ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2228–2233. © Pleiades Publishing, Ltd., 2014.

Non-Isothermal Modeling of Glycerol Oxidation Reaction and Estimation of Thermodynamic Parameters[1]

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Received October 2, 2014

Abstract—The paper presents determination of adiabatic temperature rise during the oxidation of glycerol to glyceraldehyde with hydrogen peroxide in order for estimating its potential hazardous behavior. Estimation of enthalpy of the reaction was carried out by using thermodynamic tables and the bond energy method. The Non-isothermal reaction system for glycerol oxidation was described on the basis of a dynamic modeling proposal, considering the energy balance in the reactor to describe the final stage in the process of glycerol oxidation. The objectives of the present study were determination of the physic-mathematical model for glycerol oxidation, performance of the linearization of the proposed model and determination of transfer function for control purposes.

Keywords: bond energy, enthalpy of reaction, adiabatic temperature rise, non-isothermal reactor

DOI: 10.1134/S1070363214110310

INTRODUCTION

Optimization of glycerol utilization is of considerable importance for efficient processing of surplus glycerol generated by the biodiesel industry. Glycerol oxidation is one of the alternatives of glycerol processing because it leads to the diversity of fine chemicals [1]. Given the considerable quantities of glycerol produced in biodiesel manufacturing technologies, formation of contaminating by-products can be avoided by the use of electrodes (Pt, Au) or oxidation agents (N_2O, O_2, H_2O_2).

The efficient glycerol oxidation reaction can be performed only on the basis of deep knowledge of the process thermodynamic and kinetic parameters as well as heat release and transfer at laboratory and industrial level [2]. In the case of partial oxidation of glycerol it is necessary to carry out a chemical-engineering analysis for the particular reaction, formulate a quantitative reaction kinetics model based on the estimation of the reaction mechanism and determine whether the considered system is a lumped parameter model. This means that the state values are functions of time and thus the process is described by a system of total differential equations and a distributed parameter model in which the state values are not only functions of time, but also position. In the latter case the thermodynamic system is described by a system of partial differential equations [3]. Taking into account the practical aspect, it is necessary to determine the inputs, outputs and state values.

Such approach is important for designing a simple and effective control scheme of the process and maximizing the output.

This paper is devoted to analysis of oxidation of glycerol to glyceraldehyde by H_2O_2 and calculation of the adiabatic temperature rise and enthalpy of the reaction by two different methods in order to determine its potential hazardous behavior. Modeling of the dynamic system of glycerol oxidation under non-isothermal conditions was performed on the basis of energy balance in the reactor. The physico-mathematical model that describes the oxidation of glycerol and determination of transfer function for control purposes was reached.

[1] The text was submitted by the authors in English.

Table 1. Bond enthalpies for glycerol, H_2O_2, glyceraldehyde and H_2O [8–11]

Compound	Bond	Number of bonds	Bond enthalpy per bond, kJ/mol	Sum of bond enthalpies, kJ/mol	Net change, kJ/mol
Glycerol	C–H	5	414	2070	5197
	C–O	3	351	1053	
	O–H	3	460	1380	
	C–C	2	347	694	
H_2O_2	H–O	2	460	920	1062
	O–O	1	142	142	
Glyceraldehyde	C–H	4	414	1656	4712
	C–O	2	351	702	
	O–H	2	460	920	
	C–C	2	347	694	
	C=O	1	740	740	
H_2O	H–O	2	460	920	920

Thermodynamics parameters calculation. Estimation of enthalpy of the reaction by thermodynamic tables using Eq. (38) (see Experimental) is presented in Eq. (1).

$$\Delta H_r\text{, kJ/mol} = [-598.312 - 2(285.83)] - (-668.43 - 187.8) = -313.742. \quad (1)$$

Similarly, combining the bond energy method with the values obtained from Tables 1 and 2, enthalpy change of the reaction is estimated:

$$\Delta H_r\text{, kJ/mol} = \{[(91.7 + 5197) + (51.6 + 1062)] - [(88.11 + 4712) + 2(41 + 1840)]\} = -319.81. \quad (2)$$

It is evident that the values for ΔH_r obtained using thermodynamic tables and bond energy method are related accordingly. Considering that specific heat capacity values for glyceraldehyde and glycerol are similar (0.219 kJ mol^{-1} K^{-1}) [4] and that of H_2O is equal to 0.0752 kJ mol^{-1} K^{-1} [5], the value of $\overline{C}_p$ can be deduced from the Eq. (37) of the Experimental:

$$\overline{C}_{\text{p reacrion blend}}\text{, kJ mol}^{-1}\text{ K}^{-1} = 1/3(0.219) + 2/3(0.0752) = 0.123. \quad (3)$$

