

# Model for Propane Dehydrogenation

Objective: Develop a kinetic model for Propane Dehydrogenation

In this example, we propose a simplified model for the catalytic dehydrogenation of propane to propylene on a Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. Kinetic parameters are estimated using experimental data from [1]. You may [download](#) the zip file that contains the examples for this study.

## Features Illustrated

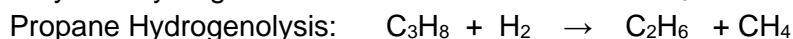
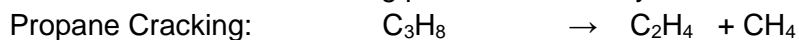
- Enforcement of Thermodynamic Constraints on Kinetic Parameters
- LHHW Site Models
- Dealing with Outlier Measurements
- Flags and color codes for kinetic parameters at bounds.
- Use of Compare Projects tool to choose between competing models

## Reaction Network

The reversible reaction for propane dehydrogenation to propylene on supported platinum catalyst is given by:



The side reactions also taking place on the catalyst surface are:



We will start with a kinetics model proposed in [1], where the main dehydrogenation reaction rate is modeled with LHHW kinetics as follows:

$$r_{Net} = \frac{k' \left( P_{C_3H_8} - \frac{P_{C_3H_6} P_{H_2}}{K_{eq}} \right)}{\left( 1 + K' P_{C_3H_6} P_{H_2}^{0.5} + K_{C_3H_6} P_{C_3H_6} + (K'' P_{H_2})^{0.5} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{C_2H_4} P_{C_2H_4} + K_{C_2H_6} P_{C_2H_6} \right)^2}$$

On the other hand, the side reactions are modeled as Mass Action (simple power law), without any LHHW sites.

## Setting up the REX Model

Partial Pressure is chosen as *concentration units* for the rates in Units Configuration node. Rate basis is catalyst mass for this fixed bed catalytic reactor. Other units chosen are shown below:

Project Explorer

- > Projects »
- ✓ **Project: Propane\_Dehyd\_1** »
  - Chemistry »
    - Units Configuration**
    - Compounds »
    - Pseudo-Compounds »
    - Reactions »
      - Properties
      - Kinetics
        - Rate Equations
        - Notes
    - Estimation »
    - Reaction Traffic »

**Units**

Reaction Rate Units will be **mmol/(gram - hour)**

Variable	Unit
Time	hour
Temperature	C
Pressure	Atm
Volume	lit
Mass	gram
Moles	mmol
Specific Energy	kJ/mol
Surface Area	m <sup>2</sup>
Rate Basis	Catalyst Mass
Concentrations	Partial Pressure

After defining the compounds and reactions, we include the pertinent directions for the reactions in the Kinetics node:

Project Explorer

- > Projects »
- ✓ **Project: Propane\_Dehyd\_1** »
  - Chemistry »
    - Units Configuration
    - Compounds »
    - Pseudo-Compounds »
    - Reactions »
      - Properties
      - Kinetics**
        - Rate Equations
        - Notes
      - Estimation »
      - Reaction Traffic »

**Reactions**

Include	Reaction	Equation
▼ <b>Direction: Forward</b>		
<input checked="" type="checkbox"/>	C3H8-Dehydrogenation	$C_3H_8 \leftrightarrow H_2 + C_3H_6$
<input checked="" type="checkbox"/>	C3H8-Cracking	$C_3H_8 \rightarrow C_2H_4 + CH_4$
<input checked="" type="checkbox"/>	C2H4-Hydrogenation	$H_2 + C_2H_4 \rightarrow C_2H_6$
<input checked="" type="checkbox"/>	C3H8-Hydrogenolysis	$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4$
▼ <b>Direction: Reverse</b>		
<input checked="" type="checkbox"/>	C3H8-Dehydrogenation	$C_3H_8 \leftrightarrow H_2 + C_3H_6$
<input type="checkbox"/>	C3H8-Cracking	$C_3H_8 \rightarrow C_2H_4 + CH_4$
<input type="checkbox"/>	C2H4-Hydrogenation	$H_2 + C_2H_4 \rightarrow C_2H_6$
<input type="checkbox"/>	C3H8-Hydrogenolysis	$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4$

In the Mass Action tab of Chemistry→Kinetics→Parameters node, all reactions have their orders to be same as their stoichiometric coefficients. In the LHHW Sites tab, the site is defined as described in previous section:

Project Explorer

- Projects »
  - Project: Propane\_Dehyd\_1 »
    - Chemistry »
      - Units Configuration
      - Compounds »
      - Pseudo-Compounds »
      - Reactions »
        - Properties
        - Kinetics
          - Parameters »
          - Kinetics Sites
          - Rate Equations
          - Notes
        - Estimation »
        - Reaction Traffic »

Sites

Site	Constant	Expression
SiteMainReaction	1	$1 + 0.1[\text{H}_2]^{0.5}[\text{C}_3\text{H}_6] + 0.1[\text{C}_3\text{H}_6] + 0.1[\text{H}_2]^{0.5} + 0.1[\text{H}_2] + 0.1[\text{CH}_4] + 0.1[\text{C}_2\text{H}_4] + 0.1[\text{C}_2\text{H}_6]$

SiteMainReaction terms

Term	Pre Exponential	Energy [kJ/mol]
Term1	1.00E-01	0.00
Term2	1.00E-01	0.00
Term3	1.00E-01	0.00
Term4	1.00E-01	0.00
Term5	1.00E-01	0.00
Term6	1.00E-01	0.00
Term7	1.00E-01	0.00

SiteMainReaction - Term1 orders

Component [Atm]	Order
H2	0.5
C3H6	1

Mass Action | LHHW Sites

The adsorption site is then assigned to the main reaction in the Kinetics→ Kinetics Site node, and site exponent is set to 2 in accordance with the rate expression for the main reaction:

Project Explorer

- Projects »
  - Project: Propane\_Dehyd\_1 »
    - Chemistry »
      - Units Configuration
      - Compounds »
      - Pseudo-Compounds »
      - Reactions »
        - Properties
        - Kinetics
          - Parameters »
          - Kinetics Sites
          - Rate Equations
          - Notes
        - Estimation »

Kinetics - Sites

Reaction	Direction	SiteMainReaction
C3H8-Dehydrogenation	Forward	<input checked="" type="checkbox"/>
C3H8-Cracking	Forward	<input type="checkbox"/>
C2H4-Hydrogenation	Forward	<input type="checkbox"/>
C3H8-Hydrogenolysis	Forward	<input type="checkbox"/>
C3H8-Dehydrogenation	Reverse	<input checked="" type="checkbox"/>

Kinetics Sites | Exponent

The screenshot shows a software interface with a 'Project Explorer' on the left and a 'Kinetics - Exponent' table on the right. The table lists two rows for the 'C3H8-Dehydrogenation' reaction, one for the forward direction and one for the reverse direction, both with an exponent of 2 and a site name 'SiteMainRea...'. The 'Kinetics Sites' and 'Exponent' tabs are visible at the bottom of the table.

