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# 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.

**Key words:** CWAO, Phenol, Trickle bed reactor, Energy recovery, Modelling, Optimisation

## 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 toxicity 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

38 temperature requiring high energy consumption in the process. Energy consumption for the pilot plant scale was  
39 negligible and natural cooling after the reaction was sufficient (no additional utility was required as the amounts  
40 reactants and products were small at pilot plant scale), thus heat recovery was not an issue in the pilot plant scale  
41 process. However, the process when scaled-up to an industrial size (**Mohammed et al., 2016**) offers the opportunity  
42 of energy savings by proper heat integration. In industrial processes, energy consumption is large and heat recovery  
43 and re-use must be taken into consideration to reduce environmental impact (in terms of CO<sub>2</sub> emission) and to  
44 reduce the cost of treatment process. The CO<sub>2</sub> emission is from the burning of fossil fuels to heat up the feed stream  
45 to desired temperature in a trickle bed reactor (**Jarullah et al., 2011**).

46 Heat integration is a very beneficial tool and is a significant phase in estimating the cost of preliminary design  
47 leading to reduced cost of design, where recovery and re-use of waste heat provides both financial and  
48 environmental benefits to process unit operators (**Khalfalla, 2009**). The possible extent of heat integration of the  
49 reactor with the rest of the process depends mainly on the reaction temperature. Changing this temperature usually  
50 has the following effects on the reaction system: (a) altering the speed of the reaction (a 10°C temperature  
51 increase typically doubles the rate), (b) altering the proportions of components produced in the output mixture  
52 (these depend on the competing reactions occurring, are highly case-specific and can again change greatly for a  
53 10°C difference), and (c) altering the heat load of the reactor, which is usually a less significant effect than the other  
54 two (**Kemp, 2007**). Heat exchangers can be used for recovering thermal energy, which may otherwise be wasted.  
55 Most industrial plants e.g. refinery processes have multiple hot and cold streams which can be matched using heat  
56 exchangers and by applying pinch design method (**Linnhoff and Flower, 1978**) an optimal heat exchanger network  
57 can be designed (**Ashaibani and Mujtaba, 2007**).

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

62

## 63 **2. Experimental Work**

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

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

73

74

75

### 76 3. Energy Consumption and Recovery in CWAO of Phenol Process

77 In this work, the process flowsheet with energy recovery and recycle for the large scale catalytic wet air oxidation of  
78 phenol is shown in Figure (2). As can be seen from this Figure, phenol feed is pumped by a pump (PU) into a heat  
79 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  
80 required temperature of reaction  $T_R$ . On the other hand, the oxygen is compressed via compressor (X1), then fed into  
81 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  
82 the reaction temperature ( $T_R$ ). Where, the reaction occurs inside a reactor (R1). After completion of the reaction, the  
83 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  
84 contacting with the main feed stock of the phenol and is further cooled via the heat exchanger 2 (H.E.2) from  $T_{out,1}$   
85 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  
86  $T_F$  via cooler (CO) by cold water at temperature  $T_{W,1}$  which is heated to  $T_{W,2}$ . The energy balance equations for the  
87 overall process are given below.

88 The operating variables  $T_{O2,1}$ ,  $T_F$ , and  $T_{W,2}$  are regarded as the main control variables due to the following reasons:  
89 increasing the value of  $T_F$  leads to increased amount of water needed to achieve the final temperature of the oxidized  
90 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  
91 2 and decreased capital cost of the furnace, but at the same time the operating cost will be increased as well as the  
92 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  
93  $T_{O2,1}$  will lead to increased total annual cost of the process and at the same time will not satisfy the constraints of the  
94 process. Therefore formulation and solutions of an appropriate optimization problem is necessary.

#### 95 3.1. Process Model

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

- 103 • Mass balance equation for oxygen in gas phase:

$$104 \frac{dC_{O2,G}}{dz} = -\left(\frac{k_{GL}a_{GL}}{u_g}\right) \left(\frac{C_{O2,G}}{H_{O2}} - C_{O2,L}\right) \quad (1)$$

- 105 • Mass balance equations in liquid phase:

106 Phenol:

$$107 \frac{dC_{ph,L}}{dz} = -\left(\frac{\eta_{LS}k_{LS}a_{LS}}{u_l}\right) (C_{ph,L} - C_{ph,L-s}) \quad (2)$$

108 Oxygen:

$$109 \frac{dC_{O2,G}}{dz} = \left(\frac{k_{GL}a_{GL}}{u_l}\right) \left(\frac{C_{O2,G}}{H_{O2}} - C_{O2,L}\right) - \left(\frac{\eta_{LS}k_{LS}a_{LS}}{u_l}\right) (C_{O2,L} - C_{O2,L-s}) \quad (3)$$

- 110 • Mass balance equations in solid phase:

111 Phenol:

$$112 \quad k_{LS} a_{LS} (C_{ph,L} - C_{ph,L-S}) = \eta_0 (1 - \varepsilon_B) R_{ph} \quad (4)$$

113 Oxygen:

$$114 \quad k_{LS} a_{LS} (C_{O_2,L} - C_{O_2,L-S}) = 7 \eta_0 (1 - \varepsilon_B) R_{ph} \quad (5)$$

115 • Chemical reaction rate:

$$116 \quad R_{ph} = \rho_{cat} K_{het} \frac{c_{ph}^n c_{O_2}^m}{(1 + K_{ph} c_{ph,L})^2} \quad (6)$$

$$117 \quad K_{ph} = \exp\left(-\frac{364.47}{T} - 2.3854\right) \quad (7)$$

118 • Heat balance equation:

$$119 \quad \frac{dT}{dz} = (-\Delta H_{r,T}) R_{ph} \rho_B \frac{\varepsilon_l}{u_g \rho_g c_p^{O_2} \varepsilon_{gg} + u_l \rho_l c_p^{ph} \varepsilon_l} \quad (8)$$

120 The equations above were solved and optimized to estimate the best kinetic parameters by **Mohammed et al. (2016)**  
 121 which are required and essential in designing the industrial reactor. Other correlations for estimating gas and liquid  
 122 properties and characteristics of the catalyst bed used at process conditions with further details of the pilot plant,  
 123 equipment and procedure, design and operations of the trickle bed reactor can be found in **Mohammed et al. (2016)**.  
 124 Beside the above equations, the equations in relation to the heat exchangers are:

125

126 **a) Heat exchanger 1 (H.E.1):**

127 Phenol feed is pumped through a pump (PU) and is heated via the heat exchanger 1 (H.E.1) from  $T_{in,0}$  to  $T_{in,1}$  with  
 128 product mixtures that leave the reactor. The product mixture is cooled from  $T_{out}$  to  $T_{out,1}$ . The heat transfer rate of  
 129 each stream can be shown in Figure (3a) and described as follow:

$$130 \quad Q_{1_{ph}} = (\rho_{ph} c_p^{ph} Q_{ph}) (T_{in,1} - T_{in,0}) \quad (9)$$

$$131 \quad Q_{1_{prod.}} = (\rho_{ph} c_p^{ph} Q_{ph} + \rho_{O_2} c_p^{O_2} Q_{O_2}) (T_{out} - T_{out,1}) \quad (10)$$

$$132 \quad Q_{1_{ph}} = Q_{1_{prod.}} \quad (11)$$

$$133 \quad Q_{1_{ph}} = U_1 A_1 \Delta T_{LM1} \quad (12)$$

$$134 \quad \Delta T_{LM1} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} \quad (13)$$

$$135 \quad \Delta T_1 = T_{out} - T_{in,1} \quad (14)$$

$$136 \quad \Delta T_2 = T_{out,1} - T_{in,0} \quad (15)$$

137 **b) Heat exchanger 2 (H.E.2):**

138 The stream of product mixture out of H.E.1 is used to heat oxygen feed into the H.E.2. In this case, the oxygen is  
 139 heated from  $T_{O_2,0}$  to  $T_{O_2,1}$  and at the same time the product mixture is cooled from  $T_{out,1}$  to  $T_{out,2}$  as shown in Figure  
 140 (3b). The equations used in H.E.2 are:

$$141 \quad Q_{2_{O_2}} = (\rho_{O_2} c_p^{O_2} Q_{O_2}) (T_{O_2,1} - T_{O_2,0}) \quad (16)$$

$$142 \quad Q_{2_{prod.}} = (\rho_{ph} cp^{ph} Q_{ph} + \rho_{O_2} cp^{O_2} Q_{O_2}) (T_{out,1} - T_{out,2}) \quad (17)$$

$$143 \quad Q_{2_{O_2}} = U_2 A_2 \Delta T_{LM2} \quad (18)$$

$$144 \quad Q_{2_{O_2}} = Q_{2_{prod.}} \quad (19)$$

$$145 \quad \Delta T_{LM2} = \frac{\Delta T_3 - \Delta T_4}{\ln\left(\frac{\Delta T_3}{\Delta T_4}\right)} \quad (20)$$

