Transient Behavior of a Chemically Reacting System in a CSTR

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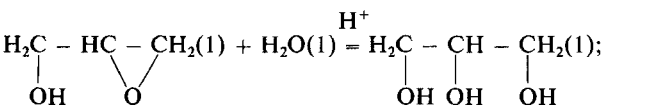
In a continuous-flow stirred-tank reactor (CSTR), the transient temperature of a reacting system and the transient concentration of a key component can be determined experimentally as a function of time. In the present paper, experimental results concerning the acid-catalyzed hydration of oxiranemethanol (OM) in a CSTR will be discussed.

For the description of the transient behavior of this reacting system use will be made of a model consisting of unsteady-state mass and energy balances and the reaction rate equation. With this model and a best-fit procedure an excellent description of the observed temperature and concentration oscillations can be obtained. It will be shown that measured oscillations of the concentration of OM agree well with the calculated oscillations based on measured temperatures only. Furthermore, runaway phenomena, resulting in violent boiling of the chemically reacting system, encountered in the course of our experiments and caused by "improper" start-up procedures, will be treated.

Reaction and Equipment

The chemical reaction used to study the transient behavior is the acid catalyzed hydration of oxiranemethanol (OM) to glycerol:



$$-\Delta H(298\ \mathrm{K}) = 88.2\ \mathrm{kJ \cdot mol^{-1}}$$

OM was purified by vacuum distillation before use. In a wide range of conditions with regard to the acidity and water content, the rate of this reaction was found to be first order in OM, proportional to the H^+ concentration and approximately independent of the H_2O concentration. According to previous publications (Frankvoort, 1977), the reaction rate can be described by:

$$r = k \cdot c_H \cdot c = k_o \cdot c_H \cdot c \cdot \exp(-T_a/T), \qquad (1)$$

in which c represents the concentration of the key component OM.

The 257 mL reactor vessel, which has been described in detail elsewhere (Vermeulen, 1986*a*, *b*), is provided with a quartz sensor for accurate temperature measurement of the chemically reacting system. The reactor is fed by two diluted streams. One feed stream is an aqueous solution of OM (about 70 wt. % OM), the other solution consists of sulfuric acid and water (about 9 wt. % H_2SO_4). The temperatures of the reactor contents and those of the two feed streams and of the coolant stream were measured and stored at time intervals of 5 s.

For the experiment concerning the approach to an orbitally stable steady state, the concentration of OM was determined at time intervals of 30 s.

Mathematical Model

The mathematical model used to describe the behavior of the chemically reacting system in the CSTR consists of a mass balance (Eq. 2) and an energy balance (Eq. 3) for unsteady-state conditions.

$$M \cdot \frac{dc}{dt} = G \cdot (c_f - c) - k_o \cdot c_H \cdot c \cdot M \cdot \exp(-T_a/T) \qquad (2)$$

$$(M \cdot C_p + mC_w) \cdot \frac{dT}{dt} = G \cdot C_{pf} \cdot (T_f - T) - US \cdot (T - T_c) + \Delta Q + k_o \cdot c_H \cdot c \cdot M \cdot (-\Delta H) \cdot \exp(-T_a/T) \qquad (3)$$

In this model it is assumed that in the reactor vessel heat exchange between liquid feed and reactor contents is so fast that their temperatures are equal before the feed participates in the chemical reaction.

The normal start-up procedure of the reaction is by filling the reactor with the feedstream solution containing sulfuric acid

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and water before the experiment is started by opening the valves that control the flow rate of the feed. The sulfate concentration c_A in a CSTR with an initial concentration $c_{A,0}$ and a feed concentration of $c_{A,f}$ can be obtained from the unsteady-state mass balance (Eq. 4).

$$M \cdot \frac{dc_A}{dt} = G\,c_{A,f} - G\,c_A \tag{4}$$

After integration of Eq. 4 we obtain:

$$c_A = c_{A,f} - (c_{A,f} - c_{A,0}) \cdot \exp(-t/\tau) \tag{5}$$

The relation between c_H and c_A can be derived from equations defining the sulfuric acid dissociation constants K_1 and K_2 and from balances commonly used in analytical chemistry. This derivation results in Eq. 6.

$$c_H^3/K_1 + c_H^2 + (K_2 - c_A) \cdot c_H - 2\,K_2 \cdot c_A = 0 \tag{6}$$

Concentration Measurements

In order to determine the OM concentration values in the reacting system, a method was devised to monitor the temperature rise ΔT_{max} of a 2 mL sample, extracted within 2 seconds from the reaction mixture, in a well-insulated plastic syringe described elsewhere (Vermeulen, 1986b).

