Development of a catalytic model system using nitrous oxide

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Abstract: - Currently, special attention is paid to partial oxidation of several sugar alcohols because it generates oxidation intermediate products with high utility value. In the present paper, we study the modelling of oxidation reaction of 1,2,3 propanotriol using an oxidizing agent in low concentrations. A major problem of such oxidation system is its low reactivity and high oxidation reactivity of products, As a result, the yield to a specific compound (i.e. dihydroxypropanal) depends on the ratio of rate constants of the consecutive reactions and also on the initial concentration of oxidizing agent. In this case, as the input value for the model calculations we chose a ratio of values of the specified rate constants and initial concentrations of nitrous oxide and 1,2,3-propanotriol. Accordingly, an experimental setup was proposed to follow the variation of temperature of the reaction blend after gradual addition of ammonium nitrate to a solution of 1,2,3 propanotriol, which can provide insights for the control of the chemical reactor.

Key-Words: - Nitrous oxide, oxidation, 1,2,3 propanotriol, dihydroxypropanal, mathematical model, control,

1 Introduction

The process of alcohol oxidation is characterized by the formation of a C-O bond and breaking of a C-H bond on the same carbon, causing a change of a bond between carbon and hydrogen, which is less electronegative, for an Oxygen atom, which is more electronegative. When only one bond of C-O is formed and one bond of C-H is broken, the product formed is an aldehyde or a ketone but in case strong oxidant is used, two oxidations can occur at the same carbon atom, and as a result, there is formation of two new C-O bonds and two C-H bonds are broken [1]. If the strong oxidant is used in primary alcohols it leads to carboxilic acids formation, with an increament in the oxidation state on carbon, while oxidation of secondary alcohols leads to ketones. As a result, no oxidation reaction occurs in tertiary alcohols [2].

These types of reactions are widely used in industry and laboratory. Additionally, they also occur in biological systems. Oxidation of alcohols using several reagents has been discussed before [3]–[7]. Some examples of these catalysts are Collins reagent, Fétizon's reagent (Silver carbonate, Ag_2CO_3 precipitated on Celite) the Swern oxidation, chromium trioxide-pyridine complex, DMSO-based oxidants, Dess-Martin Periodinane, o-Iodoxybenzoic acid and Nitrous oxide. These reagents are able to perform the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. Some of them are soluble in nonpolar solvents such as refluxing benzene or CH_2Cl_2, avoiding the formation of the hydrate and thus, allowing the oxidation to be stopped at the aldehyde. The use of an excess of alcohol and separation of aldehydes from the reaction mixture by distillation are methods that are commonly used to perform partial oxidation and avoid further oxidation steps [8].

On the contrary, reagents like alkaline potassium permanganate solution, hot concentrated HNO_3 and chromic acid solutions (H_2CrO_4 prepared *in situ* from CrO_3 with aqueous H_2SO_4, or Na_2CrO_7 with aqueous H_2SO_4) are considered strong oxidizing agents that generally lead to overoxidation of alcohols to carboxylic acids [9] unless they are used in mild conditions, like ruthenium tetroxide, which yields aldehydes with good selectivity.

Permanganate used in excess in acid (homogeneous reaction with acetic acid) or alkali (heterogenous reaction) yields aldehydes and ketones. The possible reaction mechanism occurs by hydride ion transfer from the alkoxide ion to permanganate ion. This has been proved by observing an isotope effect during the oxidation of benzyhydrol to benzophenone in which the first step was suggested to be the ionization of the alcohol followed by a number of rate-determining steps [10]. From the thermodynamic point of view, the oxidation of secondary alcohols is favored over primary ones as the oxidation potential of aldehydes

is normally higher than ketones [11]. The alkaline solution of the silver-ammonia complex ion is a mild oxidizing agent commonly used in qualitative analysis of aldehydes to distinguish from ketones. Other compound used in aldehyde identification is Tollens reagent, which contains a copper (II) complex ion and oxidize aliphatic aldehydes after reduction to copper (I).