Reaction	Direction	Site	Exponent
C3H8-Dehydrogenation	Forward	SiteMainRea...	2
C3H8-Dehydrogenation	Reverse	SiteMainRea...	2

For the reversible dehydrogenation reaction, the net rate depends on the equilibrium constant ( $K_{eq}$ ):

$$r_{Net} = r_{Forw} - r_{Rev} = \frac{k_{Forw} \left( P_{C3H8} - \frac{P_{C3H6} P_{H2}}{K_{eq}} \right)}{LHHW \text{ Site}}$$

where:

$$K_{eq} = \frac{k_{Forw}}{k_{Rev}}$$

At the average temperature of the experimental sets (600C), the equilibrium constant value is  $K_{eq}=0.303$ , while the heat of reaction is 129.6 kJ/mol.

To relate those values to the kinetics parameters, we introduce the Van't Hoff equation:

$$K_{eq} = K_0 e^{-\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

Where  $K_0$  is the equilibrium constant at temperature of  $T_0$ . We consider  $T_0=600C$  thus  $K_0=0.303$ . Combining the last two equations we have:

$$K_{eq} = K_0 e^{-\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)} = \frac{k_{Forw}}{k_{Rev}} = \frac{A_{Forw} e^{-\frac{E_{Forw}}{RT}}}{A_{Rev} e^{-\frac{E_{Rev}}{RT}}}$$

After rearranging some more we arrive at :

$$\left(K_0 e^{+\frac{\Delta H}{RT_0}}\right) e^{-\frac{\Delta H}{RT}} = \left(\frac{A_{Forw}}{A_{Rev}}\right) e^{-\frac{(E_{Forw} - E_{Rev})}{RT}}$$

From the last equality we can obtain the following relationships:

$$E_{Forw} - E_{Rev} = \Delta H$$

$$\frac{A_{Forw}}{A_{Rev}} = K_0 e^{+\frac{\Delta H}{RT_0}}$$

In Estimation→Parameter Relationships node we enforce the above constraints.

For the activation energies, a linear relationship is defined:

Include	Relation	Kinetic Parameter	Type	Expression	Constraint Type	Right Hand Side
<input checked="" type="checkbox"/>	Dehyd-Act	Activation Energy	Linear Sum	[C3H8-Dehydrogenation.F] - [C3H8-Dehydrogenation.R]	=	129.6

Reaction - Direction	Coefficient/Exponent
C3H8-Dehydrogenation - Forward	1
C3H8-Dehydrogenation - Reverse	-1

Another parameter relationship is entered for the pre-exponentials; in this case a non-linear expression:

Include	Relation	Kinetic Parameter	Type	Expression	Constraint Type	Right Hand Side
<input checked="" type="checkbox"/>	Dehyd-PreExp	PreExponential	Nonlinear Product	([C3H8-Dehydrogenation.F]) / ([C3H8-Dehydrogenation.R])	=	17200000

Reaction - Direction	Coefficient/Exponent
C3H8-Dehydrogenation - Forward	1
C3H8-Dehydrogenation - Reverse	-1

## Experimental Data

The experiments are carried out in a fixed bed reactor (PFR), where pressure and temperature are kept constant. This is defined in the Reactor node, where the gas flow is defined as *float for pressure control*, thus it is calculated automatically along the reactor:

The screenshot displays the software interface for configuring a reactor. On the left, the 'Project Explorer' shows a tree view with 'Project: Propane\_Dehyd\_1' expanded to 'Reactor'. The main window is titled 'Reactor Type / Phase Behavior' and contains a list of reactor types with radio buttons. 'PFR: Single Gas' is selected. To the right, there are two tables: 'Phases' and 'PFR Reactor Properties'.

Phase	Type	Reaction Phase
Gas	Gas	<input checked="" type="checkbox"/>

Property	Value
Flow	Float for Pressure Control
Temperature	Interpolated from Data
Pressure	Interpolated from Data
Recycle	No

In the experiments, the feed consist of propane and hydrogen with a 0.8 hydrogen to propane ratio. The experimental design allows the analysis of the following effects:

- Temperature Effect: {580, 600, 620C}
- Weighted Hourly Space Velocity (WHSV) Effect : {2, 5, 8, 11 hr<sup>-1</sup>}

We assume that all experiments are carried out with the same amount of feed. Catalyst mass is varied to obtain the desired space velocity values. Measured outlet flows of Propane, Propylene and byproducts are entered into Experiments→Measurements→ SetName nodes of the provided rex file.

## Parameter Estimation

In the Estimation node, all reactions and the LHHW site are selected for estimation. Bounds are open for pre-exponentials and activation energies of all reactions in Estimation→Parameters node. In the Weights node, we select the compounds to be reconciled, and hybrid weights are generated for them:

Project Explorer <

- > Projects »
- ▼ **Project: Propane\_Dehyd\_1** »
  - > Chemistry »
  - ▼ Estimation »
    - ▼ Parameters »
    - Relationships »
    - > Reactor
    - > Experiments »
    - > **Weights ↕**

Reconciled Measurements

Item	Total Moles	Gas
C3H8	<input checked="" type="checkbox"/>	<input type="checkbox"/>
H2	<input type="checkbox"/>	<input type="checkbox"/>
C3H6	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C2H6	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C2H4	<input checked="" type="checkbox"/>	<input type="checkbox"/>
CH4	<input checked="" type="checkbox"/>	<input type="checkbox"/>

Finally, we select “Kinetics Parameters = Estimate” in the Run→Solution Options node. The kinetic parameters are estimated by minimizing the weighted least squares prediction error of the reconciled compounds.

