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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/Al2O3 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:

Propane Dehydrogenation: $C_3H_8 \rightleftarrows C_3H_6 + H_2$

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

Propane Cracking: $C_3H_8 \rightarrow C_2H_4 + CH_4$

Ethylene Hydrogenation: $C_2H_4 + H_2 \rightarrow C_2H_6$

Propane Hydrogenolysis: $C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4$

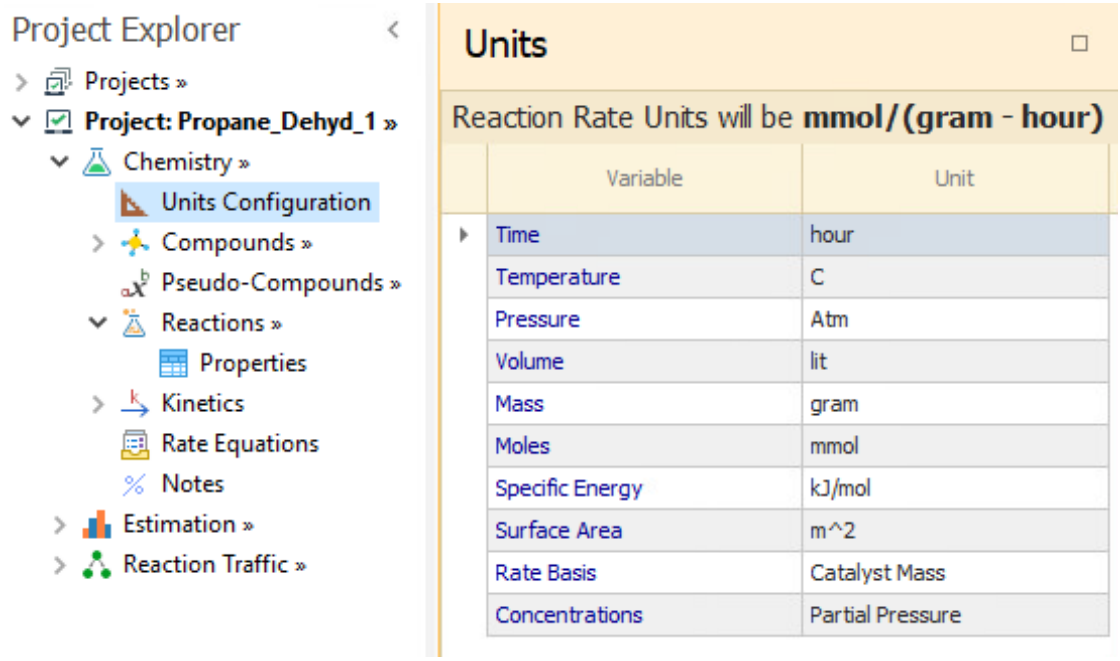
We will start with a kinetics model proposed in [1], where the main dehydrogenation reaction rate is modeled with LHHW kinetics as follows:

$$r_{Net} = \frac{k'\left(P_{C3H8} - \frac{P_{C3H6}P_{H2}}{K_{eq}}\right)}{\left(1 + K'P_{C3H6}P_{H2}^{0.5} + K_{C3H6}P_{C3H6} + (K''P_{H2})^{0.5} + K_{H2}P_{H2} + K_{CH4}P_{CH4} + K_{C2H4}P_{C2H4} + K_{C2H6}P_{C2H6}\right)^2}$$

