

Feasibility Study of Landfill Leachate Treatment by Hydrothermal Oxidation

V. Vadillo*, M. B. García-Jarana, J. Sánchez-Oneto, J. R. Portela and E. J. Martínez de la Ossa
Department of Chemical Engineering and Food Technologies, Faculty of Sciences, University of Cádiz, 11510
Puerto Real, Spain
*E-mail: violeta.vadillo@uca.es

ABSTRACT

The aim of this work is to present the results obtained in the application of the Hydrothermal Oxidation (HO) process of a landfill leachate. Few reports about landfill leachate hydrothermal oxidation process have been found. This wastewater is the liquid that moves through or drains from a landfill of urban solid waste and industrial solid waste. This liquid may either exist already in the landfill and also it may be created after rainwater mixes with the chemical waste. Typically, landfill leachate has high concentrations of nitrogen, iron, organic carbon, manganese, chloride and phenols. Other chemicals including pesticides, solvents and heavy metals may also be present. At first, Wet Air Oxidation (WAO) experiments were carried out in a batch reactor with a pressure of 180 bar, a temperature of 275°C and using air as oxidant. In a second stage, WAO and Supercritical Water Oxidation (SCWO) experiments were carried out in an isothermal plug flow reactor with low concentrations, at a constant pressure of 25 MPa and different temperatures ranging from 350 to 500 °C. Pure oxygen, from hydrogen peroxide decomposition, was used as oxidant with an oxygen excess coefficient upper than $n > 1$ that means no oxygen limitations. As the wastewater studied is a complex mixture of several compounds, the oxidation process efficiency was followed in terms of the reduction of both chemical oxygen demand (COD) and total organic carbon (TOC). The composition of the gas phase generated in the process has been also analyzed (on-line). In WAO experiments, a maximum COD removal of 75% was obtained after 120 min at a temperature of 275 °C and a pressure of 180 bar. SCWO experiments have demonstrated that the high content of salts present in the wastewater produce plugging in the tubular reactor after several hours of treatment. Besides, the presence of chlorides may generate corrosion, so it is necessary to carry out some pretreatments to remove the salts and chlorides presents in the wastewater or they must be treated in another reactor configuration as a transpiring wall.

Keywords:

Hydrothermal oxidation; Wet Air Oxidation; Supercritical Water Oxidation; Landfill; Leachate

INTRODUCTION

Landfill leachate is a wastewater with high environmental impact. It is due to the content of ammonium nitrogen, biodegradable and refractory organics and heavy metals [1-2]. Ammonium and organics are the most important components of the leachate. However, heavy

metals content is not very important due to they are present in a low concentration. The landfill leachate treatment presents some additional drawbacks as the variability in the composition and in the quantity of pollutants, which are function of the volume of water which infiltrates the landfill. Conventional technologies currently used to treat all kinds of organic and toxic wastewaters include biological methods (aerobic, anaerobic), precipitation, oxidation, adsorption, stripping, reverse osmosis, etc [3]. All these treatment methods have drawbacks and therefore may not be the best option for treating organic and toxic wastewaters [4]. Consequently, the development and application of new technologies, such as Hydrothermal Oxidation (HO) is very necessary. Nowadays few reports about HO of landfill leachate have been found [5]. Schmid et al. in 1999 reported the problem with corrosion and salts precipitation in the treatment of leachates at SUWOX facility [6]. HO consists basically of the oxidation in aqueous medium at high temperature and pressure below or above the critical point of water (374.2 °C and 22.1 MPa). The former, known as Wet Air Oxidation (WAO), is typically operated at temperatures and pressures ranging from 200 to 330°C and from 2 to 20MPa, respectively [7]. The latter, often referred to as Supercritical Water Oxidation (SCWO), is carried out at pressures and temperatures above the critical point for pure water, usually ranging from 400 to 650°C and from 25 to 35 MPa, respectively [8]. SuperCritical Water Oxidation (SCWO) has been proved to be an effective process to treat a wide variety of industrial wastewaters [9]. Above its critical point (T= 374°C, P= 22.1 MPa), water polarity changes. Under these conditions, water is a non polar solvent completely miscible with organics and gases like oxygen. In this homogeneous reaction medium do not exist have mass transfer limitations. As a result, supercritical water is a very suitable medium for the oxidation of organic and inorganic compounds [10]. In this work, the supercritical water oxidation of a landfill leachate has been studied. In a first stage, a preliminary experiment was conducted at a batch reactor. This experiment was used to check the process feasibility on this kind of wastewater. In a second stage, experiments were conducted in a continuous flow system.

