Determination of Rate Parameters of Complex Reactions by POLYMATH

Burcu Özdemir* and Selahattin Gültekin

Doğuş University, Acıbadem, Kadıköy 34722, Istanbul, Turkey

Abstract: Generally, consecutive and/or parallel reactions pose a great deal of difficulty in determining meaningful reaction rate parameters. One way to determine such parameters is to separate the whole reaction network into different regions and to study each region independently through initial rates. This method is not only tedious, but also a waste of money and time.

The other method is to use the fact that, if the reaction rates are known at any "t" time then an optimization technique in MATLAB, MATHCAD, LINDO or POLYMATH ready package programs can be used to determine rate parameters.

In this study, the POLYMATH program is chosen for a highly complex rate expression for the reaction of

$$CO + 2H_2 \xrightarrow{catalyst} CH_3OH$$

with Langmuir-Hinshelwood kinetic expression

$$-r_A = \frac{kK_{CO}K_{H2}P_{H2}P_{CO}}{(1 + K_{CO}.P_{CO} + K_{H_2}.P_{H_2} + K_{CH_3OH}.P_{CH_3OH})^2}$$

Rate parameters k, $K_{CO,}$ K_{H2} and K_{CH3OH} were determined.

INTRODUCTION

In chemical reaction engineering and in purely chemical kinetics, due to the nature of the reaction one may face very complex reaction networks. Among the complex models, the most suitable one must be determined. In this determination, well-established regression techniques are used. These regression techniques are [1]

a) Linear regression (such as $y = ax + b$)

b) Multiple regression (such as $y = a_1x_1 + a_2x_2 + ... + a_nx_n$)

c) Polynomial regression (such as $y = a_nx^n + a_{n-1}x^{n-1} + ... + a_1x + a_0$)

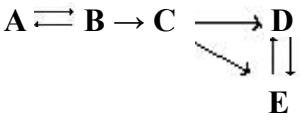
d) Non-linear regression, (such as $y = f(x_1, x_2, ..., x_n, a_1, a_2, ..., a_n)$ where n = # of experiments, m = # of parameters to be determined providing $n >$ m+1.)

This is very common and can be used almost under any condition.

In using these techniques, one has to watch for the following criteria [2]

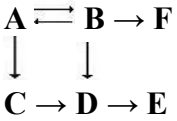
1. Variance must be minimum
2. Correlation coefficient (R) must be as close to unity as possible
3. Determined rate parameters must be physically meaningful
4. 95 % confidence interval determination is also essential in order to eliminate (ignore) certain parameters

Reactions networks such as



[3]

or



[4]

are not uncommon in reaction engineering.

REACTION RATE EXPRESSION

Reaction rate expression of

$$r_A = \frac{K_AK_Bk'P_AP_B}{(1 + K_AP_A + K_BP_B + K_CP_C)^2}$$

can be observed on a heterogeneous catalytic reaction of such as

$$CO + 2H_2 \xrightarrow{catalyst} CH_3OH$$

Then for the above reaction, we can write dual-site Langmuir-Hinshelwood model as follows:

*Address correspondence to this author at the Doğuş University, Acıbadem, Kadıköy 34722, Istanbul, Turkey; E-mail: burcuozdemir@dogus.edu.tr

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$$-r_A = \frac{kK_{CO}K_{H2}P_{H2}P_{CO}}{(1+K_{CO}.P_{CO}+K_{H_2}.P_{H_2}+K_{CH_3OH}.P_{CH_3OH})^2}$$ (dual site assumption is made)

In this study, the data given in Table **1** for the above reaction were considered for the determination of rate parameters through POLYMATH [1, 5].

Table 1. Initial Rate of Reaction at Various Partial Pressures of Reactants and Product

Experiment No	P_{CO}*	P_{H2}	P_{CH3OH}	Rate**
1	0.5	0.5	0.5	0.0457
2	1.0	0.5	0.5	0.0457
3	2.0	0.5	0.5	0.0384
4	4.0	0.5	0.5	0.0241
5	8.0	0.5	0.5	0.0141
6	1.0	1.0	0.5	0.0640
7	1.0	2.0	0.5	0.0727
8	1.0	4.0	0.5	0.0653
9	1.0	8.0	0.5	0.0474
10	1.0	1.0	1.0	0.0527
11	1.0	1.0	2.0	0.0375
12	1.0	1.0	4.0	0.0218
13	1.0	1.0	8.0	0.0100
14	0.5	1.0	0.5	0.0561
15	0.5	0.5	1.0	0.0332

* P_i = [atm], ** rate = [mole/kg cat-s].

