹) |
|------|-------------------------|---------------|----------------------|---------------------------------|------------------|----------------------|-------------------------------|------------------------|---------------------------|-------------------------|
| 33 | L=300 Ø= 11 | Air | 7.7 | 0.29-0.7 | 140 | - | 5.5 | 144 | 0.16-5 | - |
| 45 | L=200 Ø=11 | Air | 6.6 | 0.3-0.7 | 160 | - | 2 | 144 | 0.16-5.5 | 1.66-25 |
| 52 | L=200 Ø=11 | Air | 7 | 0.3-0.7 | 140 | 13.1 | 2 | 144 | - | 8,2 |
| 53 | L=305 Ø= 8.5 | Oxygen | 2.4 | 0.5-1 | 100-114 | 8 | - | 91 | 0.125-2 | - |
| 54 | L=305 Ø=8.5 | Oxygen | 1.2-2.5 | 0.5-1 | 127 | 8 | - | 91.6 | 0.125-2 | - |
| 94 | L= 500 Ø= 18 | Oxygen | 11.7 | - | 125-170 | 10-70 | - | - | - | 1-20 |
| 100 | L= - Ø=9 | Oxygen | 3 | 1.4 | 55-250 | 10.2-49.7 | 0-10.0 | 100 | 0.16-0.50 | 11.3-33.9 |
| 101 | L=200 Ø=20 | Air | 85 | - | 140 | 35 | - | 60 | 0.5 | 0.5 |
| 104 | L=200 Ø= 10 | Air | 7-7.5 | 0.3-0.7 | 120-160 | - | 2-8 | 150 | 1 | - |

Chapter 3

Materials and methods

A set of heterogeneous catalysts from the literature were tested in the wet air oxidation of rice straw black liquor. In this chapter the experimental apparatus and procedure, the catalysts used, the experimental plan, and the analysis techniques are detailed.

3.1. Experimental equipment

The oxidation runs were performed batchwise in a reactor composed of a 100 mL stainless steel vessel and a screw cap (PARR instruments). The stirring was provided by a mechanic impeller powered by a small motor from Bodine electric with a maximum rotation speed of 2500 rpm. The heating was provided by an external electrical heater (PARR instruments). Temperature and pressure inside the reactor were respectively measured with a thermocouple and a manometer (Ashcroft, model 1009) connected to the screw cap. The high-pressure oxygen gas feed line and the exit line were also connected to the screw cap together with a relief valve adjusted to 60 bar. Temperature setpoint and stirring speed were adjusted through a digital temperature controller (PARR 4842). The temperature controller receives the signal from the thermocouple and then sends the signal to the electrical heater. There is no cooling mechanism system. The experimental setup is illustrated in fig 9.

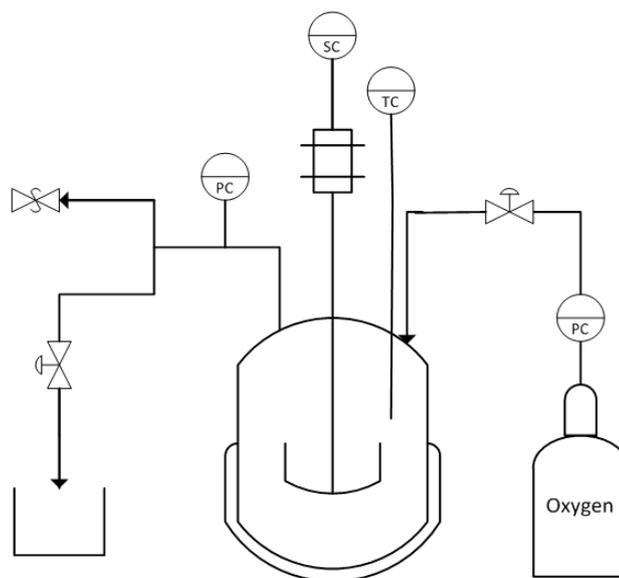


Figure 9. Experimental apparatus

3.2. Experimental procedure

The exact same procedure was followed for all the oxidation runs. The first step was to introduce 50 g of black liquor and 0.150 g of catalyst (3 g cat/1000 g black liquor) in the reactor vessel. Due to the lack of space in the reactor and the small size of the catalyst particles, the catalyst was added directly to the vessel without using any basket. The reactor vessel was then closed with the screw cap and sealed so that the oxygen could not get inside the reactor nor the gas from the reactor could go out, i.e. the reactor inlet and outlet valves were closed.

Once the reactor was sealed, it was preheated by adjusting the temperature setpoint to 170°C. The stirrer was also turned on and adjusted at maximum speed in order to ensure the absence of mass transfer limitations. When the temperature inside the reactor was between 100-105°C, the exit line was gently opened for few seconds to expel the nitrogen of remaining air inside the reactor.

Although the desired temperature of oxidation was 170°C, the valve of the oxygen gas line to the reactor was opened and rapidly shut when the temperature was between 130-140°C. The objective of letting a limited amount of oxygen in the reactor was to start the oxidation and therefore use the heat of reaction to help to reach the temperature setpoint

without exceeding it. This operation was necessary in order to avoid an overheating of the reactor content.

Finally, when the temperature inside the reactor was 170°C, the valve was completely opened. That time was considered the oxidation starting point ($t = 0$). A certain temperature variation ($\pm 10^\circ\text{C}$) was always to be expected until the temperature finally stabilized at 170°C. The stabilization time was usually less than 10 min.

The total pressure was kept constant at 12 bar during all the run. Since the vapor pressure of water at 170°C is 8 bar, the oxygen pressure inside the reactor was 4 bar. After 60 min the oxygen feed was stopped and the sealed reactor was cooled down to room temperature and finally depressurized.

The operational conditions are summarized in table 4

Table 4. Operational conditions in oxidation runs

| | |
|--------------------------|---------|
| Amount of black liquor | 50 g |
| Amount of catalyst | 0.150 g |
| Temperature of oxidation | 170°C |
| Total pressure | 12 bar |
| Oxygen partial pressure | 4 bar |

3.3. Materials

The materials used in the oxidation runs were rice straw black liquor, the catalysts and pure oxygen.

Black liquor

The black liquor used for the catalysts testing was purchased from the forest products research group in Aalto University. The conditions of the cooking are presented in table 5.

Table 5. Details of black liquor cooking

| | |
|--------------------------------------|------------|
| Feedstock | Rice straw |
| Cooking temperature | 160°C |
| Cooking time | 60 min |
| Liquid to solid ratio in the cooking | 5 |
| Sodium hydroxide charge on dry wood | 20% |

In order to test the catalyst behavior in the oxidation of black liquors with different concentration of pollutants, two different solutions were prepared from the original black liquor (BL-I and BL-II). The properties of both liquors are presented in table 6.

Table 6. Properties of BL-I and BL-II

| | Strong liquor BL-I | Weak liquor BL-II |
|---------------|-----------------------|----------------------|
| pH | 11.93 | 11.3 |
| Solid content | 22.21 % | 11.38 % |
| COD | 230654.5 mg/L | 109436.5 mg/L |
| TOC | 94957.25 mg/L | 44039.5 mg/L |

Even though the exact composition of BL-I and BL-II was unknown, the components present in non-wood black liquor are generally known. These compounds include lignin, sugar, sugar degradation products, acids, sodium salts, sodium hydroxide.

Catalysts

The election of the catalysts used in the experimental study was done according to the results reported in the articles reviewed in the literature survey. The catalysts chosen were cerium (IV) oxide (CeO_2), copper (II) oxide (CuO), iron (III) oxide (Fe_2O_3), activated carbon (AC), alumina-supported cerium oxide ($\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$), and iron supported on AC (Fe/AC). The unsupported catalysts were directly purchased whereas the supported ones were prepared as described below.

The $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was prepared using the wet impregnation method. Prior to starting the impregnation, the alumina was grinded to small particles (0.105-0.149 mm) and dried overnight at 120°C. The impregnation was carried out in a rotary evaporator at

atmospheric pressure and 50°C. Chen et al. [41,51] determined that optimal Ce content of the catalyst was 20 wt %. Therefore, a 8.05 mL distilled water solution containing 2.647 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was mixed with 4.005 g of alumina for 1 h. After the impregnation, the catalyst was dried at room temperature for 1 h and further dried in the oven at 110°C overnight. Finally it was calcinated at 300°C for 5 h.