MATERIALS AND METHODS

In a first stage, a wet air oxidation batch reactor was used. A schematic diagram of the experimental set up is shown in Figure 1. This equipment consists of a 316 stainless-steel reactor (Autoclave Engineers) with a volume of 300 mL. The vessel was fitted with a variable-speed stirrer (MagneDrive) and an electric furnace. A constant temperature was maintained at $\pm 2^\circ\text{C}$ from the set point by means of an electronic controller (PID). The experimental system incorporated a rupture disk with a burst pressure of 20 MPa as a safety device in case of pressure build-up in the reactor during an experiment. The oxidant used was synthetic air introduced in the system at the operational pressure.

Figure 1: Schematic diagram of the Hydrothermal Oxidation batch reactor.

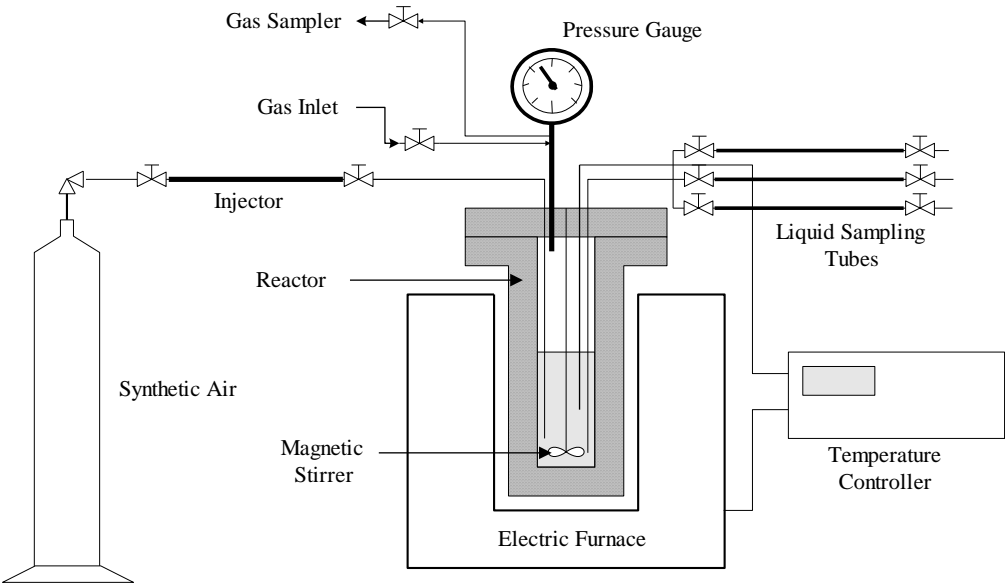
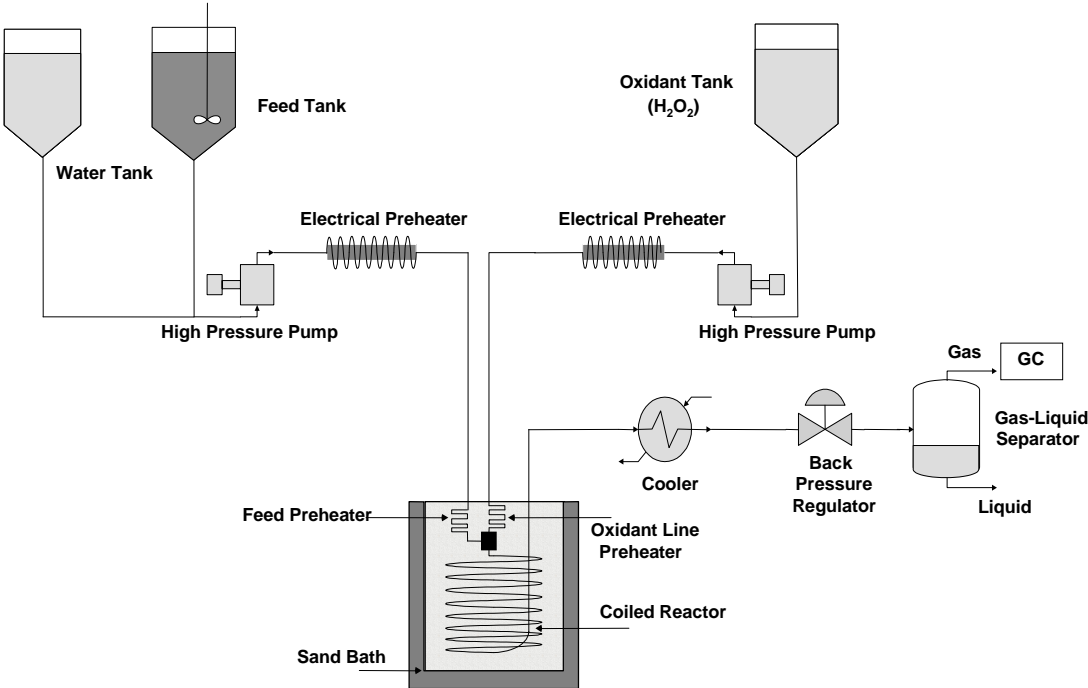


Figure 2: Schematic diagram of the continuous-flow reactor system at laboratory scale.



