

# **ANNEX I**

## **Programa NLREG versió 3.3**

En el present apèndix es mostren alguns exemples d'aplicació del programa NLREG per a l'estimació paramètrica de funcions no lineals.

## 1. Experiment TGA amb cel·lulosa Avicel PH-101 a 5 K/min

### Fitxer d'entrada de dades

**Equació cinètica**

$$-\frac{dm_t}{dt} = m_0 \left( \frac{m_t}{m_0} - \varphi \right) A \exp\left(\frac{-E}{RT}\right)$$

Els paràmetres cinètics que s'han d'ajustar són tres: el factor preexponencial ( $A$ ), el relatiu a l'energia d'activació aparent ( $c = E / R$ ) i la fracció massica de sòlid residual ( $\varphi = m_f / m_0$ ). Per als tres paràmetres, es pren un valor inicial.

**Dades**  $x = m_t$  (dada de la corba TG);  $y = -(dm_t / dt)$  (dada de la corba DTG);  $z = 1 / T$  (dada experimental).

```
Title "Fit cinetica";
Variables x,y,z;
Parameter phi=0.08 [-];
Parameter A=10^18 [s^-1];
Parameter c=28867 [K];
Function y=3.95*(x/3.95-phi)*A*exp(-c*z);
Data;
3.940 0.00005 0.001811
3.937 0.00005 0.001799
3.936 0.00002 0.001783
3.931 0.00008 0.001767
3.926 0.00008 0.001751
3.917 0.00015 0.001733
3.906 0.00018 0.001718
3.890 0.00027 0.001703
3.870 0.00033 0.001692
3.849 0.00035 0.001678
3.785 0.00110 0.001663
3.677 0.00180 0.001650
3.489 0.00310 0.001637
3.180 0.00510 0.001623
2.720 0.00770 0.001610
2.146 0.00960 0.001600
1.551 0.00990 0.001585
1.044 0.00850 0.001572
0.687 0.00590 0.001550
0.489 0.00130 0.001538
0.409 0.00037 0.001532
0.387 0.00018 0.001527
```

### Fitxer de sortida de dades

```
1: Title "Fit cinetica";
2: Variables x,y,z;
3: Parameter phi=0.08 [-];
4: Parameter A=10^18 [s^-1];
5: Parameter c=28867 [K];
6: Function y=3.95*(x/3.95-j)*A*exp(-c*z);
7: Data;
```

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```

Beginning computation...
Iteration 0. Sum of squared deviations = 5.15747E-004
Iteration 1. Sum of squared deviations = 4.82171E-005
Iteration 2. Sum of squared deviations = 2.28573E-005
Iteration 3. Sum of squared deviations = 2.26224E-005
Iteration 4. Sum of squared deviations = 2.26224E-005
Iteration 5. Sum of squared deviations = 2.26224E-005

---- Final Results ----

Fit cinetica
Number of observations = 22
Maximum allowed number of iterations = 50
Convergence tolerance factor = 1.000000E-010
Stopped due to: Singular convergence. Mutually dependent parameters?
Number of iterations performed = 5
Final sum of squared deviations = 2.26224E-005
Final sum of deviations = -5.92415E-003
Standard error of estimate = 0.00109117
Average deviation = 0.000760902
Maximum deviation for any observation = 0.0017238
Proportion of variance explained (R^2) = 0.9115 (91.15%)
Adjusted coefficient of multiple determination (Ra^2) = 0.9022 (90.22%)
Durbin-Watson test for autocorrelation = 0.530

---- Calculated Parameter Values ----

Parameter Initial guess Final estimate
-----
      phi      0.08      0.0996691323
      A      1E+018      1E+018
      c      28867      29267.326 (*)
(*) E = 243.3 kJ/mol

```

## 2. Experiment TGA amb una de les mostres de biomassa (bagàs tractat a 5 K/min)

- Primer pseudocomponent

### Fitxer d'entrada de dades

Equació cinètica 
$$\frac{dV_1}{dt} = A_1 \exp\left[\frac{-E_1}{RT}\right] (V^*_1 - V_1)$$

Paràmetres  $A_1, E_1, V^*_1$

Dades experimentals  $x = V_1; y = dV_1 / dt; z = 1 / RT$

