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An Application of MS Excel for Data Fitting with Ordinary Differential Equations in Chemical Reaction Engineering

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Abstract. Explorations of the 4th order Runge-Kutta method for ordinary differential equations (ODEs) on MS Excel spreadsheet are constructed in this paper. Appling the least square method, unknown constant(s) in ODEs can be found out by fitting given data with the desired curve using Solver Excel. Numerical solutions for two selected problems in chemical reaction engineering are also proposed and carried out. This article indicates the powerful applicability of MS Excel in mathematical engineering problems.

Keywords: numerical solution, differential equation, Solver Excel, chemical engineering

Introduction

The ordinary differential equations (ODEs) have been widely applied in engineering and science. Numerical approach for ODEs enables to find out the approximate solution for complex problems, which can not be solved by algebraic methodologies (Atkinson, Han, & Stewart, 2009). In terms of the recent powerful methods for solving ODEs such as the Euler's method, the Taylor method, the multistep methods, the Runge-Kutta method, etc., in which the Runge-Kutta (RK) method is the most popular due to its easy implementation, high stability and low error (Nirmala, Parimala, & Rajarajeswari, 2018). Therefore, many commercial software packages were programmed basing the RK method with high convenience for OEDs solution with known constant(s).

However, various OEDs models in engineering have been established for the determination of unknown constant(s) by fitting them with given data. Programmable software applications can professionally solve this problem, but they may difficult to understand and build up, especially for beginners. Based on the Generalized Reduced Gradient (GRG) method (Powell & Batt, 2008), Solver in Microsoft Excel is helpful in solving and/or optimizing various modeled processes with multi-variables. Through explaining the RK method in an Excel spreadsheet, this work suggested simple procedures for solving the above problem.

Mathematic Basics

Ordinary Differential Equations

Equation (1) is a simple ODE, which involves a function (of one variable) and its first derivative.

$$y' = f(x, y) \tag{1}$$

Here x and y are called the *independent variable* and the *dependent variable*, respectively. The particular solution of (1) can be numerically got if known initial value $y(x_0) = a$. To combine ODEs under form (1) with different dependent variables, a system of first differential equations is generated as (2)

$$\begin{cases} y_1' = f_1(x, y_1, y_2, ..., y_n) \\ y_2' = f_2(x, y_1, y_2, ..., y_n) \\ \vdots \\ y_n' = f_n(x, y_1, y_2, ..., y_n) \end{cases} \tag{2}$$

with initial conditions: $\begin{cases} y_1(x_0) = a_1 \\ y_2(x_0) = a_2 \\ \vdots \\ y_n(x_0) = a_n \end{cases}$.

For n-order ODE (3), it can be simplified to a system of first differential equations as (2) by setting $y_1 = y'$, $y_2 = y''$, … , $y_{n-1} = y^{(n-1)}$. This technique has been widely applied in almost all cases.

$$y^{(n)} + g_{n-1}(x).y^{(n-1)} + ... + g_1(x).y' + g_0(x).y = f(x) \tag{3}$$

Runge-Kutta Method

Fundamental of this method was detailed in previous report (Nirmala, Parimala, & Rajarajeswari, 2018). The RK method was expanded using Taylor's expansions. Therefore, the RK solution for ODEs is more accurate with a higher order of expansion and resulting in a more complex procedure. Formulas and parameters for different RK method orders were summarized by Arora, Joshi, and Garki (2020), and developed up 7th order by Séca and Kouass (2019). The 4th order RK method, which is used in this work, is satisfactory for engineering applications because of its easy operation and high accuracy (Séca & Kouass, 2019). From the point (x_i, y_i), an approximation of dependent variable y in (1) at a nearby value $x_{i+1} = x_i + h$ can be calculated using the recursive formula (4).

$$y_{i+1} = y_i + \frac{1}{6}h(K_1 + 2K_2 + 2K_3 + K_4) \tag{4}$$

where

$$\begin{aligned} K_1 &= f(x_i, y_i) \\ K_2 &= f\left(x_i + \frac{h}{2}, y_i + K_1\frac{h}{2}\right) \\ K_3 &= f\left(x_i + \frac{h}{2}, y_i + K_2\frac{h}{2}\right) \\ K_4 &= f(x_i + h, y_i + K_3 h) \end{aligned} \tag{5}$$

h is step-size of independent variable; K_1, K_2, K_3, K_4 are known as RK parameters; and $\phi = \frac{1}{6}(K_1 + 2K_2 + 2K_3 + K_4)$ is an average slope.

