GEARS: The α Pinene example

Jake Alan Pitt and Julio R. Banga

September 17, 2018

The α Pinene example in GEARS performs parameter estimation on the α Pinene model. The α Pinene model Tjoa and Biegler (1991) characterises a reaction that describes the thermal isomerisation of α pinene (x_1), β pyronene (x_4) and a dimer (x_5). We consider the model in the form as described by equations 1-8 and figure 1.

$$\frac{dx_1}{dt} = -(p_1 + p_2)x_1 \tag{1}$$

$$\frac{dx_2}{dt} = p_1 \cdot x_1 \tag{2}$$

$$\frac{dx_3}{dt} = p_2 \cdot x_1 - (p_3 + p_4)x_3 + p_5 \cdot x_5 \tag{3}$$

$$\frac{dx_4}{dt} = p_3 \cdot x_3 \tag{4}$$

$$\frac{dx_5}{dt} = p_4 \cdot x_3 - p_5 \cdot x_5 \tag{5}$$

$$\mathbf{x}(t_0, \boldsymbol{\theta}) = \mathbf{x}_0 \tag{6}$$

$$\mathbf{y}(t_i) = x_{1-5}(t_i) \tag{7}$$

$$\boldsymbol{\theta} = p_{1-5} \in [10^{-6}, 100] \tag{8}$$

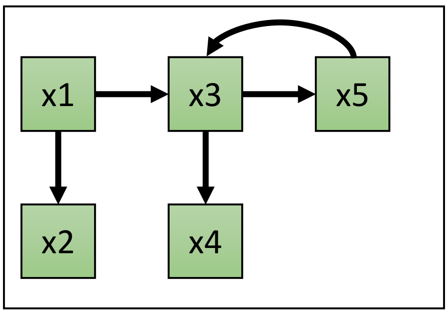


Figure 1: A visualisation of the structure of the Fitzhugh-Nagumo model.

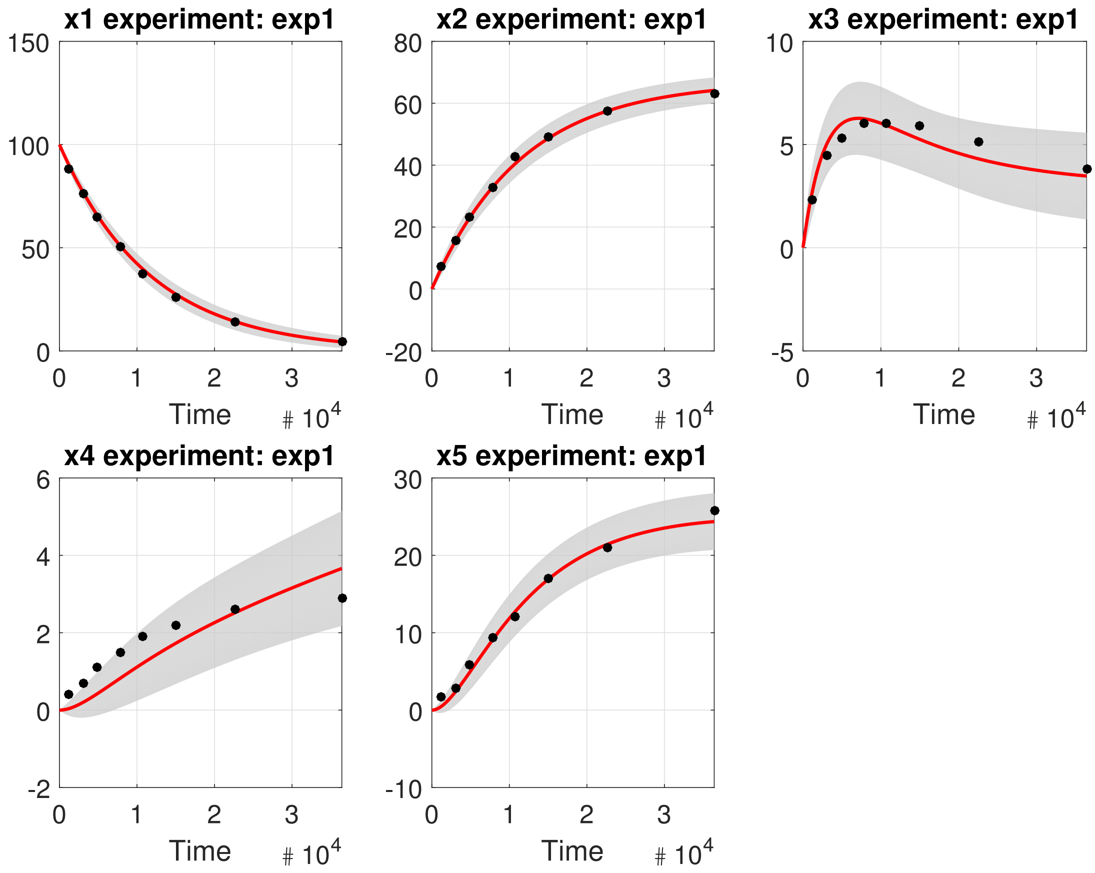
Where y is the observation function considered in the example. Data for this example was taken from Table 2 in Box et al. (1973). No standard deviation was available so ones are input. `GEARS` will normalise the residuals as no standard deviation was used in order to avoid scaling issues.