## Model 1: Results

After running the model in Propane\_Dehyd\_1.rex, we see the optimal parameter values in the Results→Parameters node:

Project Explorer

- > Projects »
- ▼ **Project: Propane\_Dehyd\_1** »
  - > Chemistry »
  - ▼ Estimation »
    - > Parameters »
    - > Reactor
    - > Experiments »
    - > Weights ↕
    - > Yield Calculations
    - > Solution Options ↕
    - > Initialization Values »
    - ▼ **Results »**
      - Parameters**

Estimated Parameters [Rate Units: mmol/(gram - hour)]

Reaction	Pre Exponential	Activation Energy [kJ/mol]	Value @ 600C	Component [Atm]	Order
<b>Direction: Forward</b>					
C3H8-Dehydrogenation	1.88E+10	129.60	3.32E+02	C3H8	1
C3H8-Cracking	7.38E+13	221.12	4.36E+00	C3H8	1
C2H4-Hydrogenation	2.78E-08	0.00	2.78E-08	C2H4	1
				H2	1
C3H8-Hydrogenolysis	1.53E+16	250.00	1.69E+01	C3H8	1
				H2	1
<b>Direction: Reverse</b>					
C3H8-Dehydrogenation	1.09E+03	0.00	1.09E+03	C3H6	1
				H2	1

Mass Action LHHW Sites

Project Explorer

- Projects »
- Project: Propane\_Dehyd\_1 »
  - Chemistry »
  - Estimation »
    - Parameters »
    - Reactor
    - Experiments »
    - Weights ↯
    - Yield Calculations
    - S= Solution Options ↯
    - Initialization Values »
    - Results »
      - Parameters

Kinetics Sites								
Site	Constant	Term	Pre Exponential	Energy [kJ/mol]	Value @ 600C	Component [Atm]	Order	
SiteMainReaction	1	Term1	2.54E-08	0.00	2.54E-08	H2	0.5	
		Term2	3.13E-08	0.00	3.13E-08	C3H6	1	
		Term3	1.74E-07	0.00	1.74E-07	H2	0.5	
		Term4	9.24E-10	-16.45	8.91E-09	H2	1	
		Term5	8.26E-06	0.00	8.26E-06	CH4	1	
		Term6	2.69E-06	-1.68	3.40E-06	C2H4	1	
		Term7	1.29E+02	0.00	1.29E+02	C2H6	1	

A parameter whose solution value lies at one of the bounds is indicated with a green arrow. Arrows pointing up indicate that the parameter reached its upper bound; downward arrows indicate the lower bound. The same can be seen in the Estimation→Parameters node if a parameter is at a bound. Relaxing the bounds may improve the model. For example, the activation energy for C3H8-Dehydrogenation reaction is upper bounded and one could increase the upper bound. However, the marginal value, which is a measure of sensitivity of the objective function to the bound, for that parameter is small as seen in Results→Marginal Values node:

Project Explorer

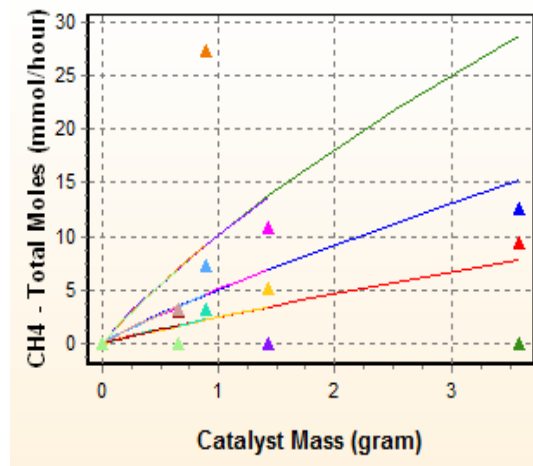
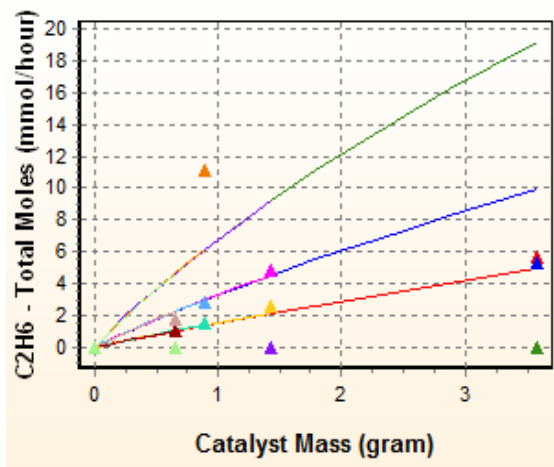
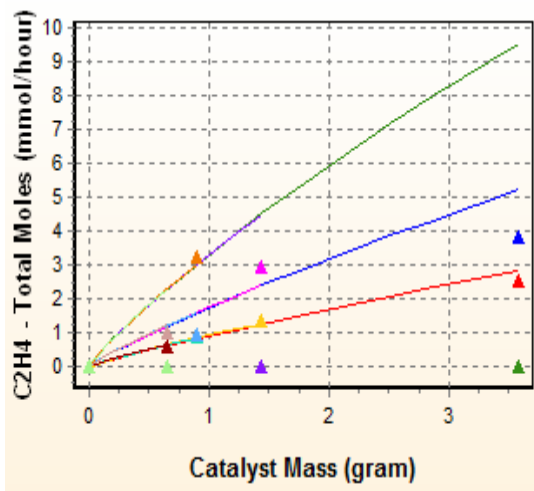
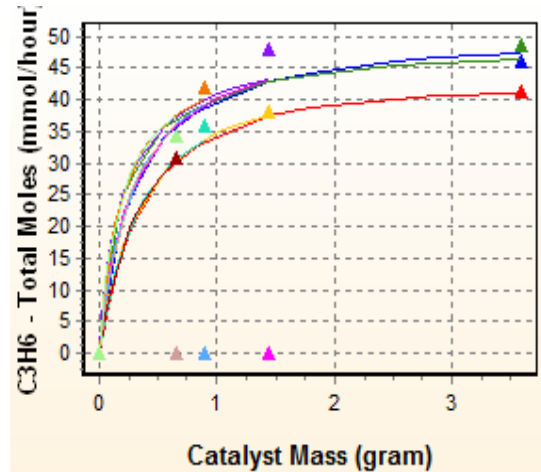
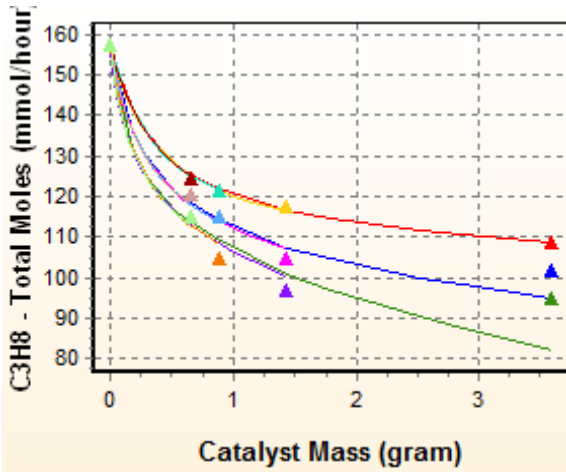
- Projects »
- Project: Propane\_Dehyd\_1 »
  - Chemistry »
  - Estimation »
    - Parameters »
    - Reactor
    - Experiments »
    - Weights ↯
    - Yield Calculations
    - S= Solution Options ↯
    - Initialization Values »
    - Results »
      - Parameters
      - Rate Equations
      - Marginal Values