$$146 \quad \Delta T_3 = T_{out,1} - T_{O_2,1} \quad (21)$$

$$147 \quad \Delta T_4 = T_{out,2} - T_{O_2,0} \quad (22)$$

148 **c) Cooler (CO):**

149 The product mixture stream out of H.E.2 will be cooled through a cooler (CO) from  $T_{out,2}$  to  $T_F$  using water as a cold  
 150 fluid at temperature  $T_{W,1}$  heated to  $T_{W,2}$ , which can be described in Figure (3c). The equations used in cooler are  
 151 written as follow:

$$152 \quad Q_{3_w} = m_w cp^w (T_{W,2} - T_{W,1}) \quad (23)$$

$$153 \quad Q_{3_{prod.}} = (\rho_{ph} cp^{ph} Q_{ph} + \rho_{O_2} cp^{O_2} Q_{O_2}) (T_{out,2} - T_F) \quad (24)$$

$$154 \quad Q_{3_w} = Q_{3_{prod.}} \quad (25)$$

$$155 \quad Q_{3_w} = U_3 A_3 \Delta T_{LM,3} \quad (26)$$

$$156 \quad \Delta T_{LM,3} = \frac{\Delta T_5 - \Delta T_6}{\ln\left(\frac{\Delta T_5}{\Delta T_6}\right)} \quad (27)$$

$$157 \quad \Delta T_5 = T_{out,2} - T_{W,2} \quad (28)$$

$$158 \quad \Delta T_6 = T_F - T_{W,1} \quad (29)$$

159 The total heat transfer area ( $A_t, m^2$ ) can be calculated as follow:

$$160 \quad A_t = A_1 + A_2 + A_3 \quad (30)$$

161 **d) Furnace (F1):**

162 Furnace is needed to further heat the feed temperature of oxygen and phenol reactants  $T_{O_2,1}$ , and  $T_{in,1}$ , respectively  
 163 in order to obtain the reaction temperature  $T_R$ . In this case, the phenol and oxygen are fed into furnace (F1)  
 164 separately to preheat the phenol  $T_{in,1}$  and oxygen  $T_{O_2,1}$  to the required temperature of the reaction  $T_R$ . The equations  
 165 of the furnace are:

$$166 \quad Q_{F_{ph}} = (\rho_{ph} cp^{ph} Q_{ph}) (T_R - T_{in,1}) \quad (31)$$

$$167 \quad Q_{F_{O_2}} = (\rho_{O_2} cp^{O_2} Q_{O_2}) (T_R - T_{O_2,1}) \quad (32)$$

$$168 \quad Q_F = Q_{F_{ph}} + Q_{F_{O_2}} \quad (33)$$

169 It is known that the physical properties such as (density, heat capacity and etc.) are temperature dependent (as a  
 170 function of temperature for each component in each equipment). Then, all the properties for each unit can be  
 171 evaluated at the following temperature:

$$172 \quad T_{av.} = \frac{T_{in.} + T_{out.}}{2} \quad (34)$$

173  $T_{in.}$  and  $T_{out.}$  are inlet and outlet temperatures for each unit.

174

175

### 176 3.2. Optimization Problem Formulation:

177

178 The optimization problem can be described as follows:

<b>Given</b>	Inlet temperature of phenol $T_{in,0}$ and oxygen $T_{O_2,0}$ , outlet product mixture $T_{out}$ , reaction temperature $T_R$ , inlet water temperature $T_{W,1}$ , volumetric flow rates of phenol $Q_{ph}$ and oxygen $Q_{O_2}$ .
<b>Optimize</b>	$T_{O_2,1}, T_F, T_{W,2}$
<b>So as to minimize</b>	The overall annual cost of the process (OAC)
<b>Subjected to</b>	Process constraints and linear bounds on all decision variables.

179 Mathematically, the optimization process is represented as follows:

180 Min  $OAC$

181  $T_{O_2,1}, T_F, T_{W,2}$

182 s.t  $f(x(z), u(z), v) = 0$  (model, equality constraints)

183  $T_F^L < T_F < T_F^U$  (inequality constraints)

184  $T_{O_2,1}^L < T_{O_2,1} < T_{O_2,1}^U$  (inequality constraints)

185  $T_{W,2}^L < T_{W,2} < T_{W,2}^U$  (inequality constraints)

186  $\Delta T_{W,2}^L < \Delta T_{W,2} < \Delta T_{W,2}^U$  (inequality constraints)

187  $\Delta T_F^L < \Delta T_F < \Delta T_F^U$  (inequality constraints)

188  $T_R = T_R^*$  (equality constraints)

189  $T_{out} = T_{out}^*$  (equality constraints)

190  $\Delta T_{W,2}$ : The temperature difference between inlet and outlet temperature of water in the cooler. Practically, the best  
 191 temperature difference between inlet and outlet water in the cooler is (5-25°C).  $\Delta T_F$ : The temperature difference  
 192 between inlet and outlet temperature of phenol in the furnace.

193 Note, as the process model including the kinetic models used in this work are the same as **Mohammed et al. (2016)**,  
 194 the reactor inlet ( $T_R$ ) and outlet ( $T_{out}$ ) temperatures are also kept the same as optimum industrial scale reactor  
 195 condition (Mohammed et al., 2016). These are ensured via the last two equality constraints. This meant that the inlet  
 196 temperature of Heat Exchanger 1 (HE 1) is fixed. Thus the number of optimisation parameters for two heat  
 197 exchangers reduces to only 3.

198

### 199 **3.2.1 Cost Function**

200 The design of equipment and cost models of the whole process (Figure2) is studied here in order to compare the  
 201 overall annual cost of the proposed CWAQ process with the conventional method. Thus, it is important to define the  
 202 overall annualized cost (OAC) of the process, which can be written as follows:

203 Overall Annual Process Cost ( $OAC$ , \$/yr) = Annualized Capital Cost ( $ACC$ , \$/yr) + Operating Cost ( $OPC$ , \$/yr) (35)

204 The Annualized Capital Cost ( $ACC$ , \$/yr) can be calculated from the total capital cost ( $TCC$ , \$), which includes the  
 205 cost of the main equipment in the unit process such as reactor, compressor, heat exchanger, pump, furnace and  
 206 separator as the following (**Smith, 2005**):

$$207 \text{ Annualized Capital Cost (ACC, \$/yr)} = \text{Total Capital Cost (TCC, \$)} \times \frac{i(1+i)^N}{(1+i)^N - 1} \quad (36)$$

208  $N$  is number of years and  $i$  is the fractional interest per year;  $N = 10$  years,  $i = 5\%$  (**Smith, 2005**).

209 The Total Capital Cost ( $TCC$ , \$) can be calculated from the following equation (**Sinnott, 2005; Jarullah, 2011**):

$$210 \text{ Total Capital Cost (TCC, \$)} = \text{Capital cost of installed equipment (CC, \$)} \times 1.45 \quad (37)$$

$$211 \text{ Capital Cost of equipment (CC, \$)} = \text{Reactor Cost (C}_r\text{)} + \text{Compressor Cost (C}_{compr}\text{)} + \text{Heat exchanger Cost}$$

$$212 \text{ (C}_{heatexch}\text{)} + \text{PumpCost (C}_{Pump}\text{)} + \text{FurnaceCost (C}_{Furn}\text{)} + \text{SeparatorCost (C}_{sep}\text{)} \quad (38)$$

213

214 The operating cost ( $OPC$ ) in equation (35) above is determined using the following equation (**Sinnott, 2005**):

$$215 \text{ Operating Cost (OPC, \$/yr)} = \text{Variable Operating Cost (VOPC)} + \text{Fixed Operating Cost (FOPC)} \quad (39)$$

$$216 \text{ Variable Operating Cost (VOPC, \$/yr)} = \text{Heating Cost (C}_{Heating}\text{)} + \text{Compression Cost (C}_{compression}\text{)} + \text{Pumping}$$

$$217 \text{ Cost (C}_{Pumping}\text{)} + \text{Cooling Cost (C}_{cooling}\text{)} + \text{CatalystCost (C}_{cat}\text{)} + \text{OxygenCost (C}_{O_2}\text{)} \quad (40)$$

218

$$219 \text{ Fixed Operating Variable Cost (FOPC, \$/yr)} = \text{Maintenance Cost (C}_{maint}\text{)} + \text{Operating Labor Cost (C}_{operat}\text{)} +$$

$$220 \text{ Laboratory Cost (C}_{lab}\text{)} + \text{Supervision Cost (C}_{superv}\text{)} + \text{Plant Overhead Cost (C}_{plant}\text{)} + \text{Capital Charge Cost (C}_{cap}\text{)}$$

$$221 \text{ + Insurance Cost (C}_{insur}\text{)} \quad (41)$$

222 Now, the capital cost ( $CC$ , \$) for each term can be calculated as follow (Douglas, 1988; Sinnott 2005):

223 • **Reactor Cost ( $C_r$ )** (\$) can estimated as follow:

$$224 C_r(\$) = \left(\frac{M\&S}{280}\right) 101.9 D_r^{1.066} L_r^{0.802} (2.18 + F_c) \quad (42)$$

225 • **Compressor Cost ( $C_{compr.}$ )** (\$) can be calculated as follow.

$$226 C_{compr.}(\$) = \left(\frac{M\&S}{280}\right) (517.5) (bhp)^{0.82} (2.11 + F_d) \quad (43)$$

227  $bhp$ , calculates from the following equations.

$$228 bhp = \frac{hp}{\eta_{ise}} \quad (44)$$

$$229 hp = \left(\frac{3.03 \times 10^{-5}}{\gamma}\right) P_{in} Q_{in} \left(\left(\frac{P_{out}}{P_{in}}\right)^{\gamma} - 1\right) \quad (45)$$

$$230 \gamma = \frac{\left(\frac{c_p^{O_2}}{c_v^{O_2}} - 1\right)}{\left(\frac{c_p^{O_2}}{c_v^{O_2}}\right)} \quad (46)$$

$$231 cv^{O_2} = cp^{O_2} - R \quad (47)$$

232  $\eta_{ise}$ : Isentropic efficiency, reported to be from 70 to 90%. Here, it is assumed 90% (Douglas, 1988; Bouton and Luyben, 2008; Jarullah et al., 2013a,b).