From the temperature rise ΔT_{max} of the sample in the syringe the concentration of OM at $t = 0$, when the sample was extracted from the reacting system, has been calculated with Eq. 7.

$$c_{in} = \frac{\Delta T_{max} \cdot (M_x \cdot C_p + m_x C_x) + U_x S_x \cdot (\langle T \rangle - T_{sur}) \cdot t_{max}}{M_x \cdot (-\Delta H)} \tag{7}$$

In Eq. 7, the heat loss of the sample is described with an average heat loss, based on the average temperature $\langle T \rangle = (T_{max} + T_{in})/2$ of the liquid in the syringe. The accuracy of Eq. 7 has been verified elsewhere (Vermeulen, 1986b). It was found that the experimental error in the concentration measurement is less than 10% and that within about 45 s all OM present in the sample is converted into glycerol.

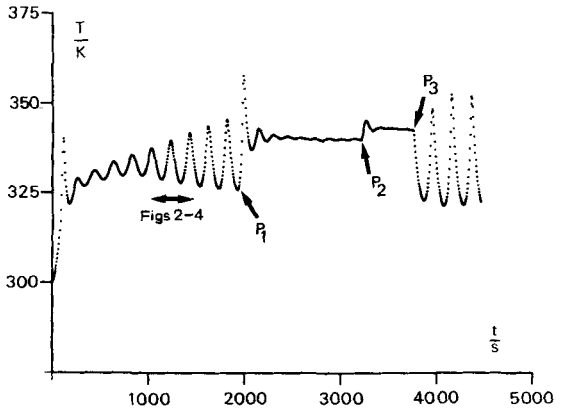

Figure 1. Measured temperatures of the reacting system for four different time intervals with different stirrer speeds.

Approach to Different Steady States

According to the procedure presented earlier, the temperature of the reacting system has been measured for the approach to an orbitally stable steady state and plotted against time in Figure 1. The dots represent temperature values measured. In the time interval 995 s $\leq t \leq$ 1,470 s, 96 temperature values and 16 OM concentration values were measured. The 96 temperature values have been used to calculate the best-fit values of all 14 physical quantities α_k in the applied model, Table 1. These best-fit values have been determined by a least-squares procedure assuming that the values of all measured physical quantities $\alpha_{k,m}$ are subject to error according to a normal distribution. The mathematical procedure applied, recently developed at our laboratory, will be described elsewhere. Application of the above-mentioned assumptions to our problem results in minimization of the value of SUM in Eq. 8, subject to the model stated.

$$\text{SUM} = \sum_{i=1}^{96} \frac{(T_{i,m} - T_{i,fit})^2}{\sigma_T^2} + \sum_{k=1}^{14} \frac{(\alpha_{k,m} - \alpha_{k,fit})^2}{\sigma_\alpha^2} \tag{8}$$

In Eq. 8, σ_T represents the experimental tolerance in the separately determined values of the temperature and σ_α the experimental tolerances of the 14 physical quantities. A value of σ_T =

Table 1. Values of the Constant Physical Quantities in Eqs. 2 and 3

Physical Quantity α_k	Measured Value $\alpha_{k,m}$	Standard Deviation σ_α	Value from Best-Fit Pr. $\alpha_{k,fit}$	Dimension
G	$1.84\ 10^{-3}$	$0.1\ 10^{-3}$	$1.808469\ 10^{-3}$	$kg \cdot s^{-1}$
M	0.30	0.005	0.3003317	kg
mC_w	392	100	427.2637	$J \cdot K^{-1}$
c_f	8.60	0.15	8.597839	$mol \cdot kg^{-1}$
C_{pf}	2,500	150	2,468.964	$J \cdot kg^{-1} \cdot K^{-1}$
C_p	2,350	150	2,373.833	$J \cdot kg^{-1} \cdot K^{-1}$
c_H	0.15	0.02	0.1616528	$mol \cdot kg^{-1}$
k_o	$85\ 10^9$	$5\ 10^9$	$86.36321\ 10^9$	$kg \cdot mol^{-1} \cdot s^{-1}$
US	30	5	29.44636	$W \cdot K^{-1}$
$-\Delta H$	$88.2\ 10^3$	$1.9\ 10^3$	$88.16624\ 10^3$	$J \cdot mol^{-1}$
ΔQ	30	15	35.47345	W
T_f	270.18	0.02	270.1800	K
T_c	300.63	0.02	300.6303	K
T_a	8,827	16	8,822.437	K

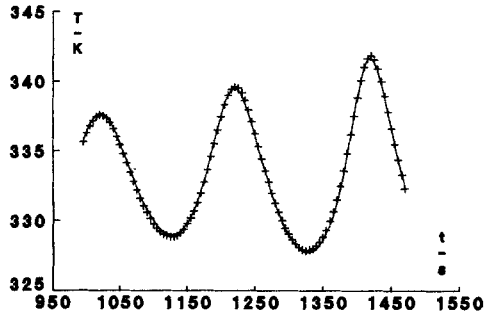

Figure 2. Transient temperature vs. time plot of the reacting system approaching an orbitally stable steady state.