The wet impregnation technique was also used in the preparation of the Fe/AC catalyst in the same exact conditions. In this case 3.876 g of AC (0.105-0.149 mm) were mixed with a 8.028 mL water solution containing 0.7468 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The respective amounts of precursors were calculated so that the Fe content in the catalyst was 2.5 wt %. The catalyst was dried at room temperature for 2.5 h and further dried in the oven at 70°C overnight. The catalyst was finally calcinated at 190°C for 6 h.

Stüber et al. [33] observed that the internal mass transfer resistance was negligible when particle size was below 0.3 mm. In order to ensure the absence of internal mass transfer resistance and thereby the kinetic nature of the reaction, all the catalysts used were grinded and sieved to particles below 0.149 mm.

The information related with the chemicals used either directly as catalysts or as precursors is presented in table 7.

Table 7. Chemicals utilized in the experimental section

Catalysts

| Compound | CAS numer | Manufacturer | Product number |
|-------------------------|-----------|---------------|----------------|
| CeO_2 | 1306-38-3 | Sigma-Aldrich | 22390 |
| CuO | 1317-38-0 | Sigma-Aldrich | 241741 |
| Fe_2O_3 | 1309-37-1 | Sigma-Aldrich | 12342 |
| AC | 7440-44-0 | Merck | 102518 |

Precursors

| Compound | CAS numer | Manufacturer | Product number |
|--|------------|---------------|----------------|
| $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ | 18618-55-8 | Alfa Aesar | A12947 |
| $\gamma\text{-Al}_2\text{O}_3$ | 1344-28-1 | Alfa Aesar | 43832 |
| $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 7782-61-8 | Sigma-Aldrich | 31233 |

Oxidant

Pure oxygen (99.99 %) purchased from AGA Finland was used as oxidant in all the experimental runs.

3.4. Experimental program

The catalyst testing was carried out in two rounds, being the feedstock for oxidation the unique difference between them. Strong black liquor was used as feedstock in the first round (BL-I) whereas weak black liquor was used in the second round (BL-II). Each round consisted of the six catalytic runs corresponding to the six different catalysts plus a control non-catalytic run that was carried out exactly in the same conditions.

The same operational conditions were applied in each run, ensuring the homogeneity and comparability of the results within runs of the same round.

Due to the limited amount of black liquor in the reactor, no intermediate samples were withdrawn. Only the final product of the oxidation was analyzed.

3.5. Analysis

The performance of the catalysts was studied by the analysis of the product of each oxidation run as well as the analysis of the liquor used in each round.

The parameters that were analyzed from each sample were the pH, solid content, COD, and TOC.

pH measurement

The pH was measured at atmospheric pressure and room temperature right after each oxidation run. The pH meter (VWR pH100) was calibrated before each round to ensure the certainty of results.

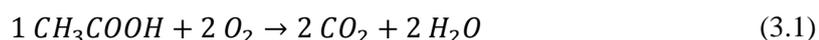
Dissolved and suspended solid content

The content of dissolved and suspended solids was measured in an elemental way. Approximately 10 g of homogeneous sample were left to evaporate overnight in an oven at 120°C and then the solid content was calculated with the weight difference. The solid content can be expressed as the mass of sample after complete water removal divided by the initial mass of the sample.

The procedure was done three times for BL-I and BL-II but just one for the oxidation products due to the limit amount available for analysis.

COD and TOC

The Chemical Oxygen Demand (COD) of a sample is an indicator of its organic content and it is usually expressed in terms of mg O₂/L. The COD can be defined as the amount of oxygen required to completely oxidize the molecules present in the sample divided by the volume of the sample. The COD of a pure compound can be theoretically calculated from its oxidation reaction. The number of oxygen molecules after balancing the reaction is the COD of the compound. For a 1M acetic acid solution the COD can be calculated as follows:



$$\frac{1 \text{ mol CH}_3\text{COOH}}{l} \cdot \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_3\text{COOH}} \cdot \frac{32 \text{ g O}_2}{\text{mol O}_2} = 64 \text{ g O}_2/l \quad (3.2)$$

The Total Organic Carbon (TOC) is also used as an indicator of the organic content of a sample. It can be expressed as the total amount of carbon less the inorganic carbon.

In the experimental work, the COD and TOC were measured using a VIS spectrophotometer (Hach Lange, model DR 3900). The COD analysis was based on the evaluation of the green coloration of Cr³⁺ after the reaction between oxidizable substances with sulphuric acid–potassium dichromate solution in the presence of silver sulphate as a

catalyst. Since the chloride concentration can interfere in the measurement, mercury sulphate is used to mask it. Both the dissolved and the suspended organic molecules contribute to the COD value.

The technique used to analyze the TOC content consists of two stages. In the first stage the total inorganic carbon (TIC) is expelled with the help of a shaker (Hach Lange, model TOC-X5). In the second stage the organic carbon is oxidized to carbon dioxide, which passes through a membrane into the indicator cuvette. The carbon dioxide causes a color change to occur, and it is this change that is evaluated with the photometer.

The cuvettes containing the reagents for COD and TOC analysis were purchased from Hach Lange (LCK 514 and LCK 387 respectively).

Due to the concentration range limitations of both COD and TOC analysis programs, the samples that needed to be analyzed were previously diluted by a certain dilution factor (DF) so that the COD and TOC were in the analyzing range. In order to double-check the results, two solutions with a different DF were prepared and analyzed for each sample.

Chapter 4

Results

4.1. Experimental conditions

The exact amounts of black liquor and catalyst for each run are presented in table 8.

Table 8. Amounts of black liquor and catalyst

| | First round | | Second round | |
|--|--------------------|------------------------|---------------------|------------------------|
| | Amount of BL-I (g) | Amount of catalyst (g) | Amount of BL-II (g) | Amount of catalyst (g) |
| Non-catalytic | 50.0 | - | 50.0 | - |
| CeO ₂ | 51.2 | 0.152 | 50.0 | 0.154 |
| CuO | 49.9 | 0.149 | 50.0 | 0.149 |
| Fe ₂ O ₃ | 51.0 | 0.153 | 49.8 | 0.151 |
| AC | 50.6 | 0.150 | 50.0 | 0.149 |
| CeO ₂ /Al ₂ O ₃ | 50.6 | 0.155 | 49.6 | 0.151 |
| Fe/AC | 49.7 | 0.149 | 50.0 | 0.149 |

Although the exact quantities of black liquor and catalyst should have been 50 g and 0.150 g respectively, the differences are considered negligible and thus it is assumed that

all the runs were performed under the exact same conditions in terms of black liquor and catalyst quantity.

4.2. Experimental results

As it has been detailed in the previous chapter, the product of each oxidation run was analyzed in order to determine the effect of the catalyst. In this section the results of the analysis are presented.

The formation of precipitates during the oxidation runs was qualitatively studied after each run. It is remarkable that precipitate only appeared when BL-I was used as feedstock.

4.2.1. Acidity (pH)

The extent of acids formation can be somewhat monitored with the pH reduction during the oxidation. Since the feedstock, and thus the initial pH is the same for all the runs belonging to the same round, the run that gives a lower pH after the oxidation will be the one with the highest acids formation. The pH of each oxidation product is presented in table 9 and fig. 10.