234 • **Heat exchanger Cost ( $C_{heatexch.}$ )** (\$):

$$235 C_{heatexch.}(\$) = \left(\frac{M\&S}{280}\right) 210.78 A_t^{0.65} (2.29 + F_c) \quad (48)$$

$$236 F_c = F_m (F_d + F_p) \quad (49)$$

237 • **Pump Cost ( $C_{Pump}$ )** (\$):

$$238 C_{Pump}(\$) = \left(\frac{M\&S}{280}\right) 9.84 \times 10^3 F_c \left(\frac{Q_p}{4}\right)^{0.55} \quad (50)$$

$$239 F_c = F_m F_p F_T \quad (51)$$

240 • **Furnace Cost ( $C_{Furn.}$ )** (\$):

$$241 C_{Furn.}(\$) = \left(\frac{M\&S}{280}\right) 5.52 \times 10^3 Q_F^{0.85} (1.27 + F_c) \quad (52)$$

$$242 F_c = F_m + F_p + F_d \quad (53)$$

243  $Q_F$ : Heat duty of the furnace, W

244  $F_m, F_p, F_c, F_d$  and  $F_T$ : Dimensionless factors that are functions of the construction material, operating pressure and  
245 temperature in addition to the design type.

246 • **Separator Cost ( $C_{sep}$ ) (\$):**

$$247 C_{sep} (\$) = \left(\frac{M\&S}{280}\right) 937.63 D_s^{1.066} L_s^{0.802} \quad (54)$$

248  $L_s$  &  $D_s$  are the length and diameter of separator, which can be estimate as follows:

249 To design the vertical separator vessel, it is necessary to estimate the settling velocity of the liquid droplets  
250 (**Gerunda, 1981**):

$$251 u_t = 0.07 \sqrt{\frac{(\rho_{ph} - \rho_{O_2})}{\rho_{O_2}}} \quad (55)$$

252  $u_t$  : Settling velocity,  $m/sec$

253  $\rho_{ph}$  : Liquid (phenol) density,  $kg/m^3$

254  $\rho_{O_2}$  : Vapor (oxygen) density,  $kg/m^3$

255 Minimum vessel diameter of the vessel ( $D_S$ ) can be estimated, follows:

$$256 D_S = \sqrt{\left(\frac{4 Q_v}{\pi u_s}\right)} \quad (56)$$

257  $D_S$ : Minimum vessel diameter,  $m$

258  $Q_v$ : gas, or vapor volumetric flow rate,  $m^3/sec$

259  $u_s = u_t$ , if a demister pad is used, and  $0.15 u_t$  for a separator without a demister pad,  $u_t$  from equation (55),  $m/sec$

260 The height of the vessel based on the liquid depth required and can estimates as follows:

$$261 L_S = V_S / A_S \quad (57)$$

262  $V_S$ : Volume held vessel separator,  $m^3$

263  $A_S$ : Cross-sectional area of vessel,  $m^2$

$$264 V_S = Q_L \times t_{hold} \quad (58)$$

265  $Q_L$ : Volumetric flow rate of liquid,  $m^3/sec$

266  $t_{hold}$ : Minimum hold-up time, assumed here 15 minute. To allow space position of level controller, it can further  
267 increases from (0.3 to 0.5 m).

268 The Variable Operating Cost ( $VOPC$ ) is estimated utilizing the following equations:

269 • **Heating Cost ( $C_{Heating}$ )** (\$/yr):

$$270 \quad C_{Heating}(\$/yr) = (Q_F(kW)) \left( \frac{0.06\$}{kWh} \right) \left( \frac{24h}{1 \text{ day}} \right) \left( \frac{342}{1yr} \right) \quad (59)$$

271 • **Compression Cost ( $C_{compression}$ )** (\$/yr) can be estimated using the following relationship based on motor  
272 efficiency of 90% (**Bouton and Luyben, 2008**) and average power price of 0.06\$/kWh (**Peral and Martín,**  
273 **2015**):

$$274 \quad C_{compression}(\$/yr) = \left( \frac{bhp(hp)}{0.9} \right) \left( \frac{1kW}{1.341 \text{ hp}} \right) \left( \frac{0.06\$}{kWh} \right) \left( \frac{24h}{1 \text{ day}} \right) \left( \frac{342}{1yr} \right) \quad (60)$$

275 • **Pumping Cost ( $C_{pumping}$ )** (\$/yr):

$$276 \quad C_{pumping}(\$/yr) = (Q_p(kW)) \left( \frac{0.06\$}{kWh} \right) \left( \frac{24h}{1 \text{ day}} \right) \left( \frac{342}{1yr} \right) \quad (61)$$

277 • **Cooling Cost ( $C_{cooling}$ )** (\$/yr) can be estimated by the following relationship with a price of cooling water  
278 (0.00375 \$/kg) (**Jarullah, 2011**):

$$279 \quad C_{cooling}(\$/yr) = \left( m_w \left( \frac{kg}{h} \right) \right) \left( \frac{0.00375\$}{kg} \right) \left( \frac{24h}{1 \text{ day}} \right) \left( \frac{342}{1yr} \right) \quad (62)$$

280 • **Catalyst Cost ( $C_{cat.}$ )** (\$/yr) can be calculated based on cycle life time ( $t_{cat.}$ ) and price of catalyst as (10 yr)  
281 and 5.8  $\frac{\$}{kg}$  (**EPA, 2015**), respectively:

$$282 \quad C_{cat.}(\$/yr) = (V_{cat}(m^3)) \left( \rho_{cat.} \left( \frac{kg}{m^3} \right) \right) \left( 5.8 \left( \frac{\$}{kg} \right) \right) \left( \frac{1}{t_{cat.}(yr)} \right) \quad (63)$$

283 • **Oxygen Cost ( $C_{Oxy.}$ )** (\$/yr) can be estimated with a price of oxygen to be (0.021\$/kg, (**Peral and Martín,**  
284 **2015**)) using the following equation:

$$285 \quad C_{Oxy.}(\$/yr) = (\rho_{O_2}(kg/m^3)) \times (Q_{O_2}(m^3/sec)) \times (0.021(\$/kg)) \times 3600 \times 24 \times 3 \quad (64)$$

286 While, the Fixed Operating Variables Cost ( $FOPC$ ) and their parameters can be estimates (**Douglas, 1988; Sinnott,**  
287 **2005**) as follow:

288 ✓ **Maintenance Cost ( $C_{maint.}$ ):** It involves the cost of materials (which involves equipment spares) and the  
289 cost of maintenance labor needed for the maintenance of the plant. Typically, the annual maintenance cost  
290 is (5-15%) of the installed capital cost.

291 ✓ **Operating Labor Cost ( $C_{operat.}$ ):** It involves a person needed to operate power to turn the plant that  
292 directly includes with running the process. The value is taken 15% of the total annual operating cost.

293 ✓ **Laboratory Cost ( $C_{lab.}$ ):** It involves the laboratory analyses required for process monitoring and quality  
294 control. The value of Laboratory Cost can be taken as 20 to 30% of the operating labor cost.

295 ✓ **Supervision Cost ( $C_{superv.}$ ):** It includes the direct operating supervision, the management directly  
296 associated with running the plant. The value is taken by 25% of the operating labors cost.

