Significant cost and energy savings opportunities in industrial three phase reactor for phenol oxidation

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ABSTRACT

Energy saving is an important consideration in process design for low cost sustainable production with reduced environmental impacts (carbon footprint). In our earlier laboratory scale pilot plant study of catalytic wet air oxidation (CWAO) of phenol (a typical compound found in wastewater), the energy recovery was not an issue due to small amount of energy usage. However, this cannot be ignored for a large scale reactor operating around 140–160 °C due to high total energy requirement. In this work, energy savings in a large scale CWAO process is explored. The hot and cold streams of the process are paired up using 3 heat exchangers recovering significant amount of energy from the hot streams to be re-used in the process leading to over 40% less external energy consumption. In addition, overall cost (capital and operating) savings of the proposed process is more than 20% compared to that without energy recovery option.

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1. Introduction

A great attention has been paid to different alternative techniques for reducing the pollution in aqueous effluent and to detoxify pollutants (mainly phenol). These techniques vary depending on the concentration of these pollutants and the physical and chemical properties of pollutants. There is no universal solution for the treatment of water polluted with different organic and mineral pollution. Depending on the initial organic content of water the processes used for water treatment is classified (Miro et al., 1999; Santos et al., 2005; Pardeep, 2010). As a general consideration, biological treatment is used for the values of pollutants lower than 1 wt% and the incineration could be an interesting process for the values higher than 10 wt%. Whereas, for high values of pollutants especially when the effluent contains hard chemical oxygen demand (i.e. low biodegradability), others processes are introduced such as catalytic wet air oxidation (CWAO) process (Pardeep, 2010). Phenolic compounds (founded in wastewater) are very harmful pollutants causing several problems in our life and most of these pollutants are organics, and may be very dangerous for human health. To reduce the environmental impact and the tox-

icity of wastewater, many studies have focused on eliminating the discharge of these toxic substances or making them less harmful.

We (Mohammed et al., 2016) most recently used CWAO in a trickle bed reactor to reduce high concentration of phenol in wastewater from 5000 ppm to 300–600 ppm (in treated water) operating the reactor at a very high temperature requiring high energy consumption in the process. Energy consumption for the pilot plant scale was negligible and natural cooling after the reaction was sufficient (no additional utility was required as the amounts reactants and products were small at pilot plant scale), thus heat recovery was not an issue in the pilot plant scale process. However, the process when scaled-up to an industrial size (Mohammed et al., 2016) offers the opportunity of energy savings by proper heat integration. In industrial processes, energy consumption is large and heat recovery and re-use must be taken into consideration to reduce environmental impact (in terms of CO_2 emission) and to reduce the cost of treatment process. The CO_2 emission is from the burning of fossil fuels to heat up the feed stream to desired temperature in a trickle bed reactor (Jarullah et al., 2011).

Heat integration is a very beneficial tool and is a significant phase in estimating the cost of preliminary design leading to reduced cost of design, where recovery and re-use of waste heat provides both financial and environmental benefits to process unit operators (Khalfalla, 2009). The possible extent of heat integration of the reactor with the rest of the process depends mainly on the reaction

temperature. Changing this temperature usually has the following effects on the reaction system: (a) altering the speed of the reaction (a 10 °C temperature increase typically doubles the rate), (b) altering the proportions of components produced in the output mixture (these depend on the competing reactions occurring, are highly case-specific and can again change greatly for a 10 °C difference), and (c) altering the heat load of the reactor, which is usually a less significant effect than the other two (Kemp, 2007). Heat exchangers can be used for recovering thermal energy, which may otherwise be wasted. Most industrial plants e.g. refinery processes have multiple hot and cold streams which can be matched using heat exchangers and by applying pinch design method (Linnhoff and Flower, 1978) an optimal heat exchanger network can be designed (Ashaibani and Mujtaba, 2007).

In the process reported in this work there is only one hot stream (reactor output), which needed to be cooled down and two cold streams which needed to be heated up before entering into the reactor. Therefore, instead of considering optimal heat exchanger network design we simply added 3 heat exchangers into the process (Fig. 3) and optimized each of them to maximize energy recovery while minimizing overall cost.

2. Experimental work

The experimental results have been reported in the literature (Safaa, 2009; Mohammed et al., 2016). A brief description about the materials, apparatus and experimental procedure used for getting the experimental results are given below for the sake of convenience of the readers:

The continuous oxidation of phenol in wastewater was carried out co-currently down-flow with pure oxygen through a fixed bed of catalyst (0.48 wt% $Pt/\gamma - Al_2O_3$, 400 °C (calcinations temperature), 0.308 cm^3/g (pore volume), 0.647 g/cm^3 (bulk density), 259.9 m^2/g (surface area), 1.6 mm (particle diameter), sphere (particle shape)). Phenol is oxidized into a trickle bed reactor as a main apparatus in the unit process. The characteristics of such reactor can be summarized as follows: 77 cm (length of reactor), 1.9 cm (inner diameter), 85 cm^3 (catalyst volume), stainless steel (construction material). The schematic representation of the experimental equipment is shown in Fig. 1.