Therefore, in order to calculate the adiabatic temperature difference, the corresponding calculated values of ΔH_r and $\overline{C}_{\text{p reacrion blend}}$, $n_r = 3$ and $(\Delta H)^{\text{vap}}_{H_2O} =$ 40.72 kJ/mol are substituted in Eq. (36) according to Eq. (4):

$$\Delta T\text{, K} = \frac{319.81 - 2(40.72)}{3(0.123)} = 645.99. \quad (4)$$

The estimation of the adiabatic temperature rise in the course of glycerol oxidation reaction demonstrates the highly exothermic behavior and as a result, the risk aspect and danger of explosion. For this reason, estimation of the above value, mass and energy balance along with economic evaluation are essential in the design of a pilot plant.

Non-isothermal modeling of glycerol oxidation. For approaching the solution of Eq. (42) of the Experimental, there is assumed no variation of density, ($\rho_1 = \rho_2 = \rho$). The solution is reached with Eq. (5) to Eq. (17) for variation of reaction temperature over oxidation time.

$$\frac{dT}{dt} = \frac{a_G(\Delta H)^0_r G}{\rho C_p V} + \frac{\dot{V}}{V}(T_1 - T), \quad (5)$$

$$\frac{dT}{dt} = \frac{a_G(\Delta H)^0_r G + \rho C_p \dot{V}(T_1 - T)}{\rho C_p V}, \quad (6)$$

$$\int \frac{\rho C_p V dt}{a_G(\Delta H)^0_r G + \rho C_p \dot{V}(T_1 - T)} = \int dt, \quad (7)$$

$$\rho C_p V dt \int \frac{dt}{a_G(\Delta H)^0_r G + \rho C_p \dot{V}(T_1 - T)} = t, \quad (8)$$

Table 2. Enthalpy change due to the vaporization stage for glycerol, H_2O_2, glyceraldehyde, and H_2O [12]

Compound	ΔH_{vap}, kJ/mol
Glycerol	91.70
H_2O_2	51.60
Glyceraldehyde	88.11
H_2O	41.00

$$-\rho C_p V \frac{1}{\rho C_p V} \ln |\, a_G (\Delta H)_r^0 G + \rho C_p \dot{V} (T_1 - T)| + C = t, \quad (9)$$

$$-V \frac{1}{V} \ln |\, a_G (\Delta H)_r^0 G + \rho C_p \dot{V} (T_1 - T)| + C = t. \quad (10)$$

For calculation of constant C, it is considered that at zero time the input and output temperatures of cooling water are equal ($t = 0$, $T = T_1$).

$$-V \frac{1}{V} \ln |\, a_G (\Delta H)_r^0 G + \rho C_p \dot{V} (T_1 - T)| + C = 0,$$

$$C = \frac{V}{\dot{V}} \ln |\, a_G (\Delta H)_r^0 G|. \quad (11)$$

Substituting the value of constant C in Eq. (10) leads to:

$$-V \frac{1}{\dot{V}} \ln |\, a_G (\Delta H)_r^0 G + \rho C_p \dot{V} (T_1 - T)| + \frac{V}{\dot{V}} \ln |\, a_G (\Delta H)_r^0 G| = t, \quad (12)$$

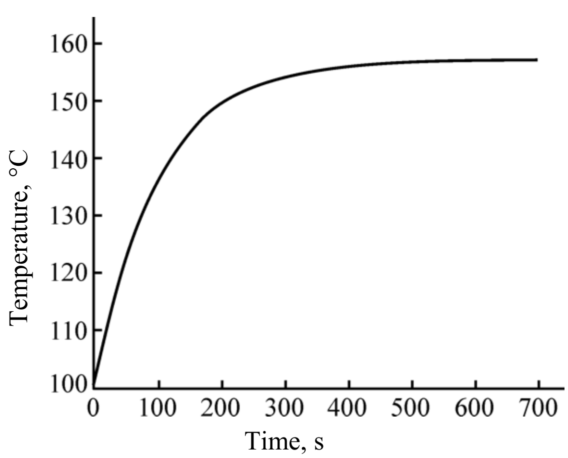

Fig. 1. Profile of temperature as function of time for glycerol oxidation to glyceraldehyde.

