REB, The Book
Example 11.5.3 Solution

The liquid-phase disproportionation of reagent A, reaction (1), is reversible. Kinetics data were generated in a 3 gal CSTR by varying the temperature, volumetric flow rate and feed concentrations of reagents A, Y, and Z from experiment to experiment. In each experiment the outlet concentration of reagent A was measured. Use the resulting data to assess the accuracy of the rate expression shown in equation (2) using a fitting function and using a linearized response model.

Note that thermodynamic data to calculate the equilibrium constant for reaction (1) are not available, so both the forward and reverse rate coefficients in the rate expression must be estimated from the experimental data.

$$A \leftrightarrows Y + Z \tag{1}$$

$$r = k_f C_A^2 - k_r C_Y C_Z \tag{2}$$

The first few data points are shown in Table 1. The full data set is available in the file, example_11_5_3_data.csv.

Table 1. First 6 of the 720 experimental data points

T (°F)	$\dot{V}$ (gal min^{-1})	$C_{A,in}$ (lbmol gal^{-1})	$C_{Y,in}$ (lbmol gal^{-1})	$C_{Z,in}$ (lbmol gal^{-1})	$C_{A,out}$ (lbmol gal^{-1})
90.0	0.5	0.01	0	0	0.007
90.0	0.5	0.01	0	0.01	0.0072
90.0	0.5	0.01	0	0.02	0.0071
90.0	0.5	0.01	0	0.03	0.0071
90.0	0.5	0.01	0.01	0	0.0067
90.0	0.5	0.01	0.01	0.01	0.0082

Assignment Summary

Reaction

$$A \leftrightarrows Y + Z \tag{1}$$

Rate Expression

$$r = k_f C_A^2 - k_r C_Y C_Z \tag{2}$$

Reactor: Steady-state, isothermal CSTR

Given Constants: V = 3 gal

Given Adjusted Experimental Inputs: $\underline{T}$, $\underline{\dot{V}}$, $\underline{C}_{A,in}$, $\underline{C}_{Y,in}$, and $\underline{C}_{Z,in}$

Given Experimental Responses: $\underline{C}_{A,out}$

Parameters to Estimate: $k_{0,f}$, E_f, $k_{0,r}$, and E_r

Deliverable: Assessment of the accuracy of the rate expression, equation (2).

Formulation of the Equations Using a Fitting Function

CSTR Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_{A,out} - rV = \epsilon_1 \tag{3}$$

$$0 = \dot{n}_{Y,in} - \dot{n}_{Y,out} + rV = \epsilon_2 \tag{4}$$

$$0 = \dot{n}_{Z,in} - \dot{n}_{Z,out} + rV = \epsilon_3 \tag{5}$$

CSTR Model Variables: $\dot{n}_{A,out}$, $\dot{n}_{Y,out}$, and $\dot{n}_{Z,out}$

Additional Computable Unknowns: $\dot{n}_{A,in}$, $\dot{n}_{Y,in}$, $\dot{n}_{Z,in}$, r, k_f, k_r, C_A, C_Y, and C_Z

$$\dot{n}_{i,in} = C_{i,in}\dot{V} \qquad i = A, Y, \text{ and } Z \tag{6}$$

$$k_i = k_{0,i} \exp\left(\frac{-E_i}{RT}\right) \qquad i = f \text{ and } r \tag{7}$$

$$C_i = \frac{\dot{n}_{i,out}}{\dot{V}} \qquad i = A, Y, \text{ and } Z \tag{8}$$

Additional Uncomputable Unknowns: $k_{0,f}$, E_f, $k_{0,r}$, and E_r

ATE Solver Inputs:

1. Initial guesses for the reactor model variables

$$\dot{n}_{i,out,guess} = \dot{n}_{i,in} = C_{i,in}\dot{V} \qquad i = A, Y, \text{ and } Z \tag{9}$$

2. Residuals function that
   a. receives guesses for the CSTR model variables, $\dot{n}_{A,out}$, $\dot{n}_{Y,out}$, and $\dot{n}_{Z,out}$
   b. has access to the parameters, $k_{0,f}$, E_f, $k_{0,r}$, and E_r
   c. calculates the additional unknowns using equations (2), (6), and (7)
   d. evaluates and returns the CSTR model residuals using equations (3) - (5)