- 297 ✓ **Plant Overhead Cost ( $C_{plant}$ ):** It involves all the general costs associated with operating the plant that are  
298 not included with other headings (such as, offices, plant security, medical, canteen, warehouses, staff and  
299 safety). This value will be taken as (50-100%) of the operating labors cost.
- 300 ✓ **Capital Charge Cost ( $C_{charge}$ ):** It is recovered as a depreciation charge. The value can be taken as 10% of  
301 the total capital cost.
- 302 ✓ **Insurance Cost ( $C_{insur}$ ):** The value of the insurance is usually taken as (1-2%) of the total capital cost.
- 303
- 304

## 305 **4. Results and Discussions**

### 306 **4.1. Evaluation of Kinetic Parameters**

307 The optimal set of kinetic parameters of CWAO reactions have been evaluated based on minimizing the sum of  
308 squared error between the experimental data and the predicted data and are reported in **Mohammed et al., (2016)**.  
309 The kinetic parameters were evaluated via two methods (linear and nonlinear method). In the first approach, non-  
310 linear regression is applied to simultaneously obtain the reaction orders of phenol ( $n$ ), hydrogen compound order ( $m$ )  
311 and reaction rate constants ( $K$ ), then linear regression using the Arrhenius equation is applied to estimate the  
312 activation energy ( $EA$ ) and pre-exponential factor ( $A^0$ ) as shown in Figure (4). In the second approach, non-linear  
313 regression is applied to determine  $n$ ,  $m$ ,  $EA$  and  $A^0$  simultaneously. These kinetic parameters have been obtained  
314 accurately for all reactions with average absolute error of less than 5%, and therefore can be confidently applied for  
315 reactor design, operation and control. The results for are summarized in Table (1) for convenience (more details  
316 related to the kinetic parameters, optimal operating conditions, temperature distribution, ... etc, can be found in  
317 **Mohamed et al., 2016**).

318 Figure (5) shows the comparison between the experimental and predicted results. This Figure shows a good  
319 agreement between the experimental and the predicted results (each point represents experimental (X-axis) and  
320 simulated (Y-axis) values at the same time with the same operating conditions for each point).

321 The relation between the experimental and simulated results for phenol are appeared to be straight line with slope to  
322 be 1.0 which indicating very good agreement between the measured and predicted results.

323

324

### 325 **4.2. The Behavior of an Industrial TBR for CWAO Process**

326 In our recent work (**Mohammed et al., 2016**), the optimal kinetic parameters, the optimal operating conditions  
327 based on maximum conversion and minimum cost in addition to the optimal distribution of the catalyst bed have  
328 been considered. Also, the optimal ratio of the reactor length to reactor diameter has also been calculated with taking  
329 into account the hydrodynamic factors (radial and axial concentration and temperature distribution) to scale up the  
330 reactor. The industrial TBR configuration for CWAO process including the optimal operating conditions, dimensions  
331 and oil feed and phenol conversion is shown in Figure 6.

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### 334 **4.3. Energy Recovery and Re-use**

335 Here, a scaled-up CWAO process with energy recovery and re-use option is considered for reducing overall energy  
336 consumption (hence reducing environmental effect). However, this leads to the addition of a number of heat  
337 exchangers in the system, requiring capital investment. The objective is to calculate a retrofit design, which can  
338 reduce the energy consumption, maximize energy recovery and consequently minimize capital investment.

339 Generally, a process plant has a number of heat exchangers and a heater and a cooler. The heater regulates the final  
340 temperature of the cold fluid to the required reaction temperature, and the cooler adjusts the final temperature of the  
341 hot fluid to requirements of the next step of the process. The exchangers, heaters and coolers used for energy  
342 recovery and energy re-use in this study are shown in Figure 2.

343 The values of constants parameters with factors, coefficients and dimensionless constants are listed in Table (2) and  
344 Table (3) respectively (Douglas, 1988; Sinnott, 2005). The results are summarized in Table (4). It is observed that  
345 the minimum overall annual cost (OAC) and amounts of cooling water ( $m_w$ ) with energy recovery option of the  
346 oxidation process are less than those obtained without energy recovery option. Also, it observed that the cost saving  
347 is (25.21%) in comparison to the cost obtained without energy recovery option to reach reaction temperature  
348 (199.72°C (472.87 K), which is the optimal reaction temperature obtained in our previous work) and to minimize the  
349 final product temperature (26°C). It is also observed that the amount of cooling water needed to reach the final  
350 temperature without energy recovery option is larger than that required with energy recovery option. It is observed  
351 that the energy saving (thus reduction is carbon footprint) is about 43% compared to those without energy recovery  
352 option.

353 For the purpose of assessing the kinetic parameters and giving enough evidence to assure that values of control  
354 parameter estimated correspond to the global minimum of the objective function so that the developed process  
355 models is accurate, sensitivity analysis for  $T_{O_2,1}$ ,  $T_F$  and  $T_{W,2}$  values were performed. The information obtained from  
356 parametric sensitivity analysis is very useful for optimization and parameter calculation. It gives us a clear indication  
357 which parameter has the biggest effect on the accuracy of the variable model. Sensitivity analysis is utilized to each  
358 of the calculated parameters by means of perturbations of the parameter value and is preferably in the range of  
359  $\pm 10\%$ , keeping the other parameters in their estimated values (Jarullah, 2011). For each perturbation in the  
360 parameter values, the objective function is re-determined and then for each parameter the perturbation percentage is  
361 plotted against the corresponding value of the objective function as shown in Figure 7 for each reaction separately  
362 (for each parameter). When all the perturbations in all the kinetic parameters give the same minimum of the  
363 objective function with their original values (0% perturbation), that means the global minimum has been achieved.  
364 On the other hand, if at least one parameter does not give the same minimum than the others at 0% perturbation,  
365 means poor nonlinear parameter evaluation. From Figure 7, it is clearly seen that the estimated parameters are the  
366 optimum since at 0% perturbation the perturbations of  $T_{O_2,1}$ ,  $T_F$  and  $T_{W,2}$  give the same minimum of the objective  
367 function (OAC) with their original values. Therefore, it is demonstrated that the global minimum has been achieved.

368

#### 369 **4.4. Overall Cost of the Process**

370 Table (5) represents the results of the overall cost of the process that includes the total capital and operating cost. In  
371 this work the total capacity of wastewater is 600 m<sup>3</sup>/day based on 50 m<sup>3</sup> of catalyst leading to 99.79 % conversion of  
372 phenol (the maximum conversion obtained with the optimal operating conditions) at temperature 472.87 K, liquid

373 hourly space velocity  $0.5 \text{ h}^{-1}$ , oxygen partial pressure 0.6 Mpa, gas flowrate 0.2 S.E., initial phenol concentration  
374  $1.0498\text{E}^{-5} \text{ mol/cm}^3$ .

375 Table (6) shows the economic results of this study in comparison with conventional method. It is observed that the  
376 overall cost of the process obtained in this study is less than those obtained in conventional method at the same plant  
377 capacity. As can be seen from these results, the biggest effect of the overall annual cost is attributed to the operating  
378 cost that changes throughout the year compared with capital cost. The cost of treatment of 1 kg of phenol was to be  
379 1.20\$ in comparison with the cost that treated in the conventional method, which is 1.58\$/kg (**Peral and Martín,**  
380 **2015**). The total cost saving of this process is about 24.53% compared to that obtained by the conventional method  
381 and 0.38\$ cost saving for each kg of phenol. This cost saving is due to many of reasons: the number of equipment  
382 used in conventional method is more than those used in this study leading to increase the operating cost and  
383 consequently increased the overall annual cost.

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## 388 5. Conclusions

389 Energy consumption and heat recovery is a big issue that should be taken into account in industrial operations,  
390 particularly when the type of reactions are exothermic, the recovery and re-use of which is very significant for  
391 maximizing not only the profitability of the process but also to reduce the carbon footprint. Also, while the  
392 energy consumption in a pilot plant scale may not be significant requiring recovery and re-use of energy, it is  
393 not the case for large scale processes. In this work, the energy recovery by pairing hot and cold streams in heat  
394 exchangers from a large scale catalytic wet air oxidation of phenol have been investigated and optimized. The  
395 optimization problem is formulated to minimize the overall annual cost (includes both capital and operational  
396 costs) of the process while optimizing oxygen outlet temperature from heat exchanger 2 ( $T_{O_2}$ ), outlet final  
397 temperature of product mixture from cooler ( $T_F$ ) and outlet water temperature from cooler ( $T_{w,2}$ ). With the  
398 introduction of 3 heat exchangers, the cost and energy savings has been found to be around 24% and 43%  
399 respectively, in comparison with the process without energy recovery option.

