Methanol to Olefins (MTO)

Objective: Estimation of kinetic parameters for MTO reaction, followed by Optimization to maximize desired yields

This example illustrates the full workflow from kinetic estimation to reactor optimization for the methanol to olefins reaction and shows how REX allows us to execute these tasks with ease. The methanol to olefins system has been studied for several decades and a discussion of mechanisms is available in [1]. In this example, we develop a LHHW (Langmuir-Hinshelwood-Hougen-Watson) model for zeolite catalysed MTO reaction. The kinetic estimation process is first illustrated (with fictitious data) and then we use the kinetic model to find the optimal temperature profile that maximizes the yield for propylene and butene. You may download the zipped rex file for this project here. A more detailed version of this document, which illustrates building this model from the ground up is available in the REX manual.

Features Illustrated
- Building a LHHW Model for the methanol to olefins (MTO) reaction
- Using the Atom Balance feature to verify experimental data consistency
- Enforcing Parameter Relationships between parameters being estimated
- Defining auxiliary variables in Pseudocompounds node
- Defining Yields to monitor and to optimize
- Reactor Optimization: finding the best Temperature profile to maximize the desired yields

Reaction Model

The simplified MTO reaction model contains two main groups of reactions:

- Methylations: Irreversible reactions where Methanol (MeOH) addition produces higher olefins:
  
  R2: $2\text{MeOH} \rightarrow \text{ETY} + 2\text{H}_2\text{O}$  *Ethylene formation*
  
  R3: $\text{MeOH} + \text{ETY} \rightarrow \text{PPY} + \text{H}_2\text{O}$  *Propylene formation*
  
  R4: $\text{MeOH} + \text{PPY} \rightarrow \text{BTE} + \text{H}_2\text{O}$  *Butene formation*
  
  R5: $\text{MeOH} + \text{BTE} \rightarrow \text{PTE} + \text{H}_2\text{O}$  *Pentene formation*
  
  R6: $\text{MeOH} + \text{PTE} \rightarrow \text{HXE} + \text{H}_2\text{O}$  *Hexene formation*

- Oligomerization/Scissions: Reversible reactions where Olefins react by merging or splitting:

  R2R2-R4: $2\text{ETY} \leftrightarrow \text{BTE}$
  
  R2R3-R5: $\text{ETY} + \text{PPY} \leftrightarrow \text{PTE}$
  
  R2R4-R6: $\text{ETY} + \text{BTE} \leftrightarrow \text{HXE}$
  
  R3R3-R6: $2\text{PPY} \leftrightarrow \text{HXE}$
  
  R3R4-R2R5: $\text{PPY} + \text{BTE} \leftrightarrow \text{ETY} + \text{PTE}$
  
  R3R5-R4R4: $\text{PPY} + \text{PTE} \leftrightarrow 2\text{BTE}$
All reactions are modeled considering adsorption of methanol and olefins by using the Langmuir Hinshelwood sites.

Setting up REX Project for Parameter Estimation

First we define the units for the project. Since this reaction is catalysed by solid catalyst, the rate is determined per unit mass of catalyst. Also, the rate expression uses partial pressure, so the Concentration type is set to Partial Pressure below:

The compounds and reactions described previously have been entered in the Chemistry node. In this project, we also need to monitor and use some additional variables, such as the total carbon content of C3 and C4 olefins. In order to do that, we create pseudo-compounds, which can be defined in the PseudoCompounds node:

- Carbon-C3C4 = 3*PPY + 4*BTE
  Since this is a linear combination of moles, we select this variable as Conserved, which allows REX to treat this like a compound and report the moles of this Carbon-C3C4 variable in the model results. If Conserved is not selected, this variable is only calculated in the concentration units.

- POlef = ETY + PPY + BTE + PTE + HXE
  This variable represents the total concentration of Olefins, which is to be used later in the kinetics model.

Next, we specify the reaction kinetics in the Kinetics node. As the methylations are all irreversible, only the forward direction is included. For scissions that are reversible, both directions must be included:
We will use a simplified kinetics model, in which all reactions have order of compounds same as their molecularity (stoichiometry coefficients). The LHHW Site for all reactions contains two terms, one for MeOH and another term for the POlef pseudocompound that represents the sum of partial pressures of all olefins. Thus, all reactions have their rate basically described as:

\[
\text{Rate} = \frac{A e^{-E/R T} P_{C1}^{n1} P_{C2}^{n2}}{1 + K_{\text{MeOH}} P_{\text{MeOH}} + K_{\text{Olef}} P_{\text{Olef}}}
\]

Here, the compound orders n1 and n2 are set to the molecularity of the compounds C1 and C2 in the reaction and we can conveniently build this by going to Kinetics → Parameters node and executing the Initialize Order action. With this action, all reactions will automatically have their compound orders set to their stoichiometric coefficients. R2R3-R5 for instance, will have order 1 for ETY and PPY in the forward direction and order 1 for PTE in the reverse direction.
An LHHW Site is defined in the LHHW Sites tab of Kinetics→Parameters node. Its constant value is 1, and it has two terms, one for MeOH and another for the pseudocompound POlef, that represents the partial pressure of all olefins. The site is then assigned to all reactions with a site exponent of 1 in the Kinetics→Kinetics Sites node.

