Toluene Benzylation

Objective: To Estimate Kinetic Parameters for Toluene Reaction with Benzyl Alcohol

In this example, an LHHW kinetic model for toluene reaction over solid catalyst in a batch reactor is formulated using the model in [1]. You may download the rex files to view the model.

Features Illustrated

- Solid Catalyzed reactions in Batch reactor
- Langmuir Hinshelwood Models
- Definition of Conversion, Yield and Selectivity calculations
- Use of Conserved Pseudo-Compounds
- Custom Axis feature for the Charts

Setting up the model in REX

The following three reactions catalyzed by sulfated zirconia powder occur in the cyclohexane reaction medium:

**Benzylation of Toluene by Benzyl Alcohol:**
R-Benzyltoluene : Toluene + Benzyl Alcohol \( \rightarrow \) Benzyltoluene + H₂O

**Dibenzytoluene formation:**
R-Dibenzytoluene : Benzyl Alcohol + Benzyltoluene \( \rightarrow \) Dibenzytoluene + H₂O

**Conversion of Benzyl Alcohol to Dibenzylether:**
R-Dibenzylether : 2 Benzyl Alcohol \( \rightarrow \) Dibenzylether + H₂O

The kinetic model suggested in [1] for the reactions above consider stoichiometric order on the reactant concentration, together with dependency on catalyst concentration. LHHW Site inhibition is proposed with exponent of two, with terms for Toluene and BenzylAlcohol. For example, the rate equation for toluene concentration \( C_{Tol} \) is indicated as:

\[
\frac{dC_{Tol}}{dt} = - \frac{C_{Cat} k_{R_{Benzytoluene}} C_{Toluene} C_{BenzylAlcohol}}{\left(1 + K_{Toluene} C_{Toluene} + K_{BenzylAlcohol} C_{BenzylAlcohol}\right)^2}
\]

In the equation above, the concentration of catalyst \( (C_{cat}) \) is in g/lit, while for the other compounds the units are in mol/lit.
In **REX**, we can implement the catalyst mass dependency on the reaction rate in the batch reactor in two ways:

- **Considering the Catalyst as a compound**
  In the Compounds node, we could load the catalyst as a compound and define the orders for it in the Parameters node. The *Rate Basis* should be selected as *Volume* in the *Kinetics→Units Configuration* node, thus the rate units will be, for example in \([\text{mol/(min-lit)}]\). In the *Experiments→Sets* node, the values loaded for the catalyst will be in mass units, even though the header states that the values should be provided in moles. In all other nodes where catalyst is shown, for example, the *Results→Model Data Comparison* node, the units will be stated as moles even though it is actually in mass units.

- **Selecting Catalyst Mass as the Rate Basis in the Units Configuration node**
  By selecting this option, we remove the need to enter the catalyst as a compound. Catalyst concentration is removed from the rate expression and the Rate units will be, for example, in \([\text{mol/(min-gcat)}]\), where gcat refers to the catalyst mass in grams. In Experiments→Sets, the experimental values for Catalyst Mass can be entered in a straightforward manner.

In this example, we choose the most direct implementation: using Catalyst Mass as rate basis. For that option, the mass balance for total moles of toluene \(N_{\text{Tol}}\) is given by:

\[
\frac{dN_{\text{Tol}}}{dt} = W_{\text{Cat}} \sum_r v_{\text{Tol},r} R_r = -W_{\text{Cat}} \frac{k_{R_{\text{Benzyloleuene}}} C_{\text{Toluene}} C_{\text{BenzyloAlcohol}}}{(1 + K_{\text{Toluene}} C_{\text{Toluene}} + K_{\text{BenzyloAlcohol}} C_{\text{BenzyloAlcohol}})^2}
\]

where, \(v_{\text{Tol},r}\) are stoichiometric coefficients of toluene in each reaction \(r\), and \(R_r\) are the rates for the \(r\) reactions per gram of catalyst mass. The equation above is equivalent to the previous mass balance from [1] after multiplying by reactor volume: \(N_{\text{Tol}} = V C_{\text{Tol}}\) represents the toluene total moles and \(W_{\text{Cat}} = V C_{\text{Cat}}\) is the catalyst mass.

You may import the *Toluene-Benzylation-1.rex* file and see the reactions entered, units selected, LHHW site definition and other related issues. For a more detailed description on how to setup LHHW kinetics, you may follow guidelines from other **Examples**, such as **Glucose-to-F6P**, or consult the REX help manual.
Experimental Data

Experimental conditions correspond to a single liquid batch reactor as entered in the Reactor node. Temperature and reactor volume are specified as Interpolated from Data. There are no inflows or outflows.

