A First Course on Kinetics and Reaction Engineering

Example 14.3

Problem Purpose

This problem illustrates differential analysis using data from a differentially operated PFR.

Problem Statement

The isomerization of cyclopropane, equation (1), was known from batch reactor studies to be first order at lower temperatures. Davis and Scott [1] used a differential plug flow reactor to determine whether it remained first order at higher temperatures. Their tubular reactor had a diameter of 0.325 cm and was 240 cm long. Use a differential analysis and their data from experiments at 1atm and 568 °C, below, to determine whether the kinetics are first order.

$$c\text{-}C_3H_6 \rightarrow C_3H_6 \qquad (1)$$

Inlet Mole Percent c-C_3H_6	***Flow Rate ($cm^3_{STP}\ s^{-1}$)***	***Outlet Mole Percent c-C_3H_6***
8	2.91	7.6
10	4.31	9.7
22	2.94	21.1
42	2.05	39.5
66	4.16	63.4
74	2.62	70.3
88	3.49	84.5

Problem Analysis

This problem provides PFR kinetics data and asks us to check the suitability of a first order rate expression using the differential method of analysis. We should check the data to make sure the reactor was operated differentially. If so, we will need to estimate the value of the derivative in the design equations using a forward difference, substitute a first order rate expression into the design equation, fit it to the data, and determine whether the resulting fit is accurate. If it is, we can use the fitting results to calculate the best value for the rate coefficient and its uncertainty.

Problem Solution

We are told that the reactor was differential, and the data given with the problem statement show that the c-C_3H_6 conversion was small in each experiment. Therefore, the use of differential analysis appears to be justified. When only one reaction takes place isothermally and at steady state in a PFR, a single mole balance design equation for any reactant or product is all that is needed to model the reactor. Writing such a mole balance design equation for cyclopropane gives equation (2). If reaction (1) is first order, then the rate expression is given by equation (3), and substitution of that rate expression into the design equation gives equation (4).

$$\frac{d\dot{n}_{c-C_3H_6}}{dz} = \frac{\pi D^2}{4} r_{c-C_3H_6,1} \tag{2}$$

$$r_{c-C_3H_6,1} = -kC_{c-C_3H_6} \tag{3}$$

$$\frac{d\dot{n}_{c-C_3H_6}}{dz} = -\frac{\pi D^2}{4} kC_{c-C_3H_6} \tag{4}$$

We are instructed to use the differential method of data analysis, so the derivative, $\frac{d\dot{n}_{c-C_3H_6}}{dz}$, in equation (4) will be treated like any other experimentally measured variable, and equation (4) will be fit directly to the experimental data. Defining x, y and m as in equations (5) through (7), and substituting into equation (4) leads to equation (8), which is clearly of the form of a straight line through the origin.

$$x = -\frac{\pi D^2}{4} C_{c-C_3H_6} \tag{5}$$

$$y = \frac{d\dot{n}_{c-C_3H_6}}{dz} \tag{6}$$

$$m = k \tag{7}$$

$$y = mx \tag{8}$$

Since the model, equation (8), is linear, linear least squares can be used to fit it to the experimental data (see Supplemental Unit S3). Linear least squares fitting can be performed manually, using a calculator, using a spreadsheet or using mathematics software. No matter which tool one chooses to use, it will be necessary to provide the following information and input data:

- the number of independent (x) variables
- whether or not the model includes an intercept (b)
- a set of experimental data points, each of which consists of a value for the dependent variable (y) and corresponding values for each of the independent variables (x_i)

Hence, we need to calculate values of x and y for each experimental data point. As noted in the informational reading for this unit, the concentration of cyclopropane that appears in equation (5) should

be the average of the inlet and outlet concentrations of cyclopropane, because when doing differential analysis of PFR data, the rate expression should be evaluated at the average composition. Hence, equation (9) should be used to calculate x. The problem statement gives the value of D as 0.325 cm. The ideal gas law can be used to calculate the total concentrations at the inlet and outlet, equations (10) and (11), and multiplying those quantities by the inlet and outlet mole fractions of cyclopropane gives its inlet and outlet concentrations, equations (12) and (13). Substitution into equation (9) then gives equation (14), which can be used to calculate a value of x for each experimental data point from the data given in the problem statement. In writing equation (14) it was noted that the inlet and outlet pressures are equal as are the inlet and outlet temperatures.