Marginal Values for the active constraints			
Type	Item	Description	Marginal Value
Parameter Relationship	Dehyd-PreExp	PreExponential	-0.65563
	Dehyd-Act	Activation Energy	0.10417
Reaction	C3H8-Hydrogenolysis - Forward	Activation Energy: Upper Bound	-0.010309
	C3H8-Dehydrogenation - Reverse	Activation Energy: Lower Bound	0.0092012
Site	SiteMainReaction	Term7 - Energy: Upper Bound	-0.0033395

The small marginal value indicates that the reduction in the weighted least square error would be small if the upper bound is increased. Thus we keep the bounds unchanged.

Now we inspect the model predictions to data in the *Model-Data Comparison* node. The compounds profiles for the reactant and products are shown below:

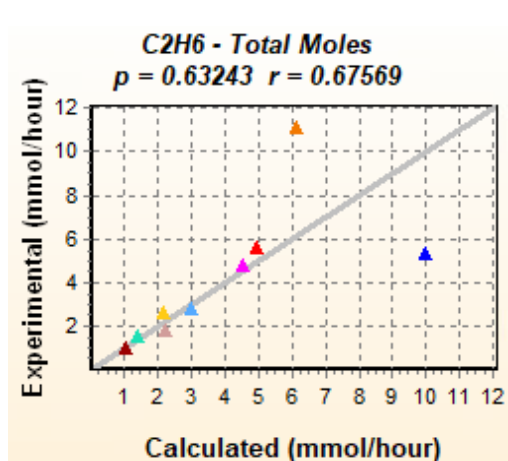
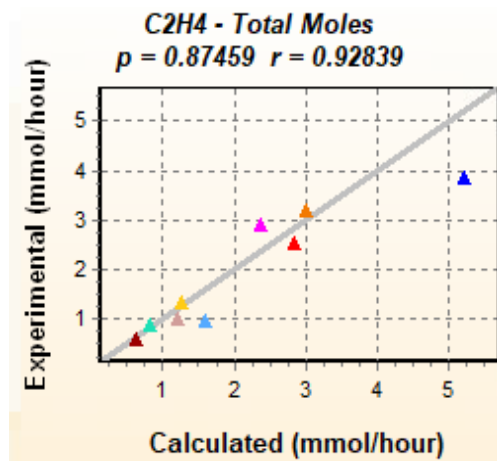
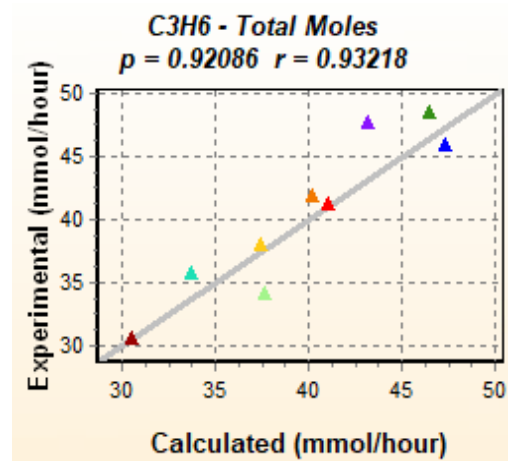
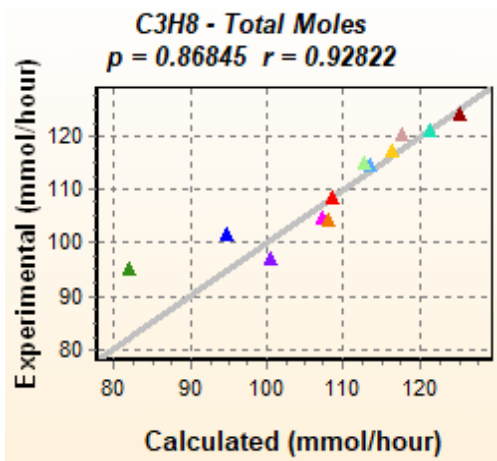