Fitting Function Inputs:

1. Experimental data: $\underline{T}$, $\underline{\dot{V}}$, $\underline{C}_{A,in}$, $\underline{C}_{Y,in}$, $\underline{C}_{Z,in}$ and $\underline{C}_{A,out}$
2. Initial guesses for the parameters being estimated

$$\beta_{f,guess} = 0 \tag{10}$$

$$E_{f,guess} = 10^4 \text{ BTU lbmol}^{-1} \tag{11}$$

$$\beta_{r,guess} = 0 \tag{12}$$

$$E_{r,guess} = 10^4 \text{ BTU lbmol}^{-1} \tag{13}$$

3. Predicted Responses Function that
    a. receives the adjusted experimental inputs and guesses for the parameters
    b. calculates the pre-exponential factors and makes them and the activation energies available to the residuals function

$$k_{0,f} = 10^{\beta_f} \tag{14}$$

$$k_{0,r} = 10^{\beta_r} \tag{15}$$

    c. loops through all of the experiments
        i. solves the CSTR model equations
        ii. calculates the model-predicted response

$$C_{A,out,pred} = \frac{\dot{n}_{A,out}}{\dot{V}} \tag{16}$$

    d. returns the predicted responses for all of the experiments

<u>Parameter Estimate Equation</u>:

$$k_{0,CI} = 10^{\beta_{CI}} \tag{17}$$

Formulation of the Equations Using a Linearized Model

<u>Linearized CSTR Model Equation:</u>

$$0 = \dot{n}_{A,in} - \dot{n}_{A,out} - rV$$

$$0 = C_{A,in} - C_{A,out} - r\frac{V}{\dot{V}}$$

$$\frac{C_{A,in} - C_{A,out}}{\tau} = r$$

$$\frac{C_{A,in} - C_{A,out}}{\tau} = k_f C_{A,out}^2 - k_r C_{Y,out} C_{Z,out}$$

$$\frac{C_{A,in} - C_{A,out}}{\tau C_{Y,out} C_{Z,out}} = k_f \frac{C_{A,out}^2}{C_{Y,out} C_{Z,out}} - k_r \quad \Rightarrow \quad y = mx + b \tag{18}$$

$$\dot{n}_{Y,out} = \dot{n}_{Y,in} + \dot{\xi} \quad \Rightarrow \quad C_{Y,out} = C_{Y,in} + \frac{\dot{\xi}}{\dot{V}} \tag{19}$$

$$C_{Z,out} = C_{Z,in} + \frac{\dot{\xi}}{\dot{V}} \tag{20}$$

$$\dot{n}_{A,out} = \dot{n}_{A,in} - \dot{\xi} \quad \Rightarrow \quad \dot{\xi} = \dot{n}_{A,in} - \dot{n}_{A,out} \tag{21}$$

<u>Linear Model Least Squares Inputs</u>: (for each same-temperature data block)

$$\underline{y} = \frac{C_{A,in} - C_{A,out}}{\tau C_{Y,out} C_{Z,out}} \tag{22}$$

$$\underline{x} = \frac{C_{A,out}^2}{C_{Y,out} C_{Z,out}} \tag{23}$$

<u>Linear Model Rate Coefficient Equations</u>: (for each same-temperature data block)

$$k_f = m \tag{24}$$

$$k_r = -b \tag{25}$$

<u>Arrhenius Expression Least Squares Inputs</u>: (for $\underline{k}_f$ and $\underline{k}_r$)

$$\underline{y} = \ln \underline{k}_j \qquad j = f \text{ and } r \tag{26}$$

$$\underline{x} = \frac{1}{\underline{T}} \qquad j = f \text{ and } r \tag{27}$$

<u>Arrhenius Parameter Equations</u>: (for k_f and k_r)

$$k_{0,j} = \exp\left(b_j\right) \qquad j = f \text{ and } r \tag{28}$$

$$E_j = -m_j R \qquad j = f \text{ and } r \tag{29}$$

<u>Coefficient of Determination Equations</u>:

$$C_{A,mean} = \frac{\sum_i C_{A,out,i}}{n_{expts}} \tag{30}$$

$$ss_{resid} = \sum_i \left(C_{A,out,i} - C_{A,out,pred,i} \right)^2 \tag{31}$$

$$ss_{total} = \sum_i \left(C_{A,out,i} - C_{A,mean} \right)^2 \tag{32}$$

$$R^2 = 1 - \frac{ss_{resid}}{ss_{total}} \tag{33}$$

Implementation of the Calculations

The Python script, example_11_5_3.py, that was written to perform the calculations accompanies this solution. It is structured as follows.