400

## 401 Nomenclature

Symbol	Definition	Unit
$A^0$	Pre-exponential factor	$\text{sec}^{-1} (\text{cm}^3/\text{mol})^{-1.108}$
$A_1$	Heat transfer area of heat exchanger 1(H.E.1)	$m^2$
$A_2$	Heat transfer area of heat exchanger 2(H.E.2)	$m^2$

$A_3$	Heat transfer area of cooler	$m^2$
$ACC$	Annualized capital cost	\$/yr
$a_{GL}$	Specific gas-liquid contact area per unit volume of bed	$cm^2/cm^3$
$a_{LS}$	Specific liquid-solid contact area per unit volume of bed	$cm^2/cm^3$
$A_S$	Cross-sectional area of separator	$m^2$
$A_t$	Total heat transfer area	$m^2$
$C_{cap.}$	Capital charge cost	\$/yr
$C_{cat.}$	Catalyst cost	\$/yr
$C_{compr.}$	Compressor cost	\$
$C_{compression}$	Compression cost	\$/yr
$C_{conversion}$	Conversion cost	\$/yr
$C_{cooling}$	Cooling cost	\$/yr
$C_{Energy}$	Energy cost	\$/yr
$C_{factor}$	Conversion factor	$\$/m^3$
$C_{FUNCTION}$	Function cost	\$/yr
$C_{Furn.}$	Furnace cost	\$
$C_{heatexch.}$	Heat exchanger cost	\$
$C_{Heating}$	Heating cost	\$/yr
$C_{insur.}$	Insurance cost	\$/yr
$C_{lab.}$	Laboratory cost	\$/yr
$C_{maint.}$	Maintenance cost	\$/yr
$C_{O_2,G}$	Concentration of oxygen in gas phase	$mol/cm^3$
$c_{O_2,L}$	Concentration of oxygen in liquid phase	$mol/cm^3$
$C_{O_2,L-s}$	Concentration of oxygen at liquid-solid Interface	$mol/cm^3$
$C_{Oxy.}$	Oxygen cost	\$/yr
$CC$	Capital cost of installed equipment	\$
$cp^{O_2}$	Specific heat capacity of oxygen	J/mol . K
$cp^W$	Specific heat capacity of water	J/g. K
$C_{Pump}$	Pump cost	\$
$cp^{ph}$	Specific heat capacity of phenol	J/mol . K
$C_{Pumping}$	Pumping cost	\$/yr

$C_{operat.}$	Operating labour Cost	\$/yr
$C_{ph,L}$	Concentration of phenol in liquid phase	mol/cm <sup>3</sup>
$C_{ph,L-s}$	Concentration of phenol at liquid-solid interface	mol/cm <sup>3</sup>
$C_{phen.}$	Phenol cost	\$/yr
$C_{plant.}$	Plant overhead cost	\$/yr
$C_r$	Reactor cost	\$
$C_{sep.}$	Separator cost	\$
$C_{superv.}$	Supervision cost	\$/yr
$cv^{02}$	Specific heat capacity for oxygen at constant volume	J/mol . K
$D_s$	Diameter of separator	m
EA	Activation energy	J/mol
$F_c, F_m, F_d, F_p, F_T$	Dimensionless constant factors are function of the construction material and operating pressure	(-)
$FOPC$	Fixed operating cost	\$/yr
$H_{O_2}$	Henry's law constant for dissolved oxygen in water	(-)
$hp$	Compressor horse power	(-)
$k_{GL}$	Gas-to-liquid mass transfer coefficient	cm/sec
$K_{het}$	Apparent reaction rate constant	sec <sup>-1</sup> (cm <sup>3</sup> /mol) <sup>1-n</sup>
$k_{LS}$	Liquid-to-solid mass transfer coefficient	cm/sec
$K_{ph}$	Adsorption equilibrium constant of phenol	cm <sup>3</sup> /mol
$L_r$	Length of reactor bed	cm
$L_s$	Length of separator	m
m	Order of oxygen partial pressure	(-)
$M \& S$	Marshal and swift index for cost escalation	(-)
m	Order of oxygen partial pressure	(-)
$m_w$	Mass flow rate of cooling water	g/sec
n	Order of phenol concentration	(-)
$OAC$	Overall annual cost	\$/yr
$OPC$	Operating cost	\$/yr
P	Partial pressure of oxygen	bar
$P_{in}$	Pressure inlet to the compressor	lb/ft <sup>2</sup>

$P_{out}$	Pressure outlet of compressor	$lb/ft^2$
$Q1_{ph}$	Heat duty of phenol in heat exchanger 1(H.E.1)	$W$
$Q1_{prod.}$	Heat duty of product mixture in heat exchanger 1 (H.E.1)	$W$
$Q2_{O2}$	Heat duty of oxygen in heat exchanger 2 (H.E.2)	$W$
$Q2_{prod.}$	Heat duty of product mixture in heat exchanger 2 (H.E.2)	$W$
$Q3_{prod.}$	Heat duty of product mixture in cooler	$W$
$Q3_w$	Heat duty of water in cooler	$W$
$Q_F$	Heat duty of the furnace	$W$
$Q_{in}$	Volumetric flowrate at compressor section	$ft^3/min$
$Q_L$	Volumetric flow rate of liquid	$m^3/sec$
$Q_{O2}$	Volumetric flow rate of oxygen	$cm^3/sec$
$Q_p$	Pump power	$kW$
$Q_{ph}$	Volumetric flow rate of phenol	$m^3/sec$
$Q_v$	Gas, or vapor volumetric flow rate	$m^3/sec$
$R_{ph}$	Rate disappearance of phenol per unit volume of catalyst	$mol/cm^3_{cat}.sec$
$T_{av}$	Average temperature between inlet and outlet temperature for item of each equipment	$^{\circ}C$
$t_{cat.}$	Cycle life time of catalyst	yr
$TCC$	Total capital cost	\$
$T_F$	Outlet final temperature of product mixture from cooler	$^{\circ}C$
$t_{hold.}$	Minimum hold-up time	min
$T_{in.}$	Inlet temperatures for item of each equipment	$^{\circ}C$
$T_{in,0}$	Inlet temperature of phenol into the heat exchanger 1 (H.E.1)	$^{\circ}C$
$T_{in,1}$	Outlet temperature of phenol from heat exchanger 1 (H.E.1)	$^{\circ}C$
$T_{O2,0}$	Oxygen inlet temperature into heat exchanger 2 (H.E.2)	$^{\circ}C$
$T_{O2,1}$	Oxygen outlet temperature from heat exchanger 2 (H.E.2)	$^{\circ}C$
$T_{out,1}$	Outlet temperature of hot product mixture from heat exchanger 1 (H.E.1)	$^{\circ}C$
$T_{out.}$	Outlet temperatures for item of each equipment.	$^{\circ}C$
$T_{out}$	Inlet temperature of hot product mixture into the heat exchanger 1 (H.E.1)	$^{\circ}C$
$T_{out,2}$	Inlet product mixture into heat exchanger 2 (H.E.2)	$^{\circ}C$
$T_{W,1}$	Inlet water temperature into cooler	$^{\circ}C$

$T_{W,2}$	Outlet water temperature from cooler	$^{\circ}\text{C}$
$U_1$	Over all heat transfer coefficient for heat exchanger 1 (H.E.1)	$\text{W}/\text{m}^2 \cdot \text{K}$
$U_2$	Over all heat transfer coefficient for heat exchanger 2 (H.E.2)	$\text{W}/\text{m}^2 \cdot \text{K}$
$U_3$	Over all heat transfer coefficient for cooler	$\text{W}/\text{m}^2 \cdot \text{K}$
$u_g$	Superficial gas velocity	$\text{cm}/\text{sec}$
$u_l$	Superficial liquid velocity	$\text{cm}/\text{sec}$
$u_t$	Settling velocity	$\text{m}/\text{sec}$
$V_{cat.}$	Volume of catalyst	$\text{m}^3$
$VOPC$	Variable operating cost	$\$/\text{yr}$
$V_S$	Volume held in vessel separator	$\text{m}^3$
$z$	Length of catalyst bed	$\text{cm}$

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404 **Greek symbols**

<b>Symbol</b>	<b>Definition</b>	<b>Unit</b>
$\epsilon_B$	Porosity	(-)
$\Delta T_{LM1}$	Log mean temperature difference for heat exchanger 1 (H.E.1)	(-)
$\Delta T_{LM,2}$	Log mean temperature difference for heat exchanger 2 (H.E.2)	(-)
$\Delta T_{LM,3}$	Log mean temperature difference for cooler	(-)
$\eta_{LS}$	Wetting efficiency	(-)
$\eta_{ise}$	Isentropic efficiency	(-)
$\rho_{O_2}$	Density of oxygen	$\text{kg}/\text{m}^3$
$\rho_{cat}$	Catalyst density	$\text{g}/\text{cm}^3$
$\rho_l$	Liquid density	$\text{kg}/\text{m}^3$
$\rho_{ph}$	Density of phenol	$\text{kg}/\text{m}^3$ , $\text{lb}/\text{ft}^3$
$\rho_v$	Vapor density	$\text{kg}/\text{m}^3$
$\gamma$	Specific heat ratio	(-)

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420 **Symbols and Abbreviations**

<b>Symbol</b>	<b>Definition</b>
CO	Cooler Equipment
$C_s$	Cost Saving
CWAO	Catalytic Wet Air Oxidation
ES	Energy Saving
F1	Furnace Equipment
gPROMS	general Process Modeling System
H.E.1	Heat Exchanger 1 Equipment
H.E.2	Heat Exchanger 2 Equipment
M & S	Marshal and Swift Index for Cost Escalation
$O_2$	Oxygen
<i>ph.</i>	Phenol
PU	Pump Equipment
R1	Reactor Equipment
SSE	Sum of Square Errors

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506 **Table 1:** Values of kinetic parameters of model estimated via first approach (Linear Method) and second approach

507

(Non-Linear Method).

