Identification methodology for stirred and plug-flow reactors

A. Bermúdez, J.L. Ferrín, N. Esteban and J.F. Rodríguez-Calo
UMI REPSOL-ITMATI
joseluis.ferrin@usc.es

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1. Introduction

2. Features of *reoptim*
   - Graphical User Interface
   - Mathematical models for the reactors
   - Mathematical methodology
   - Acceleration procedures

3. Numerical results

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Problems addressed in this presentation were proposed by the engineers of Repsol (an integrated oil and gas Company), taking into account that they can represent all the situations observed in the experimental setups they are trying to simulate.

Acknowledgments

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Objectives of the *reoptim* software tool:

1. **Simulation**
   - Species concentrations and temperature in the chemical reactor.

2. **Identification**
   - Functional forms of reaction rates.
   - Numerical values of the parameters defining the above functions.
Objectives of the *reoptim* software tool:

1. Simulation
   - Species concentrations and temperature in the chemical reactor.

2. Identification
   - Functional forms of reaction rates.
   - Numerical values of the parameters defining the above functions.
Data:

- Mathematical model of the reactor.
- Experiments at different conditions containing concentrations, temperature, inlet composition of mixture, etc., at some times.
- A catalogue of kinetic models containing the parameters to be identified.
Introduction

Chemical reactors

Reactors:

1. Stirred tank reactors (STR):
   - Transient-state Batch STR.
   - Transient-state Batch STR with computed temperature.
   - Transient-state Continuous STR.
   - Transient-state Continuous STR with computed temperature.
   - Steady-state Continuous STR.

2. Plug-flow reactors (PFR):
   - Transient-state PFR.
   - Transient-state PFR with computed temperature.
   - Steady-state PFR.
   - Steady-state PFR with computed temperature.

For simplicity we consider constant density for all reactors.
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   Mathematical models for the reactors
   Mathematical methodology
   Acceleration procedures

3 Numerical results

4 Conclusions and future work
Graphical User Interface

**Reactor type:** PFR\(\text{TS with computed temperature}\)

**Reaction number:** 1

Reactions:

1. \(y_1 + y_2 \rightarrow y_3 + y_4\)

**Species**

<table>
<thead>
<tr>
<th>N.</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A (obs.)</td>
</tr>
<tr>
<td>2</td>
<td>B (obs.)</td>
</tr>
<tr>
<td>3</td>
<td>C (obs.)</td>
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<td>4</td>
<td>D (obs.)</td>
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<tr>
<td>5</td>
<td>E (obs.)</td>
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<tr>
<td>6</td>
<td>F (obs.)</td>
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<tr>
<td>7</td>
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<td>8</td>
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<td>10</td>
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</table>

**Optimization**

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Discrimination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic models...</td>
<td>Kinetic models...</td>
</tr>
<tr>
<td>Kinetic models...</td>
<td>Concentrations...</td>
</tr>
</tbody>
</table>

**Reactions**

- **Reaction 1:**
  \(y_1 + y_2 \rightarrow y_3 + y_4\)

- **Reaction 2:**
  \(y_2 \rightarrow y_3 + 0.5y_5\)

- **Reaction 3:**
  \(y_2 \rightarrow y_9 + y_7\)

- **Reaction 4:**
  \(y_2 \rightarrow y_9 + y_9\)

- **Reaction 5:**
  \(y_2 \rightarrow y_{10} + y_{11}\)

- **Reaction 6:**
  \(y_4 + y_7 \rightarrow y_{12}\)
Mathematical models: BatchSTR@TS with computed temperature

\[ \frac{dy}{dt} = A \delta(\theta, y) \]

\[ \frac{d\theta}{dt} = -\frac{\Delta H(\theta) \cdot \delta(\theta, y) - \frac{a}{V} (\theta_{\text{ext}} - \theta)}{\hat{w}'(\theta) \cdot y} \]

\[ y(0) = y_0 \]

\[ \theta(0) = \theta_0 \]
Mathematical models

CSTR@TS with computed temperature

\[
\frac{dV}{dt}(t) = \sum_{p=1}^{P} u^p(t) - u_{\text{out}}(t),
\]

\[
\frac{dy}{dt} = A \delta(\theta, y) + \frac{1}{V} W u - \frac{1}{V} y \sum_{p=1}^{P} u^p,
\]