In a second stage, supercritical water oxidation experiments were carried out in a laboratory scale continuous flow system. A schematic diagram of the experimental set up is shown in Figure 2. All wetted parts, from the pumps to the back-pressure regulator, were made of stainless steel 316. The tubular reactor has a volume of 80 ml. The oxidant feed stream was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank was loaded with an aqueous solution of the flammable industrial wastewater. The two feed streams were pressurized in two different lines by two high-pressure metering pumps and then separately preheated. In order to ensure that all H₂O₂ decomposed to give H₂O and O₂, two in series preheating systems were used for the oxidant feed stream. Based on the studies of Croiset et al. (1997) [11], it has been proved that H₂O₂ was completely decomposed in the preheaters. A similar pre-heating system was used for the wastewater feed stream. After preheating, the two lines were mixed at the reactor inlet. Due to the reactor is submerged in a fluidized sand bath, the reaction is considered to be isothermal. Leaving the reactor, the effluent was cooled rapidly in a countercurrent heat exchanger and the pressure was subsequently reduced using a back-pressure regulator. The product stream was then separated into liquid and vapor phases. More specific details of the experimental apparatus and procedure are well described in our previous studies [12].

Some of the properties for the landfill leachate studied in this work are shown in Table 1.

Table 1: Properties of the landfill leachate.

| | |
|--------------------------------|----------------|
| pH | 9.68 ± 0.09 |
| Conductivity (mS/cm) (25°C) | 42.6 ± 1.5 |
| COD (mgO ₂ /l) | 41,959 ± 581 |
| TOC (mgC/l) | 15,913 ± 117 |
| Total Solids (mg/l) | 5.05 ± 0.11 |
| Dry extract (%) | 3.4 ± 0.01 |
| Volatile solids (%) | 1.31 ± 0.01 |
| Bicarbonates (mg/l) | 23,983 ± 4,340 |
| Chlorides (mg/l) | 8,235 ± 159 |
| Sulphates (mg/l) | 1,167 ± 404 |

The wastewater presents a high value of conductivity and a high content of salts, as can be seen in Table 1. These salts mainly consist of bicarbonates, chlorides and sulphates. Therefore, SCWO of landfill leachate could show important operational drawbacks as corrosion and salts precipitation, which can cause the reactor plugging, due to the low solubility of salts in supercritical water. On the other hand, the high chloride content may favour the corrosion phenomena at the reactor.

In the continuous flow system hydrogen peroxide (Panreac, 30%, w/v aqueous solution) was used as a source of oxygen. Diluted feed solutions of the required concentration were made using deionized water.

Chemical Oxygen Demand (COD) concentrations of liquid samples were monitored. The COD analysis was performed by closed reflux colorimetric method (5220D) according to the standard method for water and wastewater analysis [13].

Also, Total Organic Carbon (TOC) concentrations of liquid samples were monitored using a Shimadzu TOC-V CPH equipment, according to the high temperature combustion method for water and wastewater analysis (5310B) [13].

Gas samples were analyzed using an HP 6890 Series gas chromatograph with a Thermal Conductivity Detector (TCD). Two in-series columns were used to separate CO from CO₂. The first column was a Porapak-Q column and the second a molecular sieve Carvosieve column (Supelco). A temperature ramp from 55 to 160 °C (at 15 °C/min) was used. The system was calibrated with a standard gas mixture containing H₂, O₂, N₂, CO₂, CO and CH₄.

RESULTS

Since the landfill leachate is a mixture of several compounds the oxidation process efficiency has been followed in terms of reduction in the chemical oxygen demand (COD), total organic carbon (TOC) and the composition of the gas phase generated (H₂, CH₄, CO₂, and CO).

Landfill leachate Wet Air Oxidation (WAO) in a batch reactor. A landfill leachate wet air oxidation experiment was conducted in a batch reactor to check the treatment feasibility applied to this kind of wastewater. The experiment was conducted at a constant pressure of 180 bar and a temperature of 275°C as can be seen in Table 2. A volume of 220 ml of wastewater was placed in the reactor and synthetic air was introduced until getting a pressure of 180 bar.