<b>First Approach</b>			
<b>Parameter</b>	<b>Symbol</b>	<b>Unit</b>	<b>Value</b>
Order of phenol concentration	<i>n</i>	(-)	2.1086
Order of oxygen partial pressure	<i>m</i>	(-)	0.6460
Apparent reaction rate constant @ 120°C	$K_{het.1}$	$sec^{-1}(\frac{cm^3}{mol})^{-1.108}$	5440.644
Apparent reaction rate constant @ 140°C	$K_{het.2}$	$sec^{-1}(\frac{cm^3}{mol})^{-1.108}$	6900.594
Apparent reaction rate constant @ 160°C	$K_{het.3}$	$sec^{-1}(\frac{cm^3}{mol})^{-1.108}$	8690.253
Activation energy	<i>EA</i>	J/mol	16609.709
pre-exponential factor	$A^0$	$sec^{-1}(\frac{cm^3}{mol})^{-1.108}$	874143.6496
Sum of Square Errors	<i>SSE</i>	(-)	5.4078E-4
<b>Second Approach</b>			
<b>Parameter</b>	<b>Symbo l</b>	<b>Unit</b>	<b>Value</b>
Order of phenol concentration	<i>n</i>	(-)	2.1066
Order of oxygen partial pressure	<i>m</i>	(-)	0.6112
Activation energy	<i>EA</i>	J/mol	16315.735
Pre-exponential factor	$A^0$	$sec^{-1}(\frac{cm^3}{mol})^{-1.108}$	668879.2
Sum of Square Errors	<i>SSE</i>	(-)	4.8226E-4

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**Table 2:** Values of factors, coefficient and constant parameters used in this model.

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Parameter	Unit	Value
$T_{in,0}$	°C	24
$T_{O_2,0}$	°C	70
$T_{out}$	°C	199.72
$T_{W,1}$	°C	20
$U_1$	$W/m^2.K$	95
$U_2$	$W/m^2.K$	10
$U_3$	$W/m^2.K$	750
$L_s$	$m$	1.5
$D_s$	$m$	2.5

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**Table 3:** Dimensionless constants used in this model.

Dimensionless Parameters	Furnace	Pump	Heat Exchanger	Separator
$F_m$	0.75	1	3.75	3.75
$F_p$	0.15	1.9	0.625	0
$F_d$	1	0	1	1
$F_T$	0	1	0	0

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**Table 4:** Optimization results with energy recovery of CWAO process.

Variables	Without Energy Recovery	With Energy Recovery	Decision Variable Type	Optimized Value
$A_t$ ( $m^2$ )	57.72	74.43	$T_{out,1}$ ( $^{\circ}C$ )	130.81
OAC (\$/yr)	4.9735E8	3.7197E8	$T_{O2,1}$ ( $^{\circ}C$ )	130
$m_w$ (kg/hr)	3404.586	2322.04	$T_{W,2}$ ( $^{\circ}C$ )	40.0
$C_s$	-	25.21	$T_R$ ( $^{\circ}C$ )	199.72
$Q1_{ph}$ (W)	-	188378.61	$T_F$ ( $^{\circ}C$ )	26
$Q2_{O2}$ (W)	-	4630.244	$\Delta T_{W,2}$ ( $^{\circ}C$ )	20
$Q3_w$ (W)	-	215897.94	$\Delta T_F$ ( $^{\circ}C$ )	95
$Q_t$ (W)	-	2869803907	-	-
ES (%)	-	43	-	-

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**Table 5:** Total cost of CWAO Process.

Cost Function	Unit	Value
OAC	\$/yr	3.7197E8
ACC	\$/yr	5392171.5
OPC	\$/yr	366577828.5

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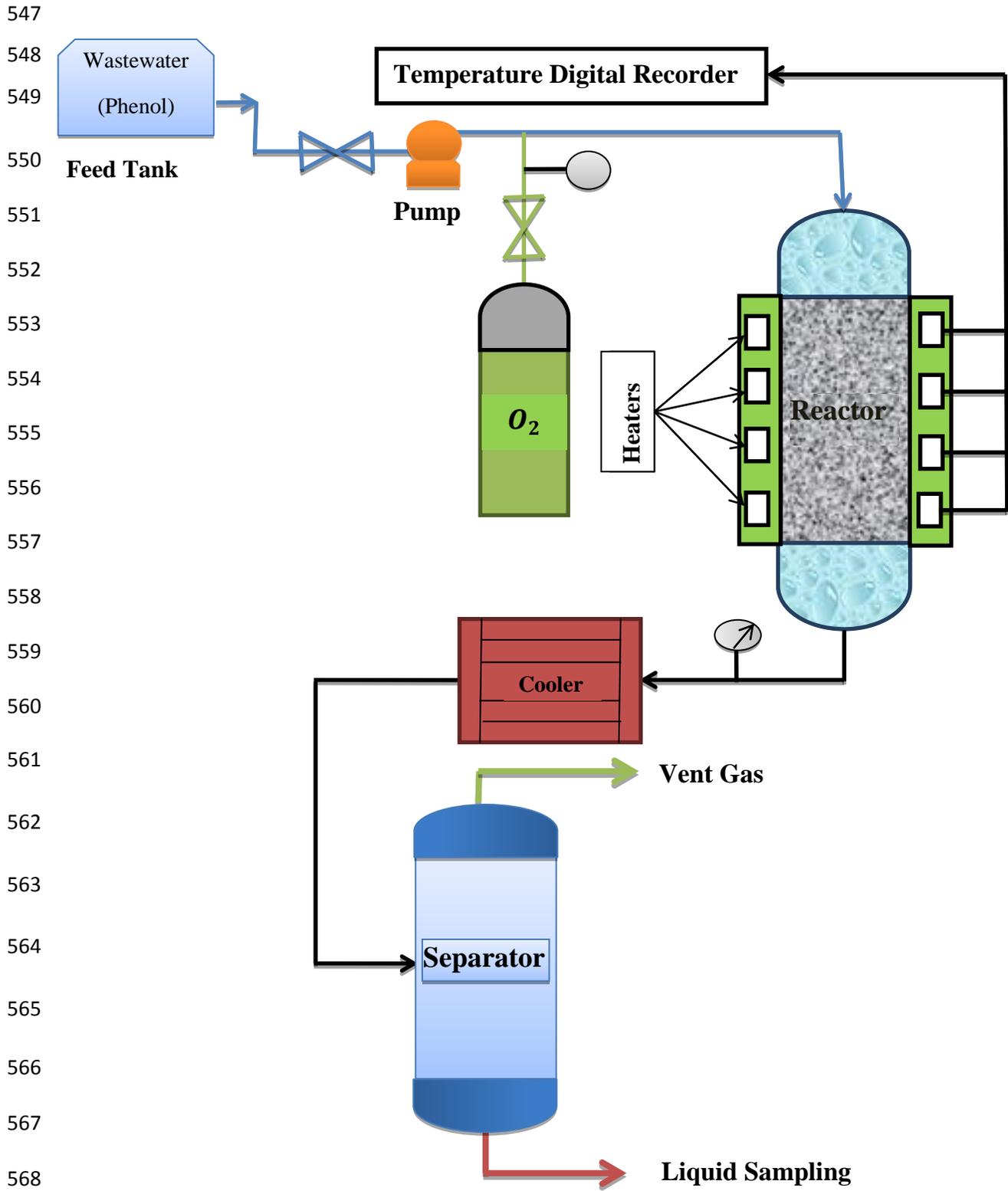
**Table 6:** Comparison results for CWAO process for phenol oxidation.

Variables	Current Study	Conventional Method
Wastewater Capacity ( $\frac{m^3}{day}$ )	600	600
OAC, (\$/yr)	3.7197E8	4.9287E8
Total Cost Saving (%)	24.53	0
Phenol Cost (\$/kg)	1.20	1.58
Cost Saving (\$/kg)	0.38	0