Table 9. pH values

| | pH | |
|--|-------------|--------------|
| | First round | Second round |
| Feedstock | 11.93 | 11.30 |
| Non-catalytic | 9.08 | 8.47 |
| CeO ₂ | 8.98 | 8.48 |
| CuO | 8.94 | 8.32 |
| Fe ₂ O ₃ | 9.17 | 9.19 |
| AC | 9.26 | 8.39 |
| CeO ₂ /Al ₂ O ₃ | 9.30 | 8.34 |
| Fe/AC | 9.04 | 8.47 |

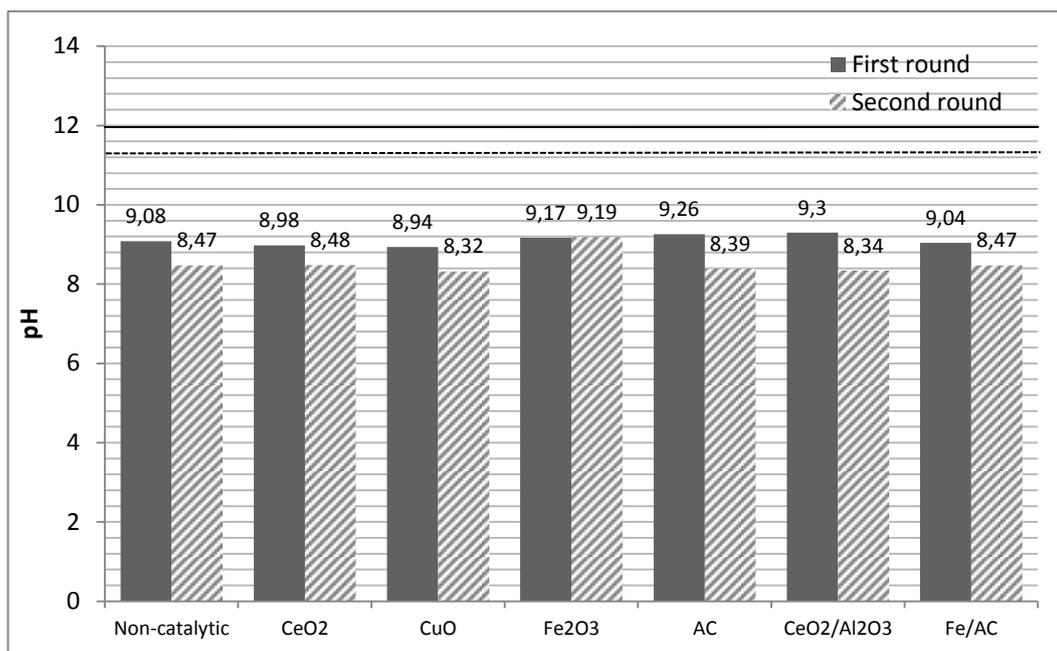


Figure 10. pH values

Despite the small differences, it can be observed that CuO gave the lowest pH in both experimental rounds and that Fe₂O₃ did not have a positive effect in terms of acids formation. The performance of AC and CeO₂/Al₂O₃ varied according to the feedstock used. Both gave the highest pH in the oxidation with strong black liquor while the oxidation using the weak black liquor led to lowest pH after CuO. The opposite happened with the CeO₂ runs. In that case the pH was considerably low in the first round but it changed to be the second highest in the second round. The pH obtained after runs using Fe/AC were in both cases nearby the intermediate positions and were very similar to the results obtained in the non-catalytic run.

4.2.2. Dissolved and suspended solid content

The solid content indicates the presence of both dissolved and suspended solids in the liquid phase. The solid content of the product of each oxidation run are presented in table 10 and fig. 11.

Table 10. Solid content values

| | Dissolved and suspended solid content (%) | |
|--|---|--------------|
| | First round | Second round |
| Feedstock | 22.21 | 11.38 |
| Non-catalytic | 22.22 | 11.01 |
| CeO ₂ | 20.90 | 9.84 |
| CuO | 20.69 | 11.24 |
| Fe ₂ O ₃ | 21.65 | 9.57 |
| AC | 23.08 | 9.80 |
| CeO ₂ /Al ₂ O ₃ | 21.24 | 11.11 |
| Fe/AC | 23.28 | 9.52 |

As it can be seen in table 10, the solid content for some of the runs was higher than the solid content of the original feedstock. This situation could be attributed to the addition of the solid catalyst. However, the amount of catalyst was so tiny that in any case would justify these values itself. This incoherence can be thereby imputed to a mistake in the solid content measurement of the feedstock. The mistake could have been done in the measurement of the oxidation samples, however, the similar solid content values of all the oxidation samples makes the first hypothesis more probable.

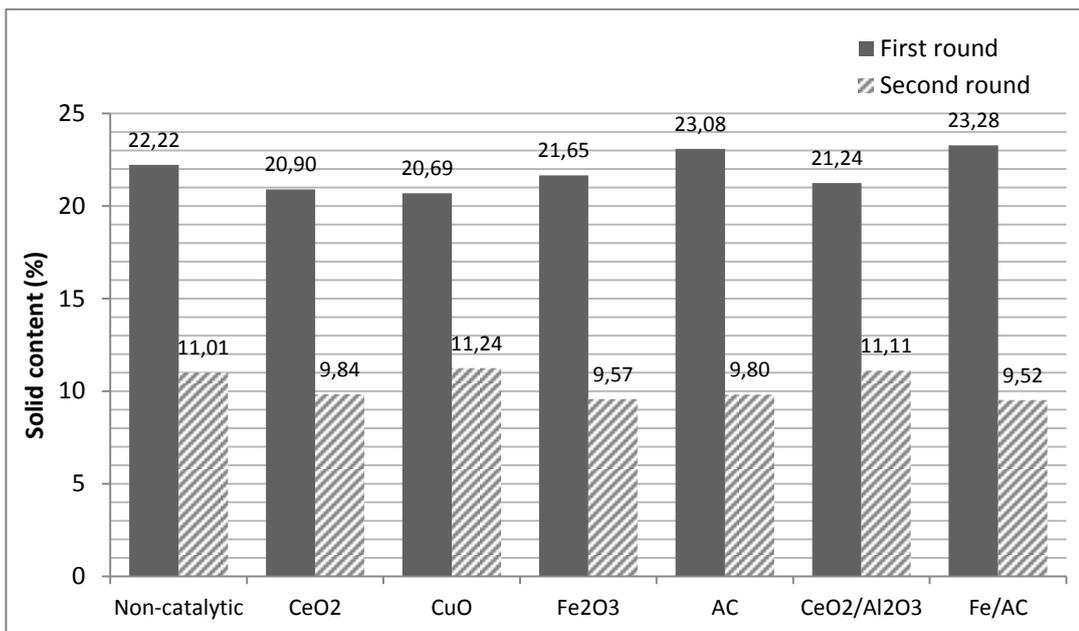


Figure 11. Dissolved and suspended solid content values

In fig. 11 it can be observed that the solid content reduction behaves very differently in the first and in the second round. Those catalysts which gave the highest solid content in the first round gave the lowest solid content in the second round and vice versa.

4.2.3. COD and TOC

The COD and TOC reduction offer reliable information about the extent of oxidation. Those catalysts which lead to high COD reduction and low TOC reduction are the most suitable catalysts for partial wet oxidation. The high COD reduction means that the organics are being oxidized while the low TOC reduction means that the organics have not been oxidized all the way to end products (i.e., carbon remains bounded to organic molecules).

The COD and TOC results are presented in table 11 and table 12 respectively.

Table 11. COD values and reduction

| | First round | | Second round | |
|--|-------------|-------------------|--------------|-------------------|
| | COD (mg/L) | COD reduction (%) | COD (mg/L) | COD reduction (%) |
| Feedstock | 230654.5 | - | 109436.5 | - |
| Non-catalytic | 194018.0 | 15.88 | 101642.0 | 7.12 |
| CeO ₂ | 192043.0 | 16.74 | 99267.5 | 9.29 |
| CuO | 197706.5 | 14.28 | 101070.5 | 7.64 |
| Fe ₂ O ₃ | 198467.5 | 13.95 | 105260.5 | 3.82 |
| AC | 201650.0 | 12.57 | 100350.0 | 8.30 |
| CeO ₂ /Al ₂ O ₃ | 201424.0 | 12.67 | 101516.5 | 7.24 |
| Fe/AC | 191730.0 | 16.88 | 98814.0 | 9.71 |