\[
\frac{d\theta}{dt} = -\frac{1}{w'(\theta) \cdot y} \left[ \Delta H(\theta) \cdot \delta(\theta, y) - \frac{g}{V} (\theta_{\text{ext}} - \theta) - \frac{1}{V} \sum_{p=1}^{P} \left( \sum_{i=1}^{N} \mathcal{M}_i W^p_i (\hat{e}_i(\theta^p) - \hat{e}_i(\theta)) \right) u^p \right]
\]

\[V(0) = V_0,\]
\[y(0) = y_0,\]
\[\theta(0) = \theta_0.\]
The mathematical models for PFR@TS with computed temperature are given by:

\[
\frac{\partial \mathbf{y}}{\partial t} + v \frac{\partial \mathbf{y}}{\partial z} = A \delta(\theta, \mathbf{y}),
\]

\[
\frac{\partial \theta}{\partial t} + v \frac{\partial \theta}{\partial z} = \frac{1}{\hat{w}'(\theta) \cdot \mathbf{y}} \left( - \Delta H(\theta) \cdot \delta(\theta, \mathbf{y}) + \frac{2h}{R} (\theta_{ext} - \theta) \right),
\]

\[
\mathbf{y}(0, t) \text{ and } \theta(0, t) \text{ are given}
\]

\[
\mathbf{y}(z, 0) = \mathbf{y}^0(z)
\]

\[
\theta(z, 0) = \theta^0(z)
\]
Numerical solution of the model equations (Algebraic, ODE or PDE):

- Finite differences.
- Second-order Backward Differentiation Formula (BDF2).
- Newton’s method.
Optimization problem: Functional form and parameters involved in it, providing a minimum of:

\[ \| x - x^e \|^* \]

being \( x \) and \( x^e \), respectively, the numerical and experimental values of the concentration of species and temperature.

Solving the optimization problem:

- Extent-based incremental identification method.
- Integral (simultaneous) identification method.
Main features:

- The identification problem is decomposed into a sequence of subproblems.
- Based on algebraic procedures for decoupling the system of equations.
- Uses the *extent* concept.
- Valid for *stirred tank reactors*.
- The catalogue of functional forms is defined by the chemist (using experience and knowledge).
Mathematical Methodology

Incremental method

Details of the incremental methodology can be seen in:

References

Mathematical Methodology

Incremental method with computed temperature

The model

\[
\begin{cases}
\frac{dy}{dt} = f(\theta, y, z, \Theta) \text{ in } [0, T], \\
\frac{d\theta}{dt} = h(\theta, y, z, \Theta), \\
y(0) = y_0 \text{ and } \theta(0) = \theta_0,
\end{cases}
\]

(1)

\[
f = A\delta(\theta, y, z, \Theta) + Ff^1 + f^2 y.
\]

\[
\Delta H(\theta) \cdot \delta(\theta, y, z, \Theta) - \frac{g}{V} (\theta_{out} - \theta) - w'(\theta) \cdot \left( F \sum_{p=1}^{P} f_p^1 (\theta_p^s - \theta) e_p \right)
\]

\[
h = \frac{w'(\theta) \cdot y}{w'(\theta) \cdot y}.
\]
Mathematical Methodology

The ODE system (1) is coupled, that is why we work in two stages.

- The concentrations equations are transformed into the extents equations:

\[
\begin{align*}
\frac{d e}{dt} &= g(\theta, e, z, \Theta) \text{ in } [0, T], \\
e(0) &= 0.
\end{align*}
\]

(2)

- The temperature equation becomes

\[
\begin{align*}
\frac{d \hat{\theta}}{dt} &= \hat{h} \text{ in } [0, T], \\
\hat{\theta}(0) &= \theta_0.
\end{align*}
\]

(3)

\[
\hat{h} = \Delta H(\hat{\theta}) \cdot \hat{\delta} - \frac{q}{V} (\theta_{out} - \hat{\theta}) - w'(\hat{\theta}) \cdot \left( F \sum_{p=1}^{P} f_p^1 (\theta^s_p - \hat{\theta}) e_p \right) / w'(\hat{\theta}) \cdot \hat{y}.
\]
Mathematical Methodology