It is easy to extend the 4th order RK method to first-order ODE systems (2). In this case, relations in the system (6) are used to approximate values of the dependent variables.

$$\begin{cases} y_{1,i+1} = y_{1,i} + \frac{1}{6}h\left(K_{11} + 2K_{21} + 2K_{31} + K_{41}\right) \\ y_{2,i+1} = y_{2,i} + \frac{1}{6}h\left(K_{12} + 2K_{22} + 2K_{32} + K_{42}\right) \\ \vdots \\ y_{n,i+1} = y_{n,i} + \frac{1}{6}h\left(K_{1n} + 2K_{2n} + 2K_{3n} + K_{4n}\right) \end{cases} \tag{6}$$

and

$$\begin{aligned} K_{1j} &= f_j\left(x_i, y_{1,i}, y_{2,i}, \ldots, y_{n,i}\right) \\ K_{2j} &= f_j\left(x_i + \frac{h}{2}, y_{i,1} + K_{11}\frac{h}{2}, y_{i,2} + K_{12}\frac{h}{2}, \ldots, y_{i,n} + K_{1n}\frac{h}{2}\right) \\ K_{3j} &= f_j\left(x_i + \frac{h}{2}, y_{i,1} + K_{21}\frac{h}{2}, y_{i,2} + K_{22}\frac{h}{2}, \ldots, y_{i,n} + K_{2n}\frac{h}{2}\right) \\ K_{4j} &= f_j\left(x_i + h, y_{i,1} + K_{31}h, y_{i,2} + K_{32}h, \ldots, y_{i,n} + K_{3n}h\right) \end{aligned} \tag{7}$$

where, $j = 1, 2, \ldots, n$.

Least Square Method

Deviation (error) e_i between each given data point $\left(x_i, y_i\right)$ and the considered curve of a function $y = f\left(x\right)$ is $e_i = y_i - f\left(x_i\right)$. According to the least square method, the best-fit curve is obtained if the sum of squared error $\sum_{i=1}^{n} e_i^2$ is minimum (Molugaram & Rao, 2017).

To evaluate the strength of relationship between the fit-curve and the given data, the squared correlation coefficient r^2 must be calculated by (8).

$$r^2 = 1 - \frac{SSE}{SSF} = 1 - \frac{\sum_{i=1}^{n} e_i^2}{\sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2} \tag{8}$$

where $\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i$ is an average value of the given dependent variable. The good fit is indicated by the close value r^2 to 1.

Engineering Problems Supposed

Problem 1

Decomposition of ozone in water is simplified by elemental chemical reactions: $2O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 3O_2$. An experiment carried out the variation of the ozone concentration C with reaction time t as following:

t, s	0	5	10	15	20	25	30	35	40
C, ppm	10.0	7.5	6.0	4.8	3.8	3.2	2.8	2.6	2.5

Kinetic constants k_1, k_{-1} of ozone decomposition can be determined using the reaction rate laws, particularly shown as (9).

$$\frac{dC}{dt} = -k_1 C^2 + \frac{3}{2} k_{-1} (C_0 - C)^3 \tag{9}$$

where C_0 is the initial concentration of ozone.

Workspace in Excel was created as illustrated in Figure 1. Procedures, formulas and explanations were detailed as following:

	A	B	C	D	E	F	G	H	I	J	K
1		Step-size	5	s							
2		k_1 =	0.0073015	1/(s.ppm)							
3		k_{-1} =	3.292E-05	1/(s.ppm^2)							
4	No	t, s	C, ppm	$C_{cal.}$	K_1	K_2	K_3	K_4	ϕ	$(e_i)^2$	SSF_i
5	1	0	10.0	10	-0.7301	-0.4882	-0.5629	-0.3781	-0.5351	0	27.04
6	2	5	7.5	7.3246392	-0.3925	-0.2962	-0.3185	-0.2437	-0.3109	0.03075	7.29
7	3	10	6.0	5.769927	-0.2462	-0.1996	-0.2081	-0.1706	-0.2054	0.05293	1.44
8	4	15	4.8	4.7431457	-0.1712	-0.145	-0.1489	-0.1274	-0.1477	0.00323	7.9E-31
9	5	20	3.8	4.004455	-0.1289	-0.1115	-0.1136	-0.1002	-0.1132	0.0418	1
10	6	25	3.2	3.4385722	-0.1019	-0.0897	-0.0909	-0.0821	-0.0908	0.05692	2.56
11	7	30	2.8	2.9844263	-0.0835	-0.0749	-0.0756	-0.0696	-0.0757	0.03401	4
12	8	35	2.6	2.6061518	-0.0696	-0.0646	-0.0649	-0.0607	-0.0649	3.8E-05	4.84
13	9	40	2.5	2.2816907	-0.0588	-0.0573	-0.0574	-0.0544	-0.0571	0.04766	5.29
14									SUM	0.26735	53.46