Nitrous oxide (Fig. 1) is a non-toxic compound with broad applications in medicine due to its anaesthetic and analgesic effects and after CO_2 and CH_4, is the third most abundant minor component of the atmosphere and together with freon and ozone plays an important role in providing earth's thermal balance [10]. The natural production of N_2O in aerobic and anaerobic biological processes is by means of denitrification. At industrial scale, is produced by decomposition of ammonim nitrate at high temperatures. Recently it has also been used as oxidizer in propellant in rocket motors, as food additive in aerosol spray propellant, as analgesic in dentistry and surgery.
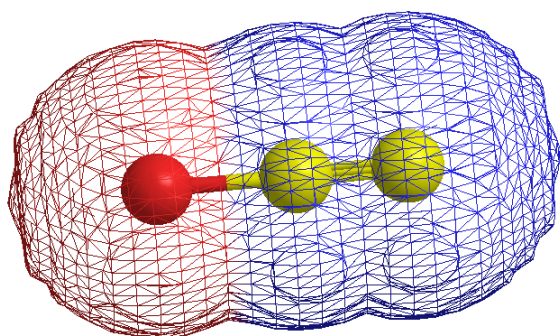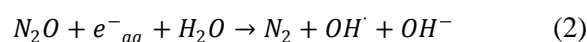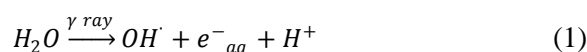

Fig.1 Chemical structure of Nitrous oxide molecule showing the solvent accessibility.

In heterogenous catalysis, several metal oxides have been extensively used in chemical reactions. Among the most effective catalysts are iron-containing acidic zeolites which yield surface-activated iron-oxo species (α-Oxygen). Ohtani reported that the oxidation of organic compounds at room temperature can be performed by the reductive decomposition of N_2O to produce hydroxyl radical ($\cdot OH$) selectively, however it is observed only under limited reaction conditions, such as γ-radiolysis, photolisis or electrolisis [12]. N_2O is used as a trap for hydrated electron as well as hydroxyl radical ($\cdot OH$) generated by γ-radiolysis of water via reactions (1) and (2)

$$H_2O \xrightarrow{\gamma\, ray} OH^{\cdot} + e^{-}{}_{aq} + H^{+} \qquad (1)$$

$$N_2O + e^{-}{}_{aq} + H_2O \rightarrow N_2 + OH^{\cdot} + OH^{-} \qquad (2)$$

Generally, chemical reactions are accompanied by various relatively complex simultaneous reactions resulting in a complicated blend of intermediate products. As a general model, the oxidation reaction of sugar alcohols (S) using nitrous oxide (N) for the production of derivatives (A) and (B) in isothermal conditions is discussed next. The diagram of the system is presented in Fig. 2 having three inputs (F, C_{N0}, and C_{S0}), four state variables (A, N, S and B) and four output variables (A, N, S, and B) [13]–[17].
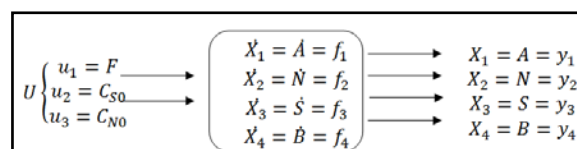

Fig.2 Scheme of the oxidation of 1,2,3 propanotriol with N_2O describing the input, state variable and output.

2 Experimental

Experimentally, the oxidation reaction is performed as described in Fig.3. Briefly, the reactant is heated at 202 °C and ammonium nitrate is added while monitoring the reaction temperature. The minimum and maximum temperature registered after the addition. This information is described in Table 1 and Fig.4. Accordingly, to understand the thermodynamics of the reaction, it is important to use the values of the enthalpy of formation to calculate the reaction enthalpy, adiabatic heat, specific heat of reaction mixture and finally adiabatic heat temperature of the reaction for safety purposes.
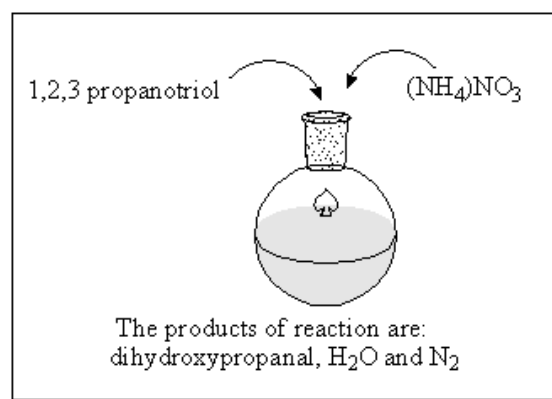

Fig.3 Reaction procedure for oxidation of 1,2,3 propanotriol with $(NH_4)NO_3$.

