Kinetic Analysis of a Non-Isothermal Reactor

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BACKGROUND

The destruction of low concentrations (typically less than 1000 ppm) of volatile organic compounds (VOC) by incineration is an industrial technique for controlling certain air pollution problems. Because of the excess oxygen, such reactions are often modeled using first order kinetics for hydrocarbon destruction (Hemsath and Susey, 1974; Lee et al., 1979), that is,

$$-\frac{dC}{dt} = kC \tag{1}$$

Well-insulated tubular flow reactors are often used as VOC incinerators. These reactors typically operate at atmospheric pressure, and at temperatures which may range from 800 to 1200°K. Such a device is often modelled as an isothermal plug flow reactor (PFR) although it is recognized that there will always be some deviation from isothermality (which may in fact be substantial). The analysis of an isothermal PFR for an irreversible, first-order reaction with Arrhenius kinetics is quite simple. When the rate expression is integrated, a plot of $-\ln(f/f_o)$ vs. time (length divided by velocity) yields a straight line with slope = k, the rate constant.

THEORY

Consider now a non-isothermal PFR, which at steady state has some concentration and temperature profiles along its length. For a small increment of reactor length, ΔX, located at the ith position in the reactor, over which the temperature change is small, the rate constant and velocity are reasonably well represented by a linear average of their inlet and outlet values. Treating the average values as constants, integration of the differential equation yields

$$\frac{f_i}{f_{i-1}} = e^{-\bar{k}_i \frac{\Delta X}{\bar{U}_i}} \tag{2}$$

The mole fraction exiting the nth increment is related to the inlet mole fraction by

$$\frac{f_n}{f_o} = e^{\sum_{i=1}^{n}\left(-\bar{k}_i \frac{\Delta X}{\bar{U}_i}\right)} \tag{3}$$

Note that if both k_i and U_i are constant throughout the reactor, Eq. 3 reduces to the familiar form for the isothermal PFR:

$$\frac{f_x}{f_o} = e^{-\frac{kX}{U}} \tag{4}$$

If the rate constant, k, is represented by the Arrhenius form, then

$$\frac{\bar{k}_x}{k_o} = \frac{Ae^{-E/R\bar{T}_x}}{Ae^{-E/RT_o}} \tag{5}$$

Equation 5 can be rewritten as

$$\bar{k}_x = k_o F_x \tag{6}$$

where

$$F_x \equiv e^{-\left[\frac{E}{RT_o}\left(\frac{T_o}{\bar{T}_x} - 1\right)\right]}$$

Now if we denote position X by $i\Delta X$ we can denote $\bar{k}_x$ as $\bar{k}_i$ and F_x as F_i. Using this notation, taking logs of Eq. 3 and substituting Eq. 6 for $\bar{k}_i$ yields:

$$\ln\frac{f_n}{f_o} = -\sum_{i=1}^{n} k_o F_i \frac{\Delta X}{\bar{U}_i} \tag{7}$$

Defining the residence time for increment i by

$$\Delta t_i = \frac{\Delta X}{\bar{U}_i} \tag{8}$$

Equation 7 becomes

$$\ln\frac{f_n}{f_o} = -\sum_{i=1}^{n} k_o F_i \Delta t_i \tag{9}$$

Now, if we view F_i as a transformation factor for Δt_i we can define a transformed time increment by

$$\Delta t_i' = F_i \Delta t_i \tag{10}$$

and Eq. 9 becomes

$$\ln\frac{f_n}{f_o} = -\sum_{i-1}^{n} k_o \Delta t_i' \tag{11}$$

A transformed reaction time is defined by summing the transformed time increments.

$$t' = \sum_{i=1}^{n} \Delta t_i' \tag{12}$$

Taking exponentials of both sides of Eq. 11 and substituting Eq. 12 into the result yields

$$\frac{f_n}{f_o} = e^{-k_o t'} \tag{13}$$

Plotting f_n/f_o vs. transformed time on a semilog plot will yield a straight line of slope $-k_o$, the reaction rate constant at the inlet temperature T_o. Thus, transformed reaction time technique is a method of linearizing the kinetic data for known deviations from isothermality without disturbing the concentration measurements themselves. The transformed time, t', is simply the time it would have taken to reach the given concentration (measured at time t) had the reaction occurred isothermally at the inlet temperature.

The temperature may vary non-linearly with axial distance in the reactor and the gas velocity will vary with position due to temperature changes. However, if there are enough temperature measurements to estimate a profile, these data can be used to numerically calculate a transformation factor and average velocity for each small increment of the reactor, and thus a transformed reaction time can be calculated for each position along the reactor. A simple computer program can be written to calculate and sum the transformed time increments up to any arbitrary real time (length of reactor).