Measurements at 45°C are reported below from [1]:

![Graph showing reaction data]

Example of kinetic run for the reaction of toluene with benzyl alcohol

<table>
<thead>
<tr>
<th>t (min)</th>
<th>$C_{\text{tol}}$ (mol/l)</th>
<th>$C_{\text{BzOH}}$ (mol/l)</th>
<th>$C_{\text{M}}$ (mol/l)</th>
<th>$C_{\text{T}}$ (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0474</td>
<td>0.0009</td>
<td>0.0008</td>
<td>0.0000</td>
</tr>
<tr>
<td>20</td>
<td>0.0458</td>
<td>0.0016</td>
<td>0.0009</td>
<td>0.0001</td>
</tr>
<tr>
<td>30</td>
<td>0.0439</td>
<td>0.0024</td>
<td>0.0013</td>
<td>0.0001</td>
</tr>
<tr>
<td>60</td>
<td>0.0592</td>
<td>0.0045</td>
<td>0.0013</td>
<td>0.0001</td>
</tr>
<tr>
<td>90</td>
<td>0.0644</td>
<td>0.0068</td>
<td>0.0020</td>
<td>0.0001</td>
</tr>
<tr>
<td>120</td>
<td>0.0280</td>
<td>0.0097</td>
<td>0.0022</td>
<td>0.0002</td>
</tr>
<tr>
<td>150</td>
<td>0.0247</td>
<td>0.0110</td>
<td>0.0028</td>
<td>0.0002</td>
</tr>
<tr>
<td>180</td>
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<td>0.0133</td>
<td>0.0032</td>
<td>0.0003</td>
</tr>
<tr>
<td>210</td>
<td>0.0148</td>
<td>0.0148</td>
<td>0.0039</td>
<td>0.0004</td>
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<tr>
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<td>0.0091</td>
<td>0.0174</td>
<td>0.0047</td>
<td>0.0006</td>
</tr>
<tr>
<td>270</td>
<td>0.0072</td>
<td>0.0175</td>
<td>0.0054</td>
<td>0.0007</td>
</tr>
<tr>
<td>300</td>
<td>0.0020</td>
<td>0.0188</td>
<td>0.0071</td>
<td>0.0011</td>
</tr>
<tr>
<td>330</td>
<td>0.0006</td>
<td>0.0180</td>
<td>0.0090</td>
<td>0.0017</td>
</tr>
</tbody>
</table>

Run in cyclohexane at 45°C; $C_{\text{tol}}^0 = 1.500$ mol/l; $C_{\text{BzOH}}^0 = 0.050$ mol/l; $C_{\text{M}} = 10.0$ g/l. For kinetic purposes, the reaction up to $t = 270$ min was considered.
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In the table above, $C_M$ refers to Benzyltoluene concentration and $C_D$ to DibenzylToluene concentration. Values provided for the compounds are all molar concentrations; we assume the reaction volume to be 1 lit. Of the two reactants, Toluene is in excess, so the limiting reactant is Benzyl alcohol. Cyclohexane is the solvent. The amount of cyclohexane is not reported in [1]. However, we do not really need this information. We specify the reactor volume to be 1 lit and use the concentrations provided above to enter the experimental mole values into REX as shown below. As the catalyst concentration is reported to be 10 g/lit, we enter the catalyst mass in REX as 10 g. We show below the data loaded for the experimental set above. We entered all data, including those for time higher than 270 min that are not used in [1] for the parameter estimation:

![Experimental Data Table](image)

Measurements at 300 and 330 min are not to be considered for reconciliation in accordance with [1]. Thus, we have them un-included above.

Parameter Estimation

In the Estimation—Parameters node, the pre-exponential factor bounds are open for both the Mass Action and LHHW site. Activation energies are kept fixed to zero since tabular data is only available at one temperature (45°C). In the Weights node, we select the measured compounds: Benzyl Alcohol, Benzyl Toluene, Dibenzyl ether and Dibenzyl Toluene. Hybrid weights are generated for them, unlike the uniform weights used in [1].

After running the Estimation, you may see the solution parameters in the Results—Parameters node:
The profiles of the experimental and calculated profiles can be seen in the Model Data Comparison node:

![Graphs showing experimental and calculated profiles](image)

While the predictions are reasonably close to measurements, the kinetic parameters in this example differ somewhat from those in [1] because we used only one experiment for which the tabular values were provided. Furthermore, some parameters were fixed in [1] and uniform weights were used in
their work. This model can of course be easily expanded to consider additional data sets if numeric measurement values are available.

The carbon traffic for the reaction network may be visualized by selecting the Reaction Traffic→Options node:

The carbon moles traffic option can be enabled above because the carbon content of compounds was previously loaded in the Chemistry→Compounds→Formula node. The arrow widths in the generated network show the relative amount of carbon traveling in those paths:
Conversion, Yield and Selectivity Definition

You may easily define and display additional variables such as Conversion, Yield and Selectivity. This extra information does not affect the simulation or parameter estimation. We now show how to enable these calculations.

In the Estimation→Yield Calculations node, you may define the conversion of desired compounds:
You may import the Toluene-Benzylation-2.dat file that has the conversion selected as above. After rerunning the project, the conversion values are reported in the Results→Yield Conversions node:

The line shows the conversion predicted by the model, while experimental conversion values are indicated by triangles. For toluene, the experimental conversion is reported as 100% for the non-initial data points. This is because in the Experiments→Sets node, there are no toluene values (zeros loaded) except for the initial point, resulting in an incorrect calculation of 100% experimental conversion.