$$x = -\frac{\pi D^2}{4}\left(\frac{C^0_{c-C_3H_6} + C_{c-C_3H_6}}{2}\right) \tag{9}$$

$$C^0_{tot} = \frac{\dot{n}^0_{tot}}{\dot{V}^0} = \frac{P^0}{RT^0} \tag{10}$$

$$C_{tot} = \frac{\dot{n}_{tot}}{\dot{V}} = \frac{P}{RT} \tag{11}$$

$$C^0_{c-C_3H_6} = y^0_{c-C_3H_6} C^0_{tot} \tag{12}$$

$$C_{c-C_3H_6} = y_{c-C_3H_6} C_{tot} \tag{13}$$

$$x = -\frac{\pi D^2}{4}\left(\frac{y^0_{c-C_3H_6} + y_{c-C_3H_6}}{2}\right)\frac{P}{RT} \tag{14}$$

As noted in the informational reading, for differential analysis of PFR data, the derivative in equation (6) is estimated using a forward difference, equation (15). The problem states that the reactor length, L, was 240 cm. The total inlet molar flow rate can be calculated from the inlet volumetric flow rate, which is given at STP in the problem statement, using equation (16). Noting that the reaction does not change the total number of moles (one cyclopropane is converted to one propene), equation (16) also gives the outlet total molar flow rate. The inlet and outlet flow rates of cyclopropane are then found by multiplying the total molar flow rate by the corresponding mole fraction of cyclopropane, equations (17) and (18). Substitution into equation (15) leads to equation (19), which can be used to calculate a value of y for each experimental data point from the data given in the problem statement.

$$y = \frac{d\dot{n}_{c-C_3H_6}}{dz} = \frac{\dot{n}_{c-C_3H_6} - \dot{n}^0_{c-C_3H_6}}{L} \tag{15}$$

$$\dot{n}_{tot}^{0} = \frac{P_{STP}\dot{V}_{STP}}{RT_{STP}} \tag{16}$$

$$\dot{n}_{c-C_3H_6}^{0} = y_{c-C_3H_6}^{0}\frac{P_{STP}\dot{V}_{STP}}{RT_{STP}} \tag{17}$$

$$\dot{n}_{c-C_3H_6} = y_{c-C_3H_6}\frac{P_{STP}\dot{V}_{STP}}{RT_{STP}} \tag{18}$$

$$y = \frac{y_{c-C_3H_6} - y_{c-C_3H_6}^{0}}{L}\frac{P_{STP}\dot{V}_{STP}}{RT_{STP}} \tag{19}$$

Thus, we can generate a set of (x,y) data using equations (14) and (19). The model has only one independent variable, x, and it does not include an intercept. With this information and input data we have everything needed to fit the model to the data. Upon doing so, using whichever linear least squares fitting tool one chooses to employ, the resulting output shows that the correlation coefficient, r^2, is equal to 0.97 and the best value of the slope, m, is equal to 0.022 ± 0.002 s^{-1} (95% confidence limits based upon the data given in the problem statement). The fitting tool may also produce a model plot like that shown in Figure 1, but if such a plot is not created, one can be generated easily.

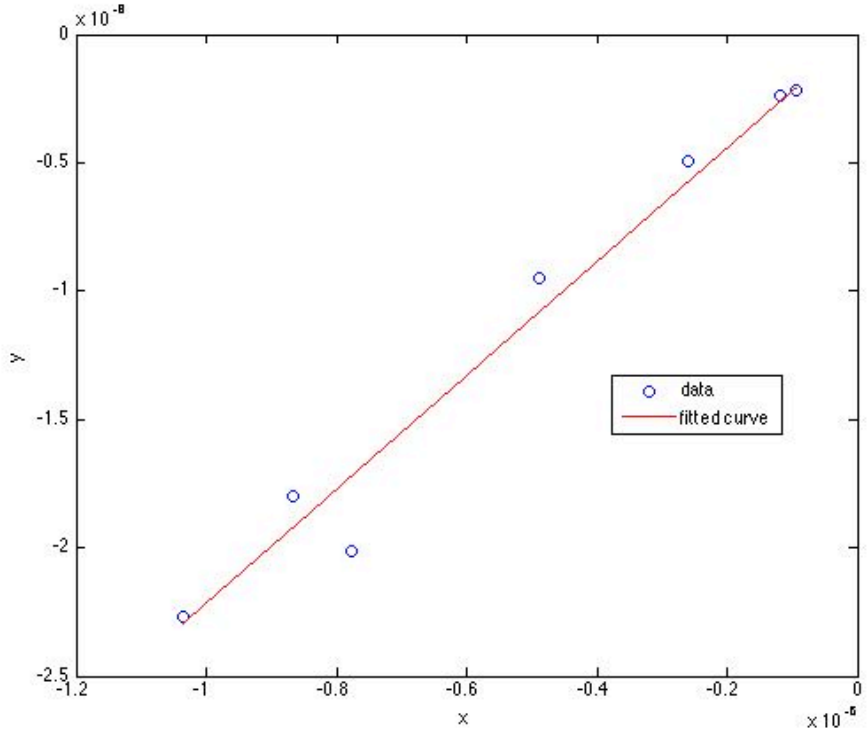

Figure 1. Model plot showing the experimental data as points and the model's predictions as a line.