1. Import necessary libraries.
2. Make the given constants, adjusted experimental inputs, and measured responses available wherever they are needed.
3. Declare global variables for quantities that cannot be passed to the residuals function as arguments.
4. Define the CSTR model, CSTR derivatives, and predicted responses functions as described above.
5. Perform the analysis using a fitting function
    a. Define an initial parameter guess and fit the CSTR model to the data using a fitting function.
    b. Calculate the experiment residuals
6. Perform the analysis using the linear model
    a. Separate the data into same-temperature blocks and for each block
        i. calculate x and y

ii. fit the straight line, $y = mx + b$, to the $x - y$ data using least squares

iii. calculate k_f and k_r from the estimates for the slope and intercept

b. Fit the Arrhenius expression to the $\left(T - k_f\right)$ and $\left(T - k_r\right)$ data from step 6a using least squares

c. Calculate the predicted responses and coefficient of determination for all of the experiments using the Arrhenius expression parameters from the the linearized model analysis.

d. Calculate the experiment residuals

7. Tabulate, graph, and save the results, as appropriate.

The fitting function did not converge using the initial guess for the parameters shown in equations (10) through (13), so other guesses had to be tried until convergence was achieved. The ATE solver did converge using the guesses listed above.

Results and Discussion

The fitting function approach yields pre-exponential factors and activation energies that are each estimated using all of the experimental data points. The results for this set of data are presented in Table 2. The parity plot is included in Figure 1, and the residuals plots, in Figure 2.

Table 2. Fitting Function Parameter Estimation Results

Parameter	Value	95% CI	Units
$k_{0,f}$	6.12 x 10^5	[2.5 x 10^5, 1.5 x 10^6]	gal $lbmol^{-1}$ min^{-1}
E_f	11,900	[10,900, 12,900]	BTU $lbmol^{-1}$
$k_{0,r}$	9.46 x 10^7	[1.9 x 10^7, 4.7 x 10^8]	gal $lbmol^{-1}$ min^{-1}
E_r	18,900	[17,100, 20,700]	BTU $lbmol^{-1}$
R^2	0.986		

The data points in the parity plot show a small amount of scatter about the parity line. The data in the residuals plots show that the scatter is random, with equal positive and negative deviations and with no trends relative to any of the adjusted experimental inputs. These graphical indicators, together with a coefficient of determination of 0.986, indicate that the model is accurate and adequately captures the effect of each adjusted input on the reaction rate.