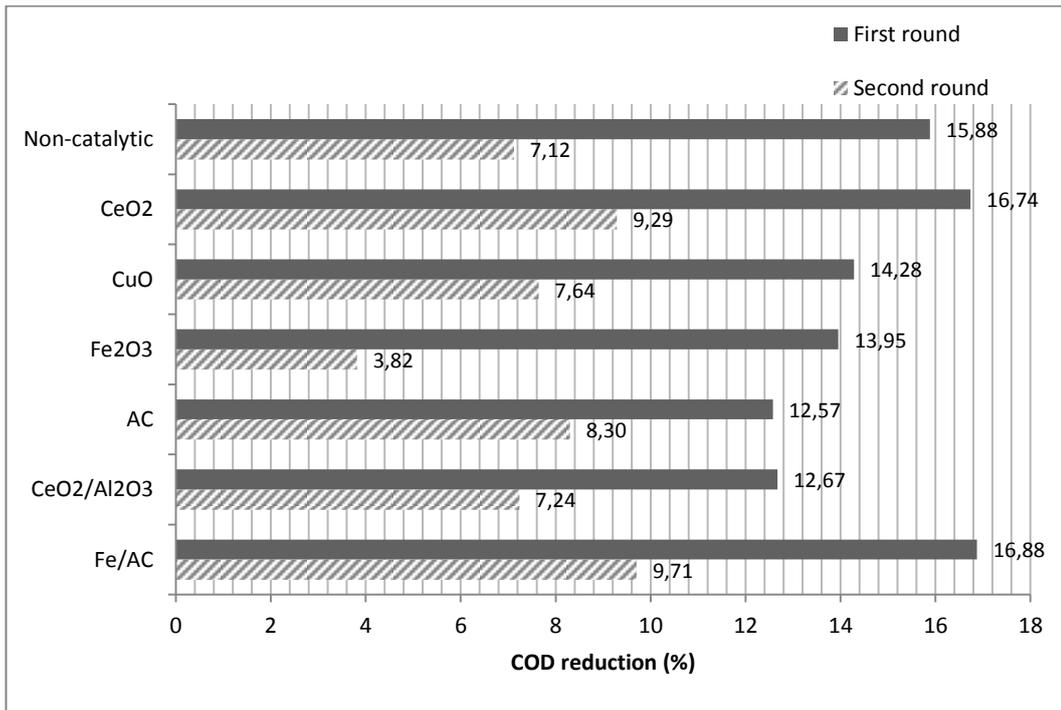


Figure 12. COD reduction

In fig. 12 it can be seen that Fe/AC and CeO₂ are the most effective catalysts in terms of COD reduction, being the former slightly superior to the latter. In the runs with strong black liquor only these two reached a higher COD reduction than the non-catalytic run,

whereas in the second round the non-catalytic run had very poor reduction in comparison with the catalyzed runs. The AC catalyst gave a very low COD reduction in the oxidation with strong black liquor but it was the third best catalyst in the second round. The catalysts that offered the poorest COD reduction were Fe₂O₃ and CeO₂/Al₂O₃.

Table 12. TOC values and reduction

| | First round | | Second round | |
|--|-------------|-------------------|--------------|-------------------|
| | TOC (mg/L) | TOC reduction (%) | TOC (mg/L) | TOC reduction (%) |
| Feedstock | 94957.25 | - | 44039.5 | - |
| Non-catalytic | 77458.5 | 18.43 | 41033.5 | 6.83 |
| CeO ₂ | 79368.0 | 16.42 | 38288.5 | 13.06 |
| CuO | 78574.8 | 17.25 | 39450.0 | 10.42 |
| Fe ₂ O ₃ | 81957.0 | 13.69 | 39098.0 | 11.22 |
| AC | 77543.0 | 18.34 | 39497.0 | 10.31 |
| CeO ₂ /Al ₂ O ₃ | 80836.0 | 14.87 | 39304.0 | 10.75 |
| Fe/AC | 76556.5 | 19.38 | 39157.0 | 11.09 |

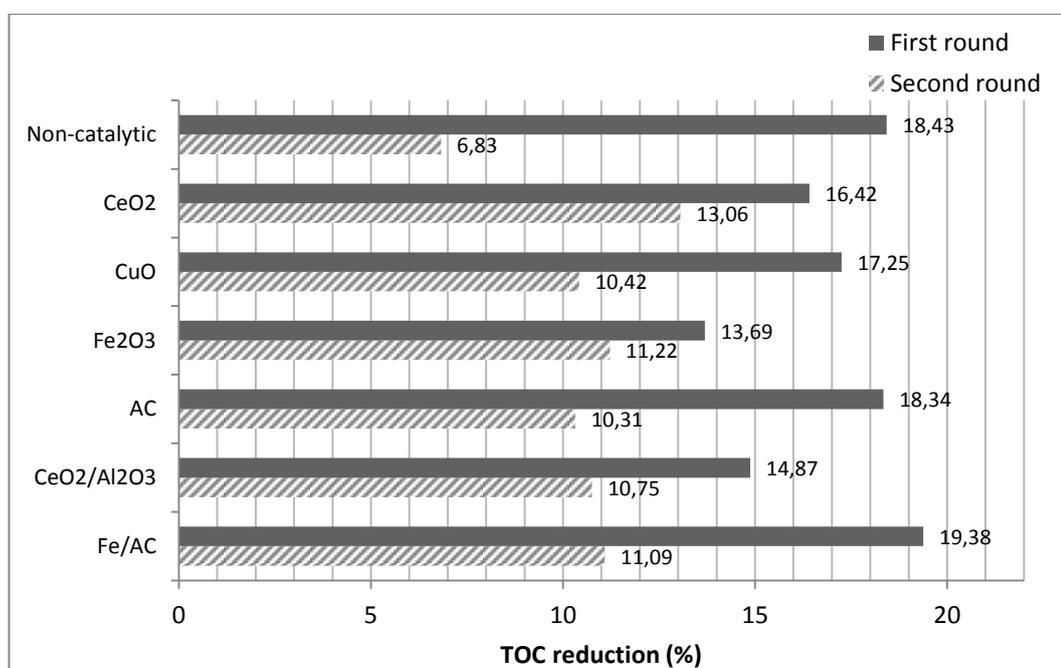


Figure 13. TOC reduction

In the same line that the COD analysis, in fig. 13 it can be observed the different behavior of the catalysts between the first and the second round in the TOC reduction. This difference can be specially appreciated in the comparison of the catalytic runs with the non-catalytic one. In the oxidation of the strong black liquor the TOC reduction for the non-catalytic run is higher than the reduction for most of the catalytic runs. However, when weak black liquor was used, all the catalytic runs outperformed the control one.

From the results of the second round it can be observed that the TOC reduction of the CeO₂ run was much higher than the reduction for the rest of the catalytic runs, which had very similar results in terms of TOC reduction.

4.2.3.1. Combined parameters

There are a few parameters that can be calculated from COD and TOC that can be useful in the determination of which catalyst is more selective toward the partial oxidation. The most important are the Average Oxidation State of Carbon atoms (AOSC) and the COD to TOC ratio.

Average oxidation state of carbon atoms

The AOSC gives an idea of the oxidation state of the organic compounds. The reference values for AOSC are 0 for acetic acid, 2 for formic acid, and 3 for oxalic acid. The AOSC can be calculated with eq. 4.1 using molar concentrations for COD and TOC [105].

$$AOSC = 4 \cdot \frac{TOC - COD}{TOC} \quad (4.1)$$

The AOSC values for each run are presented in table 13.

Table 13. AOSC values

| | AOSC | |
|--|-------------|--------------|
| | First round | Second round |
| Non-catalytic | 0.243 | 0.284 |
| CeO ₂ | 0.371 | 0.111 |
| CuO | 0.226 | 0.157 |
| Fe ₂ O ₃ | 0.368 | -0.038 |
| AC | 0.099 | 0.189 |
| CeO ₂ /Al ₂ O ₃ | 0.262 | 0.126 |
| Fe/AC | 0.243 | 0.215 |

As it can be observed from table 13 all the AOSC values are very close to 0, which means that the average oxidation state is equivalent to acetic acid.

COD to TOC ratio

The COD to TOC ratio is a useful tool to analyze which catalysts have better selectivity toward the acids formation. Accordingly to what have been detailed in section 4.2.3., a low COD to TOC ratio represents a high selectivity towards the acid formation.

The COD to TOC ratio for each run (in molar concentration) is presented in table 14.

Table 14. COD to TOC ratio

| | COD/TOC | |
|--|-------------|--------------|
| | First round | Second round |
| Non-catalytic | 0.939 | 0.929 |
| CeO ₂ | 0.907 | 0.972 |
| CuO | 0.944 | 0.961 |
| Fe ₂ O ₃ | 0.908 | 1.010 |
| AC | 0.975 | 0.953 |
| CeO ₂ /Al ₂ O ₃ | 0.934 | 0.969 |
| Fe/AC | 0.939 | 0.946 |

In table 14 it can be observed that CeO_2 and Fe_2O_3 runs have the lowest ratio in the first round whereas they have the worst in the second round. Fe/AC and AC runs have the lowest ratio in the second round, followed by CuO.

