Power Recovery Study from Phenol Wet Air Oxidation Process

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Abstract—Several studies have investigated the recovery of the heat produced by the highly exothermic reaction of oxidation in Wet Air Oxidation processes (WAO) by the estimation of effluent concentrations from which the process becomes autotherm, but little works has been devoted to the recovery of electricity and especially the exact calculation of the organic pollutant concentrations from which energetic self sufficiency is achieved by the process. In this present work, we are interested in the recovery of energy in the form of heat and electricity consumed and produced by the process in the treatment of water polluted by phenol. The objective is the calculation of the exact value of the autotherm point and also the autoelectric point in the process and the determination of the influence of operating pressure and temperature on electrical production and self-sufficiency.

Index Terms—wet air oxidation, phenol oxidation, energy recovery, electricity production, wastewater treatment, SuperPro Designer

I. INTRODUCTION

Wet Air Oxidation (WAO) is the liquid phase oxidation of organics or oxidizable inorganic components at high temperatures (125–320°C) and pressures (0.5–20MPa) using a gaseous source of oxygen (O₂ or air) as oxidant.

The solubility of O₂ in aqueous solutions is greatly enhanced at elevated temperatures and pressures, which provide the strong driving force for oxidation [1].

The development of the wet air oxidation process is attributed to Frederick J. Zimmerman, more than 40 years ago; he realized the air combustion of organic compounds dissolved in liquid water at relatively high pressure and temperature, producing only carbon dioxide and water [2].

Many compounds have been oxidized using sub and supercritical water: methane, methanol, ethanol, propane, nitrogen, phenol, acetic acid, dinitrophenol, chlorinated hydrocarbons, etc. [3].

Several works studied hydrothermal oxidation of phenol as a pollutant: experimental works deals essentially with kinetic studies to obtain data for the process [4]. Mathematical modeling studied, concentration and temperature profiles resulting from mass, momentum and energy differential equations resolution, it provides a comprehensive way to understand experimental results, equipment design and the scale-up of the process [5], [6].

The WAO, is an efficient treatment method, it is a clean way to remove the pollutant at 95% under certain operation conditions [7], without toxic by-products and even with energy recovery opportunities from the highly exothermic reaction.

Different methods have been used to optimize energy recovering from processes including hot and cold streams, [8], [9], the most important one is the Pinch technology. Its principal objective is to match cold and hot process streams with a network of exchangers, minimizing demands for externally supplied utilities [10].

As the oxidation of organic compounds is exothermic, and the process consume and produce heat and electricity, the WAO can become self-sustaining, if the energy production exceeds the demand of the process. The aim of this work is to study the energy recovery opportunities from phenol WAO process, the influence of organic pollutant concentration in the effluent to treat and also the influence of operating condition: pressure and temperature, on the energy recovery. The chemical oxygen demand COD, is used to represent the organic concentration of phenol in the effluent.

II. THEORY

To study the energy recovery from wet air oxidation process, we first, performed mass and energy balances, for the proposed flow diagram on SuperPro Designer software. We obtain material and energy results for every stream in the process, for different initial concentration of phenol in the effluent. Then, we used the new feature of the software to match operations that require cooling at a high temperature with operations that require heating at a low temperature without using explicit heat exchangers. The objective of this step is to have the exact COD concentration from which the energy of the exothermic reaction is sufficient to heat the effluent: the autotherm point. In addition, it is also possible to recycle power generated by the gas expansion, and estimate the COD concentration and operation condition from which the
power production became equal or superior to the power demand of the process: the autoelectrical point. Varying initial effluent concentration, pressure and temperature, we estimate the power consumption and generation in the process. The savings in cost utility due to heat and power recovery are also reported according to effluent COD.

The schematic flow sheet used to study WAO process consists mainly of a high-pressure pump, an air oxygen compressor, a heat-exchangers, an oxidation reactor, a gas expansion and a downstream separator [1], [11].

In this work, we used WAO to treat a water-phenol effluent by oxidation reaction, which is highly exothermic:

\[
C_6H_5OH + 7 O_2 \rightarrow 6CO_2 + 3H_2O + \Delta H
\]

where \( \Delta H \) is the energy produced by the reaction.

We perform a flow diagram of the process presented in Fig. 1 in SuperPro Designer v9.0. Both, air (source of oxygen \( O_2 \) as oxidant) and effluent streams enter the oxidizer at 180°C and 101 bars. An effluent flowrate of 100 kg/h (water-phenol) is compressed in a fluid pump and heated before the reactor. The products are expanded and cooled before the separation phase. We used adiabatic reactor, with 100% of oxygen in excess and a 95% of reaction conversion.

### III. RESULTS AND DISCUSSION

#### A. Heat Recovery

The WAO process has many operations that either consume or generate heat. Using energy recovery module of SuperPro Designer, we can obtain the heat recovery opportunities by matching operations that require cooling at a high temperature with operations that require heating at a low temperature without using explicit heat exchangers (Fig. 1) [12].

To determine the autotherm point: COD concentration from which the heat load produced by the cooling can be used by the heating to raise the temperature of the effluent to 180°C, we use the energy recovery feature of the software varying initial effluent COD. In Table I, we present some results of this application. This table shows all the operations that require cooling, their required cooling loads and their inlet and outlet temperatures. As an example, for 2% in mass of phenol (COD = 47.41 g O/l), operation P-5 that produces heating load can be matched with operation P-7 that requires heating, but P-5 produces only 74.3Kw, which is inadequate since operation P-7 needs 79.2Kw, that is why, SuperPro Designer displays a red cross for this matching (Table I-a).