Table 1. Record of temperature variation after addition of NH_4NO_3

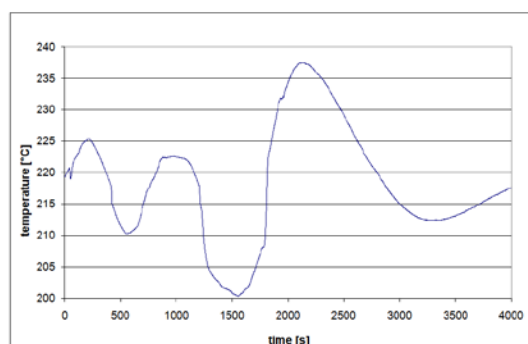| m[g]	t_{min} [°C]	t_{max} [°C]
0,62	206	218
0,52	210	215
0,53	203	213
0,55	206	214
0,53	208	220
0,51	212	223
0,51	211	221
0,49	203	216
0,50	210	220
0,51	213	223
0,48	211	225
0,51	211	226
0,48	212	223
0,53	208	218
0,50	200	214
0,52	206	220

Fig.4 Temperature profile versus time of addition for the oxidation of 1,2,3 propanotriol in ammonium nitrate.

3 Mathematical model of oxidation reaction with N_2O

The consecutive irreversible reaction carried out in a reactor can be described by the next equations

$$S + N \xrightarrow{k_1} A \qquad (3)$$

$$A + N \xrightarrow{k_2} B \qquad (4)$$

The simple mole balances for sugar alcohol (S) and product derivative (A) are:

$$\frac{dS}{dt} = -k_1 \cdot S \cdot N \qquad (5)$$

$$\frac{dA}{dt} = k_1 \cdot S \cdot N - k_2 \cdot A \cdot N \qquad (6)$$

Dividing dA/dt by dS/dt

$$\frac{dA}{dS} - \frac{k_2 \cdot A}{k_1 \cdot S} = -1 \qquad (7)$$

If we change A/S for v, then:

$$A = vS \qquad (8)$$

$$\frac{dA}{dS} = v\frac{dS}{dS} + S\frac{dv}{dS} = v + S\frac{dv}{dS} \qquad (9)$$

Proceeding to substitute the new variables into the differential equation

$$v + S\frac{dv}{dS} - \frac{k_2}{k_1}v = -1 \qquad (10)$$

$$\frac{dv}{-1-v\left(1-\frac{k_2}{k_1}\right)} = \frac{dS}{S} \qquad (11)$$

The previous equation is integrated, rearranged and after substitution of v for A/S, we obtain

$$S^{\frac{k_1}{k_2-k_1}} = \left(\left[\frac{k_2}{k_1} - 1\right]\frac{A}{S} - 1\right)c \qquad (12)$$

$$A = \left(cS^{\frac{k_1}{k_2-k_1}} + 1\right)\frac{S}{\frac{k_2}{k_1}-1} \qquad (13)$$

The value of c (integration constant) is obtained after application of boundary conditions $A=A_0=0$, $S=S_0=1$

$$c = \left[\frac{AS}{\frac{k_2-k_1}{k_1}} - 1\right]\bigg/ S^{\frac{k_1}{k_2-k_1}} \qquad (14)$$

$$c = -\frac{1}{1^{\frac{k_1}{k_2-k_1}}} \qquad (15)$$

Hence, the number of moles of A in terms of S is

$$A = \left(-\frac{1}{1^{\frac{k_1}{k_2-k_1}}}S^{\frac{k_1}{k_2-k_1}} + 1\right)\frac{S}{\frac{k_2}{k_1}-1} \qquad (16)$$

For a ratio of $k_2/k_1 = 2$

$$A = (-S + 1)S \qquad (17)$$

The mole balance for product B in terms of S and A is calculated as described next:

$$B = B_0 + S_0 + A_0 - S - A \qquad (18)$$

While the mole balance for N in terms of S and A is

$$N = N_0 - (S_0 - S) - [S_0 - S + A_0 - A] \quad (19)$$

Then, the total mole balance (M) is

$$M = S + N + A + B \quad (20)$$

As an example, of these modeling, if we consider that we add double amount of oxidant (N_0) to the initial amount of alcohol ($S_0=1$ mol), when the alcohol concentration has decreased to $S=0.5$, then the concentration of alcohol and products can be calculated as:

$$A = (-0.5 + 1)(0.5) = 0.25 \quad (21)$$
$$B = 0 + 1 + 0 - 0.5 - 0.25 = 0.25 \quad (22)$$
$$N = 2 - (1 - 0.5) - [1 - 0.5 + 0 - 0.25] = 1.25 \quad (23)$$
$$M = 0.5 + 1.25 + 0.25 + 0.25 = 2.25 \quad (24)$$