```

Title "Fit cinetica";
Variables x,y,z;
Parameter V*=2 [mg];
Parameter A=1.7E12 [s^-1];
Parameter E=160000 [J/mol];
Function y=A*exp(-E*z)*(V*-x);

```

## Data;

0.549	0.001866667	0.000216329
0.669	0.002000000	0.000214020
0.836	0.002783333	0.000212507
1.018	0.003033333	0.000210646
1.240	0.003700000	0.000208456
1.484	0.004066667	0.000207021
1.744	0.004333333	0.000205254

## Fitxer de sortida de dades

```

1: Title "Fit cinetica";
2: Variables x,y,z;
3: Parameter V*=2 [mg];
4: Parameter A=1.7E12 [s-1];
5: Parameter E=160000 [J/mol];
6: Function y=A*exp(-E*z)*(V*-x);
7: Data;

```

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Beginning computation...

Iteration	0.	Sum of squared deviations =	1.26943E-001
Iteration	1.	Sum of squared deviations =	1.66255E-002
Iteration	2.	Sum of squared deviations =	2.05822E-003
Iteration	3.	Sum of squared deviations =	2.18360E-004
Iteration	4.	Sum of squared deviations =	1.53797E-005
Iteration	5.	Sum of squared deviations =	8.59628E-007
Iteration	6.	Sum of squared deviations =	5.40599E-007
Iteration	7.	Sum of squared deviations =	5.34472E-007
Iteration	8.	Sum of squared deviations =	5.34469E-007
Iteration	9.	Sum of squared deviations =	5.34469E-007

---- Final Results ----

```

Fit cinetica
Number of observations = 7
Maximum allowed number of iterations = 50
Convergence tolerance factor = 1.000000E-010
Stopped due to: Singular convergence. Mutually dependent parameters?
Number of iterations performed = 9
Final sum of squared deviations = 5.34469E-007
Final sum of deviations = 4.26984E-004
Standard error of estimate = 0.000365537
Average deviation = 0.000226322
Maximum deviation for any observation = 0.000506063
Proportion of variance explained (R^2) = 0.9054 (90.54%)
Adjusted coefficient of multiple determination (Ra^2) = 0.8581 (85.81%)
Durbin-Watson test for autocorrelation = 1.429

```

---- Calculated Parameter Values ----

Parameter	Initial guess	Final estimate
V*	2	2.34284415 (*)
A	1.7E+012	4.7E+015
E	160000	200021.847

(\*)paràmetre que serà sotmès a un procés d'ajust amb  $f_1=0.752$

- Segon pseudocomponent

### Fitxer d'entrada de dades

**Equació cinètica** 
$$\frac{dV_2}{dt} = A_2 \exp\left[\frac{-E_2}{RT}\right] (V^*_2 - V_2)$$

**Paràmetres**  $A_2, E_2, V^*_2$

**Dades experimentals**  $x = V_2; y = dV_2 / dt; z = 1 / RT$

```

Title "Fit cinetica";
Variables x,y,z;
Parameter V*=5 [mg];
Parameter A=1E18 [s-1];
Parameter E=243300 [J/mol];
Function y=(V*-x)*A*exp(-E*z);
Data;
2.75334131      0.007382358      0.000190919
3.28933403      0.008933212      0.000189118
3.89333338      0.010066656      0.000187936
4.50733334      0.010233333      0.000186190
5.07033333      0.009383333      0.000185045
5.53233333      0.007700000      0.000183632
5.85733333      0.005416667      0.000182241

```

### Fitxer de sortida de dades

```

1: Title "Fit cinetica";
2: Variables x,y,z;
3: Parameter V*=5 [mg];
4: Parameter A=1E18 [s-1];
5: Parameter E=243300 [J/mol];
6: Function y=(V*-x)*A*exp(-E*z);
7: Data;

```

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Beginning computation...