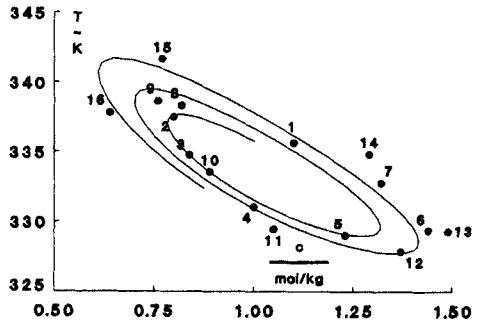

Figure 4. Transient temperature vs. transient OM concentration.

0.5 K has been used. The values of σ_x are shown in Table 1. Because no accurate data are available concerning the heat capacity of aqueous solutions containing OM, glycerol and sulfuric acid, the values of the heat capacity C_{pf} of the feed and the average heat capacity C_p of the reacting system have been estimated by taking 80% of the sum of the values obtained by multiplication of each of the mass fractions of a component and its specific heat capacity. This method has been described by Wasburn (1929).

It can be concluded from Table 1 (column 4) that all the best-fit values of physical quantities are within the possible experimental error of the measured values. Figures 2, 3 and 4 show the observed and the calculated transient values of temperature and OM concentration of the reacting system for the above-mentioned time interval. The symbols in these figures represent measured values and the solid lines represent the values calculated with the above-mentioned best-fit procedure. The temperature oscillations of the reacting system approaching an orbitally stable steady state are shown in Figure 2. The concentration of the key component OM for the same time interval is shown in Figure 3. In Figure 4, the temperature of the reacting system has been plotted against the concentration of the key component OM.

During the experiment presented in Figure 1, the stirrer speed was reduced from $n = 75\ s^{-1}$ to $n = 50\ s^{-1}$ at $t(P_1) = 1{,}925$ s. From Figure 1, it can be seen that the original oscillatory behavior of the temperature immediately changes into an approach to a point stable steady state, because the heat transfer from the reacting system to the coolant is reduced. From empirical correlations, it can be calculated that a decrease of the stirrer speed by 33.3% results in a decrease of about 20% of the *US* value presented in Table 1 (column 2). At $t(P_2) = 3{,}220$ s, the stirrer speed was further reduced to $n = 41.67\ s^{-1}$, resulting in an approach to another point-stable steady state with a slightly higher value of T. At $t(P_3) = 3{,}760$ s, the stirrer speed was increased to its original value of $n = 75\ s^{-1}$, resulting in a return to oscillatory behavior.

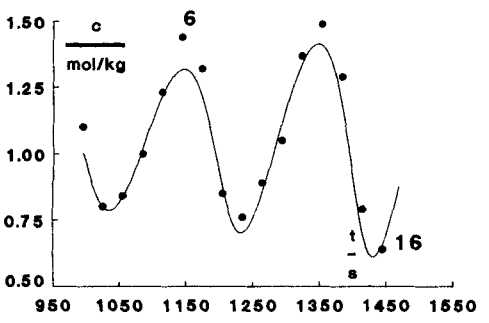

Figure 3. Transient concentration of OM vs. time for the time domain 995 s ≤ t ≤ 1,470 s (see Figure 1).

Procedures Resulting in a Runaway

The start-up of the reaction in the CSTR was discussed earlier when the reactor was prefilled with the aqueous sulfuric acid solution. The transient behavior of the reacting system concerning three other start-up procedures will be discussed here.

Figure 5 shows the transient temperature of the reacting system when the reactor was initially filled with three other aqueous solutions. Curve 1 refers to the situation when the reactor was prefilled with the OM-containing feedstream solution; curve 2 refers to the situation when the reactor was initially filled with water only and curve 3 shows the behavior when the starting liquid was an aqueous 50 wt. % glycerol solution.

The symbols in Figure 5 indicate temperature values measured sequentially at time intervals of 5 s. The values of the physical quantities of the starting liquid are presented in Table 2. From Figure 5, it can be concluded that after an initial slow increase of the temperature, runaway suddenly occurs, then the bubble point (380 K) is passed and the reactor contents is blown off. The curves in these figures represent the values calculated by numerical integration of the mass and energy balances. During this integration, Eqs. 5 and 6 were used to calculate the concentrations of OM and sulphuric acid and the mass fractions of all components in the liquid. These fractions are used to calculate the value of the heat capacity of the liquid contents C_p according to the method mentioned previously.