Accordingly, from the parameters described in Fig.2, the set of equations that describe the mass balance, including of chemical reactions in which are supposed to be of the first order mechanism, of the components is presented in (25) to (28)

$$\frac{dA}{dt} = k_1 \cdot S \cdot N - k_2 \cdot A \cdot N - \frac{F}{V}A \quad (25)$$
$$\frac{dN}{dt} = -k_1 \cdot S \cdot N - k_2 \cdot A \cdot N + \frac{F}{V}C_{N0} - \frac{F}{V}N \quad (26)$$
$$\frac{dS}{dt} = -k_1 \cdot S \cdot N + \frac{F}{V}C_{S0} - \frac{F}{V}S \quad (27)$$
$$\frac{dB}{dt} = k_2 \cdot A \cdot N - \frac{F}{V}B \quad (28)$$

The described system is non-linear. The elements of matrix A, B, are the following [18]–[20]:

$$a_{11} = \frac{\partial f_1^0}{\partial A} = -k_2 N^0 - \frac{F^0}{V}; a_{12} = \frac{\partial f_1^0}{\partial N} = k_1 S^0 - k_2 A^0; a_{13} = \frac{\partial f_1^0}{\partial S} = k_1 N^0; a_{14} = \frac{\partial f_1^0}{\partial B} = 0 \quad (29)$$

$$a_{21} = \frac{\partial f_2^0}{\partial A} = -k_2 N^0; a_{22} = \frac{\partial f_2^0}{\partial N} = -k_1 S^0 - k_2 A^0 - \frac{F^0}{V}; a_{23} \frac{\partial f_2^0}{\partial S} = -k_1 N^0; a_{24} = \frac{\partial f_2^0}{\partial B} = 0 \quad (30)$$

$$a_{31} = \frac{\partial f_3^0}{\partial A} = 0; a_{32} = \frac{\partial f_3^0}{\partial N} = -k_1 S^0; a_{33} = \frac{\partial f_3^0}{\partial S} = -k_1 N^0 - \frac{F^0}{V}; a_{34} = \frac{\partial f_3^0}{\partial B} = 0 \quad (31)$$

$$a_{41} = \frac{\partial f_4^0}{\partial A} = k_2 N^0; a_{42} = \frac{\partial f_4^0}{\partial N} = k_2 A^0; a_{43} = \frac{\partial f_4^0}{\partial S} = 0; a_{44} = \frac{\partial f_4^0}{\partial B} = -\frac{F^0}{V} \quad (32)$$

Considering the control variables, equations (11) to (14) are obtained:

$$b_{11} = \frac{\partial f_1^0}{\partial F} = -\frac{A^0}{V}; b_{12} = \frac{\partial f_1^0}{\partial C_{S0}} = 0; b_{13} = \frac{\partial f_1^0}{\partial C_{N0}} = 0 \quad (33)$$

$$b_{21} = \frac{\partial f_2^0}{\partial F} = \frac{(C_{N0} - N^0)}{V}; b_{22} = \frac{\partial f_2^0}{\partial C_{S0}} = 0; b_{23} = \frac{\partial f_2^0}{\partial C_{N0}} = \frac{F^\circ}{V} \quad (34)$$

$$b_{31} = \frac{\partial f_3^0}{\partial F} = \frac{(C_{S0} - S^0)}{V}; b_{32} = \frac{\partial f_3^0}{\partial C_{S0}} = \frac{F^\circ}{V}; b_{33} = \frac{\partial f_3^0}{\partial C_{N0}} = 0 \quad (35)$$

$$b_{41} = \frac{\partial f_4^0}{\partial F} = -\frac{B^0}{V}; b_{42} = \frac{\partial f_4^0}{\partial C_{S0}} = 0; b_{43} = \frac{\partial f_1^0}{\partial C_{N0}} = 0 \quad (36)$$