Chapter 5

Discussion and conclusions

5.1. Discussion

The comparison between the COD and TOC reduction levels in the experimental section of this work and the reduction levels reported by the authors reviewed in the literature shows that the extent of oxidation has been much lower in this work. These poor results were not only observed in the catalytic runs but also in the non-catalytic runs and therefore they cannot be attributed to a bad catalysts performance. The mild temperature could justify the poor results; however other authors that used very similar conditions of temperature reported much higher rates of oxidation. In this work the COD reduction for the non-catalytic oxidation of BL-II was 7.12% while Dhakhwa et al. [1] reported 32% COD reduction after 240 min of non-catalytic oxidation of a weak black liquor (COD = 5120 mg/L) at 170°C, pH of 7.5 and total oxygen pressure of 9.5 bar. It could be suggested that the difference in the COD of the feedstock is the cause for such different results. Nevertheless, according to the kinetics the higher the concentration the higher the reaction rate and thus the extent of reaction, meaning that the COD reduction should be higher in the experimental run performed in this work than in the results reported by Dhakhwa et al. It is therefore probable that either the length of oxidation or the pH of the feedstock play an important role in the extent of the organics oxidation. The scavenging effect of the stainless steel walls on the free radicals could also explain the poor results.

This effect usually can be neglected when reactor dimensions are sufficiently big, however, the effect can be significant in small reactors like the one used in this work.

In the COD and TOC results it can be observed the different behavior of catalysts when different feedstock (BL-I and BL-II) were used. When BL-I was used as feedstock, the results showed that most of the catalysts had an adverse effect on the oxidation. It could be suggested that none of the catalysts is suitable for wet oxidation processes. However, when BL-II was utilized, the trend changed and some of the catalyst that had an adverse effect on the reaction using BL-I turned out to be effective in the COD and TOC reduction of the black liquor. This situation suggests that the catalyst activity was limited as a consequence of the high concentration of black liquor. When using BL-I, the COD reduction for AC was 12.57% while the reduction for the non-catalytic run was 15.88%. However, in the second round, the COD reduction for AC was more than one point above the reduction of the control run (8.30% to 7.12%). Focusing on the reference of the non-catalyzed reaction it is obvious that in the first round the presence of AC was prejudicial to the extent of oxidation, whereas in the second round (diluted black liquor), the AC clearly enhanced the extent of oxidation.

It could be suggested that the catalyst deactivation was due to lignin precipitation and deposition on the catalyst active sites. This theory is consistent with (i) the formation of precipitate after the oxidation runs of the first round and (ii) the different performance of AC in the oxidation of BL-I and BL-II. The AC can only enhance the oxidation rates by providing active sites for the organic compounds to adsorb on. The formation of carbonaceous deposits on the surface catalysts and hence the blocking of the activation sites would explain the bad result of the AC in the first round. The active sites blockage as a cause for the bad performance of the catalysts in the oxidation of BL-I would be in agreement with a number of authors [11,58-62], which observed that the formation of carbonaceous deposits was promoted in low temperature and low catalyst concentration conditions.

Assuming that the strong liquor negatively affects the catalyst activity, it is wise to base the evaluation of the catalysts suitability on the second experimental round. In the evaluation of the six proposed catalysts, more importance has been given to the COD and TOC values as well as the COD/TOC ratio.

The Fe/AC is the catalyst that gave the highest COD reduction and the lowest COD to TOC ratio, meaning that it promotes the formation of intermediates rather than the

complete oxidation to carbon dioxide and steam. The positive effect of impregnating AC with Fe was suggested to be due to (i) the increase in acidity that the Fe itself causes, (ii) the promoter role of Fe on phenol oxidation, and (iii) the limited formation of deposits on metal-doped catalysts [54,63-67]. The higher resistance to deactivation of Fe/AC reported in the literature seems to be in agreement with the results obtained in the first round. In the oxidation of BL-I the Fe/AC run outperformed the non-catalytic run (in terms of COD and TOC reduction) while the AC run had very poor results due to deactivation.

In the oxidation of BL-II, the non-catalytic run gave a lower pH and a lower COD to TOC ratio than Fe/AC, meaning that the formation of acid is higher in the non-catalytic run. It could be suggested that there is no need for a catalyst in the partial wet oxidation processes because the non-catalytic run gave better acid formation. However, the conversion of the non-catalytic run was rather poor in comparison with the catalyzed runs, meaning that the product of oxidation still contains high-molecular-weight organics.

The CeO₂ has been shown an effective catalyst for the complete oxidation of organic pollutants when it is not affected by the formation of deposits (COD reduction of 9.29% and TOC reduction of 13.06%). However, the formation of deposits led to a diminution of its TOC reduction (using the non-catalytic run as a reference) while maintaining the COD reduction at a high level (COD reduction of 16.74% and TOC reduction of 16.42%)..

The catalyst that gave the second lowest COD to TOC ratio was AC. The good performance of AC is believed to be related to its high adsorption capacity and potential to generate oxygenated free radicals [33]. The nature of AC as a provider of active sites makes the catalyst extremely susceptible to deactivation. The fact that AC based catalysts had the best performances might suggest that the effect of the catalysts in the wet oxidation is more dependent on the number of active sites than on interactions with the metal.

The CuO catalyst gave the lowest pH in both oxidation rounds and even though neither its COD nor TOC reductions were extremely high, the COD to TOC ratio is the highest among the metal-based catalysts. The relatively low COD to TOC ratio seems to be in agreement with the results reported by Duarte [23], which among a set of heterogeneous metal-based catalysts (including CeO₂ and Fe₂O₃), reported the lowest COD to TOC ratio for CuO.

The oxidation runs in presence of CeO₂/γ-Al₂O₃ had very poor result in comparison with the runs catalyzed with unsupported CeO₂. Chen et al. [41,51] reported that the CeO₂/γ-

Al_2O_3 was not as effective as CeO_2 but the cheaper price of the former made it interesting for the industrial oxidation process. However, the difference between both catalysts obtained in the experimental testing was significant (COD reduction of 9.29% for CeO_2 and of 7.64% for $\text{CeO}_2/\text{Al}_2\text{O}_3$).

Finally, the Fe_2O_3 had the worst performance among all the catalysts. The presence of Fe_2O_3 in the oxidation medium not only did not enhance the reaction but also affected it negatively (COD reduction of 7.12% for control run and 3.82% for Fe_2O_3). According to the results it could be suggested that the presence of Fe_2O_3 inhibits the oxidation. This might be due to the reducing nature of iron i.e. its oxidation is promoted instead of the oxidation of organic matter.

5.2. Conclusions

The strength of the black liquor, namely, the concentration of pollutants in the stream is of utmost importance for the catalyst activity. The formation of carbonaceous deposits is dependent on the concentration of the liquor. The catalytic oxidation of streams with high concentration of organics is likely to be troublesome due to the blockage of the active sites of the catalyst, especially in small-scale reactors. The reduction of catalyst activity due to carbonaceous deposition may vary from catalyst to catalyst. The metal-doped catalysts are more resistant to the formation of carbonaceous deposition than the rest.

When the catalyst activity was not affected by the active sites blockage, the catalysts that offered a better performance in terms of partial oxidation are Fe/AC, AC and CuO in order of importance. It has been proved the positive effect of adding impregnating AC with Fe. Both Fe/AC and AC are cheap and easy to obtain and to the best of our knowledge there is not any remarkable inconvenience derived from their use either in small or big-scale processes. The CuO did not have as good results as Fe/AC and AC in terms of COD and TOC reduction. Nonetheless, the low pH obtained after the CuO oxidation run might suggest its good performance in the promotion of acids production. The high leaching rates of CuO reported by other authors might be a problem for its application to industrial scale processes. However, this problem has not been studied in this work and therefore no comments can be done about it. Regarding the price, without being an expensive chemical, it is much more expensive than the AC and the Fe/AC. The

CeO₂ is a suitable catalyst for the complete oxidation of organics and thus is not so interesting for the partial wet oxidation.

The high yield of acids formation in the non-catalytic run may suggest that there is no need for a catalyst in the partial wet oxidation processes. However, the absence of the catalyst effect on the organic pollutants destruction should be compensated with high energetic conditions or higher oxidation times, increasing the operational costs of the process. Besides, the low oxidation of organics achieved in the non-catalytic runs derives in a lower contribution of the heat of reaction to the temperature in the reactor, which in turns represent a higher requirement of external heating.

The yield of acids formation in the WAO of lignocellulose feedstock is enhanced when the feedstock has small lignin content.