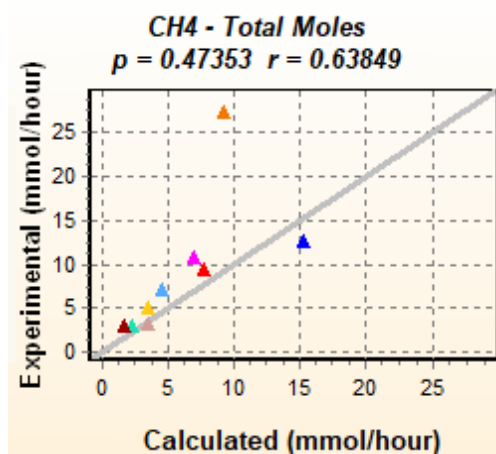


- |                   |                    |                   |                    |
|-------------------|--------------------|-------------------|--------------------|
| ▲ SV2-T580 - Exp  | — SV2-T580 - Calc  | ▲ SV2-T600 - Exp  | — SV2-T600 - Calc  |
| ▲ SV2-T620 - Exp  | — SV2-T620 - Calc  | ▲ SV5-T580 - Exp  | — SV5-T580 - Calc  |
| ▲ SV5-T600 - Exp  | — SV5-T600 - Calc  | ▲ SV5-T620 - Exp  | — SV5-T620 - Calc  |
| ▲ SV8-T580 - Exp  | — SV8-T580 - Calc  | ▲ SV8-T600 - Exp  | — SV8-T600 - Calc  |
| ▲ SV8-T620 - Exp  | — SV8-T620 - Calc  | ▲ SV11-T580 - Exp | — SV11-T580 - Calc |
| ▲ SV11-T600 - Exp | — SV11-T600 - Calc | ▲ SV11-T620 - Exp | — SV11-T620 - Calc |

In the above charts, some of the experimental points (labeled) are not consistent with the experimental trends and are likely to be outliers. For example, C<sub>2</sub>H<sub>4</sub> data increases with temperature, with the only exception of SV2-T600 where less C<sub>2</sub>H<sub>4</sub> is produced than the SV2-T580 set.

Parity Charts are an alternative way of displaying the experimental and predicted values. Points on the 45 degree mean exact model match to data, while overpredicted values are located to the right of that line and underprediction to the left:





Comparing the pre-exponential values of the site terms, we see that inhibition from  $C_2H_6$  is most significant. Other inhibition terms are negligible. However, on further analysis, we found that this model has multiple solutions. One way to see this is by fixing all but one of the pre-exponential terms in the LHHW site to zero. The results of this study are summarized below:

Run Trial	Weighted LSQ
<i>All Terms estimated (Model 1)</i>	28.055
Only $C_3H_8$ Term estimated - Other Terms fixed to zero	33.763
Only $C_3H_6$ Term estimated - Other Terms fixed to zero	33.683
Only $H_2$ (Term 3) estimated - Other Terms fixed to zero	51.660
Only $H_2$ (Term 4) estimated - Other Terms fixed to zero	52.699
Only $CH_4$ Term estimated - Other Terms fixed to zero	28.080
Only $C_2H_4$ Term estimated - Other Terms fixed to zero	28.090
Only $C_2H_6$ Term estimated - Other Terms fixed to zero	28.055

From these runs, it can be seen that the solution with all the terms optimized has nearly the same prediction error (Weighted LSQ) as the last three runs. We may draw two conclusions from these runs:

- We can eliminate the inhibition effect of  $C_3H_8$ ,  $C_3H_6$  and  $H_2$ . They are zero when estimating all terms, while estimating them separately leads to higher LSQ.
- With the available data, there is no way to separate the effects of  $CH_4$ ,  $C_2H_4$  and  $C_2H_6$  inhibition factors. The solution obtained is very similar irrespective of whether they are all estimated simultaneously or individually. Thus, we could consider a single inhibition effect for them as a whole.

In next section, we proceed with model improvements based on this analysis.

## Model 2 : Simplified LHHW Inhibition for Main Reaction

First, we ignore the effect of the outlier experimental points on the parameter estimation. This can be manually done in the Weights→Sets node, where the weights are set to zero for these outlier points. Then, we modify the LHHW Site definition in order to consider only one combined inhibition term for CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. To do this, in the pseudo-compounds node, the *ByProducts* variable is created as the sum of the above compounds:

The screenshot shows the 'Project Explorer' on the left and the 'Pseudo-Compounds' configuration window on the right. The 'Project Explorer' is expanded to 'Project: Propane\_Dehyd\_2' > 'Chemistry' > 'Pseudo-Compounds'. The 'Pseudo-Compounds' window displays a table with the following data:

Pseudo-Compound	Type	Constant Term	Expression	Conserved
ByProducts	Linear Sum	0	[CH4] + [C2H4] + [C2H6]	<input type="checkbox"/>
				<input checked="" type="checkbox"/>

Below this table, the 'ByProducts terms' section is expanded, showing a table of terms:

Compound	Coefficient/Exponent
CH4	1
C2H4	1
C2H6	1

Then, we define a new Site, that has only one term corresponding to the ByProducts pseudo-compound:

Project Explorer <

- Projects »
- Project: Propane\_Dehyd\_2 »
  - Chemistry »
    - Units Configuration
    - Compounds »
    - Pseudo-Compounds »
    - Reactions »
    - Kinetics
      - Parameters »
      - Kinetics Sites
      - Rate Equations
      - Notes
    - Estimation »
    - Reaction Traffic »

Sites

Site	Constant	Expression
SiteMainReaction	1	$1 + 0.1[H_2]^{0.5}[C_3H_6] + 0.1[C_3H_6] + 0.1[H_2]^{0.5} + 0.1[H_2] + 0.1[CH_4] + 0.1[C_2H_4] + 0.1[C_2H_6]$
SiteMainReaction2	1	$1 + 0.1[ByProducts]$

SiteMainReaction2 terms

Term	Pre Exponential	Energy [kJ/mol]
Term1	1.00E-01	0.00

SiteMainReaction2 - Term1 orders

Component [Atm]	Order
ByProducts	1

Mass Action LHW Sites

We can delete the older site (SiteMainReaction), or we can keep it without assigning it to any reaction: that way the old site will not be used in the model. The new site is selected for the main reaction:

Project Explorer <

- Projects »
- Project: Propane\_Dehyd\_2 »
  - Chemistry »
    - Units Configuration
    - Compounds »
    - Pseudo-Compounds »
    - Reactions »
    - Kinetics
      - Parameters »
      - Kinetics Sites
      - Rate Equations