Therefore, the representation of the state vector is given by:

$$\begin{pmatrix} \frac{dA}{dt} \\ \frac{dN}{dt} \\ \frac{dS}{dt} \\ \frac{dB}{dt} \end{pmatrix} = $$

$$\begin{pmatrix} -\left(k_2 N^0 + \frac{F^\circ}{V}\right) & k_1 S^0 - k_2 A^0 & k_1 N^0 & 0 \\ -k_2 N^0 & -\left(k_1 S^0 + k_2 A^0 + \frac{F^\circ}{V}\right) & k_1 N^0 & 0 \\ 0 & -k_1 S^0 & -\left(k_1 N^0 + \frac{F^\circ}{V}\right) & 0 \\ k_2 N^0 & k_2 A^0 & 0 & -\frac{F^\circ}{V} \end{pmatrix} \begin{pmatrix} \Delta A \\ \Delta N \\ \Delta S \\ \Delta B \end{pmatrix} +$$

$$\begin{pmatrix} -\frac{A^0}{V} & 0 & 0 \\ \frac{(C_{N0} - N^0)}{V} & 0 & \frac{F^\circ}{V} \\ \frac{(C_{S0} - S^0)}{V} & \frac{F^\circ}{V} & 0 \\ -\frac{B^0}{V} & 0 & 0 \end{pmatrix} \begin{pmatrix} \Delta F \\ \Delta C_{S0} \\ \Delta C_{N0} \end{pmatrix} \quad (37)$$

The multiplication procedure leads to the next group of equations:

$$\frac{d\Delta A}{dt} = -\left(k_2 N^0 + \frac{F^\circ}{V}\right)\Delta A + (k_1 S^0 - k_2 A^0)\Delta N + (k_1 N^0)\Delta S - \frac{A^0}{V}\Delta F \quad (38)$$

$$\frac{d\Delta N}{dt} = -(k_2 N^0)\Delta A - \left(k_1 S^0 + k_2 A^0 + \frac{F^\circ}{V}\right)\Delta N + (k_1 N^0)\Delta S + \frac{(C_{N0} - N^0)}{V}\Delta F + \frac{F^\circ}{V}\Delta C_{N0} \quad (39)$$

$$\frac{d\Delta S}{dt} = -(k_1 S^0)\Delta A - \left(k_1 N^0 + \frac{F^\circ}{V}\right)\Delta S + \frac{1}{V}(C_{S0} - S^0)\Delta F + \frac{F^\circ}{V}\Delta C_{S0} \quad (40)$$

$$\frac{d\Delta B}{dt} = (k_2 N^0)\Delta A + (k_2 A^0)\Delta N - \left(\frac{F^\circ}{V}\right)\Delta B - \left(\frac{B^0}{V}\right)\Delta F \quad (41)$$

For the purpose of control, it is necessary to introduce the following dimensionless parameters

$$A^* = \frac{A}{S^0} \therefore A = A^* \cdot S^0 \tag{42}$$

$$N^* = \frac{N}{N^0} \therefore N = N^* \cdot N^0 \tag{43}$$

$$S^* = \frac{S}{S^0} \therefore S = S^* \cdot S^0 \tag{44}$$

$$B^* = \frac{B}{S^0} \therefore B = B^* \cdot S^0 \tag{45}$$

$$F^* = \frac{F}{F^0} \therefore F = F^* \cdot F^0$$

$$C_{S0}{}^* = \frac{C_{S0}}{S^0} \therefore C_{S0} = C_{S0}{}^* \cdot S^0 \tag{46}$$

$$C_{N0}{}^* = \frac{C_{N0}}{N^0} \therefore C_{N0} = C_{N0}{}^* \cdot N^0$$

After substitution of dimensionless dependencies, equations (25) to (28) are obtained:

$$\frac{d\Delta A^* \cdot S^0}{dt} = -\left(k_2 N^0 + \frac{F^\circ}{V}\right)\Delta A^* \cdot S^0 + (k_1 S^0 - k_2 A^0)\Delta N^* \cdot N^0 + (k_1 N^0)\Delta S^* \cdot S^0 - \frac{A^0}{V}\Delta F^* \cdot F^0 \tag{47}$$

$$\frac{d\Delta N^* \cdot N^0}{dt} = -(k_2 N^0)\Delta A^* \cdot S^0 - \left(k_1 S^0 + k_2 A^0 + \frac{F^\circ}{V}\right)\Delta N^* \cdot N^0 + (k_1 N^0)\Delta S^* \cdot S^0 + \frac{(C_{N0} - N^0)}{V}\Delta F^* \cdot F^0 + \frac{F^\circ}{V}\Delta C_{N0}{}^* \cdot N^0 \tag{48}$$