Next we must decide whether the final model is sufficiently accurate. In this case, the accuracy of the model can be assessed using the correlation coefficient and the model plot. The closer the correlation coefficient is to a value of 1.0, the better the fit of the model to the data. In this case, the correlation coefficient of 0.97 indicates a good fit. Additionally, if the fit is accurate, then the scatter of the experimental data about the model should be small and random; there should not be any systematic deviations of the data from the model. Examining the model plot, Figure 1, it is apparent that these criteria are fairly well satisfied. In fact, the deviations are small except for one point, but at the same time, there is a slight curvature of the data above the model line for all of the data except that one point. Since differential analysis is only meant to offer a quick, preliminary assessment, the rate expression can be accepted at this point. However, before this rate expression is used for other calculations or reactor design, additional experiments should be performed, and the data should be analyzed using an integral analysis. For this problem, the rate coefficient is equal to the slope, and therefore no further calculations are needed.

Calculation Details Using MATLAB

Three MATLAB script files for linear least squares are provided with Supplemental Unit S3. The file names indicate the number of independent variables and whether or not the model has an intercept. The script named FitLinmSR is used when the model has one independent variable (x) and ***does not*** include the intercept (b). FitLinmbSR is used when the model has one independent variable and ***does*** include the intercept, and FitLinSR is used when the model has two or more independent variables. (With MATLAB, when the model has two or more independent variables, it must have an intercept; Supplemental Unit S3 describes how to convert a model without an intercept into a model that has an intercept.) In this problem the model has one independent variable, but no intercept, so the script file named FitLinmSR will be used. To do so, the script file must be located in the current MATLAB working directory or in the MATLAB search path.

Before executing FitLinmSR, the experimental values of x must be stored in a vector named `x`, and the experimental values of y must be stored in a vector named `y_hat`. Upon execution of the script, it will return the correlation coefficient, r^2, as `r_squared`, the slope, m, as `m`, and the 95% confidence limits on the slope, λ_m, as `m_u`. It will also generate a model plot. In this problem, since the model parameter, k, is equal to the slope, m, no additional calculations are needed. The commands for performing these tasks can be entered at the MATLAB command prompt, but here they have been recorded in the MATLAB file named Example_14_3.m which accompanies this solution.

Example_14_3.m is shown in Listing 1. It begins with the entry of the data from the problem statement and a few additional universal constants. The values of x and y are then calculated and stored in the arrays `x` and `y_hat`. FitLinmSR is then called to perform the fitting. This generates the model plot shown previously as Figure (1) along with the output shown in Listing 2.

```
% MATLAB file used in the solution of Example 14.3 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
T=568.0 + 273.15; % K
P0=1.0; % atm
Diam=0.325; % cm
L=240; % cm
y0 = [8      10     22     42     66     74     88]'; % mol % cyclopropane
y0 = y0/100; % mol fraction cyclopropane
Vfr = [2.91   4.31   2.94   2.05   4.16   2.62   3.49]'; % cm3(stp)/s
y = [7.6     9.7    21.1   39.5   63.4   70.3   84.5]'; % mol % cyclopropane
y = y/100; % mol fraction cyclopropane

% Other known constants
Rgas=82.06; % cm^3 atm / (K mol)
Pstp = 1; % atm
Tstp = 273.15; % K
% Calculate x and y using equations (14) and (19) from the solution
x = (-pi()*Diam^2/4)*(P0/Rgas/T)*(y0 + y)/2;

y_hat = zeros(7,1);
for i = 1:7
    y_hat(i) = (Pstp*Vfr(i)/Rgas/Tstp)*(y(i) - y0(i))/L;
end

% Use the MATLAB script file "FitLinmSR.m" from "A First Course on
% Kinetics and Reaction Engineering" to fit a straight line through the
% origin to the data.
FitLinmSR
```

Listing 1. Code from Example_14_3.m used to solve this problem.

```
>> Example_14_3

r_squared =

    0.9733

m =

    0.0222

m_u =

    0.0021
```

Listing 2. Output from the execution of Example_14_3.m.

References Cited

[1] Davis, B. R. and D. S. Scott, “Rate of Isomerization of Cyclopropane in a Flow Reactor,” *Ind. Eng. Chem. Fundamentals* **3**(1), 20-23 (1964).