$$-\frac{V}{\dot{V}} \left\{ \ln |\, a_G (\Delta H)_r^0 G| + \ln \left| 1 + \frac{\rho C_p \dot{V} (T_1 - T)}{a_G (\Delta H)_r^0 G} \right| \right\} + \frac{V}{\dot{V}} \ln |\, a_G (\Delta H)_r^0 G| = t, \quad (13)$$

$$-\frac{V}{\dot{V}} \ln \left| 1 + \frac{\rho C_p \dot{V} (T_1 - T)}{a_G (\Delta H)_r^0 G} \right| = t, \quad (14)$$

$$-\frac{t\dot{V}}{V} = \ln \left| 1 + \frac{\rho C_p \dot{V} (T_1 - T)}{a_G (\Delta H)_r^0 G} \right|, \quad (15)$$

$$e^{-\frac{t\dot{V}}{V}} = 1 + \frac{\rho C_p \dot{V} (T_1 - T)}{a_G (\Delta H)_r^0 G}, \quad (16)$$

and solving for T:

$$T = \frac{a_G (\Delta H)_r^0 G}{\rho C_p \dot{V}} \left(1 - e^{-\frac{t\dot{V}}{V}} \right) + T_1. \quad (17)$$

The profile of temperature as function of time in glycerol oxidation to glyceraldehyde is represented by the above Eq. (17) and Fig. 1. The influence of a_G, time, and G on temperature is presented accordingly in Figs. 2 and 3. This system, as a real one, fulfils the strong physical condition of the feasibility (the outputs are functions only of the state variables). Considering the input variables as T_1, G, $\dot{V}$, and a_G, and the output variable as T, the system becomes:

$$\Delta \dot{X}_{1x1} = A_{1x1}\, \Delta X_{1x1} + B_{1x4}\, \Delta U_{4x1},$$

$$\Delta Y = \Delta X, \quad (18)$$

where A is the state matrix of dimension 1×1 and B is the control matrix of dimension 1×4. The elements of both matrices A and B correspond to the systems presented in Eqs. (19) and (20) respectively and are expressed in Eq. (21):

$$\frac{\partial f^0}{\partial T} = \frac{\dot{V}^0}{V} = a_{11}, \quad (19)$$

$$\frac{\partial f^0}{\partial T_1} = \frac{\dot{V}^0}{V} = b_{11}; \quad \frac{\partial f^0}{\partial G} = \frac{a_G^0 (\Delta H)_r^0 G}{\rho C_p V} = b_{12};$$

$$\frac{\partial f^0}{\partial \dot{V}} = \frac{T_1^0 - T^0}{V} = b_{13}; \quad \frac{(\Delta H)_r^0 G^0}{\rho C_p V} = b_{14}, \quad (20)$$

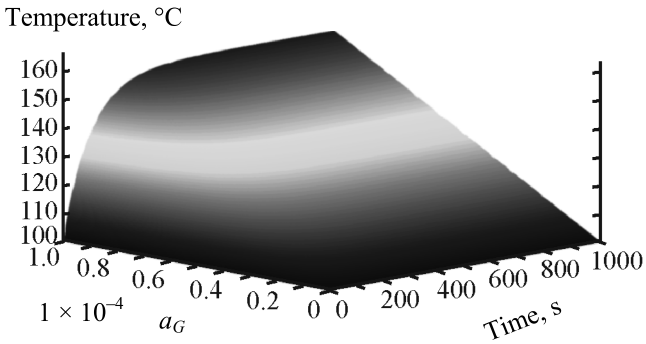

Fig. 2. Determination of reaction temperature during the oxidation reaction of glycerol to glyceraldehyde at different values of mass flow input of dilute glycerol.

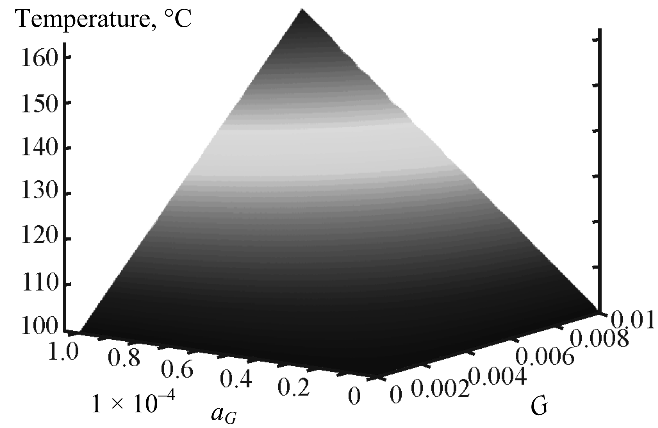

Fig. 3. Profile of reaction temperature as function of a_G and mass flow input of glycerol for glycerol oxidation to glyceraldehyde.