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570 **Figure 1**

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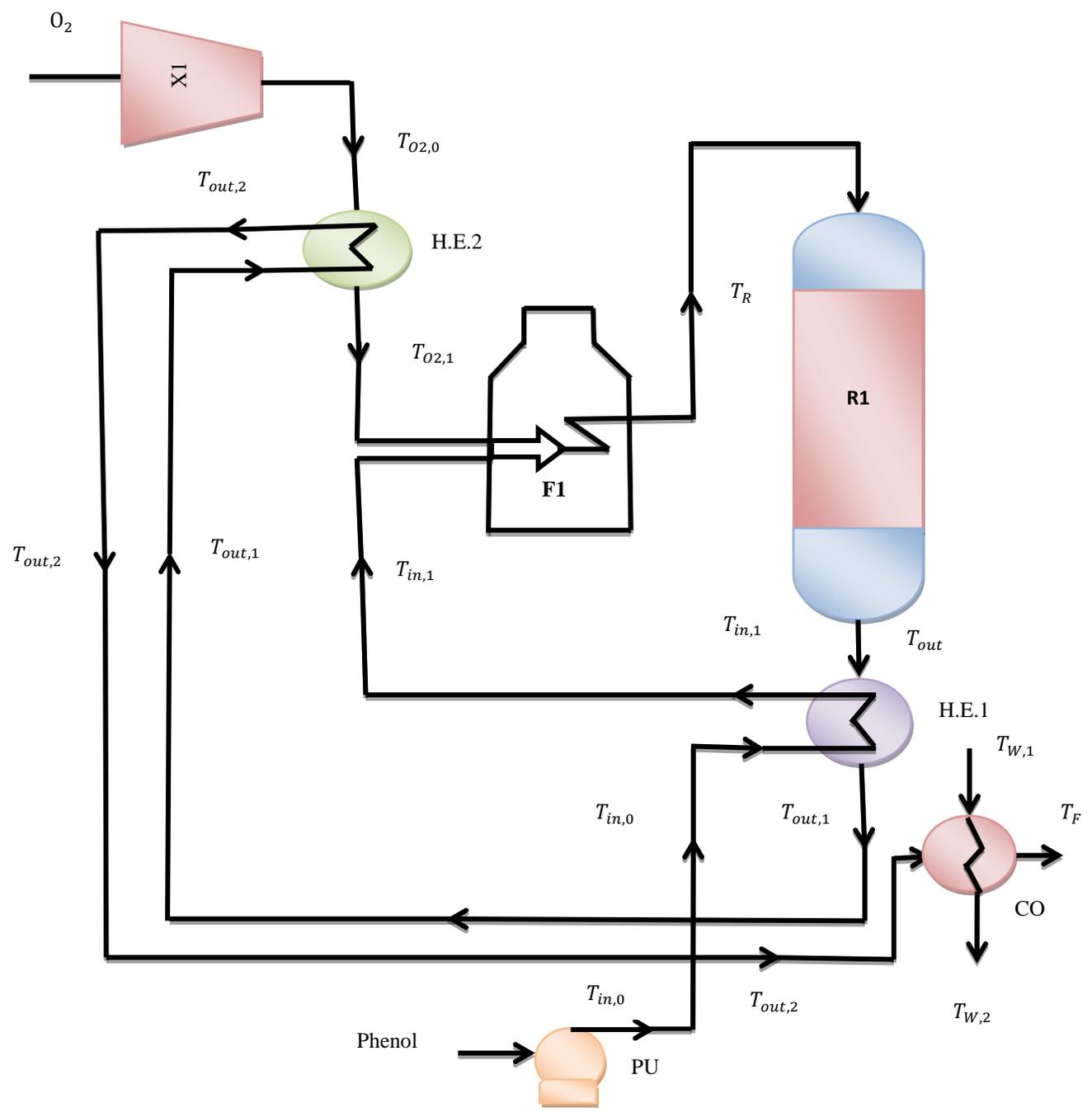


Figure 2

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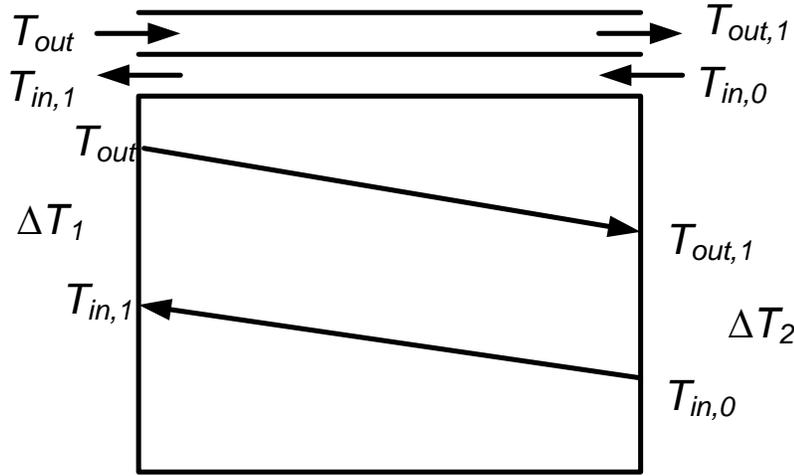
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602 **Figure 3a**

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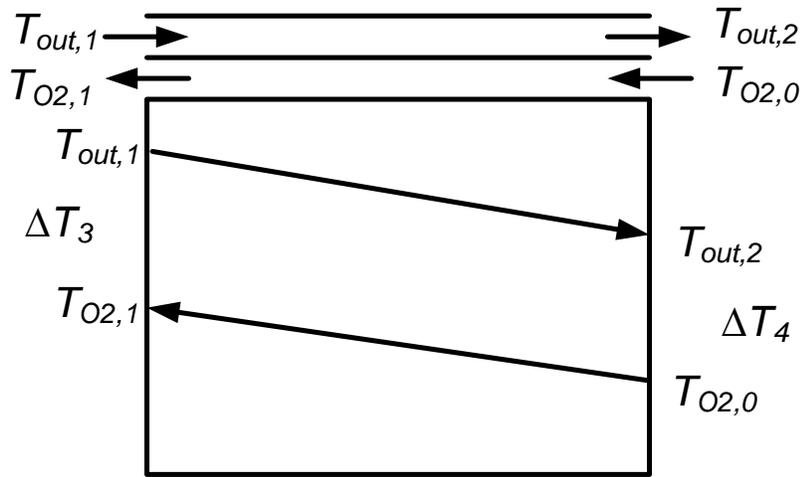
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611 **Figure 3b**

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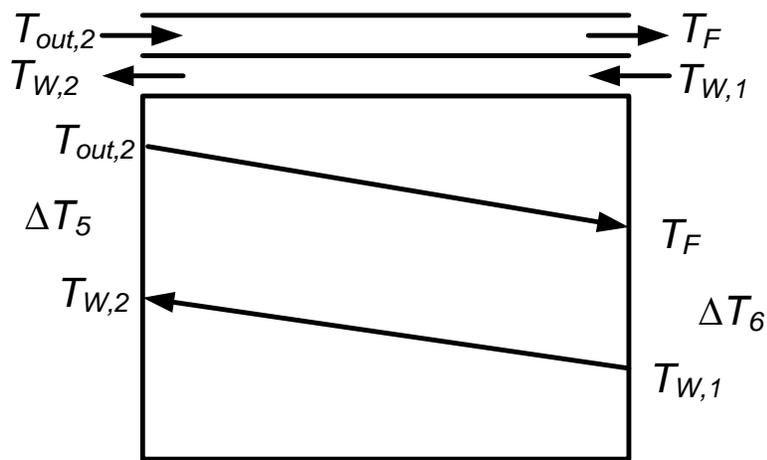
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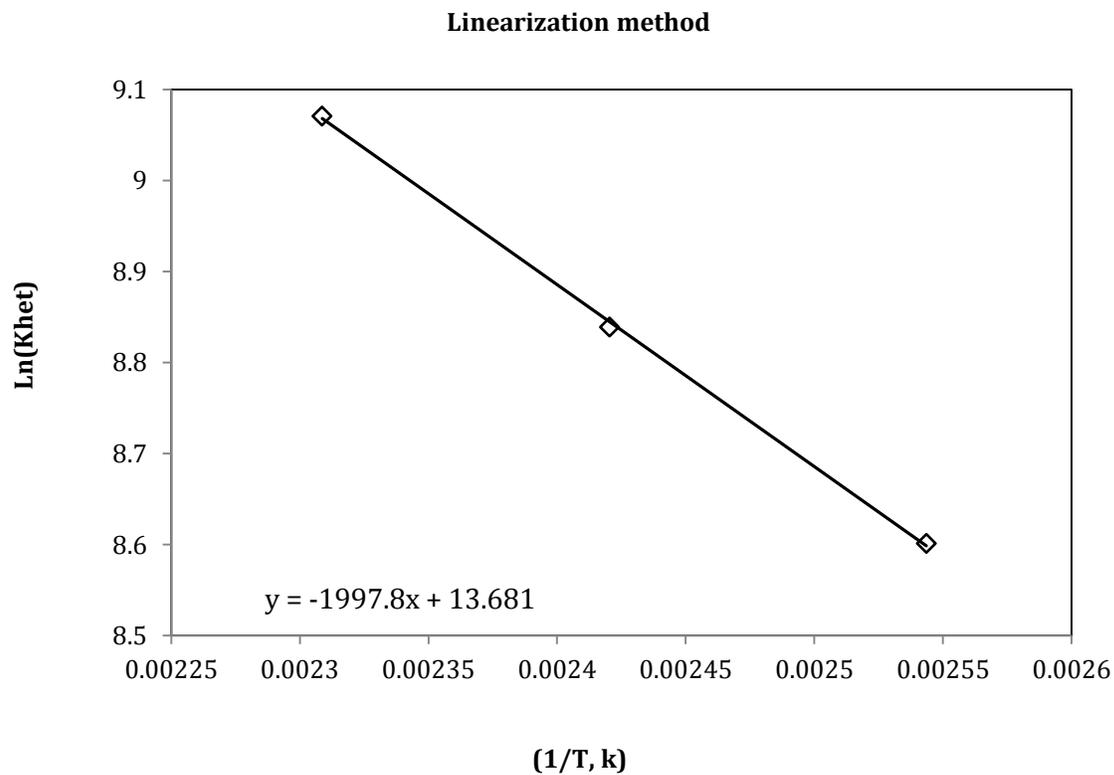
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619 **Figure 3c**