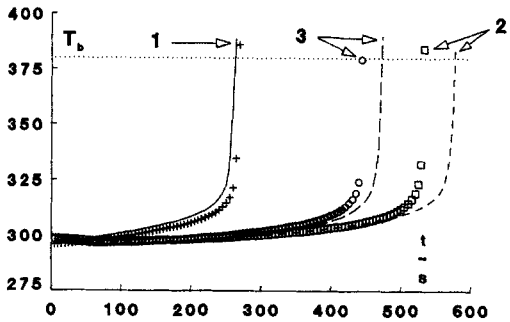

Figure 5. Approach to a runaway of the reacting system in a CSTR for three different start-up procedures.

Table 2. Values of the Constant Physical Quantities Used to Calculate the Runaway of the Reacting System (See Figure 5)

Physical Quantity	Aqueous OM Solution*	Water**	Aq. Glycerol Solution†	Dimension
T_f	272.72	272.78	272.77	K
T_c	298.15	298.18	298.17	K
T_0	295.66	298.14	298.14	K
c_0	10.78	0.0	0.0	mol · kg^{-1}
G	1.80 10^{-3}	1.80 10^{-3}	1.80 10^{-3}	kg · s^{-1}
M	0.30	0.30	0.30	kg
mC_w	392	392	392	J · K^{-1}
c_f	9.17	9.17	9.17	mol · kg^{-1}
C_{pf}	2,500	2,500	2,500	J · kg^{-1} · K^{-1}
k_o	85 10^9	85 10^9	85 10^9	kg · mol^{-1} · s^{-1}
US	47.5	35	25	W · K^{-1}
$-\Delta H$	88.2 10^3	88.2 10^3	88.2 10^3	J · mol^{-1}
ΔQ	30	30	30	W
T_a	8,827	8,827	8,827	K

*See curve 1.
**See curve 2.
†See curve 3.

We found that the values of US and C_p are of crucial importance in accurately predicting the transient temperature values of the reacting system. The heat transfer coefficients mentioned in Table 2 were obtained from heat transfer correlations and mean values of transport properties published elsewhere (Vermeulen, 1986b).

Conclusions

From the experiments on the approach to an orbitally stable steady state and the least-squares procedure applied to experimental results presented in this paper, it can be concluded that the observed oscillatory behavior of the temperature and the composition of a reacting system can be described quantitatively by a model consisting of mass and energy balances (Eqs. 2 and 3).

Furthermore it has been observed that a change in the stirrer speed, resulting in a change of the heat transfer to the coolant, can alter the original oscillatory behavior into a point-stable steady state.

According to the experiments and calculations concerning three different start-up procedures resulting in runaways, the predicted behavior agrees well with the observed behavior if a model consisting of Eqs. 2, 3, 5 and 6 is applied and proper values of the mean heat transfer coefficient are used, and the value of the heat capacity of the reacting liquid is updated after each numerical integration step (0.05 s).

Acknowledgment

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Notation

c = concentration of the key component oxiranemethanol, mol · kg^{-1}
c_A = total concentration of sulphate-containing components, mol · kg^{-1}
c_H = H^+ concentration, mol · kg^{-1}
C_p = average heat capacity of the reacting liquid, J · kg^{-1} · K^{-1}
C_w = heat capacity of the solid parts of the reactor, J · kg^{-1} · K^{-1}
G = mass flow rate, kg · s^{-1}
ΔH = reaction enthalpy, J · mol^{-1}
K_1, K_2 = dissociation constants of H_2SO_4, mol · kg^{-1}
k = second-order reaction rate constant, kg · mol^{-1} · s^{-1}
k_o = second-order frequency factor, kg · mol^{-1} · s^{-1}
M = mass of the reaction liquid in the reactor, kg
m = mass of the solid parts of the reactor, kg
n = stirrer speed, s^{-1}
r = mass based reaction rate, mol · kg^{-1} · s^{-1}
ΔQ = heat production due to mixing and stirring, W
S = heat transfer surface area of the cooling coil, m^2
SUM = parameter defined in Eq. 8, 1
T = temperature of the reacting system in the reactor, K
$\langle T \rangle$ = average temperature of the liquid in the syringe, K
T_a = activation temperature, K
T_c = inlet temperature of the coolant, K
T_{in} = temperature of the sample in the syringe at $t = 0$, K
T_{max} = maximum temperature of the sample in the syringe, K
ΔT_{max} = maximum temperature rise of the sample in the syringe ($\Delta T_{max} = T_{max} - T_{in}$), K
T_{sur} = temperature of the surrounding air, K
t = time, s
t_{max} = time corresponding to $T = T_{max}$, s
U = overall heat transfer coefficient of the cooling coil, W · m^{-2} · K^{-1}
α_k = physical quantity ($k = 1$ to 14)
σ = standard deviation
τ = residence time ($\tau = M/G$), s

Subscripts

f = concerning the feed
fit = refers to a best-fit value
i, j = refer to measurements i, j
m = refers to separately measured value
T = refers to the reacting-system temperature
x = refers to the syringe
α = refers to a physical quantity

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