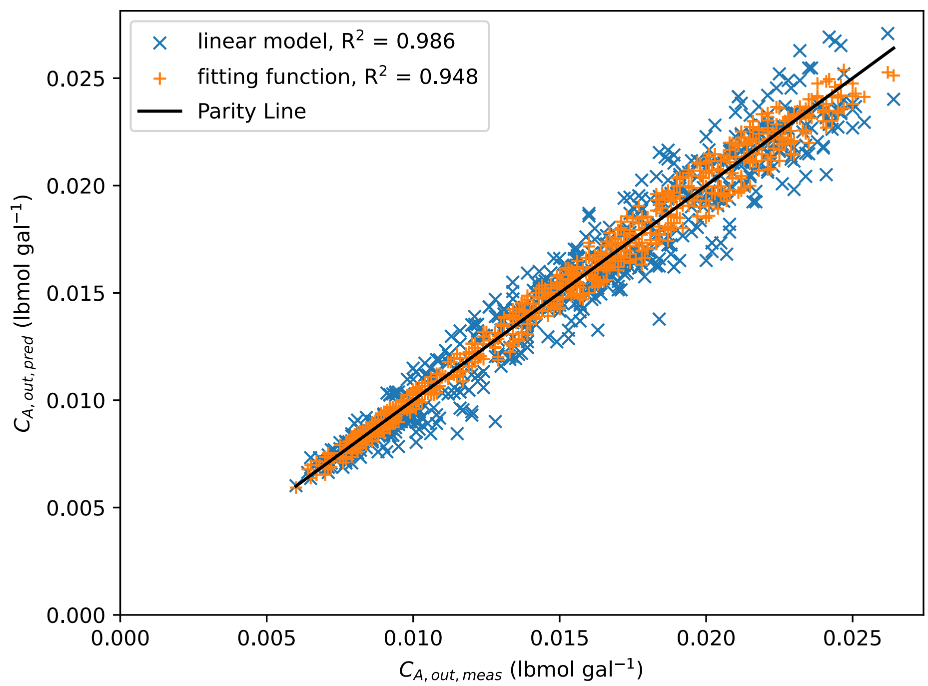

Figure 1. Parity plots for both the fitting function (blue) and linear model (green) approaches.

The confidence interval for $k_{0,f}$ is between 41 and 245 % of the estimated value, while that for $k_{0,r}$ is between 20 and 497% of its estimated value. It is often found that pre-exponential factors have relatively large uncertainties. The confidence interval for E_f is between 92 and 108% of its estimated value, and for E_r between 90 and 110% of its estimated value. These much narrower confidence intervals indicate that there is much less uncertainty in the activation energies.