5.3. Recommendations

Trickle bed reactor has been reported as the most suitable reactor configuration for the catalytic wet oxidation. The features that make TBR interesting from the industrial CWAO process are (i) the low liquid hold up and (ii) the low catalyst deactivation. The low liquid hold up promotes the partial wetting of the catalyst, which is desired in highly concentrated streams like black liquor [83,89].

As it has been suggested in the conclusions section (5.2.) the most promising catalysts for CWAO and therefore the catalysts that should be studied into more detail in further studies are Fe/AC, AC, and CuO. In table 3 it can be observed that the catalyst particles size ought not to be less than 0.3 mm and that it can go as high as 1 mm. A smaller pellet size would lead to high pressure drop in the catalytic bed while the internal mass resistance would negatively affect the conversion rates if pellets size was bigger than 1 mm. [8]. The catalyst loading strongly depends on the reactor dimensions. Usual catalyst loading ranges are 1-10 g.

From table 3 it can also be observed that the author used either pure oxygen or air indistinctly as oxidizing agent. However, the cheaper price of air and the hazards derived from the use of pure oxygen make the air option more recommendable.

According to the authors reviewed in table 3, the optimal temperature for TBR operation ranges from 120 to 170°C and oxygen partial pressure in the reactor from 2-10 bar.

The optimal gas flow rate depends on the oxidizing agent. Gas flow rates around 100 mL/min (STP) are recommended when using oxygen and around 150 mL/min (STP) when air is used as oxidizing agent.

Finally, the liquid flow rate should take values from 0.16 to 5 mL/min, that depending on the exact dimensions of the reactor would give LHSV values ranging from 1-30 h⁻¹.

References

1. Dhakhwa, S., Bandyopadhyay, S., Majozi, T., Garg, A., Efficacy of Chemical Oxidation and Coagulation for COD and Color Reduction from Pulp Mill effluent, *J. Environ. Eng.* **138** (2012) 1194-1199.
2. Garg, A., Mishra, I. M., Chand, S., Catalytic Oxidative Treatment of Diluted Black Liquor at Mild Conditions Using Copper Oxide/cerium Oxide Catalysts, *Water Environ. Res.* **80(2)** (2008) 136-141.
3. Hammett, A.L., Youngs, R. L., Sun, X., Chandra, M., Non-wood fibers as an alternative to wood fiber in China's pulp and paper industry, *Holzforschung.* **55** (2001) 219-224.
4. Biermann, C.J., *Essentials of pulping and papermaking*, Academic press, San Diego (CA) 1993.
5. Bhargava, S. K., Tardio, J., Prasad, J., Föger, K., Akolekar, D. B., Grocott, S. C., Wet Oxidation and Catalytic Wet Oxidation, *Ind. Eng. Chem. Res.* **45** (2006) 1221-1258.
6. Akolekar, D. B., Bhargava, S. K., Shirgoankar, I., Prasad, J., Catalytic wet oxidation: an environmental solution for organic pollutant removal from paper and pulp industrial waste liquor, *Appl. Catal., A.* **236** (2002) 255-262.
7. Heponiemi, A., Rahikka, L., Lassi, U., Kuokkanen, T., Catalytic Oxidation of Industrial Wastewater Under Mild Conditions, *Top. Catal.* **54** (2011) 1034-1041.
8. Kolaczowski, S.T., Plucinski, P., Beltran, F.J, Rivas, F.J., McLurgh, D.B., Wet air oxidation: a review of process technologies and aspects in reactor design, *Chem. Eng. J.* **73** (1999) 143-160.
9. Flynn, B.L., Wet air oxidation of waste streams, *Chem. Eng. Prog.* **75(4)** (1979) 66-69.

10. Chou, C.L., Verhoff, F.H., Process for power generation from wet air oxidation with application to coal gasification waste waters *Ind. Eng. Chem. Process. Des. Dev.* **20** (1981) 12-19.
11. Kim, K.H., Ihm, S.K., Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review, *J. Hazard. Mater.* **186** (2011) 16-34.
12. Vaidya, P. D., Mahajani, V. V., Insight into sub-critical wet oxidation of phenol. *Adv. Environ. Res.* **6** (2002) 429-439
13. Myréen, B., A new approach to the non-wood black liquor problem, 2001 *TAPPI Pulping Conference*.
14. Tikka, P., *Chemical pulping part II. Recovery of chemicals and energy*, 2nd edition, Paper Engineers' Association, Finland 2008.
15. Ekblom, T., Lindblom, M., Berglin, N., Ahlvik, P., *Technical and Commercial Feasibility Study of Black Liquor Gasification with Methanol/DME Production as Motor Fuels for Automotive uses – BLGMF*, 2003.
16. Zhang, Q., Chuang, K. T., Kinetics of wet oxidation of black liquor over a Pt-Pd-Ce/alumina catalyst, *Appl. Catal., B.* **17** (1998) 321-332.
17. Pruden, B.B., Le, H., Wet air oxidation of soluble components in wastewater, *Can. J. Chem. Eng.* **54(4)** (1976) 319-325.
18. Levenspiel, O., *Chemical Reaction Engineering*, 2nd Edition, Wiley, New York 1972.
19. Beyrich, J., Gautschi, W., Regenass, W., Wiedmann, W., Design of reactors for the wet air oxidation of industrial wastewater by means of computer simulation, *Comput. Chem. Eng.* **3(1-4)** (1979) 161-165.
20. Debellefontaine, H., Chakchouk, M., Foussard, J.N., Tissot, D., Striolo, P., Treatment of organic aqueous wastes: Wet air oxidation and wet peroxide oxidation, *Environ. Pollut.* **92(2)** (1996) 155-164.
21. Guo, J., Al-Dahhan, M., Kinetics of Wet Air Oxidation of Phenol over a Catalyst, *Ind. Eng. Chem. Res.* **42** (2003) 5473-5481.
22. Pray, H.A., Schweickert, C.E., Minnich, B.H., Solubility of Hydrogen, Oxygen, Nitrogen and Helium in Water at Elevated Temperatures, *Ind. Chem. Eng.* **44** (1952) 1146-1151.
23. Duarte, D., *Catalytic Wet Air Oxidation of Spent Kraft Pulping Liquors*, Heritage Branch, Ottawa 2004.

24. Broden, A., Simonson, R., Solubility of Oxygen. Part 2. Solubility of Oxygen in Sodium Hydrogen Carbonate and Sodium Hydroxide Solutions at Temperatures ≤ 5 Mpa, *Sven. Papperstidn.* **82(16)** (1978) 497-491.
25. Imamura, S., Catalytic and Noncatalytic Wet Oxidation. *Ind. Eng. Chem. Res.* **38(5)** (1999) 1743-1753.
26. Robert, R., Barbati, S., Ricq, N., Ambrosio, M., Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterization of hydrogen peroxide, *Water Res.* **36** (2002) 4821-4829.
27. Hamoudi, S., Larachi, F., Cerrella, G., Cassanello, M., Wet Oxidation of Phenol Catalyzed by Unpromoted and Platinum-Promoted Manganese/Cerium Oxide, *Ind. Eng. Chem. Res.* **37(9)** (1998) 3561-3566.
28. Jin, F., Cao, J., Zhou, Z., Moriya, T., Enomoto, H., Effect of Lignin on Acetic Acid Production in Wet Oxidation of Lignocellulosic Wastes, *Chem. Lett.* **33(7)** (2004) 910-911.
29. Luan, M., Jing, G., Piao, Y., Liu, D., Jin, L., Treatment of refractory organic pollutants in industrial wastewater by wet air oxidation, *Arabian J. Chem. B* (2012).
30. Belkacemi, K., Larachi, F., Sayari, A., Lumped Kinetics for Solid-Catalyzed Wet Oxidation: A Versatile Model, *J. Catal.* **193** (2000) 224-237.
31. Li, L., Chen, P., Gloyna, E.F., Generalized kinetic model for wet oxidation of organic compounds, *AIChE J.*, **37(11)** (1991) 1687-1697.
32. Verenich, S., Laari, A., Kallas, J., Wet oxidation of concentrated wastewaters of paper mills for water cycle closing, *Waste Manage.* **20** (2002) 287-293.
33. Stüber, F., Polaert, I., Delmas, H., Font, J., Fortuny, A., Fabregat, A., Catalytic wet air oxidation of phenol using active carbon: performance of discontinuous and continuous reactors, *J. Chem. Technol. Biotechnol.* **76** (2011) 743-751.
34. Lin, S.S., Weng, H.S., Liquid-phase oxidation of cyclohexane over CoAPO-5: Synergism effect of coreactant and solvent effect, *Appl. Catal., A* **118(1)** (1994) 21-31.
35. Rivas, F.J., Kolaczek, S.T., Beltrán, F.J., McLurgh, D.B., Development of a model for the wet oxidation of phenol based on a free radical mechanism, *Chem. Eng. Sci.* **53(14)** (1998) 2575-2586.
36. Chang, D.J., Chen, I.P., Chen, M.T., Lin, S.S., Wet air oxidation of a reactive dye solution using CoAlPO₄-5 and CeO₂ catalysts, *Chemosphere* **52** (2003) 943-949.
37. Lin, S.S., Chang, D.J., Wang, C., Chen, C.C., Catalytic wet oxidation of phenol by CeO₂ catalyst – effect of reactions conditions, *Water Res.* **37** (2003) 793-800.