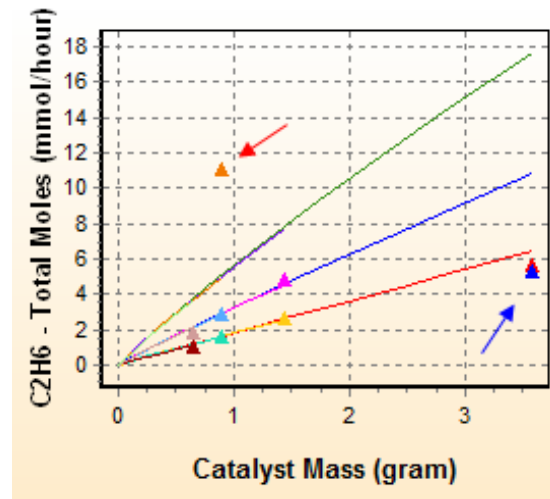
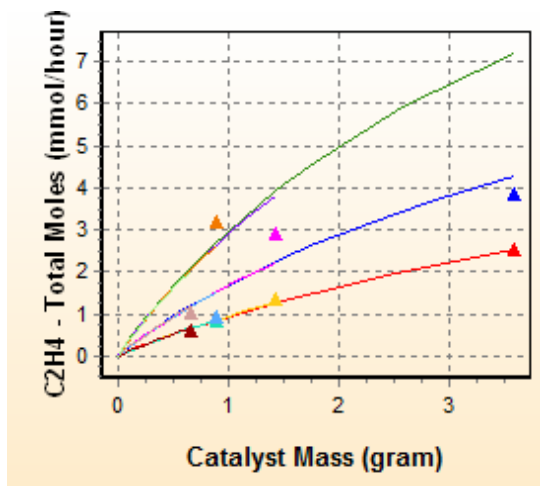
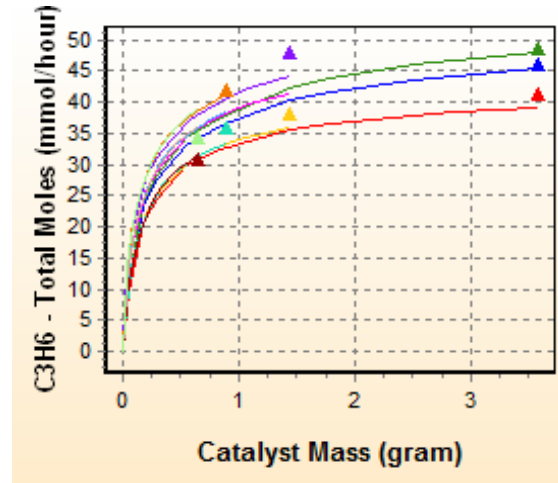
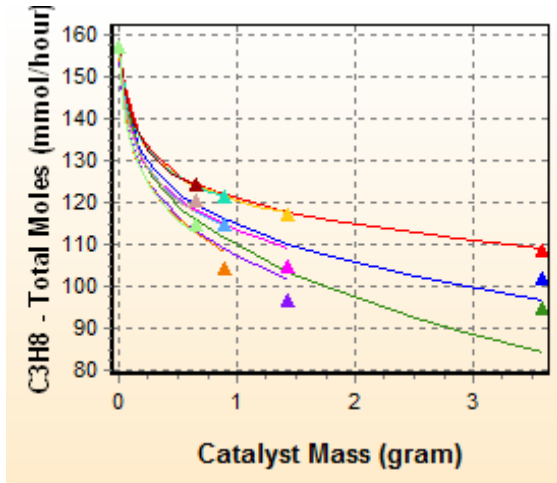
Kinetics - Sites

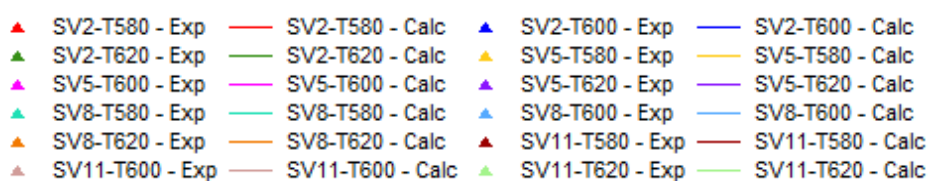
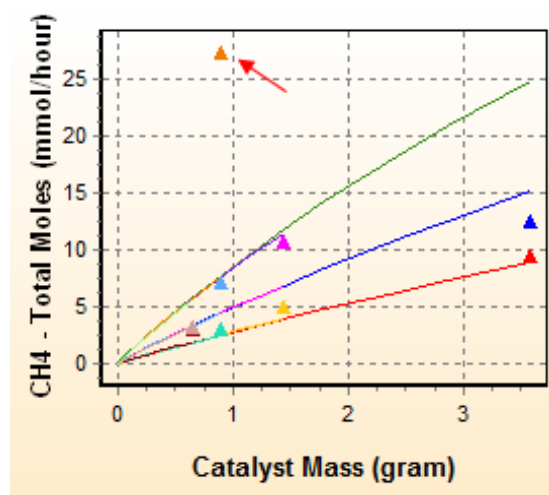
Reaction	Direction	SiteMainReaction	SiteMainReaction2
C3H8-Dehydrogenation	Forward	<input type="checkbox"/>	<input checked="" type="checkbox"/>
C3H8-Cracking	Forward	<input type="checkbox"/>	<input type="checkbox"/>
C2H4-Hydrogenation	Forward	<input type="checkbox"/>	<input type="checkbox"/>
C3H8-Hydrogenolysis	Forward	<input type="checkbox"/>	<input type="checkbox"/>
C3H8-Dehydrogenation	Reverse	<input type="checkbox"/>	<input checked="" type="checkbox"/>