When estimating kinetic parameters, we would like to enforce thermodynamic constraints on the activation energies of the scission reactions so that the difference between forward and reverse activation energy values is equal to the heat of reaction. These constraints are added in the Estimation→Parameter Relationships node, where the Right Hand Side values are the heat of reaction:

\[
[R2R3-$\Delta$H] = [-90.5]
\]

In the Reactor node, we selected Single Gas PFR (fixed bed) reactor with no recycle. Pressure and Temperature are constant. The pressure is specified in the experimental data, so the Flow is selected as *Float for Pressure Control*.

After loading experimental values for all sets, we can analyze the consistency of the data in the Experiments→Check Atom Balance node. As the carbon numbers for each species is loaded in the Compounds→Formula node, we can get the carbon error in the data sets:
Based on this analysis, you may choose to remove or de-emphasize some data sets from reconciliation. However, since the average carbon error here is quite small, we try to match all data sets. In this example, we select all the olefins and MeOH as the compounds to be reconciled to estimate the parameters. Weighting factors are generated with the Hybrid method.

Parameter Estimation Results
After running the project, you may review all the results in the Results tree. The estimated mass action kinetic parameters are shown below. The reaction network and carbon traffic can be visualized in Reaction Traffic node. In the Results→Parameters node, pre-exponentials for both forward and reverse directions of $R2R2-R4$ reaction are zero. This reaction can be eliminated from the model by un-including it from either the Chemistry→Reactions or Chemistry→Kinetics nodes.
In the Results→Model Data Comparison node, you may compare the model predictions with the experimental data. For example, the charts below show sets that only differ in the amount of MeOH feed.
To visualize the accuracy of the model predictions for several sets together, the Parity Plots may be used:

**Reactor Optimization**

Having established the kinetics, we can use the optimization features in REX to improve the reactor performance. We will now show how to maximize the carbon yield of (PPY + BTE) with respect to carbon from the main reactant (MeOH).

In order to proceed with this example, the imported rex file must be switched to optimization mode. This is done by right-clicking on the project name, and selecting Mode→Change to Optimization.
In the Optimization→Yields Calculations node, we define the Yield of pseudocompound = Carbon-C3C4 with respect to MeOH:

The Carbon-C3C4 variable defined in PseudoCompounds node adds the carbon content for Propylene and Butene, while carbon moles for the reactant MeOH is just the moles of MeOH. Other Yields, Conversions or Selectivities can be defined here to be monitored. However, only those that have non-zero weights in the Objective node are considered for the optimization.

In this example, we want only to maximize the yield of Carbon-C3C4. Thus, a weight of 1 is entered for Carbon-C3C4 and all other variables have zero weights:
In Case Design node, we enter the Specifications and Initial Charge bounds. In this case, the initial charge for all compounds are fixed, while Catalyst Mass and Temperature are opened to find their optimal values. Pressure is fixed while the Flow has open bounds to maintain pressure at its setpoint.

After running the project, the maximum yield obtained is 70.71%, which is reported in the Results node.

In the Results→Reactor Summary node, we see that the optimal Catalyst Mass is 23.189 mg, while the optimal Temperature value is 417.78°C.

Next, we attempt to improve yield further, by allowing the Temperature to have a profile (non-constant) along the reactor. This is done by executing the Enable Control Profiles action by right-clicking on the Optimization node. The Control Profiles tree appears, where the Temperature must be selected to be optimized. In the Profile Optimize node, the reactor length is split into three periods of nearly equal length as shown below. For all of them, a linear profile is selected for the Temperature:
Finally, in the Profile Bounds node, Temperature bounds and values are entered for each period:

With the optimized temperature profile, the yield now increases to 77.33% in comparison to the 70.71% yield obtained when optimizing with constant temperature. The optimal temperature profiles can be seen in the Results → Profiles node:
The Temperature stays at the lower bound for the first and second period, then goes up in the third period. The reason is that in the beginning, lower temperature promotes the higher olefins (because they have lower activation energy). Once MeOH is depleted, these higher olefins can be split to C3 and C4 by increasing temperature. The reaction R2 that produces Ethylene has the highest activation energy. If we run higher temperature in the beginning, the Ethylene fraction becomes higher and that Ethylene cannot be converted to Butene once the Methanol is exhausted. This is because the R2R2-R4 reaction has zero rate. This optimal profile allows less of the MeOH to be stored as Ethylene in the beginning and once Methanol is depleted, higher temperature promotes the scission of higher olefins to increase C3 (mainly) and C4 olefins. MeOH decreases from the reactor inlet and becomes negligibly small close to the reactor outlet.
References