In the chart above, it may seem that toluene conversion calculated from the model is always zero. That is not actually the case. As toluene is in excess, its calculated conversion is very small. The small values can be seen in the Values tab of Results→Yield Conversion node. You can also see this in the Charts by enabling Custom Axis, available on right-clicking on the chart:
A grid is then shown in the Select Sets to View tab. There you can change the Min and Max values for the chart axis. For example, if changing the Y axis max to 1, the chart will now be as follows, showing the low toluene conversion values:

![Chart showing toluene conversion](image)

Selectivity calculations can also be enabled. For example, the selectivity of benzyl toluene with respect to a basis compound(s) can be enabled as shown in the grid below. Here, Benzyl Alcohol and Toluene are both chosen as the basis, and thus the selectivity feature will calculate the moles of Benzyl Toluene formed divided by the sum of the moles of Benzyl alcohol and Toluene that are converted, in percentage units(x100).

![Selectivity grid](image)

Selectivity of other products can be similarly defined and the values can be seen after running the model in the Results→Yield - Conversion node. By right clicking on this node (or using the icon on the toolbar), you may enable the Single Set view of variables. This allows you to show more than one variable for a given set. If we display all selectivities together, we have as shown below:
The Experimental Selectivity values reported are all obtained from the experimental data entered in Measurements→Sets. As we mentioned earlier, values for toluene are not available except for the initial content, where it is in excess with respect to the other reactant. Thus, the relatively small experimental values of benzyltoluene produced when are divided by the (apparently) high amount of toluene converted, results in a very small experimental selectivity. Therefore, the experimentally calculated selectivities should be ignored here. Only the calculated values are accurate.

The sum of calculated selectivities does not equal 100% because they are based on compound moles. A more suitable way to report selectivities would be on a carbon atom basis. Carbon based selectivity would relate the carbon atoms of a given product with respect to carbon atom lost by the reactants.

In order to do that, we first create auxiliary variables in Pseudo-Compounds node that will represent the carbon content of reactants and products. For example, we enter C-Toluene and define it as seven times toluene (C7H8) moles. The pseudocompound is selected as Conserved, so that reported values will correspond to the carbon moles contained in toluene:

Similar definitions are are entered for the other compounds, as you can see in Pseudo-Compounds node.
Then we go back to Yield-Calculations node and choose the selectivities shown next:

We enabled the selectivity of C-Benzyltoluene with respect to C-BenzylAlcohol and C-Toluene. Given the definition of those pseudocompounds, the resulting values will represent the selectivity in carbon basis: carbon moles of Benzyltoluene produced with respect to carbon moles of BenzylAlcohol and Toluene consumed.

You may notice that after the definition of the new selectivities, a Method for PseudoCompound child node appears under the Yield Calculations node. This node is used to specify how the experimental values for pseudocompounds are determined when calculating experimental Conversions, Yields or Selectivities.

To better understand the options of this node, we have defined the conversion of C-BenzylAlcohol in the Yield Calculations node. If C-BenzylAlcohol is unselected in the Conversion tab of the Method for PseudoCompounds node, then the reported experimental values for it will be depending on the data loaded for C-BenzylAlcohol in Experiments→Measurements→Set node. As they are all zero, the resulting experimental conversion is reported as zero as can be seen in the Results→Yield-Conversion node:

If you load other experimental values for C-BenzylAlcohol in Measurements→Set node, then after rerunning the project the experimental values for the conversion will be reported according to the new
On the other hand, if you select the _Formula_ checkbox for C-BenzylAlcohol in the conversion tab of the _Method for Pseudocompounds_ node, the reported experimental conversion is based on the experimental values of the compounds involved in the formula that defines the pseudocompound. In this case, that means that the experimental values of the BenzylAlcohol compound will be used. Thus you will see the following chart for C-BenzylAlcohol conversion:

You can compare the chart above with the one of BenzylAlcohol conversion and note that they are identical. This is because the experimental values of C-BenzylAlcohol are internally computed in REX from the experimental values of BenzylAlcohol. In all these charts, you can also see that the calculated values are invariant with respect to the option chosen for the pseudocompound.

The above described method for calculating pseudocompound experimental values applies also for yields and selectivities.

Coming back to our original goal of calculating carbon based selectivities: we keep the default option for them, thus no checkbox is selected for Selectivities in _Method for Pseudocompounds_ node. The reported experimental selectivity of C-Benzyltoluene with respect to C-Toluene and C-BenzylAlcohol is then based on the pseudocompounds values entered in Measurements—Sets node. We have all zero values for them; consequently the experimental selectivities for the pseudocompounds are shown as zero.

Now, if you display all products selectivity in the chart, you can verify that the sum of the values is 100%. This allows you to compare the product formation on a consistent basis:
The above Dibenzyl ether carbon selectivity values imply that close to 80% of all Toluene and Benzyl Alcohol carbon that reacts is used to produce Dibenzyl ether.

Further Studies
You may also enable confidence interval calculations in Run→Solution Options node to see the uncertainties in the parameters. You can find more information about Pseudo-compound types and about calculating Conversions, Yields and Selectivities in the REX help. Help is available by pressing F1 key on any REX node.

References