Kinetics Sites Exponent

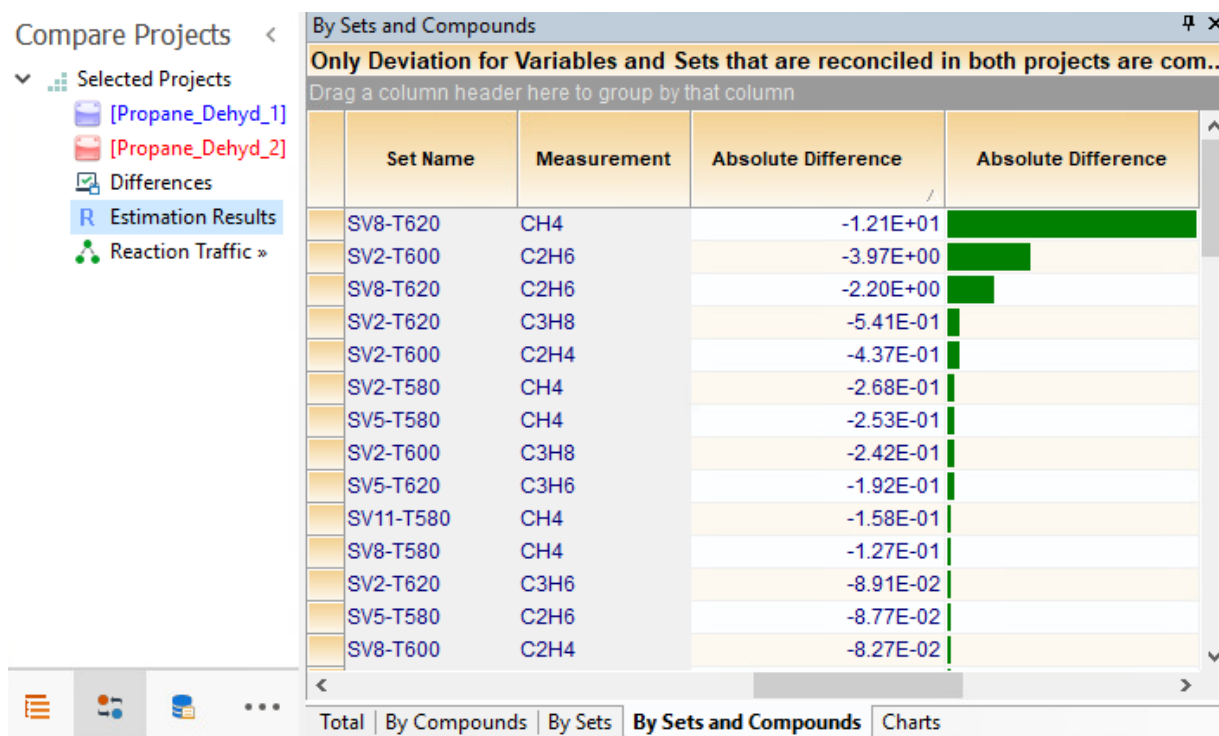
We assign an exponent of 1 for this site in the Exponent tab.

After opening bounds for the new site in the Estimation→Parameters node, we can run this project, as shown in the Propane Dehyd 2.rex file. The compound profiles are shown below. The outliers that are not reconciled are indicated by arrows:





The LSQ decreases from 28.05 in Model 1 to 8.38 in Model 2. 91% of the reduction is due to the zeroing of weights for the outliers. You may use the Compare Projects tool to do further analysis. The basics for using Compare Projects are described in the last section of the Methanol Synthesis [example](#). In the *By Sets and Compounds* tab, by clicking on the Absolute Difference header to sort the values, we see that the outlier points have the highest reduction in the weighted least square error:



LSQ reductions are indicated with a green bar, while increases are shown in red. If you scroll down, you will see a few measurements whose LSQ worsened from Model 1 to Model 2.

## Model 3 & 4: Effect of Site Inhibition on Byproduct Reactions

So far we considered Site inhibition for the main reaction only, while the reactions for byproduct formation were modeled without LHHW Sites. A look at the predicted byproduct profiles shows that the increase of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> is almost linear with catalyst mass. On the other hand, the data indicates a decrease in their formation rate as catalyst mass increases, suggesting an inhibition effect. That could be due to product inhibition; we will assume that the byproducts inhibit their own formation due to competitive adsorption.

We can try assigning the same site we are using for all reactions, as it models byproduct inhibition. Thus we switch the CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> formation reactions from Mass Action to LHHW in Chemistry→Kinetics node. Then the LHHW site is assigned for all of these reactions in Kinetics→Kinetics Site node. After running this modified project, weighted LSQ actually increases, as you will see by importing the Propane\_Dehyd\_3.rex file. The LSQ worsens from 8.38 to 12.5; thus we discard this model.

We can define an additional site for byproduct inhibition, to be assigned only for byproduct reactions. This new site also has only one term for the pseudo-compound that adds CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The main reaction will have the original site, as seen in the Kinetics→Kinetics Sites node of Propane\_Dehyd\_4.rex file:



Project Explorer

- Projects »
- Project: Propane\_Dehyd\_4 »
  - Chemistry »
    - Units Configuration
    - Compounds »
    - Pseudo-Compounds »
    - Reactions »
    - Kinetics
      - Parameters »
      - Kinetics Sites**
      - Rate Equations
      - Notes

Kinetics - Sites

Reaction	Direction	SiteMainReaction2	SiteForByProducts
C3H8-Dehydrogenation	Forward	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C3H8-Cracking	Forward	<input type="checkbox"/>	<input checked="" type="checkbox"/>
C2H4-Hydrogenation	Forward	<input type="checkbox"/>	<input checked="" type="checkbox"/>
C3H8-Hydrogenolysis	Forward	<input type="checkbox"/>	<input checked="" type="checkbox"/>
C3H8-Dehydrogenation	Reverse	<input checked="" type="checkbox"/>	<input type="checkbox"/>

Kinetics Sites Exponent

In the Estimation→Parameters node, we open the bounds for the pre-exponential and activation energy in the new site. We also open bounds between one and two for the order of the ByProducts in order to allow for stronger inhibition as byproducts build up:

Project Explorer

- Projects »
- Project: Propane\_Dehyd\_4 »
  - Chemistry »
  - Estimation »
    - Parameters »
    - Reactor
    - Experiments »
    - Weights ▾
    - Yield Calculations
    - S= Solution Options ▾
    - Initialization Values »
    - Results »
    - Reaction Traffic »

Sites

Site	Constant Min	Constant	Constant Max
SiteMainReaction2	1	1	1
SiteForByProducts	1	1	1

SiteMainReaction2 terms

Term	PreExponential Min	PreExponential	PreExponential Max	Energy Min	Energy [kJ/mol]	Energy Max
Term1	1.00E-04	5.62E+02	1.00E+04	-50.00	0.00	0.00