```

Iteration 0. Sum of squared deviations = 3.13241E-003
Iteration 1. Sum of squared deviations = 4.08506E-004
Iteration 2. Sum of squared deviations = 2.78675E-005
Iteration 3. Sum of squared deviations = 9.91914E-007
Iteration 4. Sum of squared deviations = 8.86762E-007
Iteration 5. Sum of squared deviations = 8.86762E-007
Iteration 6. Sum of squared deviations = 8.86762E-007
Iteration 7. Sum of squared deviations = 8.86762E-007

```

---- Final Results ----

```

Fit cinetica
Number of observations = 7
Maximum allowed number of iterations = 50
Convergence tolerance factor = 1.000000E-010
Stopped due to: Singular convergence. Mutually dependent parameters?
Number of iterations performed = 7
Final sum of squared deviations = 8.86762E-007

```

```

Final sum of deviations = 2.66607E-004
Standard error of estimate = 0.00047084
Average deviation = 0.00028812
Maximum deviation for any observation = 0.000590388
Proportion of variance explained (R^2) = 0.9502 (95.02%)
Adjusted coefficient of multiple determination (Ra^2) = 0.9253 (92.53%)
Durbin-Watson test for autocorrelation = 2.432

```

---- Calculated Parameter Values ----

Parameter	Initial guess	Final estimate
V*	5	6.15606589 (*)
A	1E+018	1E+018
E	243300	249597.474

(\*) paràmetre que serà sotmès a un procés d'ajust amb  $f_2=0.757$

### • Tercer pseudocomponent

#### Fitxer d'entrada de dades

**Equació cinètica** 
$$\frac{dV_3}{dt} = A_3 \exp\left(\frac{-E_3}{RT}\right) \frac{(V^*_3 - V_3)^3}{(V^*_3)^2}$$

**Paràmetres**  $A_3, E_3, V^*_3$

**Dades experimentals**  $x = V_3; y = dV_3 / dt; z = 1 / RT$

```

Title "Fit cinetica";
Variables x,y,z;
Parameter V*=2 [mg];
Parameter A=407.7 [s^-1];
Parameter E=65400 [J/mol];
Function y=A*exp(-E*z)*((V*-x)^3/(V*^2));
Data;
1.668 0.0004167 0.0001706
1.694 0.0004333 0.0001694
1.718 0.0004000 0.0001682
1.742 0.0004000 0.0001671
1.764 0.0003667 0.0001661
1.784 0.0003333 0.0001650
1.804 0.0003333 0.0001639
1.823 0.0003167 0.0001628
1.838 0.0002500 0.0001617
1.853 0.0002500 0.0001606

```

#### Fitxer de sortida de dades