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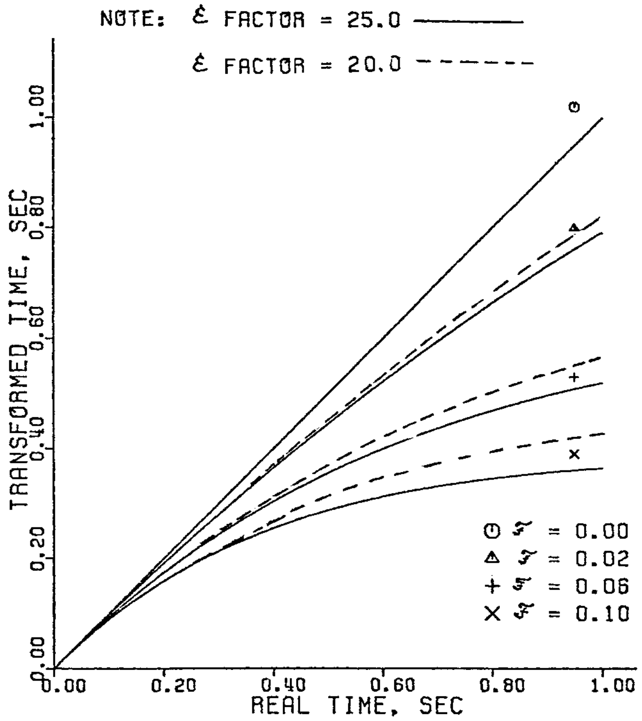

Figure 1. Effect of ℰ and ℱ factors on transformed time.

APPLICATION TO VOC INCINERATORS

Assuming no change in moles due to reaction and assuming constant pressure, the velocity at any point is given by

$$U_i = U_{i-1}\frac{T_i}{T_{i-1}} \tag{14}$$

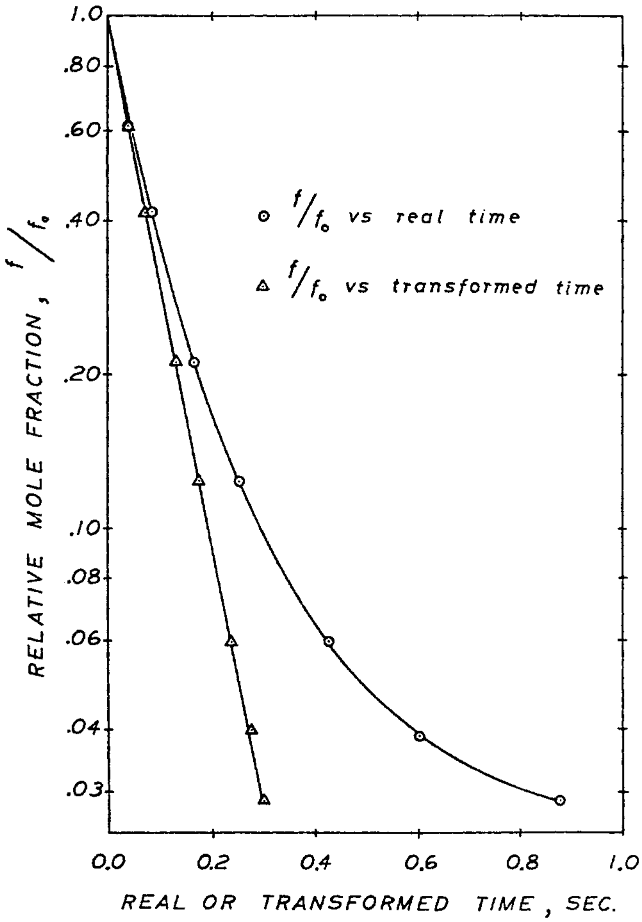

Figure 2. Results from transformed reaction time sample problem.

TABLE 1. "DATA" AND RESULTS FOR TRANSFORMED REACTION TIME SAMPLE PROBLEM

	T (°K)	U (m/s)	L (m)	E (cal/gmol)	A, s^{-1}
Inlet Conditions	1000	12	10	50000	1.0 $(10)^{12}$

Sample Location (m)	T (°K)	$\frac{f_i}{f_o}$	Reaction Time (s)	Transformed Time (s)
0.0	1000	1.000	0.000	0.000
0.5	995	0.633	0.042	0.040
1.0	990	0.418	0.084	0.074
2.0	980	0.211	0.168	0.132
3.0	970	0.124	0.254	0.177
5.0	950	0.060	0.427	0.238
7.0	930	0.039	0.605	0.274
10.0	900	0.029	0.878	0.301

Let us further assume a linear temperature decline along the reactor in order to investigate the relationships between transformed time and real time. Let a dimensionless group, the fractional temperature drop across the entire reactor, $\mathscr{F}$, be defined as follows:

$$\mathscr{F} = \frac{L}{T_o}\left(\frac{-dT}{dX}\right) \tag{15}$$

Also define a dimensionless activation energy by:

$$\mathscr{E} = \frac{E}{RT_o} \tag{16}$$

Further, define dimensionless distance along the reactor by dividing by reactor length, L, so that Z varies from zero to one. Finally, define a relative velocity as the inlet velocity divided by L. Thus, a relative velocity of 1.0 s^{-1} would yield a residence time of 1.0 s under isothermal conditions. With these dimensionless parameters Eq. 10 becomes

$$\Delta t_i' = e^{-\mathscr{E}\left(\frac{\mathscr{F}Z}{1-\mathscr{F}Z}\right)}\Delta t_i \tag{17}$$

Equations 14 and 17 were solved numerically with $U_o = 1.0$ and summed to yield t' and t for various values of $\mathscr{E}$ and $\mathscr{F}$. Forty increments were used. The results are illustrated by Figure 1. As can be seen, larger values of either $\mathscr{E}$ or $\mathscr{F}$ produce larger transformations.