Incremental method with computed temperature

We proceed with the following steps:

1. Fitting experimental observations with cubic splines:
   1.1 Compute $\frac{d\hat{e}^e}{dt}$ from $\hat{e}^e$ with $e \in \mathcal{E}$.
   1.2 From the expression of $g$ we deduce:

   $$\hat{\delta}^e = \frac{d\hat{e}^e}{dt} - Sf_1^1 - f_2^2 \hat{e}^e, \ e \in \mathcal{E}.$$  

   1.3 Solve initial value problem (3) to give $\hat{\theta}$.

2. With $\hat{\theta}$, we apply the same methodology as for the incremental method without temperature for solving (2).
Optimization problem (weighted least squares)

\[
\min_{\Theta} J(\Theta),
\]

being

\[
J(\Theta) := \sum_{e \in \mathcal{E}} \sum_{i=1}^{N+1} \sum_{t_n^e \in \mathcal{S}^e} \omega_{ien} (x_{i}^{e,n}(\Theta) - \hat{x}_{i}^{e,n})^2,
\]

where \(x_{i}^{e,n}(\Theta)\) is the \(i\)-th component of the solution of the model at time \(t_n \in \mathcal{S}^e\).
- **Optimization**: algorithm where the objective function is obtained from the solution provided by the solver.

  - **Initial value of $\Theta$**:
    - **STR** - Solution provided by the incremental method.
    - **PFR** - Multistart.

  - **Global optimization**:
    - VNS perturbations.
Acceleration procedures

Parallelization of the incremental method
Acceleration procedures

Parallelization of the integral method

Optimal kinetic

Parallel tasks

- Perturbation 1
- Perturbation 2
- \ldots
- Perturbation P

- Optimization with the integral method
- Optimization with the integral method
- \ldots
- Optimization with the integral method

Choice of the best objective value

Numerical results
Conclusions and future work
Acceleration procedures

Gradient of the discrete objective function

\[ J_d(\Theta) = J_{h,\Delta t}(x_h(\Theta), \Theta) := \sum_{e \in E} \sum_{i=1}^{N+1} \sum_{t_e^n \in S_e} \omega_{ien} (x_{d,i}^{e,n}(\Theta) - \hat{x}_{e,n}^{e,n})^2. \]

Adjoint method:

1. Solve the discretized state equation:

\[ \tilde{B}x_h = \tilde{F}. \]

2. Compute the adjoint state \( p \) as the solution of the following linear system:

\[ \tilde{B}^t p = \nabla_x J_{h,\Delta t}(x_h(\Theta), \Theta). \]

3. Compute the gradient \( \nabla_{\Theta} J_d(\Theta) \) in terms of the adjoint state:

\[ \nabla_{\Theta} J_d(\Theta) = \nabla_{\Theta} Fp + \nabla_{\Theta} J_{h,\Delta t}(x_h, \Theta). \]
<table>
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<th>Title</th>
</tr>
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<td>Features of <em>reoptim</em></td>
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<td></td>
<td>Graphical User Interface</td>
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<td></td>
<td>Mathematical models for the reactors</td>
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<tr>
<td></td>
<td>Mathematical methodology</td>
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<td></td>
<td>Acceleration procedures</td>
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<tr>
<td>3</td>
<td>Numerical results</td>
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<tr>
<td>4</td>
<td>Conclusions and future work</td>
</tr>
</tbody>
</table>
We consider a reaction system with 12 species involved in 6 reactions as follows, catalyzed by 1 catalyst:

\[ E_1 + E_2 \rightarrow E_3 + E_4, \]
\[ E_2 \rightarrow E_3 + \frac{1}{2}E_5, \]
\[ E_2 \rightarrow E_6 + E_7, \]
\[ E_2 \rightarrow E_8 + E_9, \]
\[ E_2 \rightarrow E_{10} + E_{11}, \]
\[ E_4 + E_7 \rightarrow E_{12}, \]
"Exact" expressions of the components of the reaction velocity vector are