$$\Delta T^0 = -\frac{\dot{V}^0}{V}\,\Delta T + \begin{bmatrix} \dfrac{\dot{V}^0}{V} & \dfrac{a_G^0(\Delta H)_r^0}{\rho C_p V} & \dfrac{T_1^0 - T^0}{V} & \dfrac{(\Delta H)_r^0 G^0}{\rho C_p V} \end{bmatrix} \begin{bmatrix} \Delta T_1 \\ \Delta G \\ \Delta \dot{V} \\ \Delta a_G \end{bmatrix}. \quad (21)$$

The multiplication step leads to expression (22).

$$\frac{d\Delta T}{dt} = -\frac{\dot{V}^0}{V}\,\Delta T + \frac{\dot{V}^0}{V}\,\Delta T_1 + \frac{a_G^0(\Delta H)_r^0}{\rho C_p V}\,\Delta G + \frac{T_1^0 - T^0}{V}\,\Delta \dot{V} + \frac{(\Delta H)_r^0 G^0}{\rho C_p V}\,\Delta a_G\ . \quad (22)$$

For control purpose it is necessary to introduce the following dimensionless dependences, represented with "*":

$$\Delta T^* = \frac{\Delta T}{T^0};\ \Delta T_1{}^* = \frac{\Delta T_1}{T^0};\ \Delta G^* = \frac{\Delta G}{G^0};\ \Delta \dot{V}^* = \frac{\Delta \dot{V}}{\dot{V}^0};\ \Delta a_G{}^* = \frac{\Delta a_G}{a_G{}^0}. \quad (23)$$

Implementation of the above dimensionless relations in Eq. (22), followed by the multiplication of both sides of the equation by $V/(T^0V^0)$ gives:

$$\frac{d(\Delta T^* T^0)}{dt} = -\frac{V^0}{V}\,(\Delta T^* T^0) + \frac{V^0}{V}\,(\Delta T_1{}^* T^0) + \frac{a_G^0(\Delta H)_r^0}{\rho C_p V}\,(\Delta G^* G^0) + \frac{(T_1^0 - T^0)}{V}\,\Delta \dot{V}\dot{V}^0 + \frac{(\Delta H)_r^0 G^0}{\rho C_p V}\,\Delta a_G{}^* a_G{}^0, \quad (24)$$

$$\Delta \dot{T}^* = -(\Delta T^*) + (\Delta T_1{}^*) + \frac{a_G^0(\Delta H)_r^0}{T^0\dot{V}^0\rho C_p}\,(\Delta G^* G^0) + \frac{(T_1^0 - T^0)}{T^0}\,\Delta \dot{V} + \frac{(\Delta H)_r^0 G^0}{T^0\dot{V}^0\rho C_p}\,(\Delta a_G{}^* a_G{}^0). \quad (25)$$

This can be also expressed in matrix form as in Eq. (26).

$$\Delta \dot{T}^* = -[\Delta T^*] + \begin{bmatrix} 1 & \dfrac{a_G^0(\Delta H)_r^0 G^0}{T^0\dot{V}^0\rho C_p} & \dfrac{T^0{}_1 - T^0}{T^0} & \dfrac{(\Delta H)_r^0 G^0 a_G^0}{T^0\dot{V}^0\rho C_p} \end{bmatrix} \begin{bmatrix} \Delta T_1{}^* \\ \Delta G^* \\ \Delta \dot{V}^* \\ \Delta a_G{}^* \end{bmatrix}. \quad (26)$$

With elements A and B:

$$A^* = [-1],$$

$$B^* = \begin{bmatrix} 1 & \dfrac{a_G^0(\Delta H)_r^0 G^0}{T^0\dot{V}^0\rho C_p} & \dfrac{T^0{}_1 - T^0}{T^0} & \dfrac{(\Delta H)_r^0 G^0 a_G^0}{T^0\dot{V}^0\rho C_p} \end{bmatrix}. \quad (27)$$