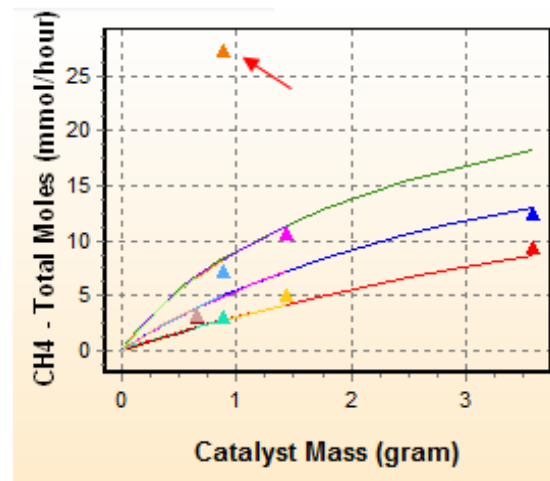
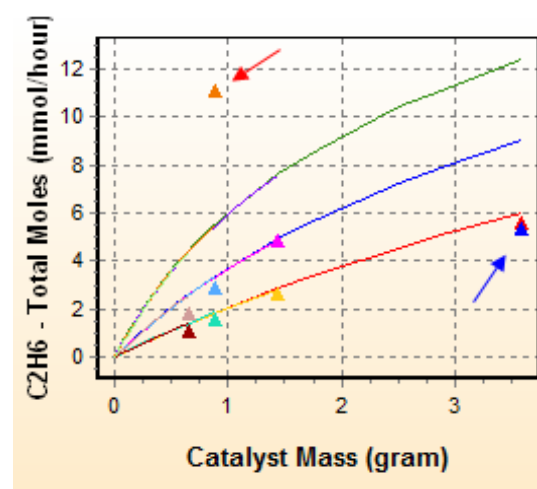
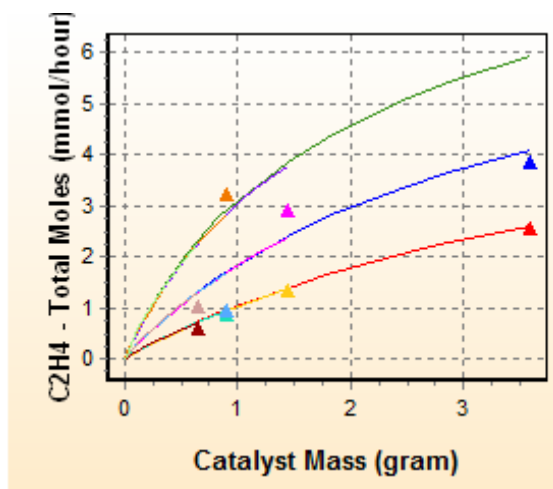
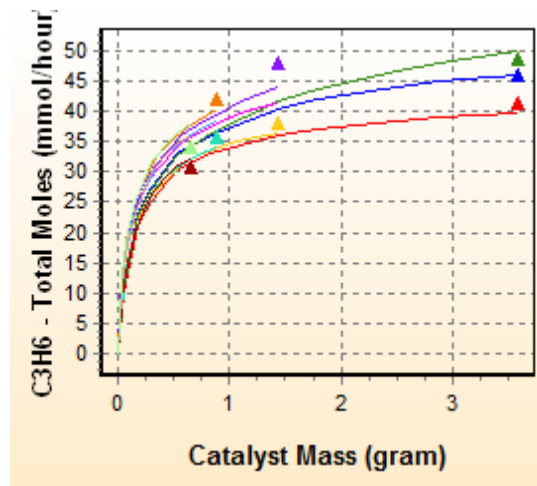
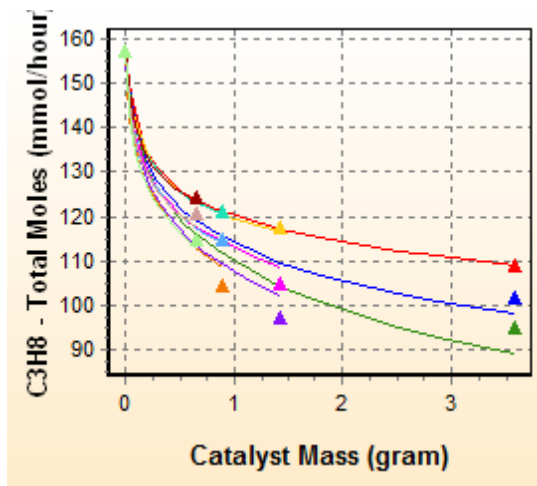
SiteMainReaction2 - Term1 orders

Component [Atm]	Order Min	Order	Order Max
ByProducts	1	1	1

Mass Action LHHW Sites Rate Bounds

After running the project we now get a 25% reduction of LSQ, from 8.38 (Model 2) to 6.29 in this Model 4.

You can see the more curved profile for the byproduct in the chart below. (Outliers not reconciled are indicated with arrows)



- |                   |                    |                   |                    |
|-------------------|--------------------|-------------------|--------------------|
| ▲ SV2-T580 - Exp  | — SV2-T580 - Calc  | ▲ SV2-T600 - Exp  | — SV2-T600 - Calc  |
| ▲ SV2-T620 - Exp  | — SV2-T620 - Calc  | ▲ SV5-T580 - Exp  | — SV5-T580 - Calc  |
| ▲ SV5-T600 - Exp  | — SV5-T600 - Calc  | ▲ SV5-T620 - Exp  | — SV5-T620 - Calc  |
| ▲ SV8-T580 - Exp  | — SV8-T580 - Calc  | ▲ SV8-T600 - Exp  | — SV8-T600 - Calc  |
| ▲ SV8-T620 - Exp  | — SV8-T620 - Calc  | ▲ SV11-T580 - Exp | — SV11-T580 - Calc |
| ▲ SV11-T600 - Exp | — SV11-T600 - Calc | ▲ SV11-T620 - Exp | — SV11-T620 - Calc |

## Further Studies

The Reaction Traffic node shows that  $C_2H_6$  is produced from two reactions. By enabling the carbon traffic feature, it is clear that one of these paths is very small. You may eliminate the weaker path and check the impact on the predictive ability of the model.

## References

1. A. Farjoo, F. Khorasheha, S. Niknaddaf, M. Soltani "Kinetic modeling of side reactions in propane dehydrogenation over Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst". *Scientia Iranica C* (2011) 18 (3), 458–464