\[
\begin{align*}
\delta_1(\theta, y) &= 5 \cdot 10^{10} e^{-62737/\mathcal{R}\theta} y_1 y_2 z_1, \\
\delta_2(\theta, y) &= 2 \cdot 10^{10} e^{-71097/\mathcal{R}\theta} y_2^2 z_{1.5}, \\
\delta_3(\theta, y) &= 10^{10} e^{-66914/\mathcal{R}\theta} y_2^2 z_1, \\
\delta_4(\theta, y) &= 5 \cdot 10^9 e^{-85734/\mathcal{R}\theta} y_2 z_{1.1}, \\
\delta_5(\theta, y) &= 4 \cdot 10^9 e^{-133829/\mathcal{R}\theta} y_2 z_{0.5}, \\
\delta_6(\theta, y) &= 2 \cdot 10^9 e^{-63987/\mathcal{R}\theta} y_4 y_7 z_{1.2}.
\end{align*}
\]
Numerical results

An example in a PFR@TS with computing temperature

<table>
<thead>
<tr>
<th></th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$E_4$</th>
<th>$E_5$</th>
<th>$E_6$</th>
<th>$E_7$</th>
<th>$E_8$</th>
<th>$E_9$</th>
<th>$E_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_1(0, t)$ [mol/l]</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1.5</td>
<td>1</td>
<td>1.1</td>
<td>1.3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1.5</td>
<td>1.5</td>
<td>1.25</td>
<td>2</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>$y_2(0, t)$ [mol/l]</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
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<td></td>
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<td>2</td>
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<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>$y_3(0, t)$ [mol/l]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>$y_4(0, t)$ [mol/l]</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>$y_5(0, t)$ [mol/l]</td>
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<td>0</td>
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<tr>
<td>$y_6(0, t)$ [mol/l]</td>
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<td>0</td>
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<td>0</td>
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<tr>
<td>$y_7(0, t)$ [mol/l]</td>
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<td>$y_8(0, t)$ [mol/l]</td>
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<tr>
<td>$y_{10}(0, t)$ [mol/l]</td>
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<td>$y_{11}(0, t)$ [mol/l]</td>
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<tr>
<td>$y_{12}(0, t)$ [mol/l]</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\theta(0, t)$ [K]</td>
<td>383</td>
<td>373</td>
<td>383</td>
<td>373</td>
<td>383</td>
<td>373</td>
<td>383</td>
<td>373</td>
<td>383</td>
<td>373</td>
</tr>
<tr>
<td>$u_{in}(t)$ [l/s]</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.001</td>
<td>0.1</td>
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<td>0.01</td>
<td>0.01</td>
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</tr>
</tbody>
</table>

Table 1: Inlet conditions for the experiments
Numerical results  Performance of the adjoint method

Computing the gradient of the objective function with $K = 256, J = 64$ and $N_p = 68$.

**Performance improvement:**

<table>
<thead>
<tr>
<th>Method</th>
<th>Computer time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adjoint method</td>
<td>5 min 38.65 s</td>
</tr>
<tr>
<td>Incremental quotients</td>
<td>223 min 56.85 s</td>
</tr>
</tbody>
</table>

Table 2: Computer time for evaluating the gradient of the objective function for a PFR@TS with computed temperature, using a Scilab implementation and running in an Intel i5-4670 at 3.4 GHz

With the data used in this demo, the adjoint method is almost 40 times faster than the incremental quotients for calculating the gradient of the objective function.
Numerical results

Numerical solution provided by the identification methodology

a) Experiments 1 to 5

b) Experiments 6 to 10

Numerical vs Experimental concentrations for species $E_1$
Introduction  Features of reoptim  Numerical results  Conclusions and future work

**Numerical results**

Numerical solution provided by the identification methodology

---

### **Numerical results**

#### a) Experiments 1 to 5

[Graph showing temperature vs time for experiments 1 to 5]

#### b) Experiments 6 to 10

[Graph showing temperature vs time for experiments 6 to 10]

---

**Numerical vs Experimental concentrations for temperature**
Numerical results

More numerical experiments can be seen in:

References


- M. Benítez, A. Bermúdez and J.F. Rodríguez-Calo. Adjoint method for inverse problems in chemical reaction systems, Submitted.

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| 4 | Conclusions and future work |
Conclusions and future work

Conclusions:

- *reoptim* is being successfully used in reactors with real data by the Spanish energy company Repsol in its Technology Center.

Future work:

- Other chemical reactors can be considered.
- Extension to reactor networks.
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