$$\frac{d\Delta S^* \cdot S^0}{dt} = -(k_1 S^0)\Delta A^* \cdot S^0 - \left(k_1 N^0 + \frac{F^\circ}{V}\right)\Delta S^* \cdot S^0 + \frac{1}{V}(C_{S0} - S^0)\Delta F^* \cdot F^0 + \frac{F^\circ}{V}\Delta C_{S0}{}^* \cdot S^0 \tag{49}$$

$$\frac{d\Delta B^* \cdot S^0}{dt} = (k_2 N^0)\Delta A^* \cdot S^0 + (k_2 A^0)\Delta N^* \cdot N^0 - \left(\frac{F^\circ}{V}\right)\Delta B^* \cdot S^0 - \left(\frac{B^0}{V}\right)\Delta F^* \cdot F^0 \tag{50}$$

Accordingly, multiplying either by $V/F^0 G^0$ or by $V/F^0 N^0$, the next sets of equations are obtained:

$$\frac{d\Delta A^*}{dt^*} = -\left(\frac{k_2 N^0 V}{F^0} + 1\right)\Delta A^* + \left(\frac{V k_1 N^0}{F^0} - \frac{V k_2 A^0 N^0}{F^0 S^0}\right)\Delta N^* + \frac{V k_1 N^0}{F^0}\Delta S^* - \frac{A^0}{S^0}\Delta F^* \tag{51}$$

$$\frac{d\Delta N^*}{dt^*} = -\frac{V k_2 S^0}{F^0}\Delta A^* - \left(\frac{V k_1 S^0}{F^0} + \frac{V k_2 A^0}{F^0} + 1\right)\Delta N^* + \frac{V k_1 S^0}{F^0}\Delta S^* + \frac{(C_{N0} - N^0)}{N^0}\Delta F^* + \Delta C_{N0}{}^* \tag{52}$$

$$\frac{d\Delta G^*}{dt^*} = -\frac{V k_1 G^0}{F^0}\Delta A^* - \left(\frac{V k_1 N^0}{F^0} + 1\right)\Delta S^* + \frac{(C_{S0} - S^0)}{S^0}\Delta F^* + \Delta C_{S0}{}^* \tag{53}$$

$$\frac{d\Delta B^*}{dt^*} = \frac{V k_2 N^0}{F^0}\Delta A^* + \frac{V k_2 A^0 N^0}{F^0 S^0}\Delta N^* - \Delta B^* - \frac{B^0}{S^0}\Delta F^* \tag{54}$$

where the term $t^* = \left(F^\circ \cdot t/V\right)$ implies a dimensionless parameter (dimensionless time). As a result, the system transforms into (55)

$$
\begin{pmatrix} \frac{d\Delta A^*}{dt^*} \\ \frac{d\Delta N^*}{dt^*} \\ \frac{d\Delta S^*}{dt^*} \\ \frac{d\Delta B^*}{dt^*} \end{pmatrix}
= \begin{pmatrix}
-\left(\frac{V k_2 N^0}{F^\circ}+1\right) & \frac{V k_1 N^0}{F^0} - \frac{V k_2 A^0 N^0}{F^0 S^0} & \frac{V k_1 N^0}{F^\circ} & 0 \\
-\left(\frac{V k_2 S^0}{F^\circ}\right) & -\left(\frac{V k_1 S^0 + V k_2 A^0 + F^\circ}{F^\circ}\right) & \left(\frac{V k_1 S^0}{F^\circ}\right) & 0 \\
-\left(\frac{V k_1 S^0}{F^\circ}\right) & -\left(\frac{V k_1 N^0}{F^\circ}+1\right) & 0 & 0 \\
\left(\frac{V k_2 N^0}{F^\circ}\right) & \left(\frac{V k_2 A^0 N^0}{F^\circ S^0}\right) & 0 & -1
\end{pmatrix}
\begin{pmatrix} \Delta A^* \\ \Delta N^* \\ \Delta S^* \\ \Delta B^* \end{pmatrix}
$$
$$
+ \begin{pmatrix}
-\frac{A^0}{S^0} & 0 & 0 \\
\frac{(C_{N0} - N^0)}{N^0} & 0 & 1 \\
\frac{(C_{S0} - G^0)}{G^0} & 1 & 0 \\
-\left(\frac{B^0}{S^0}\right) & 0 & 0
\end{pmatrix}
\begin{pmatrix} \Delta F^* \\ \Delta C_{S0} \\ \Delta C_{N0} \end{pmatrix} \tag{55}
$$