In order to determine the transfer function to represent the dynamic system, it is required to obtain the Laplace Transform of expression (18) as presented in Eq. (28) to Eq. (32):

$$s\Delta X_L = A\Delta X_L + B\Delta U_L, \quad (28)$$

$$(s - A)\Delta X_L = B\Delta U_L, \quad (29)$$

$$\Delta X_L = \Delta Y_L, \quad (30)$$

$$(s - A)\Delta Y_L = B\Delta U_L, \quad (31)$$

$$(\Delta Y_L)/(\Delta U_L) = (s - A)^{-1}B. \quad (32)$$

The term $(\Delta Y_L)/(\Delta U_L)$, represents the relationship between the output and the input of the process. It is also known as the Transfer function. The substitution of Eq. (27) into Eq. (32) leads to expressions (33) and (34):

$$\frac{\Delta Y_L}{\Delta U_L} = G(s) = [s+1]^{-1}$$
$$\times\left[1 \quad \frac{a_G^0(\Delta H)_r^0 G^0}{T^0\dot{V}^0\rho C_p} \quad \frac{T^0{}_1 - T^0}{T^0} \quad \frac{(\Delta H)_r^0 G^0 a_G^0}{T^0\dot{V}^0\rho C_p}\right], \qquad (33)$$

$$G(s)$$
$$=\left[\frac{1}{(s+1)} \quad \frac{a_G^0(\Delta H)_r^0 G^0}{T^0\dot{V}^0\rho C_p(s+1)} \quad \frac{T^0{}_1 - T^0}{T^0(s+1)} \quad \frac{(\Delta H)_r^0 G^0 a_G^0}{T^0\dot{V}^0\rho C_p(s+1)}\right]. \qquad (34)$$

Estimation of adiabatic temperature rise during the highly exothermic reactions is the most common method for determination of hazardous behavior. According to the value obtained from Eq. (2), ΔH_r = –319.81 kJ/mol the partial oxidation of glycerol is highly exothermic reaction. In exothermic reactions the energy evolved may appear in many forms, but for practical purposes it is usually obtained in the form of heat. In view of several legal and economic implications of disastrous explosion and catastrophic effects it is essential to cool the reaction down to eliminate runaway conditions. So, intensive research has been performed for avoiding the danger of explosion by reducing the heat caused by the reaction [6]. If the heat released by the reaction is not removed fast enough, a severe non-uniform temperature distribution can occur within the reactor, which in turn can lead to different rates of reaction. The effect of heat and mass transfer becomes more important for faster reaction rates, when these become rate controlling in heterogeneous reactions. Temperature distribution can be controlled by varying the tube diameter, residence time and cooling rate.

Estimation of the transfer function is particularly important in the control of a chemical reactor calculated specifically for a non-isothermic reaction system. Such system implies higher oxidation and rate of conversion of glycerol. Another important indicator of the technology is the adiabatic temperature difference in the reaction mixture and it is necessary to know also the standard enthalpy of the reaction. The values are estimated from published thermodynamic tables and the bond energy using bond enthalpies, achieving very good agreement between the calculated values of heat of the reaction for both procedures.

EXPERIMENTAL

Estimation of thermodynamics parameters. In order to analyze variation of adiabatic temperature in the course of glycerol oxidation a reaction model using H_2O_2 is presented and discussed.

$$C_3H_8O_2 + H_2O_2 \rightarrow C_3H_6O_3 + 2H_2O. \qquad (35)$$

Calculation of adiabatic temperature difference of the reaction (35) is performed using Eq. (36):

$$\Delta T = \frac{-(\Delta H)_r - 2(\Delta H)_{H_2O}^{vap}}{n_r C_{p\ \text{reaction blend}}}. \qquad (36)$$

The term n_r corresponds to the number of mols in the reaction blend, C_p represents the specific heat of the reaction blend and can be calculated using Eq. (37). The numerator represents enthalpy of the reaction and enthalpy of vaporization of water (40.74 kJ/mol).

$$C_{p\ \text{reaction blend}} = (1/3)C_{p\ \text{glyceraldehyde}} + (2/3)C_p(H_2O). \qquad (37)$$

In order to evaluate the enthalpy change of the reaction ΔH_r, two different methods are discussed. The first one involves the use of values obtained from thermodynamic tables and the second method applies the bond energy. Based on thermodynamic tables [7], values of the energy of formation ΔH_f of glycerol (–668.43 kJ/mol), glyceraldehyde (598.312 kJ/mol), H_2O_2 (–187.8 kJ/mol), and H_2O (–285.83 kJ/mol) were applied in Eq. (38) to calculate enthalpy of the reaction. In this equation n and m stand for the number of reactants and products respectively.

$$(\Delta H)_r = \sum_{i=1}^{n} (\Delta H)_{f\ \text{products}}^{298\ \text{K}} - \sum_{i=1}^{m} (\Delta H)_{f\ \text{reactants}}^{298\ \text{K}}. \qquad (38)$$

The second procedure involved the Eq. (39).

$$(\Delta H)_r = \sum_{i=1}^{n} (\Delta H)_{\text{bonds broken}} - \sum_{i=1}^{m} (\Delta H)_{\text{bonds formed}}. \qquad (39)$$

The bond enthalpies are presented in Table 1.