A selection of the expected results achieved by running the AP example in `GEARS` can be found below. For the full collection of the expected results of the example please consult the expected results folder in the AP example folder.

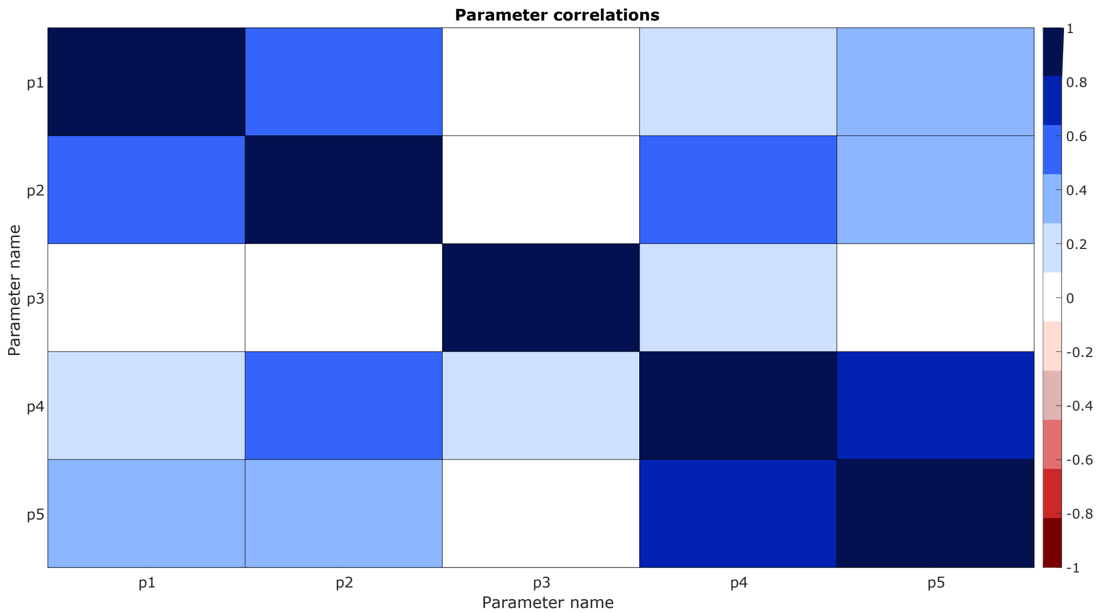
One particular issue that should be considered for the AP model is a lack of identifiability for the p_4 and p_5 parameters. This is due to the high correlation between said parameter where they have some capability of counteracting each other. This can be seen in the correlation matrix in figure 2b. This can also be seen in the model structure in figure 1 where the rate between x_3 and x_5 are controlled by a reaction in either direction of which a change in one rate could be counteracted by the other.

Parameter	Value	Confidence (95%)	Coeff of variation (%)	Bounds status
p_1	5.7688e-05	± 8.5753e-05	148.6495	Bounds not active
p_2	2.8325e-05	± 3.4929e-05	123.3175	Bounds not active
p_3	2.1783e-05	± 3.0977e-05	142.2093	Bounds not active
p_4	0.00026805	± 0.00062808	234.3158	Bounds not active
p_5	3.4818e-05	± 0.00018153	521.3728	Bounds not active

Table 1: A summary of the results from the `GEARS` analysis of the AP model.



(a) The fit of the AP model to the fitting data with uncertainty intervals.



(b) The correlation matrix for the AP model at the estimated parameter values.

Figure 2

References

Box, G. E., Hunter, W. G., Macgregor, J. F., and Erjavec, J. (1973). Some problems associated with the analysis of multiresponse data. *Technometrics*, 15(1):33–51.

Tjoa, I.-B. and Biegler, L. (1991). Simultaneous Solution and Optimization Strategies for Parameter Estimation of Differential-Algebraic Equation systems. *Process Engineering and Design*, 30:376–385.