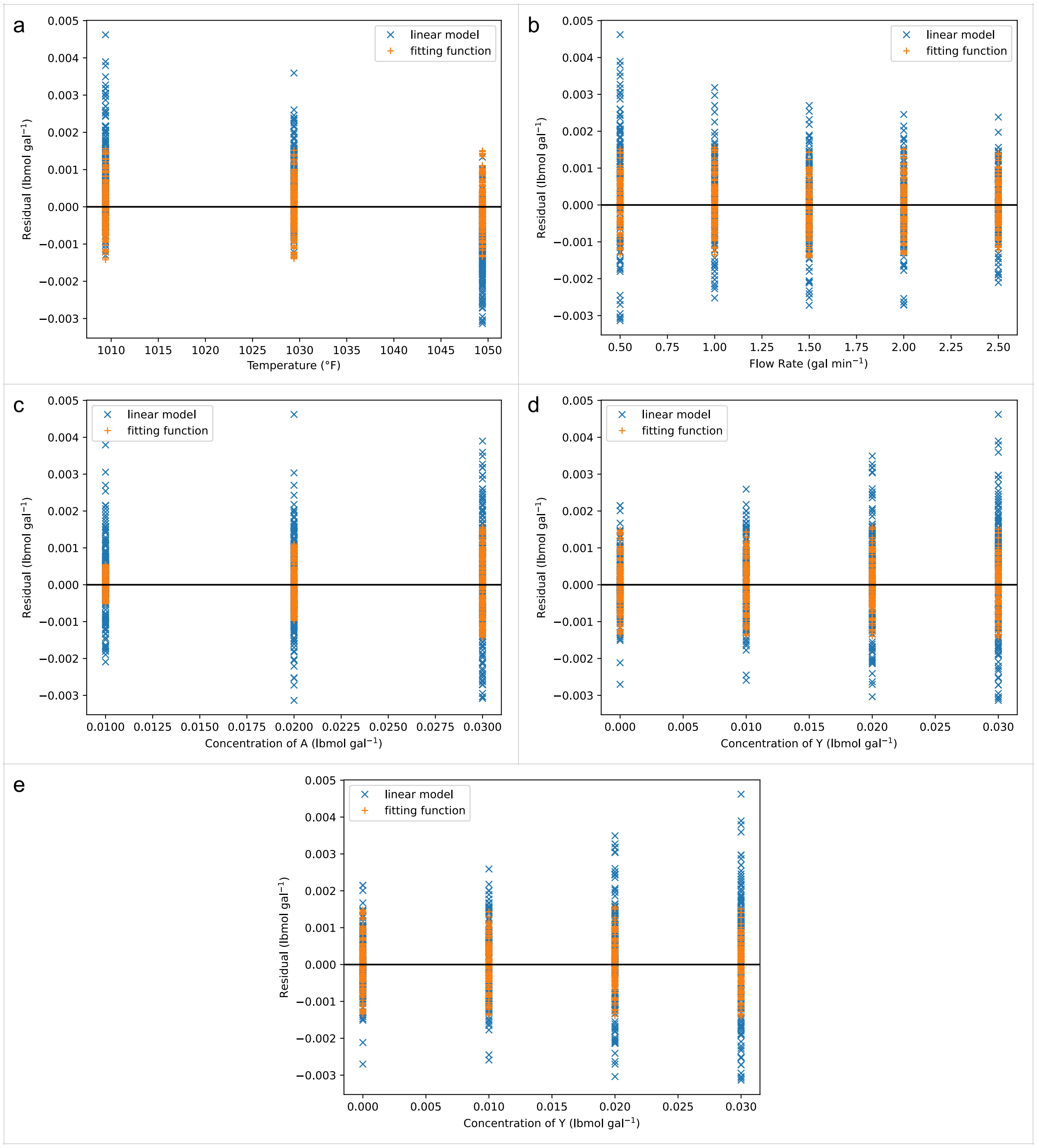

Figure 2. Residuals plots for a) temperature, b) volumetric flow rate, and feed concentrations of c) reagent A, d) reagent Y, and e) reagent Z for both the fitting function (blue) and linear model (green) approaches.

Overall, with the parameters estimated using the fitting function approach, equation (2) is an acceptably accurate rate expression. The uncertainty in the estimated parameters is reasonable and there are no indications that the rate expression fails to capture effects associated with the adjusted experimental inputs.

In the linear model approach the data are separated into same temperature blocks. The rate coefficients estimated for each block only use the data from that block, not the complete data set. Figure 3 shows the model plots for the three temperatures used in the experiments. Both a visual examination and the coefficients of determination included in the figure legends indicate that the fit of the linear model to the 110 °F data is a little less accurate than for the other temperatures.

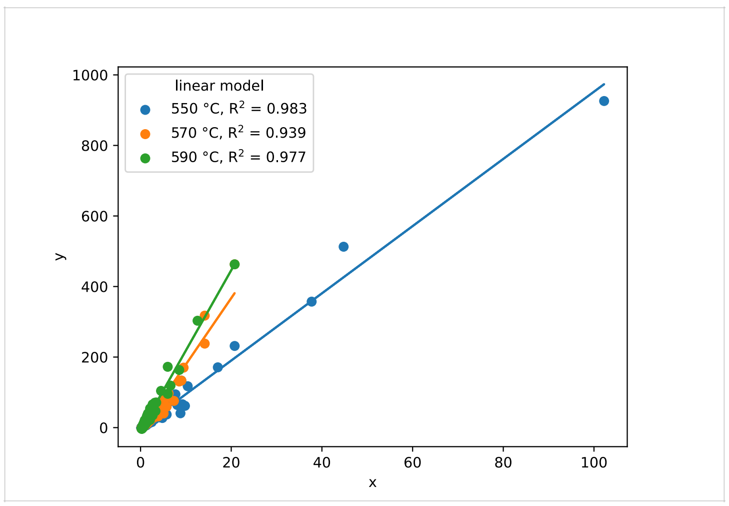

Figure 3. Model plots for linear model.

The forward and reverse rate coefficients at the three data block temperatures are found from slopes and intercepts of the model plots. The Arrhenius expression is then fit to the $(T-k)$ data as shown in Figure 4. The fit for the forward rate coefficient is relatively good, but for the reverse rate coefficient it is unacceptable.