Table 2 exhibits the values of enthalpy change in vaporization stage ΔH_{vap} (kJ/mol).

Non-isothermal modeling of glycerol oxidation. A linear mathematical model including input, output and inner-state variables for oxidation of glycerol is proposed to describe the final stage in the process. In this model the heat transfer between the coolant and the reactor can be determined using the enthalpy values of the oxidation reaction, the mass flow input of glycerol, the volume flow rate, the mass fraction of pure glycerol in the mass flow, and the input

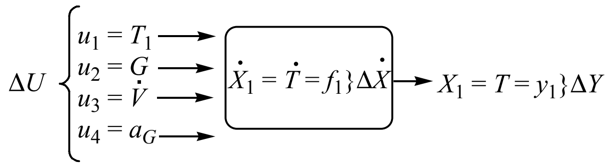

Fig. 4. Scheme of the system presenting the input, state variables and output.

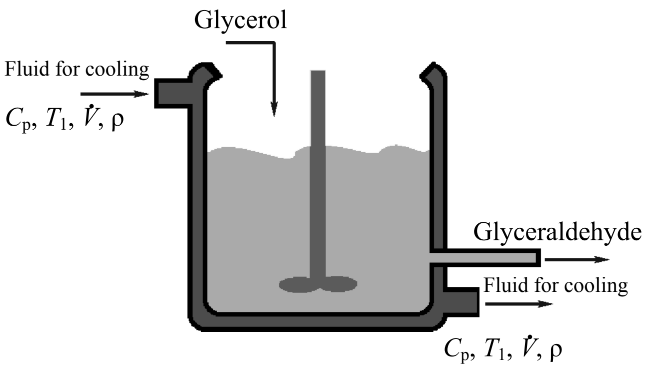

Fig. 5. Scheme of the chemical reactor for oxidation of glycerol considering glyceraldehyde as the main product.

temperature of coolant as input parameters. The diagram of the system is presented in Fig. 4. The analog nonlinear system is presented by Eqs. (40).

$$\dot{X} = F(X, U);\ Y = G(X, U), \tag{40}$$

where X is the state vector, U is the input vector, Y is the output vector, F and G are vectors functions, and $\dot{X}$ is time derivative from state variables as presented in Eq. (41).

$$\dot{X} = dX/dt. \tag{41}$$

The reactor configuration is presented in Fig. 5. Considering a non-isothermal system, in order to approach the modeling of the glycerol oxidation reaction, it is necessary to perform an energy balance as presented in Eq. (42).

$$G\Delta H_r^0 a_G + \rho_1 \dot{V} T_1 C_p = \dot{V}\rho_2 C_p T + \rho_2 C_p V(dT/dt), \tag{42}$$

where G is the mass flow input of dilute glycerol (kg/s), ΔH_r^0 is the enthalpy of the oxidation reaction of glycerol to glyceraldehyde (J/kg), a_G is the mass fraction of pure glycerol in the mass flow, ρ is density (kg/m^3), $\dot{V}$ the volume flow rate (m^3/s), T_1 and T the input and output temperatures of the cooling water (°C) respectively, C_p is the specific heat (J deg^{-1} kg^{-1}), V is the volume of reactor (m^3), and t is time (s). Solution of the above equation leads to estimation of the temperature profile, which can be applied also to evaluation of the influence that any input parameter has on temperature response at different intervals of time.

CONCLUSIONS

In the present research the adiabatic temperature change in the course of oxidation of glycerol is studied. The reaction is exothermic which makes the control of temperature to be essential to guarantee safety of the process, particularly at the industrial scale. For this purpose, a mathematical model is proposed. The transfer function describes the system and represents the relation between the input parameters and the response (variation of temperature) during the exothermic reaction.

ACKNOWLEDGMENTS

The project was financially supported by the European Regional Development Fund under the Project CEBIA-Tech no. CZ.1.05/2.1.00/03.0089 and Tomas Bata University Internal Grant (IGA/FAI/2014/011). J.C.B-P. author also thanks the doctoral scholarship provided by the National Council of Science and Technology (CONACYT) in Mexico.

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