Desired values

Experimental data

RK area

Figure 1. Excel workspace for Problem 1

- Step-size (cell C1) is 5 due to the interval of reaction time from experiment.
- Desired values of k_1, k_{-1} (cells C2, C3) were first randomly chosen. If the troubleshoot occurs in RK calculations (next steps), these values need to be reset.
- The initial value (cell D5) is equal to the ozone concentration at $t = 0$ (cell C5).
- RK parameters K_1, K_2, K_3, K_4 were calculated using (5).
- All of the cells else in the RK area were similarly calculated.

Parameter	Formula
K_1 (cell E5)	=-$C$2*D5^2-1.5*$C$3*($C$5-C5)^3
K_2 (cell F5)	=-$C$2*(D5+E5*$C$1/2)^2-1.5*$C$3*($C$5-(D5+E5*$C$1/2))^3
K_3 (cell G5)	=-$C$2*(D5+F5*$C$1/2)^2-1.5*$C$3*($C$5-(D5+F5*$C$1/2))^3
K_4 (cell H5)	=-$C$2*(D5+G5*$C$1)^2-1.5*$C$3*($C$5-(D5+G5*$C$1))^3
ϕ (cell I5)	=(E5+2*F5+2*G5+H5)/6
$(e_i)^2$ (cell J5)	= (C5-D5)^2 (squared error between experimental and calculated values)
SSF_i (cell K5)	= (C5-AVERAGE($C$5:$C$13))^2
y_{i+1} (cell D6)	= D5+I5*$C$1 (approximate value of concentration at next reaction time)

The sum of $(e_i)^2$ (cell J14) from J5 to J13 must be minimized by adjusting the values of k_1, k_{-1} with Excel Solver. The Solver Parameter box is opened by selecting Data tab → Solver. Main parameters were entered into this window as presented in Figure 2a).

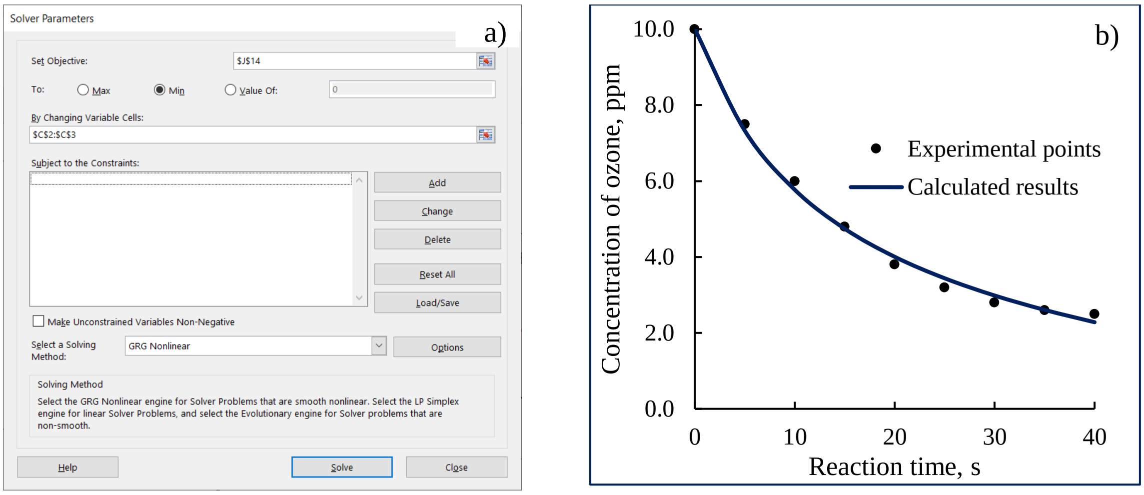

Figure 2. a) Solver Parameters box and b) correlation between experimental and calculated results in Problem 1

After the Solver option was selected, desired kinetic constants k_1, k_{-1} were found to be 7.30×10^{-5} ($s^{-1}ppm^{-1}$) and 3.29×10^{-5} ($s^{-1}ppm^{-2}$), respectively. As consequently, the good fit between experimental results and fit-curve (Figure 2b) was indicated by the value of $r^2 = 0.9950$ according to (8).