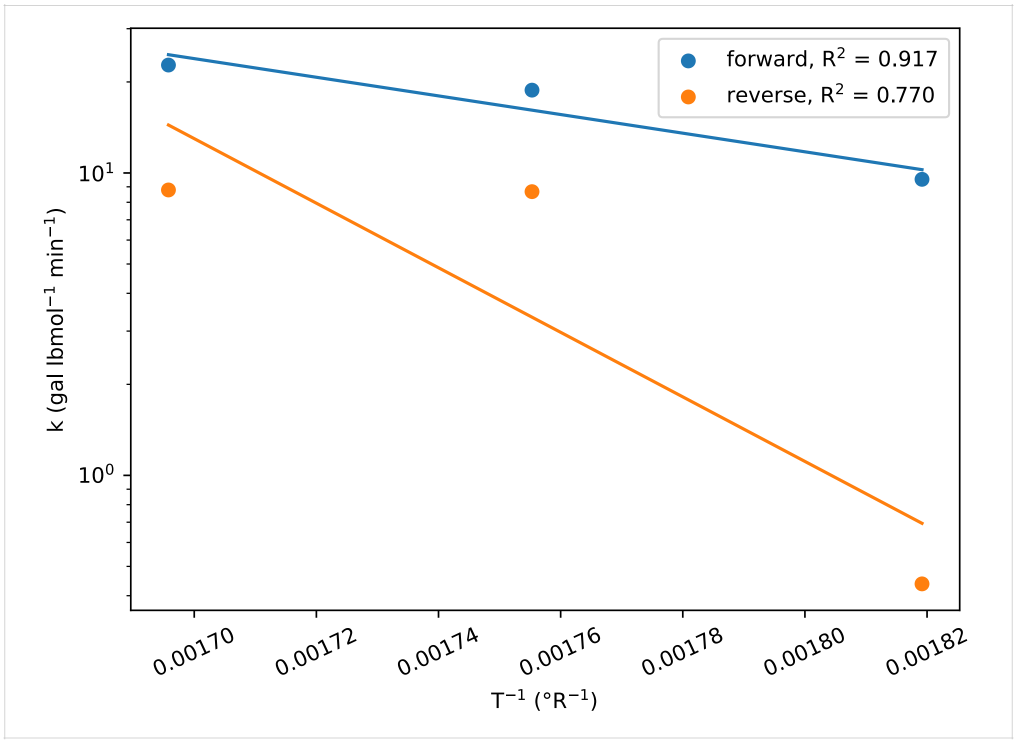

Figure 4. Arrhenius plots for the a) forward and b) reverse rate coefficients estimated using same-temperature data blocks.

Table 3 compares the Arrhenius parameters for the two approaches. As expected from the Arrhenius plots, the pre-exponential factor and activation energy for the reverse rate coefficient have huge uncertainty. Their values are also vastly different from those found using the fitting function approach. While the Arrhenius parameters for the forward rate coefficient are closer to those from the fitting function approach, their 95% confidence intervals are also unacceptable.

Given the high uncertainty in the rate expression parameters found using the linear model, it is somewhat surprising that coefficients of determination in Table 3 are both well above 0.9, and the data, shown in green, still fall close to the parity plot in Figure 1. The deviations are larger, but don't, in themselves, indicate that the rate expression is unacceptable. The larger deviations are also seen in the residuals plots of Figure 2. There appears to be a trend in the deviations as a function of temperature for the linear model, but not for the fitting function approach.

While the linear model gives a reasonably accurate overall model, the uncertainties in the individual parameters are too large, and it should not be accepted. Additional experiments should be performed, particularly at 110 °F, to get better estimates.

Table 3. Comparison of the Estimated Rate Expression Parameters

Approach	Parameter	Value	95% CI
fitting function	$k_{0,f}$	6.12×10^5 gal lbmol^{-1} min^{-1}	[2.5×10^5, 1.5×10^6]
	E_f	11907 BTU lbmol^{-1}	[10900, 12914]
	$k_{0,r}$	9.46×10^7 gal lbmol^{-1} min^{-1}	[1.9×10^7, 4.71×10^8]
	E_r	18913 BTU lbmol^{-1}	[17092, 20735]
	R^2	0.986	
linear model	$k_{0,f}$	4.14×10^6 gal lbmol^{-1} min^{-1}	[7.43×10^{-15}, 2.3×10^{27}]
	E_f	14098 BTU lbmol^{-1}	[-39908, 68105]
	$k_{0,r}$	1.82×10^{19} gal lbmol^{-1} min^{-1}	[1.42×10^{-111}, 2.33×10^{149}]
	E_r	48838 BTU lbmol^{-1}	[-289868, 387544]
	R^2	0.948	

Deliverables

Using a fitting function approach, the parameter values shown in Table 2 were estimated. With those parameters, the rate expression shown in equation (2) is acceptably accurate.