SAMPLE PROBLEM

A simple example was chosen to demonstrate this technique. Consider a PFR in which sampling points and thermocouples are located at the inlet and at various positions downstream. From the data in Table 1, a fractional temperature drop of 0.01 per meter was calculated yielding an $\mathscr{F}$ value of 0.10 for this 10-m reactor. From a previous estimate of the activation energy, an $\mathscr{E}$ factor of 25.2 was calculated. It should be noted that to use this technique requires an estimate of the activation energy of the reaction. With an unknown $\mathscr{E}$, an initial estimate is made and if several different inlet temperatures are studied, one or two iterations of this technique will be sufficient to determine the actual activation energy (and, subsequently, the pre-exponential factor). Figure 2 presents the results of this technique.

CONCLUSIONS

In the laboratory or in industry it is difficult to maintain isothermality for reactions which occur in a plug flow reactor at high temperatures (800-1200°K). A technique has been developed to analytically account for the effect of temperature variation. With this technique, one may analyze the data and obtain specific Arrhenius constants (pre-exponential factor and activation energy) corresponding to the inlet temperature Analysis of non-isothermal incineration data is facilitated by use of this technique because simple linear arithmetic and graphical techniques can be used in place of more complex non-linear methods. It should also be noted that this technique can be used with other than first order reactions, since we are adjusting only for temperature effects.

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NOTATION

A = pre-exponential factor (s^{-1})
E = activation energy (kcal/gmol)
$\mathscr{E}$ = dimensionless activation energy
F_i = transformation factor for the ith increment of reactor distance
F_x = transformation factor, equal to F_i for $X = i\Delta X$
f_i = mole fraction at the ith increment of reactor distance
f_x = mole fraction, equal to f_i for $X = i\Delta X$
$\mathscr{F}$ = dimensionless fractional temperature drop across the entire reactor
i = index for number of distance increments
k = first-order reaction rate constant (s^{-1})
$\bar{k}_i$ = average value of rate constant over ith increment of reactor distance (s^{-1})
k_o = first order rate constant at the inlet temperature, T_o (s^{-1})
L = overall reactor length (m)
R = gas constant (0.001987 kcal/gmol°K)
T = absolute temperature (°K)
T_o = absolute temperature at reactor inlet (°K)
$\bar{T}_x$ = average temperature over ith reactor increment located at $X = i\Delta X$
t = time (s)
t' = transformed time (s)
U = linear velocity in the reactor (m/s)
$\bar{U}_i$ = average velocity in the ith increment of the reactor (m/s)
X = axial distance (m)
Z = dimensionless axial distance
Δt, $\Delta t'$ = incremental time, increment transformed time (s)
ΔX = incremental reactor distance (m)

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Estimation of Kinetic Parameters—Initial Guess Generation Method

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Estimates of chemical kinetic equation parameters are obtained from calculation procedures which utilize the experimental data and consist of minimization of a suitable criterion function. A number of methods with criteria of various forms, using different calculation techniques, have been described (Froment, 1975; Himmelblau et al., 1967; Pexidr, 1974; Seinfeld, 1970; Van den Bosch and Hellinckx, 1974). In most cases the above problem is solved by means of an iterative procedure. The convergence of the algorithm depends on the goodness of the initial guesses. The importance of this aspect of calculations is emphasized in all papers dealing with estimation of parameters in the sets of both algebraic and differential equations. Various ways and preparation methods of initial estimations are discussed and illustrated by Kittrell et al. (1965). An independent algorithm for generation of preliminary parameter values is proposed apart from the accurate parameter determination algorithm (Seinfeld and Gavalas, 1970). This provides considerable economy of calculation time. This paper discusses the calculation technique for estimating initial parameters for the set of non-linear first-order ordinary differential equations.

CALCULATION FORMULAS

Let us consider a set of differential equations with the preset initial condition:

$$\frac{dx}{dt} = f(t, x, k); \quad x(0) = x_o \tag{1}$$

Equation 1 may be solved by one of the known differential-difference methods (Lapidus and Seinfeld, 1971). The differential-difference method generating equation may be written, by using first derivatives, as follows:

$$x_{n+1} = \sum_{i=0}^{p} a_i x_{n-i} + h \sum_{i=-1}^{p} b_i x'_{n-i} \tag{2}$$

where $h = (t_{n+1} - t_n)$ is the integration step and $p + 1$ is the number of previous x values required for calculation of $x_{n+1} = x(t_{n+1})$. Depending on the numerical values of coefficients a_i, b_i and the values of p, Eq. 2 has different accuracies. The remainder may be expressed by the equation:

$$T_n = ch^{q+1} \frac{d^{q+1}}{dt^{q+1}} x(\eta); \quad t_n < \eta < t_{n+1} \tag{3}$$

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