Problem 2

Primary reaction $2A \xrightarrow{k} B$ taken place in an ideal plug flow reactor as schemed in Figure 3. Concentration of A along with length x ($0 \le x \le 1$) of reactor were recorded as following:

x, m	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
C, M	1.00	0.98	0.97	0.94	0.91	0.88	0.83	0.77	0.42	0.27	0.12

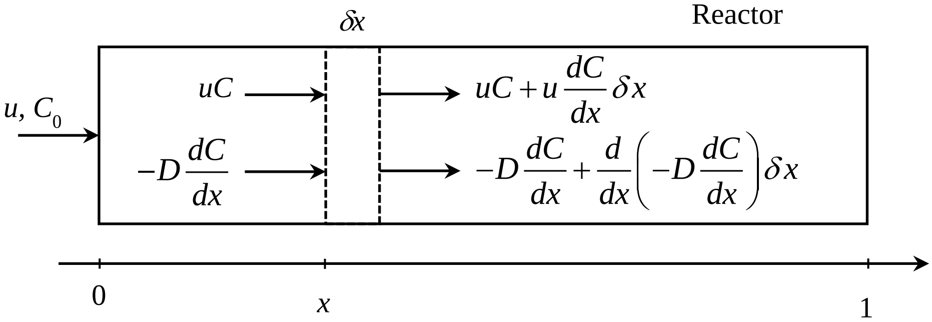

Figure 3. Scheme of plug flow reactor

Mass balance is applied for the element with length δx from x, resulting in (10).

$$\underbrace{\left[uC+\left(-D\frac{dC}{dx}\right)\right]}_{input}-\underbrace{\left[\left(uC+u\frac{dC}{dx}\delta x\right)+\left(-D\frac{dC}{dx}+\frac{d}{dx}\left(-D\frac{dC}{dx}\right)\delta x\right)\right]}_{output}-\underbrace{r_A\delta x}_{reaction}=\underbrace{0}_{accumulation} \qquad (10)$$

Reduce and rearrange (10), the reactor was modeled by the 2nd order ODE (11).

$$D\frac{d^2C}{dx^2}-u\frac{dC}{dx}-kC^2=0 \qquad (11)$$

where u = 2 mm/s is velocity of fluid, D: diffusion coefficient (m^2/s), k: reaction rate constant (L/mol.s) and C: concentration of A (mol/L). Herein, D and k are parameters that must be determined.

By setting $z = \frac{dC}{dx}$, the 2nd order OED (11) converts to the system of first-order ODEs (12).

$$\begin{cases} \dfrac{dC}{dx} = z \\ \dfrac{dz}{dx} = kC^2 + \dfrac{u}{D} z \end{cases} \tag{12}$$

Apparently, $z(0) = 0$.

Applying (6) and (7), workspace was created with chosen D and k values of 10^{-3} as Figure 4. Herein, groups of (C_1, C_2, C_3, C_4) and (Z_1, Z_2, Z_3, Z_4) are the RK parameters for the dependent variable C and z.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1		Step-size	0.1	[-]													
2		u =	2.00E-03	m/s													
3		D =	6.32E-04	m^2/s													
4		k =	3.56E-04	L/(mol.s)													
5	No.	x, [-]	C	$C_{cal.}$	z	C_1	Z_1	C_2	Z_2	C_3	Z_3	C_4	Z_4	ϕ_C	ϕ_z	$(e_i)^2$	SSF_i
6	1	0	1	1	0	0	-0.563607	0	-0.652789	0	-0.666901	0	-0.774661	0	-0.66294	0	0.058037
7	2	0.1	0.98	1	-0.06629	-0.066294	-0.773407	-0.069609	-0.892057	-0.069775	-0.910646	-0.073272	-1.053762	-0.06972	-0.90543	0.0004	0.048801
8	3	0.2	0.97	0.993028	-0.15684	-0.156837	-1.052117	-0.164679	-1.209855	-0.165071	-1.23438	-0.173344	-1.424437	-0.16495	-1.2275	0.00053	0.044483
9	4	0.3	0.94	0.976533	-0.27959	-0.279587	-1.422275	-0.293567	-1.632051	-0.294266	-1.664487	-0.309014	-1.917132	-0.29404	-1.65541	0.001335	0.032728
10	5	0.4	0.91	0.947129	-0.44513	-0.445129	-1.914284	-0.467385	-2.193708	-0.468498	-2.236764	-0.491979	-2.573372	-0.46815	-2.22477	0.001379	0.022774
11	6	0.5	0.88	0.900314	-0.66761	-0.667605	-2.569611	-0.700986	-2.942965	-0.702655	-3.000414	-0.737871	-3.450626	-0.70213	-2.9845	0.000413	0.014619
12	7	0.6	0.83	0.830101	-0.96606	-0.966055	-3.445639	-1.014358	-3.946977	-1.016773	-4.024182	-1.067733	-4.629859	-1.01601	-4.00297	1.03E-08	0.005028
13	8	0.7	0.77	0.728501	-1.36635	-1.366352	-4.623208	-1.43467	-5.301291	-1.438086	-5.406053	-1.510161	-6.227626	-1.437	-5.37759	0.001722	0.000119
14	9	0.8	0.61	0.5848	-1.90411	-1.904111	-6.218688	-1.999317	-7.145052	-2.004077	-7.289021	-2.104519	-8.415973	-2.00257	-7.25047	0.000635	0.022228
15	10	0.9	0.34	0.384543	-2.62916	-2.629158	-8.403838	-2.760616	-9.686377	-2.767189	-9.887469	-2.905877	-11.45613	-2.76511	-9.83461	0.001984	0.175637
16	11	1	0.12	0.108033	-3.61262	-3.612619	-11.43943	-3.79325	-13.24594	-3.802281	-13.53258	-3.992847	-15.75727	-3.79942	-13.459	0.000143	0.408437
17															**SUM**	0.008541	0.832891