38. Sheldon, R.A., Kochi, J.K., *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, London, 1981.
39. Cavani, F., Trifiro, F., Classification of industrial catalysts and catalysis for the petrochemical industry, *Catal. Today* **34** (1997) 269-279.
40. Sadana, A., Katzer, J.R., Involvement of free-radicals in aqueous-phase catalytic-oxidation of phenol over copper oxide, *J. Catal.* **35** (1974) 140-152.
41. Chang, L., Chen, I.P., Lin, S.S., An assessment of the suitable operating conditions for the CeO₂/γ-Al₂O₃ catalyzed wet air oxidation of phenol, *Chemosphere*. **58** (2005) 485-492.
42. Gunale, T.L., Mahajani, V.V., An insight into Ru/TiO₂ catalyzed wet air oxidation of N-ethylethanolamine in an aqueous solution, *Chem. Eng. J.* **159** (2010) 17-23.
43. Fortuny, A., Bengoa, C., Font, J., Castells, F., Fabregat, A., Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, *Catal. Today* **53** (1999) 107-114.
44. Eftaxias, A., Font, J., Fortuny, A., Giralt, J., Fabregat, A., Stuber, F., Kinetic modeling of catalytic wet air oxidation of phenol by simulated annealing, *Appl. Catal. B: Environ.* **33** (2001) 175-190.
45. Eftaxias, A., Font, J., Fortuny, A., Fabregat, A., Stüber, F., Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst, *J. Chem. Technol. Biotechnol.* **80** (2005) 677-687.
46. Lin, S.H., Ho, S.J., Wu, C.L., Kinetic and Performance Characteristics of Wet Air Oxidation of High-Concentration Wastewater, *Ind. Eng. Chem. Res.* **35** (1996) 307-314.
47. McGinnis, G. D., Wilson, W. W., Prince, S. E., Chen, C.C., Conversion of Biomass into Chemicals with High-Temperature Wet Oxidation, *Ind. Eng. Chem. Prod. Res. Dev.* **22** (1983) 633-636.
48. McGinnis, G.D., Wilson, W.W., Mullen, C.E., Biomass pretreatment with water and high-pressure oxygen. The wet-oxidation process, *Ind. Eng. Chem. Prod. Res. Dev.* **22**(2) (1983) 352-357.
49. Kim, S.K., Ihm, S.K., Nature of carbonaceous deposits on the alumina supported transition metal oxide catalysts in the wet air oxidation of phenol. *Top Catal.* **33** (2005) 171-179.
50. Kim, S.K., Kim, K.H., Ihm, S.K., The characteristics of wet air oxidation of phenol over CuO_x/Al₂O₃ catalysts: effect of copper loading, *Chemosphere* **68** (2007) 287-292.

51. Chen, I.P., Lin, S.S., Wang, C.H., Chang, L., Chang, J.S., Preparing and characterizing an optimal supported ceria catalyst for the catalytic wet air oxidation of phenol, *Appl. Catal. B: Environ.* **50** (2004) 49-58.
52. Suarez-Ojeda, M.E., Stüber, F., Fortuny, A., Fabregat, A., Carrera, J., Font, J., Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, *Appl. Catal., B.* **58** (2005).
53. Quintanilla, A., Casas, J.A., Mohedano, A.F., Rodríguez, J.J., Reaction pathway of the catalytic wet air oxidation of phenol with a Fe/activated carbon catalyst, *Appl. Catal., B.* **67** (2006) 206-216.
54. Quintanilla, A., Casas, J.A., Rodríguez J.J., Catalytic wet air oxidation of phenol with modified activated carbons and Fe/activated carbon catalysts, *Appl. Catal., B.* **76** (2007) 135-145.
55. Mohamed, W. T., Ghani, S. A., Rasheed, S. M., Fe/Activated Carbon as a Catalyst in Wet Oxidation of Phenolic Compounds in a Trickle Bed Reactor, *Energy Sources, Part A.* **35** (2013) 299-311.
56. Tukac, V., Hanika, J., Catalytic effect of active carbon black chezacarb in wet oxidation of phenol. *Collect. Czech Chem. Commun.* **61** (1996) 1010-1017.
57. Fortuny, A., Miró, C., Font, J., Fabregat, A., Three-phase reactors for environmental remediation: catalytic wet oxidation of phenol using active carbon. *Catal. Today* **48** (1999) 323-328.
58. Mikulová, J., Barbier, J., Rossignol, S., Mesnard, D., Duprez, D., Kappenstein, C., Wet air oxidation of acetic acid over platinum catalysts supported on cerium-based materials: influence of metal and oxide crystallite size, *J. Catal.* **251** (2007) 172-181.
59. Masende, Z.P.G., Kuster, B.F.M., Ptasinski, K.J., Janssen, F., Katima, J.H.Y., Schouten, J.C., Platinum catalyzed wet oxidation of phenol in a stirred slurry reactor-the role of oxygen and phenol loads on reaction pathways, *Catal. Today* **79** (2003) 357-370.
60. Cybulski, A., Trawczynski, J., Catalytic wet air oxidation of phenol over platinum and ruthenium catalysts, *Appl. Catal. Environ.* **47** (2004) 1-13.
61. Pintar, A., Levec, J., Catalytic liquid-phase oxidation of refractory organics in waste water, *Chem. Eng. Sci.* **47** (1992) 2395-2400.
62. Pintar, A., Levec, J., Catalytic oxidation of organics in aqueous solutions. I. Kinetics of phenol oxidation, *J. Catal.* **135** (1992) 345-357.

63. Kim, K.H., Kim, J.R., Ihm, S.K., Wet oxidation of phenol over transition metal oxide catalysts supported on $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ prepared by continuous hydrothermal synthesis in supercritical water, *J. Hazard. Mater.* **167** (2009) 1158-1162.
64. Nousir, S., Keav, S., Barbier, J., Bensitel, M., Brahmi, R., Duprez, D., Deactivation phenomena during catalytic wet air oxidation (CWAO) of phenol over platinum catalysts supported on ceria and ceria-zirconia mixed oxides, *Appl. Catal. B: Environ.* **84** (2008) 723-731.
65. Hamoudi, S., Sayari, A., Belkacemi, K., Bonneviot, L., Larachi, F., Catalytic wet oxidation of phenol over $\text{Pt}_x\text{Ag}_{1-x}\text{MnO}_2/\text{CeO}_2$ catalysts, *Catal. Today* **62** (2000) 379-388.
66. Hussain, S.T., Sayari, A., Larachi, F., Novel K-doped Mn-Ce-O wet oxidation catalysts with enhanced stability, *J. Catal.* **201** (2001) 153-157.
67. Hussain, S.T., Sayari, A., Larachi, F., Enhancing the stability of Mn-Ce-O WETOX catalysts using potassium, *Appl. Catal. B: Environ.* **34** (2001) 1-9.
68. Alejandre, A., Medina, F., Rodriguez, X., Salagre, P., Cesteros, Y., Sueiras, J.E., Cu/Ni/Al layered double hydroxides as precursors of catalysts for the wet air oxidation of phenol aqueous solution, *Appl. Catal. B: Environ.* **30** (2001) 195-207.
69. Alejandre, A., Medina, F., Salagre, P., Fabregat, A., Sueiras, J.E., Characterization and activity of copper and nickel catalysts for the oxidation of phenol aqueous solutions, *Appl. Catal. B: Environ.* **18** (1998) 307-315.
70. Alejandre, A., Medina, F., Fortuny, A., Salagre, P., Sueiras, J.E., Characterization of copper catalysts and activity for the oxidation of phenol aqueous solutions, *Appl. Catal. B: Environ.* **16** (1998) 53-67.
71. Miro, C., Alejandre, A., Fortuny, A., Bengoa, C., Font, J., Fabregat, A., Aqueous phase catalytic oxidation of phenol in a trickle bed reactor: effect of the pH, *Water Res.* **33** (1999) 1005-1013.
72. Kouraichi, R., Delgado, J.J., Lopez-Castro, J.D., Stitou, M., Rodriguez-Izquierdo, J.M., Cauqui, M.A., Deactivation of $\text{Pt}/\text{MnO}_x\text{-CeO}_2$ catalysts for the catalytic wet oxidation of phenol: formation of carbonaceous deposits and leaching of manganese, *Catal. Today* **154** (2010) 195-201.
73. Santos, A., Yustos, P., Quintanilla, A., Rodriguez, S., Garcia-Ochoa, F., Route of the catalytic oxidation of phenol in aqueous phase, *Appl. Catal. B: Environ.* **39** (2002) 97-113.
74. Santos, A., Yustos, P., Quintanilla, A., Garcia-Ochoa, F., Influence of pH on the wet oxidation of phenol with copper catalyst, *Top. Catal.* **33** (2005) 181-192.