We obtain the same decision (Table I-b), for the concentration effluent of 4% in mass (COD=94.96 g O/l), where the heat produced by the cooler (80.9Kw) is higher than that required for heating (77.8Kw), but SuperPro Designer displays a red cross for this matching because of temperature infeasibility, the temperature difference at the ends of the flow is less than the specified minimum approach of 5°C.

So, by varying COD concentrations and reporting energy recovery opportunities, we found that from the exact concentration of 4.16% in mass of phenol (98.78 g O/l COD), matching operation P-5 with P-7, becomes possible (Table I-c). Thus, the real autotherm point for this process is reached at 98.78g O/l COD, for the considered operation conditions and the available hot stream can be used to heat the effluent to treat.

### TABLE I. HEAT RECOVERY OPPORTUNITIES PROPOSED BY SUPERPRO DESIGNER

<table>
<thead>
<tr>
<th>COD Concentration</th>
<th>Heat Recovery Opportunities Matched</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>P-5\rightarrow P-7 (74.3Kw)</td>
</tr>
<tr>
<td>4%</td>
<td>P-5\rightarrow P-7 (79.2Kw)</td>
</tr>
<tr>
<td>4.16%</td>
<td>P-5\rightarrow P-7 (80.9Kw)</td>
</tr>
</tbody>
</table>

#### B. Power Recovery

In addition to heat recovery, the power is consumed by the gas compressor, the pump, the heater, the cooler and the oxidizer, and it is produced by the expander. The produced power can also be recycled. SuperPro Designer gives the total power consumed by the process and the power generated by gas expansion. In Fig. 2, we can see that unlike the heat recovery, power generation is higher than the demand for the low concentrations; the process is self sufficient until 2% in mass of phenol. This result reminds that of Akse et al. [13], when they found that no mechanical energy recovery were possible for the studied case, the energy produced remains below the power demand of the process.

![Figure 2. Power consumed and generated by the process](image-url)
C. Utilities Saving Costs

We have also reported the cost saving in utilities due to heat recovery and power recycle. Heat recovery is possible only from the autotherm point reported above, that is why its saving cost is zero before this point. The amount of energy due to heat recovery is greater than thus due to power recycled (Table I and Fig. 2), this difference appears in utilities cost savings, reported in Fig. 3. These results are obtained by the economic evaluation report of the software varying initial concentration of phenol.

D. Temperature and Pressure Effect on Power Recovery

In this section we consider only the electricity consumption and generation by the process, and we assume the heat recycling scheme of Fig. 4. The objective is to study the effect of operating condition: pressure and temperature on the autoelectric point.

At a fixed pressure of 100 bars and varying temperatures from 150°C to 300°C, we obtain the point from which the power generated is equal to power consumed by the process for every initial temperature. The results are reported in Fig. 5. Then, at a fixed temperature of 180°C and by varying pressure from 50 to 150 bars, we can estimate the autoelectric point for each effluent pressure; the results are presented in Fig. 6.

The results shows that for high temperatures the process is self sustainable until high COD concentration, but for low temperatures the electricity self sufficiency is limited to moderate concentrations; by against the pressure effect is opposite. On the other hand, we notice that the pressure has a greater effect on the autoelectric point that the temperature.

Thus, for process electric autonomy, it is necessary to adapt the operating conditions depending on the effluent concentration. For highly concentrated effluents, we have to work at high temperatures and moderate pressures. Finally, from the results, even if the process of WAO, is not totally self sufficient in electricity for high concentration, the power produced by the expansion of the reaction products remains high and can reach 62% of the process power demand (for concentrations near 359 g O/L), Fig. 2.

IV. Conclusion

Several studies have reported that WAO process is authotherm for wastes COD of about 15-600 g O/L [1], [13], and in reference [14], it is mentioned that WAO process is self-sustaining for a feed COD about 170 g/l with propanol-2 and butanol-1 as an organic pollutant effluent.

In this work, we reported the energy recovery opportunities using Superpro Designer software, and we studied the energy recovery (power and heat) available in the process. The calculation procedure allows estimating the self-sustaining point: the exact COD effluent concentration from which the process becomes autotherm and the point from which it becomes autoelectric. For the operating conditions studied, from about 98.78 g/l organic effluent concentration, the energy produced by the exothermic reaction can be sufficient to heat the feed. In the other hand, the power produced by the gas
expansion exceeds the power consumption until the COD of about 50g/L.

The savings cost in utilities due to heat and power recovery, self sustainability and the treatment efficiency of the process confirm that WAO wastewater treatment is a clean and alternative way to remove organic concentration in water.

The results of temperature and pressure influence on process energy recovery show opposite effects, which imply a careful choice of the operating conditions for an energetic self-sufficiency depending on concentration of the effluent to be treated.

The WAO electricity production remains important and can exceed 50% of its consumption for very high pollutant concentrations for which electric self-sufficiency cannot be achieved.

The calculating procedure developed in this work allows producing exact auto-sufficient points for other substances, and other operating conditions, by only changing the input data of the process to be studied.

REFERENCES


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