Table 2: Operational conditions and results in the landfill leachate HO in a batch reactor.

| | |
|------------------------------------|-------|
| Pressure (bar) | 180 |
| Temperature (°C) | 275 |
| Oxygen excess coefficient (n) | 1.2 |
| Initial COD (mg O ₂ /l) | 3,390 |
| Final COD (mg O ₂ /l) | 782 |
| COD removal (%) | 75 |
| Reaction time (h) | 2 |
| H ₂ (%) | 0 |
| CH ₄ (%) | 0 |
| CO ₂ (%) | 4 |
| CO (%) | 0 |
| O ₂ (%) | 12 |
| N ₂ (%) | 84 |

After two hours of reaction the COD removal was 75% due to the low value of temperature. In order to reach higher removal efficiencies with these operational conditions, the use of a catalyst would be necessary [14]. On the other hand, the application of WAO as a pre-treatment previous to a biological treatment is an interesting option [15-16]. Thus, the WAO objective is not to get a high removal efficiency but to improve the wastewater biodegradability. Therefore it is not necessary to work at severe conditions, which reduces the reactor corrosion and decreases the necessary investment. Collivignarelli and Bissolotti [17] checked the increase in biodegradability of landfill leachate, paint industry wastewater and oil wastewater when they were treated by WAO.

So, it would be necessary to study the effluent biodegradability to check the biological treatment feasibility.

Landfill leachate Hydrothermal Oxidation (HO) in a continuous flow system. A set of 5 experiments with low concentration have been conducted in order to determine the feasibility of the landfill leachate supercritical water oxidation process. All experiments were conducted at a constant pressure of 250 bar and different temperatures ranging from 350 to 500 °C. i.e. from subcritical to supercritical conditions. The first temperature studied was 350°C because the landfill leachate had not been previously studied. The highest temperature studied at laboratory scale was 500°C due to experimental equipment limitations. The initial waste concentration (expressed as COD) was around 3,500 mg O₂/l in experiment 1 to 4 and 8,000 mg O₂/l in experiment 5. In all cases oxygen excess coefficient (n) was higher than 1 to ensure the absence of oxygen limitations. Thus, it has been used an oxygen excess between 1.4 and 2.1 what means an oxygen excess from 40% to 110%. Table 3 shows the operational conditions used in the laboratory scale experiments. As it is shown in Table 3, all experiments have been practically conducted in isothermal conditions which mean that the temperature was nearly constant in all cases.

Table 3: Operational conditions and results in the landfill leachate SCWO in a continuous flow system.

| Experiment | Average temperature (°C) | Oxygen excess coefficient (n) | Residence time (s) | Initial COD (mg O ₂ /l) | COD removal (%) | TOC removal (%) |
|------------|--------------------------|-------------------------------|--------------------|------------------------------------|-----------------|-----------------|
| 1 | 351 | 2.10 | 128 | 3,396 | 37.3 | 25.4 |
| 2 | 397 | 1.40 | 28 | 3,686 | 56.4 | 52.7 |
| 3 | 450 | 1.70 | 17 | 3,304 | 71.4 | 65.8 |
| 4 | 502 | 1.75 | 15 | 3,496 | 87.9 | 78.7 |
| 5 | 501 | 1.50 | 13 | 8,096 | 92.5 | 87.9 |

Experimental results for experiments 1-4 in COD and TOC disappearance are shown in Figure 3 and Figure 4 respectively. In experiments with similar residence times a higher temperature involves a higher COD and TOC removal. Results have shown that landfill leachate is difficult to oxidize because of experiment conducted at 350°C yielded a COD removal of 37% with a residence time around two minutes. As can be seen in Table 3, a higher temperature provides a higher COD removal although the reaction time decreases due to the decrease in the fluid density. In experiment 4, the temperature was 500°C and a COD

removal of 88% was reached with a reaction time of 15 s. In order to obtain efficiencies around 99% is necessary to increase the residence time until around 60 s or to increase the temperature to 550°C which were not possible due to experimental equipment limitations.