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628 **Figure 4**

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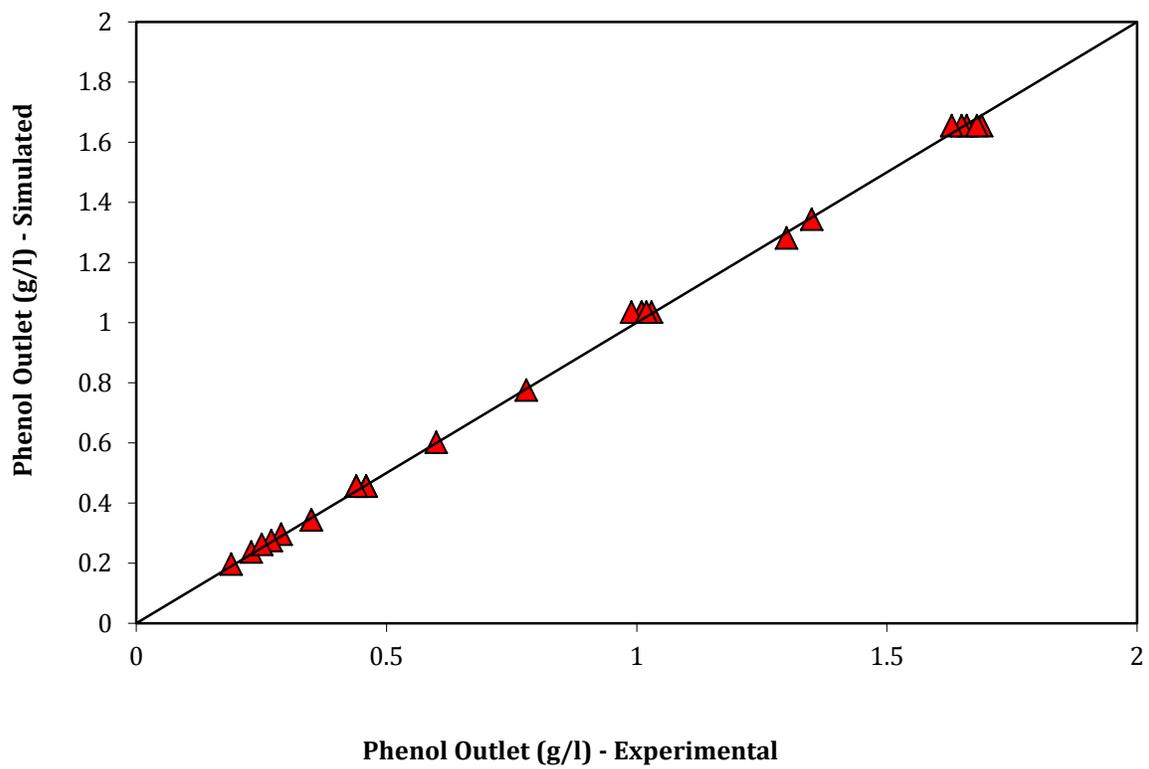
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644 **Figure 5**

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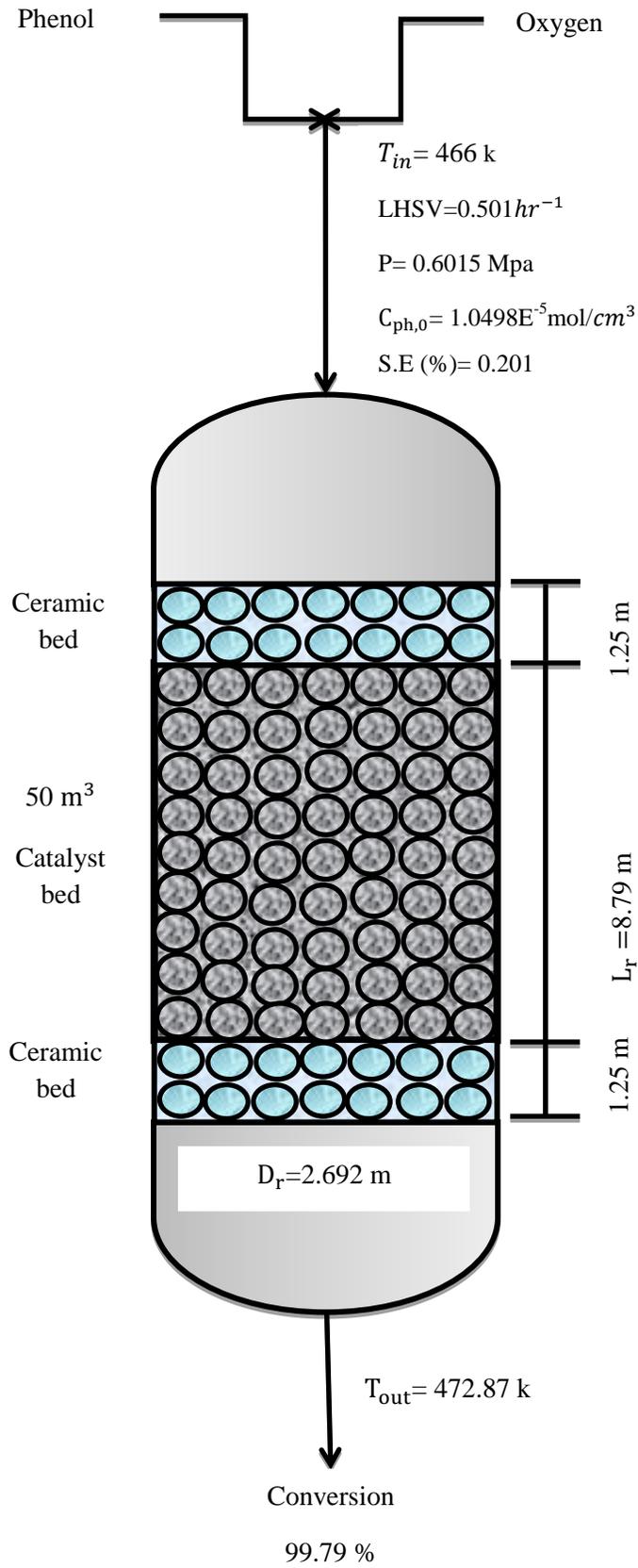
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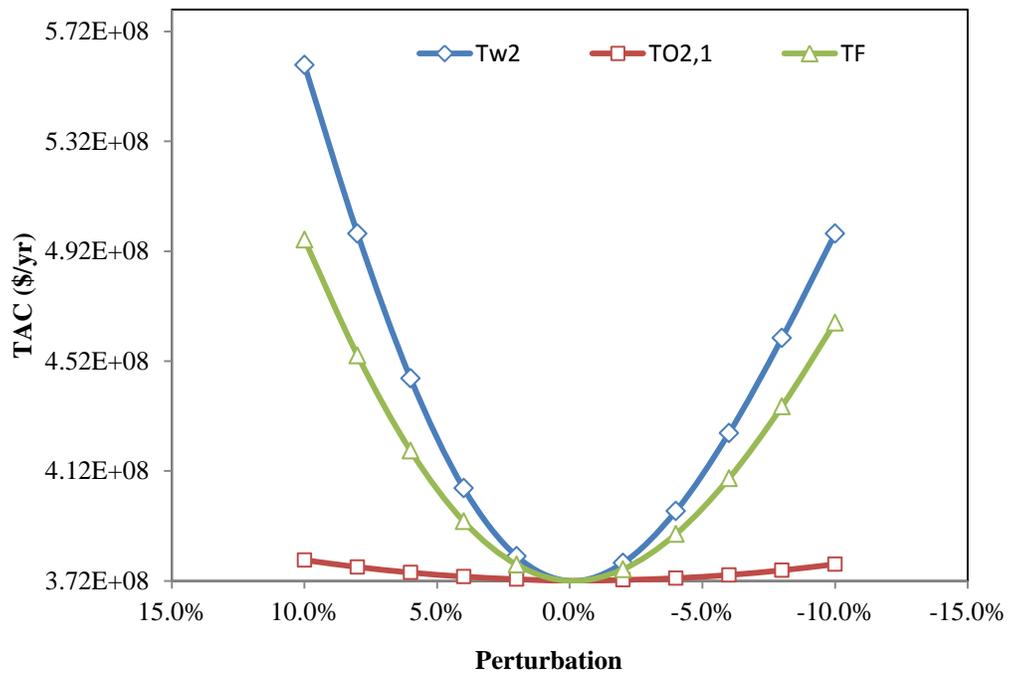
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**Figure 6**

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695 **Figure 7**

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