Furthermore, as the transfer function G(s) is given by $(s) = (sI - A)^{-1}B$, firstly it is necessary to calculate $(sI - A)$. Therefore, we need to define the next elements of matrix A:

$$a_{11} = \left(\frac{V k_2 N^0}{F^\circ}+1\right); a_{12} = \frac{V k_1 N^0}{F^0} - \frac{V k_2 A^0 N^0}{F^0 S^0};$$
$$a_{13} = \frac{V k_1 N^0}{F^\circ} \tag{56}$$

$$a_{21} = \left(\frac{V k_2 N^0}{F^\circ}\right); \quad a_{22} = \left(\frac{V k_1 S^0 + V k_2 A^0 + F^\circ}{F^\circ}\right); \quad a_{23} = \left(\frac{V k_1 S^0}{F^\circ}\right) \tag{57}$$

$$a_{31} = \left(\frac{V k_1 S^0}{F^\circ}\right); a_{32} = \left(\frac{V k_1 N^0}{F^\circ}+1\right) \tag{58}$$

$$a_{41} = \left(\frac{V k_2 N^0}{F^\circ}\right); a_{42} = \left(\frac{V k_2 A^0 N^0}{F^\circ S^0}\right) \tag{59}$$

$$(sI - A) = \begin{pmatrix}
s + a_{11} & -a_{12} & -a_{13} & 0 \\
a_{21} & s + a_{22} & -a_{23} & 0 \\
a_{31} & a_{32} & s & 0 \\
-a_{41} & -a_{42} & 0 & s + 1
\end{pmatrix} \tag{60}$$

In order to simulate the process, the next input parameter values are taken into account: F=0.1 m³·s⁻¹, C_{S0}=1 mol·m⁻³, C_{N0}=1 mol·m⁻³ k_1=0.32 h⁻¹, k_2=0.49 h⁻¹, k_3=0.27 h⁻¹, V=1 m³, N=0.2 mol·m⁻³, S=0.3 mol·m⁻³, A=0.5 mol·m⁻³, B=0.2 mol·m⁻³. As a result, the respective transfer functions are given by the following set of equations:

From input u_1=F to output

$$y1: G(s) = \frac{-1.6667s^3 - 11.49s^2 - 12.2919s - 2.4619}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (61)$$

$$y2: G(s) = \frac{4s^3 + 16.61s^2 + 18.8436s + 6.2336}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (62)$$

$$y3: G(s) = \frac{2.3333s^3 + 12.2833s^2 + 20.7807s + 10.8307}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (63)$$

$$y4: G(s) = \frac{-0.6667s^3 + 0.64s^2 + 4.656s + 5.2533}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (64)$$

from input $u_2 = C_{S0}$ to output

$$y1: G(s) = \frac{0.6400s^2 + 2.5088s + 1.8688}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (65)$$

$$y2: G(s) = \frac{0.9600s^2 + 1.9200s + 0.96}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (66)$$

$$y3: G(s) = \frac{1s^3 + 7.39s^2 + 13.6616s + 7.2716}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (67)$$

$$y4: G(s) = \frac{2.1952s + 3.3994}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (68)$$

from input $u_3 = C_{N0}$ to output

$$y1: G(s) = \frac{-0.9933s^2 - 2.0429s - 1.0496}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (69)$$

$$y2: G(s) = \frac{s^3 + 2.98s^2 + 2.5944s + 0.6144}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (70)$$

$$y3: G(s) = \frac{-1.64s^2 - 3.9336s - 2.2936}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (71)$$

$$y4: G(s) = \frac{1.6333s^2 + 2.2605s - 0.0251}{s^4 + 7.39s^3 + 15.8504s^2 + 12.8288s + 3.3684} \quad (72)$$