Output

$$rate = k \cdot K_{CO}K_{H_2} \cdot P_{CO} / (1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{CH_3OH} \cdot P_{CH_3OH})^2$$

Variable	Initial Guess	Value	95% Confidence
k	0.5	0.4002314	9.014E-06
Kco	7.0	5.984377	0.0003698
KH2	4.5	3.994414	0.0002109
KCH3OH	3.0	2.495249	0.0001844

Precision

R^2	0.9999993
R^2 adj	0.9999991
Rmsd	4.015E-06
Variance	3.297E-10

Source Data Points and Calculated Data Points

	P_{H2}	Pco	P_{CH3OH}	rate	rate calc.	Delta rate
1	0.5	0.5	0.5	0.0457	0.0456671	3.287E-05
2	0.5	1.0	0.5	0.0457	0.0457161	-1.610E-05
3	0.5	2.0	0.5	0.0364	0.0363936	6.397E-06
4	0.5	4.0	0.5	0.0241	0.0240912	8.764E-06
5	0.5	8.0	0.5	0.0141	0.0140876	1.240E-05
6	1.0	1.0	0.5	0.0640	0.0640007	-7.269E-07
7	2.0	1.0	0.5	0.0727	0.0727222	-2.221E-05
8	4.0	1.0	0.5	0.0653	0.0652929	7.104E-06
9	8.0	1.0	0.5	0.0474	0.0473909	9.065E-06
10	1.0	1.0	1.0	0.0527	0.0526972	2.798E-06
11	1.0	1.0	2.0	0.0375	0.0375156	-1.562E-05
12	1.0	1.0	4.0	0.0218	0.0217776	2.242E-05
13	1.0	1.0	8.0	0.0100	0.0099936	6.430E-06
14	1.0	0.5	0.5	0.0561	0.0560986	1.386E-06
15	0.5	0.5	1.0	0.0332	0.0332243	-2.431E-05

Table 2. Model Equation, Data and The Results with Statistical Analysis

rate= $k*K_{CO}*K_{H2}*P_{H2}*P_{CO}/(1+K_{CO}*P_{CO}+K_{H2}*P_{H2}+K_{CH3OH}*P_{CH3OH})^2$

Initial Guess for Model Parameters	
Model Parameters	Initial Guess
k	0.5
K_{CO}	7
K_{H2}	4.5
K_{CH3OH}	3

Variables	
Dependent Variables	Reaction rate
Independent Variable	P_{H2}, P_{CO}, P_{CH3OH}
Model Variable/s	k, K_{CO}, K_{H2}, K_{CH3OH}
Available Variables	Experiment, P_{CO}, P_{H2}, P_{CH3OH}

Output			
Variable	Initial guess	Value	95% confidence
k	0.5	0.4002314	9.014E-06
K_{CO}	7.0	5.984377	0.0003698
K_{H2}	4.5	3.994414	0.0002109
K_{CH3OH}	3.0	2.495249	0.0001844

Precision	
R^2	0.9999993
R^2 adj	0.9999991
Rmsd	4.015E-06
Variance	3.297E-10

As can be seen from the output information (Table **2**) adsorption equilibrium constants K_i's as well as rate constant, k have physical meaning. For example, non of K_i's is expected to be negative, as they must be not only positive, but they must also decrease with increasing temperature [6].

CONCLUSIONS

Experimental data can be used easily to determine rate parameters for any suggested model by usage of readily available POLYMATH or any other similar program. In the example given in this paper, Langmuir-Hinshelwood rate model with dual-site adsorption were used and then four rate parameters k, $K_{CO,}$ K_{H2} and K_{CH3OH} were determined.

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