Figure 3: COD removal percentage as a function of residence time and temperature

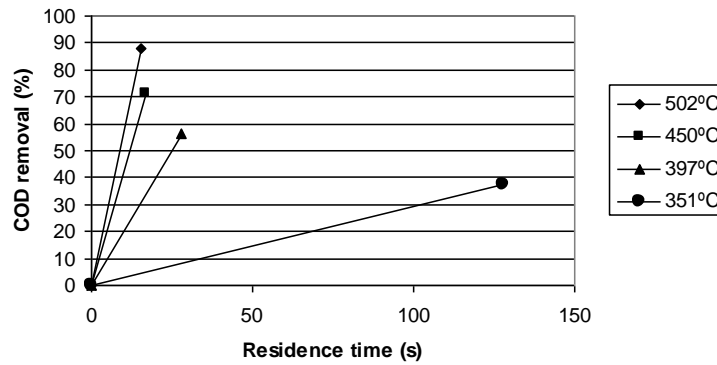
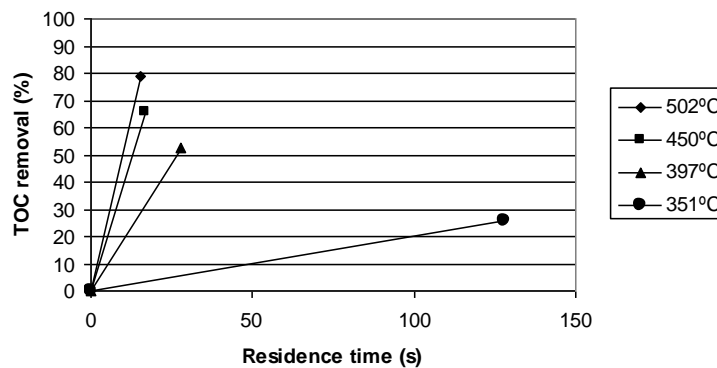


Figure 4: TOC removal percentage as a function of residence time and temperature



In relation to COT, results are similar to COD although removal efficiencies are lower. It is due to the formation of intermediate compounds as acetic acid in the liquid phase [18] instead of CO and CO₂ formation so only a reduction in COD was observed. The production of acids as reaction intermediates can be seen as a reduction in the effluent pH in relation to the feed pH. This fact is shown in Table 4.

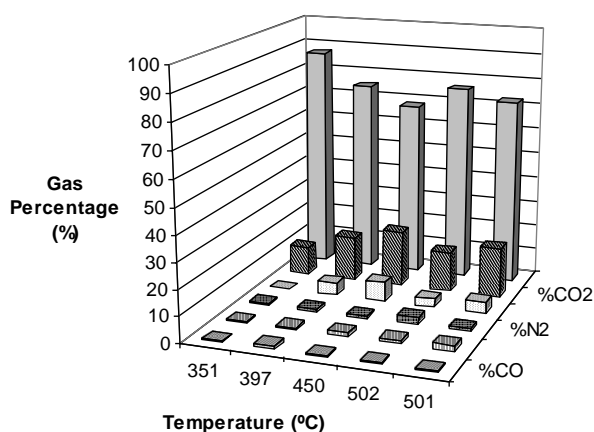
Table 4: Results in the landfill leachate SCWO in a continuous flow system.

| Experiment | Carbon Balance (%) | Initial pH | Final pH | Initial Conductivity (mS) | Final Conductivity (mS) |
|------------|--------------------|------------|----------|---------------------------|-------------------------|
| 1 | 65.3 | 7.81 | 7.60 | 8.95 | 6.21 |
| 2 | 56.2 | 7.75 | 7.66 | 9.49 | 5.88 |
| 3 | 57.7 | 7.85 | 7.56 | 8.74 | 4.63 |
| 4 | 52.8 | 7.73 | 7.44 | 8.71 | 4.13 |
| 5 | 43.7 | 8.01 | 7.60 | 16.72 | 9.67 |

In all experiments the percentage of CO in the gas effluent was less than 1.3%. It was due to the little presence of incomplete oxidation reactions as can be seen in Figure 5.

Although no operational drawbacks such as plugging, problems in the preheating and pressurization, etc. have been observed, Table 4 shows that carbon balance was less than 100% in all experiments. Therefore, organic matter has been retained into the system. The retention can be due to salts precipitation because the landfill leachate has a high content in bicarbonates.

Figure 5: Gas composition in the gas stream as a function of temperature



CONCLUSION

WAO experiments at 275 °C showed a maximum COD removal of 75% was obtained after 120 min. Therefore, it would be necessary to study the biological treatment feasibility after WAO.

Landfill leachate has demonstrated to be difficult to oxidize by means of SCWO process so it is necessary a temperature of 500°C to get a removal efficiency of 92% with a residence time of 13 s. however, SCWO process in a tubular reactor is not suitable for long-term treatment of the landfill leachate since severe plugging appears in the reactor after several hours due to the high salt content. Therefore it is necessary to use another reactor configuration or to remove salts in a pre-treatment.

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