3. Energy consumption and recovery in CWAO of phenol process

In this work, the process flowsheet with energy recovery and recycle for the large scale catalytic wet air oxidation of phenol is shown in Fig. 2. As can be seen from this Figure, phenol feed is pumped by a pump (PU) into a heat exchanger 1 (H.E.1) and heated from $T_{in,0}$ to $T_{in,1}$, then fed into a Furnace (F1) to further heating from $T_{in,1}$ to required temperature of reaction T_R. On the other hand, the oxygen is compressed via compressor (X1), then fed into heat exchanger 2 (H.E.2) and is heated from $T_{O2,0}$ to $T_{O2,1}$ and then immediately introduced into a furnace to achieve the reaction temperature (T_R). Where, the reaction occurs inside a reactor (R1). After completion of the reaction, the hot product stream is leaving the reactor and is cooled from T_{out} to $T_{out,1}$ via the heat exchanger 1 (H.E.1) by contacting with the main feed stock of the phenol and is further cooled via the heat exchanger 2 (H.E.2) from $T_{out,1}$ to $T_{out,2}$ by contacting with the cold stream of oxygen $T_{O2,0}$. The final product temperature is cooled from $T_{out,2}$ to T_F via cooler (CO) by cold water at temperature $T_{W,1}$ which is heated to $T_{W,2}$. The energy balance equations for the overall process are given below.

The operating variables $T_{O2,1}$, T_F, and $T_{W,2}$ are regarded as the main control variables due to the following reasons: increasing the value of T_F leads to increased amount of water needed to achieve
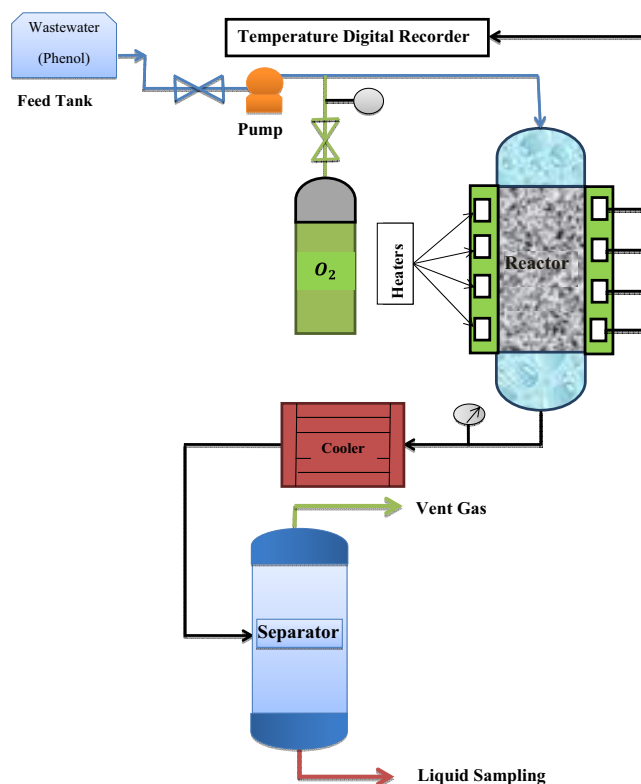

Fig. 1. Schematic representation of the experimental equipment (Safaa, 2009).

the final temperature of the oxidized phenol and as a result $T_{W,2}$ will be decreased and reflected to the $T_{O2,1}$ leading to decreased capital cost of H.E.1 and 2 and decreased capital cost of the furnace, but at the same time the operating cost will be increased as well as the target value (T_R), which will not be achieved. On the other hand, decreasing the value of T_F and $T_{W,2}$ and increasing $T_{O2,1}$ will lead to increased total annual cost of the process and at the same time will not satisfy the constraints of the process. Therefore formulation and solutions of an appropriate optimization problem is necessary.

3.1. Process model

The aim of this work is to reduce the energy consumption and maximizing the heat recovery during the catalytic wet air oxidation process of industrial scale. The behavior of industrial reactors is different from pilot plant reactors. While, a pilot plant is operated in ideal behavior and in isothermal mode; and the industrial reactor operates in non-isothermal mode. This means that the heat balance must be included in the process model. Mathematical models are usually developed from the pilot-plant experiments and are used to simulate the performance of scaled-up industrial reactor. The main mass balance equations, energy balance and chemical reaction rate equations used can briefly be shown as follow:

• Mass balance equation for oxygen in gas phase:

$$\frac{dC_{O2,G}}{dz} = -(\frac{k_{GL}a_{GL}}{u_g})(\frac{C_{O2,G}}{H_{O2}} - c_{O2,L}) \qquad (1)$$

• Mass balance equations in liquid phase:

Phenol:

$$\frac{dC_{ph,L}}{dz} = -(\frac{\eta_{LS}k_{LS}a_{LS}}{u_l})(C_{ph,L} - C_{ph,L-s}) \qquad (2)$$