75. Arena, F., Giovenco, R., Torre, T., Venuto, A., Parmaliana, A., Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol. *Appl. Catal. B: Environ.* **45** (2003) 51-62.
76. Fenoglio, R.J., Massa, P.A., Ivorra, F.D., Haure, P.M., Conventional and wet proofed CuO/Al₂O₃ catalysts for phenol oxidation: deactivation studies in a trickle bed reactor, *J. Chem. Technol. Biotechnol.* **82** (2007) 481-487.
77. Massa, P., Ivorra, F., Haure, P., Fenoglio, R., Optimized wet-proofed CuO/Al₂O₃ catalysts for the oxidation of phenol solutions: enhancing catalytic stability, *Catal. Commun.* **10** (2009) 1706-1710.
78. Massa, P., Ivorra, F., Haure, P., Cabello, F.M., Fenoglio, R., Catalytic wet air oxidation of phenol aqueous solutions by 1% Ru/CeO₂-Al₂O₃ catalysts prepared by different methods, *Catal. Commun.* **8** (2007) 424-428.
79. Chen, I.P., Lin, S.S., Wang, C.H., Chang, S.H., CWAO of phenol using CeO₂/γ-Al₂O₃ with promoter – effectiveness of promoter addition and catalyst regeneration, *Chemosphere* **66** (2007) 172-178.
80. Luck, F., A review of industrial catalytic wet air oxidation processes, *Catal. Today* **27(1-2)** (1996) 195-202.
81. Ishii, T., Mitsui, K., Sano, K., Inoue, A., Method for treatment of wastewater, Eur. Patent No. 431932, 1991.
82. NS-LC Wastewater Treatment System-Catalytic Oxidation, Technical Leaflet, Nippon Shokubai.
83. Larachi, F., Catalytic wet oxidation: micro-meso-macro methodology from catalyst synthesis to reactor design, *Top. Catal.* **33** (2005) 109-134.
84. Iliuta, I., Larachi, F., Wet air oxidation solid catalysis analysis of fixed and sparged three-phase reactors, *Chem. Eng. Process.* **40** (2001) 175-185.
85. Eftaxias, A., Larachi, F., Stüber, F., Modelling of trickle bed reactor for the catalytic wet air oxidation of phenol, *Can. J. Chem. Eng.* **81(3-4)** (2003) 784-794.
86. Pöpken, T., Geisler, R., Götze, L., Brehm, A., Moritz, P., Gmehling, J., Reaction kinetics and reactive distillation – on the transfer of kinetic data from a batch reactor to a trickle-bed reactor, *Chem. Eng. Technol.* **21** (1999) 401-404.
87. Bergault, I., Rajashekharam, M.V., Chaudhari, R.V., Schweich, D., Delmas, H., Modeling and comparison of acetophenone hydrogenation in trickle-bed and slurry air lift reactors. *Chem. Eng. Sci.* **52(21-22)** (1997) 4033-4043.

88. Lopes, R. J. G., Quinta-Ferreira, R.M., Numerical Studies of Catalyst Wetting and Total Organic Carbon Reaction on Environmentally Based Trickle-Bed Reactors, *Ind. Eng. Chem. Res.* **49** (2010) 10730-10743.
89. Green, D.W., Perry, R.H., *Perry's Chemicals Engineer's Handbook*, 8th edition, McGraw-Hill, New York 2008.
90. Emanuel, N.M., Zaikov, G.E., Maitus, Z.K., *Oxidation of Organic Compounds. Medium Effects in Radical Reactions*, Pergamon Press, Oxford 1980.
91. Kolaczkowski, S.T., Beltran, F.J., McLurfh, D.B., Rivas, F.J., Wet air oxidation of phenol: Factors that may influence global kinetics, *Process Safety Environ. Protect.* **75(4)** (1997) 257-265.
92. Nigam, K.D.P., Larachi, F., Process intensification in trickle-bed reactors, *Chem. Eng. Sci.* **60** (2005) 5880-5894.
93. Tukac, V., Simícková, M., Chyba, V., Lederer, J., Kolena, J., Hanika, J., Jiricný, V., Stanek, V., Stavárek, P, The behavior of pilot trickle-bed reactor under periodic operation, *Chem. Eng. Sci.* **62** (2007) 4891-4895.
94. Tukac, V., Hanika, J., Chyba, V., Periodic state of wet oxidation in trickle-bed reactor, *Catal. Today.* **79-80** (2003) 427-431.
95. Kastanek, F.Z.J., Kratochvil, J., Cermak, J., *Chemical Reactors for Gas-Liquid Systems*, Ellis Horwood, New York 1993.
96. Shah, Y.T., Kelkar, B.G., Godbole, S.P., Deckwer, W.D., Desing parameters estimations for bubble column reactors, *AIChE J.* **28(3)** (1982) 353-379.
97. Ishii, T., Mitsui, K., Sano, K., Inoue, A., Nippon Shokubai Kagaku Kogyo Company Ltd., Method for treatment of wastewater, 1991, Eur. Pat. Application 90313238.9, Publication Number 0 431 932 A1.
98. Luck, F., Djafer, M., Bourbigot, M.M., Catalytic wet air oxidation of biosolids in a monolithic reactor, *Catal. Today* **24** (1995) 73-78.
99. Debellefontaine, H., Crispel, S., Reilhac, P., Péirié, F., Foussard, J.N., Wet air oxidation (WAO) for the treatment of industrial wastewater and domestic sludge: design of bubble column reactors, *Chem. Eng. Sci.* **54** (1999) 4953-4959.
100. Pintar, A., Batista, J., Tisler, T., Catalytic wet-air oxidation of aqueous solutions of formic acid, acetic acid and phenol in a continuous-flow trickle-bed reactor over Ru/TiO₂ catalysts, *Appl. Catal., B.* **84** (2008) 30-41.
101. Yang, S., Zhu, W., Wang, J., Chen, Z., Catalytic wet air oxidation of phenol over CeO₂-TiO₂ catalyst in the batch reactor and the packed-bed reactor, *J. Hazard. Mater.* **153** (2008) 1248-1253.

102. Gianetto, A., Specchia, V., Trickle-bed reactors: state of art and perspectives. *Chem. Eng. Sci.* **47** (1992) 3197-3213.
103. Fortuny, A., Ferrer, C., Bengoa, C., Font, J., Fabregat, A., Catalytic removal of phenol from aqueous phase using oxygen or air as oxidant. *Catal. Today* **24** (1995) 79-83.
104. Stüber, F., Smith, K.M., Baricot Mendoza, M., Marques, R.R.N., Fabregat, A., Bengoa, C., Font, J., Fortuny, A., Pullket, S., Fowler, G.D., Graham, N.J.D., Sewage sludge based carbons for catalytic wet air oxidation of phenolic compounds in batch and trickle bed reactors, *Appl. Catal., B.* **110** (2011) 81-89.
105. Hellenbrand, R., Mantzavinos, D., Metcalfe, I.S., Livingston, A.G., Integration of wet oxidation and nanofiltration for treatment of recalcitrant organics in wastewater, *Ind. Eng. Chem. Res.* **36** (1997) 5054-5062.