4 Algorithm design

As an example, we describe next how to determine the respective transfer function for two inputs using the next algorithm developed in Matlab

```
syms s V F k1 k2 k3 CA R G K cg0
 A=[s+((V*k2*R/F)+1) -((V*k1*G/F)-
(V*k2*CA/F)) -(V*k1*R/F) 0;   (V*k2*R/F)
s+((V*k1*G+V*k2*CA+F)/F) -(V*k1*R/F)
0;(V*k1*G/F)((V*k1*R/F)+1) s 0;-(V*k2*R/F) -
(V*k2*CA/F) 0 s+1];
inv(A)
B=[CA/G 0;-R/G 0;-(cg0-G)/G 1/G;-K/G 0];
G=inv(A)*B

F=0.1; %m3 s-1
ca0=1; %mol m-3
k1=0.032; %h-1
k2=0.49; %h-1
k3=.27; %h-1
V=1; %m3
ca=0.6;
cb=0.3;
cc=0.05;
cd=0.05;
```

```
A = [ -((V*k1/F)+1) 0 0 0; (V*k1/F) -((V*k2/F)+1)
0 0;  0 (V*k2/F) -((V*k3/F)+1) 0; 0 0 (V*k3/F) -1];
 B=[(ca0-ca)/ca 1/ca0; -cb/V 0;-cc/V 0;-cd/V 0];

C=[1 0 0 0; 0 1 0 0; 0 0 1 0; 0 0 0 1];
D=[0 0;0 0;0 0;0 0];
[num1,den1]=ss2tf(A,B,C,D,1) % iu = 1
[num2,den2]=ss2tf(A,B,C,D,2) % iu = 2
```

where iu corresponds to the input we are analyzing (i.e. when we have 2 inputs, first we consider *iu=1* (first input), this allow us to obtain the transfer functions from input 1 to output 1 and from input 1 to output 2. Then we proceed with *iu = 2*, which give the transfer functions from input 2 to output 1 and input 2 to output 2.

The response to a unit step input *(F and C_{S0} respectively)* for the transfer functions described in previous equations is presented in Fig. 5 and Fig. 6.
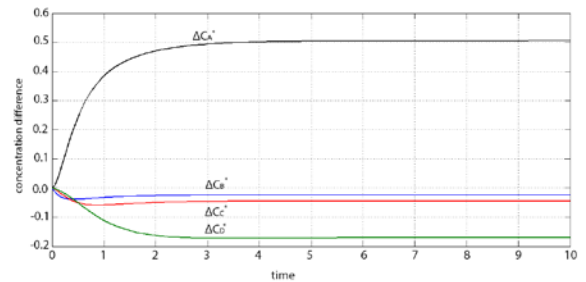

Fig.5 Response to a unit step input of F and the effect on the respective outputs (—ΔC_A; —ΔC_B; —ΔC_C; —ΔC_D)
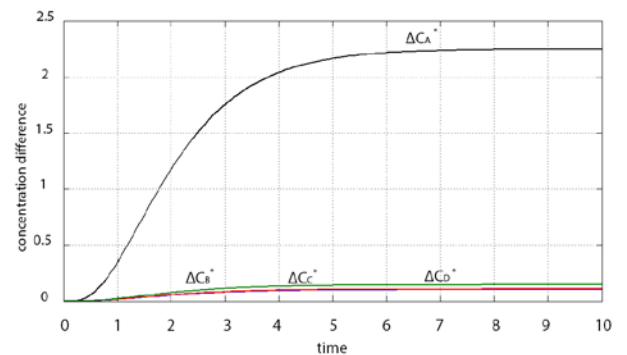

Fig.6 Response to a unit step input of C_{S0} and the effect on the respective outputs (—ΔC_A; —ΔC_B; —ΔC_C; —ΔC_D)

5 Conclusions

Extensive research is performed currently in the area of partial oxidation of several sugar alcohols because it gives oxidation intermediate products with high utility value. However, a major problem of these reaction lies in its low reactivity and high

oxidation reactivity of intermediates, which is expressed by different values of the rate constants of oxidation in the first step of the reaction and in subsequent steps of the oxidation reaction. The yield mainly depends on the ratio of rate constants. In this paper we have covered the mathematical model of partial oxidation of 1,2,3 propanotriol to dihydroxypropanal using N_2O considering 3 input values, two are related to the oxidant (flow and concentration) and one to the reactant (concentration). We analyze the use of an oxidizing agent in low concentrations, which is able to suppress subsequent over oxidation steps due to the very low residual concentrations of the oxidizing agent. For simulation purposes, specified constants and initial concentrations of nitrous oxide and reactant can be specified to obtain the transfer function equations. Experimental procedure was followed to perform the oxidation reaction determining the minimum and maximum values of temperature after addition of ammonium nitrate to avoid risk of explosion. Further research will be performed to use the transfer function equations that were determined for purposes of controlling the reaction.

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