Figure 4. Excel workspace for Problem 2

Fitting curve with Solver released the D and k values of 6.23×10^{-4} and 3.56×10^{-4}, respectively, resulting in $r^2 = 0.9897$. The relationship between fit-curve and given data can be observed as in Figure 5.

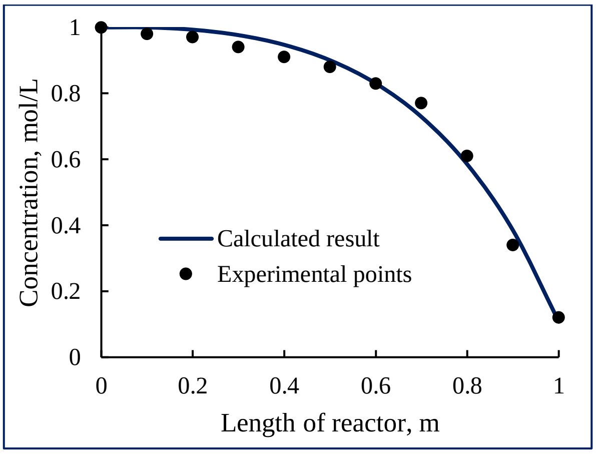

Figure 5. Correlation between experimental and calculated result in Problem 2

Conclusion

The MS Excel application for ODEs fitting was developed in this paper. Procedures for solving ODEs with the 4th order Runge-Kutte method are visually shown on the Excel spreadsheet. From using the least square method, unknown constants in two supposed problems were determined by fitting the desired curve to given data with the Solver Excel. The approach in this paper can be extended for other mathematical problems in easy-to-use.

References

Arora, G., Joshi, V. & Garki, I. S. (2020). Developments in Runge–Kutta Method to Solve Ordinary Differential Equations. In M. Ram (Ed.), *Recent Advances in Mathematics for Engineering* (pp. 193-202). Boca Raton, Florida, US: CRC Press.

Atkinson, K., Han, W., & Stewart, D. E. (2009). *Numerical Solution of Ordinary Differential Equations.* New Jersey, Canada: Wiley.

Molugaram, K. & Rao, G. S. (2017). Curve Fitting. In *Statistical Techniques for Transportation Engineering* (pp. 281-292). Cambridge, US: Elsevier.

Nirmala V., Parimala V. & Rajarajeswari P. (2018). *Application of Runge-Kutta method for finding multiple numerical solutions to intuitionistic fuzzy differential equations*. International Conference on Applied and Computational Mathe, Conf. Series, 1139, 01201.

Powell, S. G., & Batt, R. J. (2008). *Modeling for Insight: A Master Class for Business Analysts*. New Jersey, Canada: Wiley.

Séca, H. & Kouassi, A. R. (2019). A New Seventh Order Runge-kutta Family: Comparison with the Method of Butcher and Presentation of a Calculation Software. *Mathematics and Computer Science, 4*(3), 68-75.