```

1: Title "Fit cinetica";
2: Variables x,y,z;
3: Parameter V*=2 [mg];
4: Parameter A=407.7 [s^-1];
5: Parameter E=65400 [J/mol];
6: Function y=A*exp(-E*z)*((V*-x)^3/(V*^2));
7: Data;

```

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Beginning computation...

Iteration	0.	Sum of squared deviations =	1.17175E-006
Iteration	1.	Sum of squared deviations =	5.87359E-007
Iteration	2.	Sum of squared deviations =	1.35948E-007
Iteration	3.	Sum of squared deviations =	3.70307E-008
Iteration	4.	Sum of squared deviations =	4.88278E-009
Iteration	5.	Sum of squared deviations =	4.80309E-009
Iteration	6.	Sum of squared deviations =	4.80309E-009
Iteration	7.	Sum of squared deviations =	4.80309E-009
Iteration	8.	Sum of squared deviations =	4.80222E-009
Iteration	9.	Sum of squared deviations =	4.80128E-009
Iteration	10.	Sum of squared deviations =	4.80033E-009
Iteration	11.	Sum of squared deviations =	4.79931E-009
Iteration	12.	Sum of squared deviations =	4.79856E-009
Iteration	13.	Sum of squared deviations =	4.79608E-009
Iteration	14.	Sum of squared deviations =	4.79496E-009
Iteration	15.	Sum of squared deviations =	4.79369E-009
Iteration	16.	Sum of squared deviations =	4.79239E-009
Iteration	17.	Sum of squared deviations =	4.79103E-009
Iteration	18.	Sum of squared deviations =	4.78970E-009
Iteration	19.	Sum of squared deviations =	4.78842E-009
Iteration	20.	Sum of squared deviations =	4.78716E-009
Iteration	21.	Sum of squared deviations =	4.78589E-009
Iteration	22.	Sum of squared deviations =	4.78462E-009
Iteration	23.	Sum of squared deviations =	4.78335E-009
Iteration	24.	Sum of squared deviations =	4.78207E-009
Iteration	25.	Sum of squared deviations =	4.78078E-009
Iteration	26.	Sum of squared deviations =	4.77949E-009
Iteration	27.	Sum of squared deviations =	4.77819E-009
Iteration	28.	Sum of squared deviations =	4.77688E-009
Iteration	29.	Sum of squared deviations =	4.77557E-009
Iteration	30.	Sum of squared deviations =	4.77425E-009
Iteration	31.	Sum of squared deviations =	4.77293E-009
Iteration	32.	Sum of squared deviations =	4.77160E-009
Iteration	33.	Sum of squared deviations =	4.77026E-009
Iteration	34.	Sum of squared deviations =	4.76891E-009
Iteration	35.	Sum of squared deviations =	4.76756E-009
Iteration	36.	Sum of squared deviations =	4.76621E-009
Iteration	37.	Sum of squared deviations =	4.76484E-009
Iteration	38.	Sum of squared deviations =	4.76347E-009
Iteration	39.	Sum of squared deviations =	4.76210E-009
Iteration	40.	Sum of squared deviations =	4.76072E-009
Iteration	41.	Sum of squared deviations =	4.75933E-009
Iteration	42.	Sum of squared deviations =	4.75793E-009
Iteration	43.	Sum of squared deviations =	4.75653E-009
Iteration	44.	Sum of squared deviations =	4.75512E-009
Iteration	45.	Sum of squared deviations =	4.75371E-009
Iteration	46.	Sum of squared deviations =	4.75229E-009
Iteration	47.	Sum of squared deviations =	4.75086E-009
Iteration	48.	Sum of squared deviations =	4.74943E-009
Iteration	49.	Sum of squared deviations =	4.74799E-009
Iteration	50.	Sum of squared deviations =	4.74655E-009
Iteration	50.	Sum of squared deviations =	4.74655E-009

---- Final Results ----

Fit cinetica  
Number of observations = 10  
Maximum allowed number of iterations = 50  
Convergence tolerance factor = 1.000000E-010

Stopped due to: Function did not converge before iteration limit reached.  
 Number of iterations performed = 50  
 Final sum of squared deviations = 4.74655E-009  
 Final sum of deviations = 1.55501E-006  
 Standard error of estimate = 2.60399E-005  
 Average deviation = 1.86761E-005  
 Maximum deviation for any observation = 3.44512E-005  
 Proportion of variance explained ( $R^2$ ) = 0.8762 (87.62%)  
 Adjusted coefficient of multiple determination ( $R_a^2$ ) = 0.8408 (84.08%)  
 Durbin-Watson test for autocorrelation = 1.388

---- Calculated Parameter Values ----

Parameter	Initial guess	Final estimate
V*	2	2.27937783
A	407.7	208.906666
E	65400	58166.1761