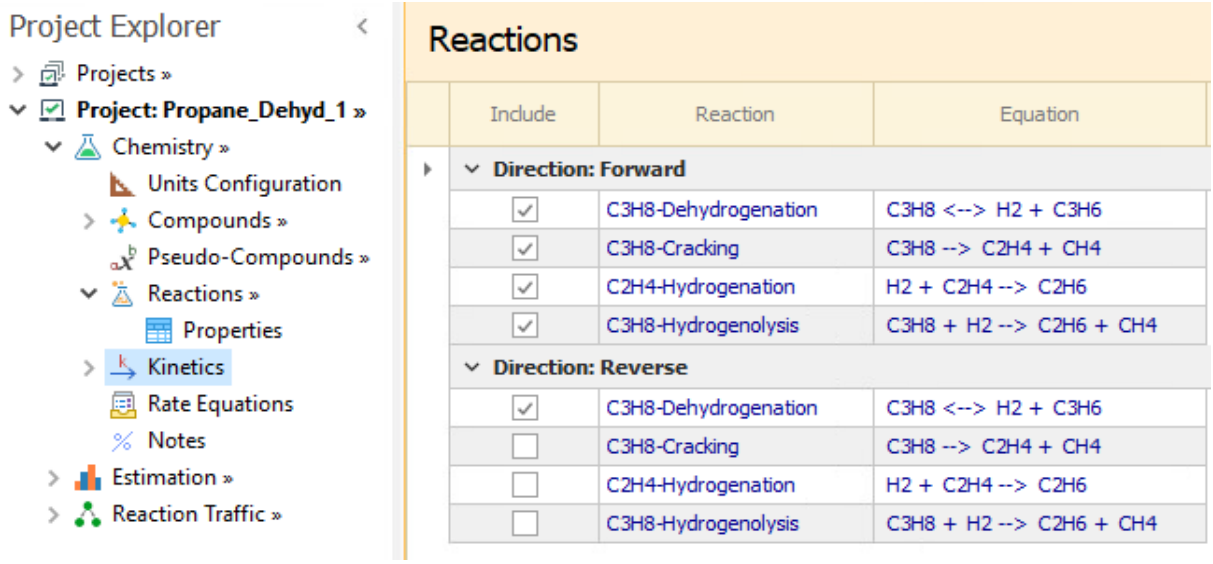
On the other hand, the side reactions are modeled as Mass Action (simple power law), without any LHHW sites.

Setting up the REX Model

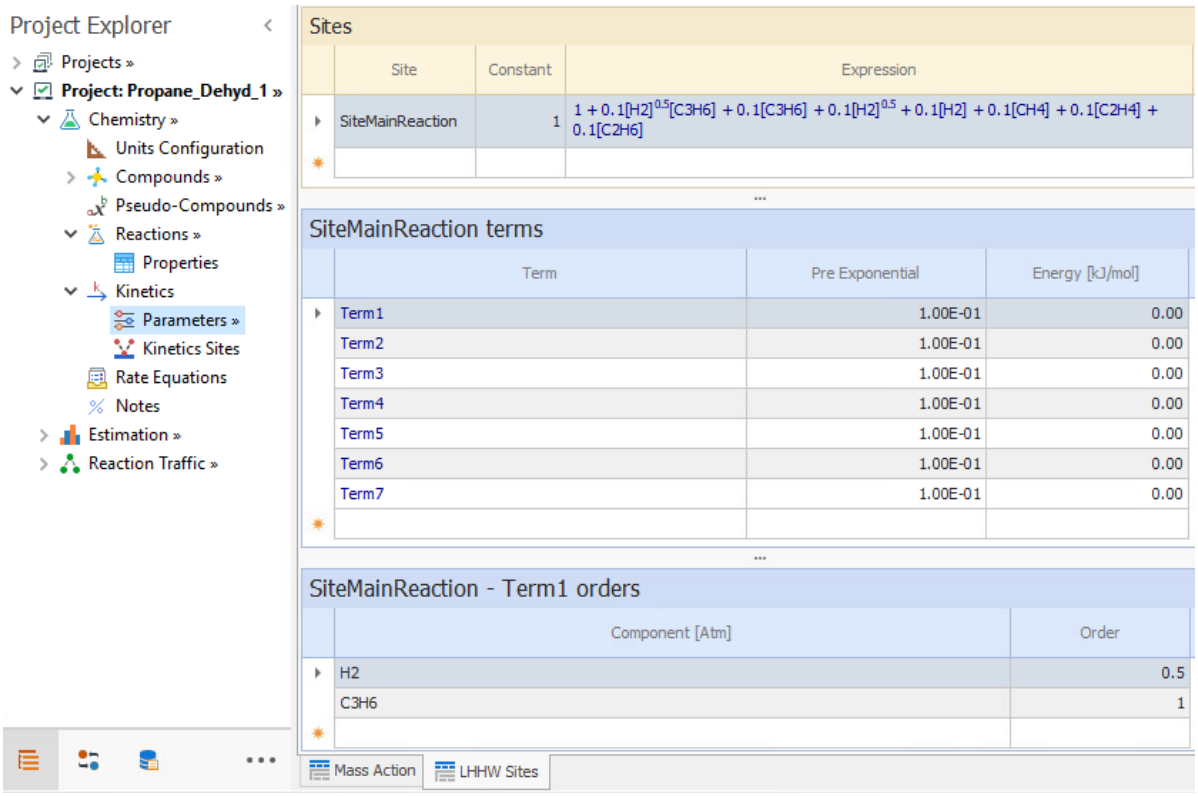
Partial Pressure is chosen as *concentration units* for the rates in Units Configuration node. Rate basis is catalyst mass for this fixed bed catalytic reactor. Other units chosen are shown below:



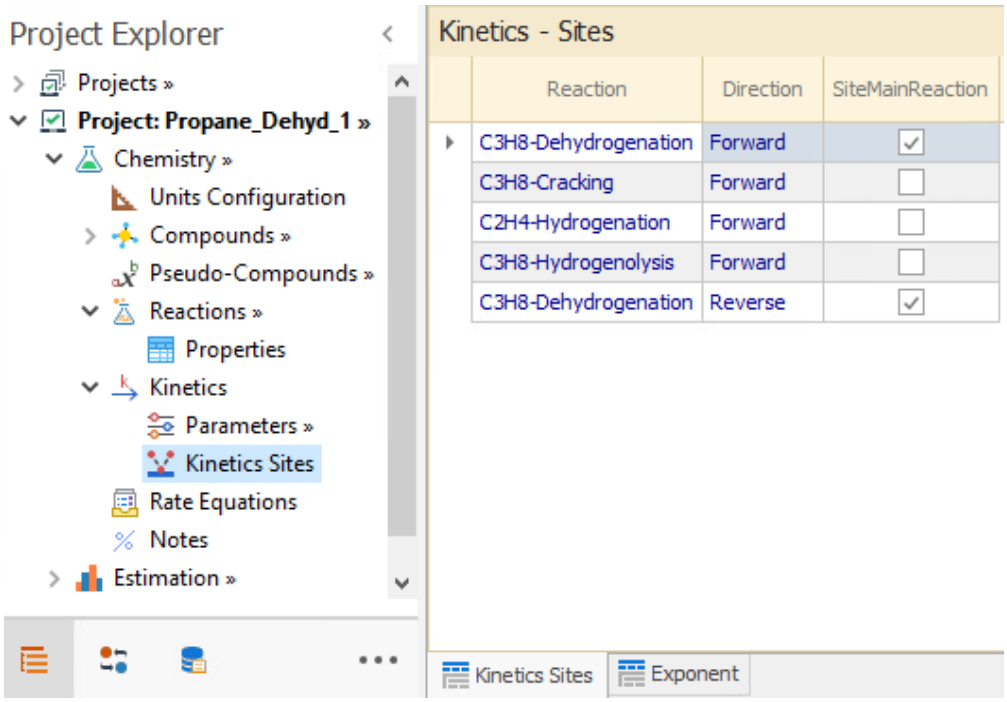
After defining the compounds and reactions, we include the pertinent directions for the reactions in the Kinetics node:

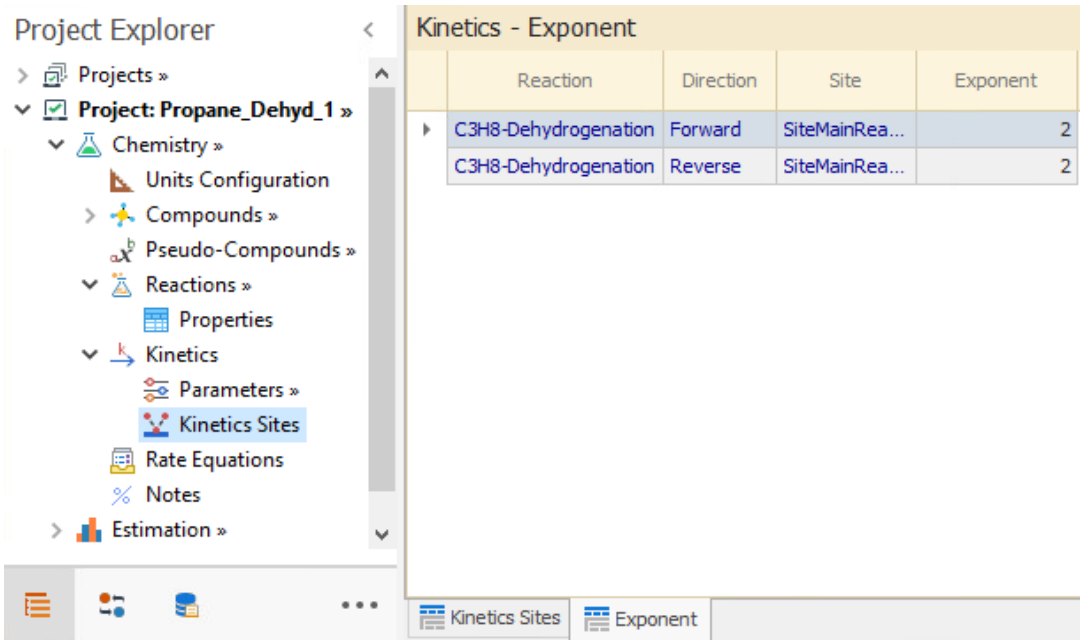


In the Mass Action tab of Chemistry→Kinetics→Parameters node, all reactions have their orders to be same as their stoichiometric coefficients. In the LHHW Sites tab, the site is defined as described in previous section:



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:





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

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

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 :

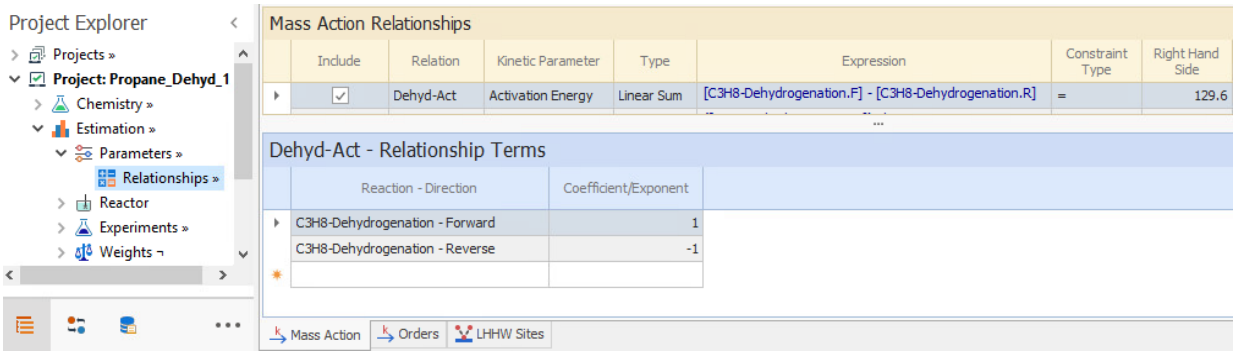
$$\left(K_0 e^{+\frac{\Delta H}{RT_0}}\right) e^{-\frac{\Delta H}{RT}} = \left(\frac{A_{Forw}}{A_{Rev}}\right) e^{-\frac{(E_{Forw}-E_{Rev})}{RT}}$$

From the last equality we can obtain the following relationships:

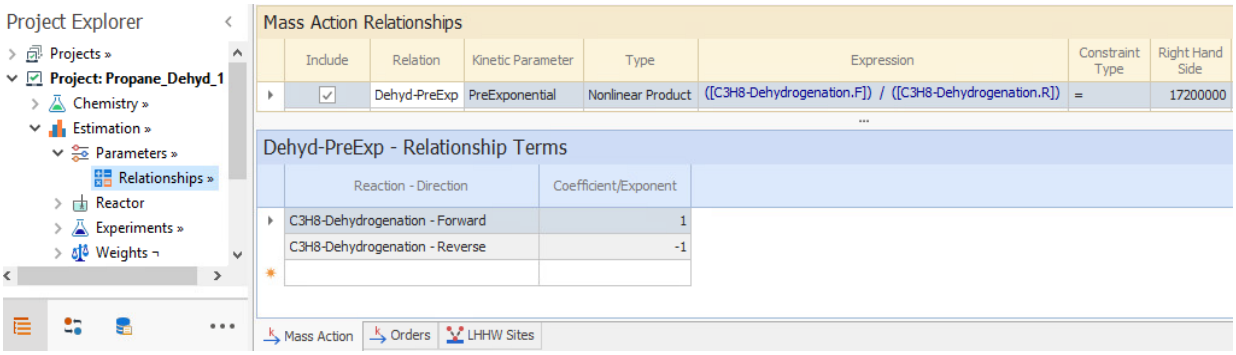
$$E_{Forw} - E_{Rev} = \Delta H$$

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

In Estimation→Parameter Relationships node we enforce the above constraints.
For the activation energies, a linear relationship is defined:

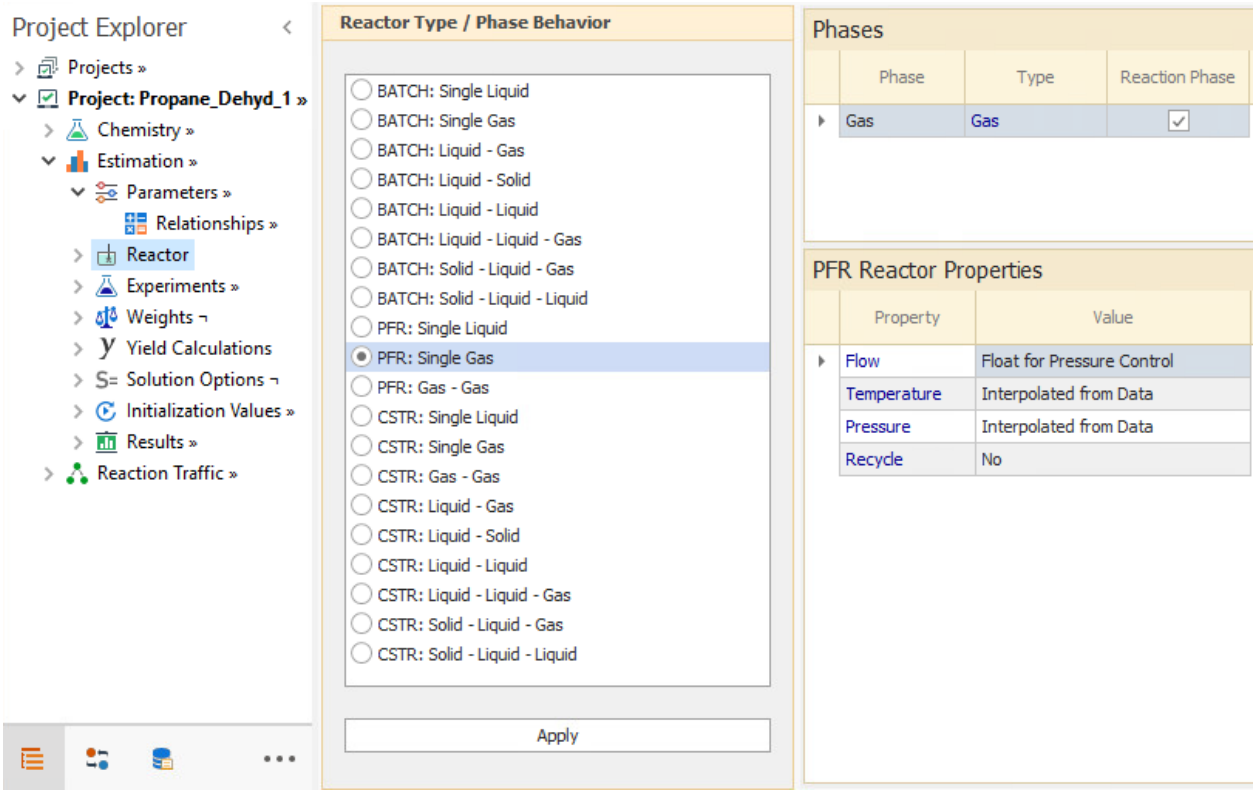


Another parameter relationship is entered for the pre-exponentials; in this case a non-linear expression:



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:



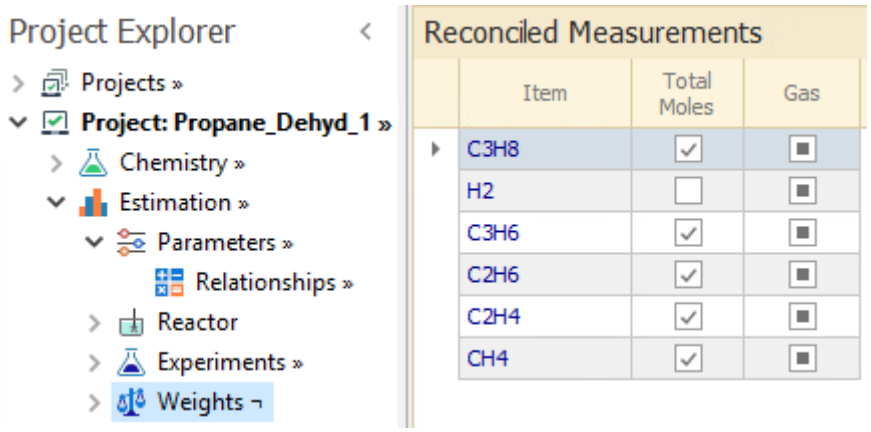
In the experiments, the feed consist of propane and hydrogen with a 0.8 hydrogen to propane ratio. The experimental design allows the analysis of the following effects:

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

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

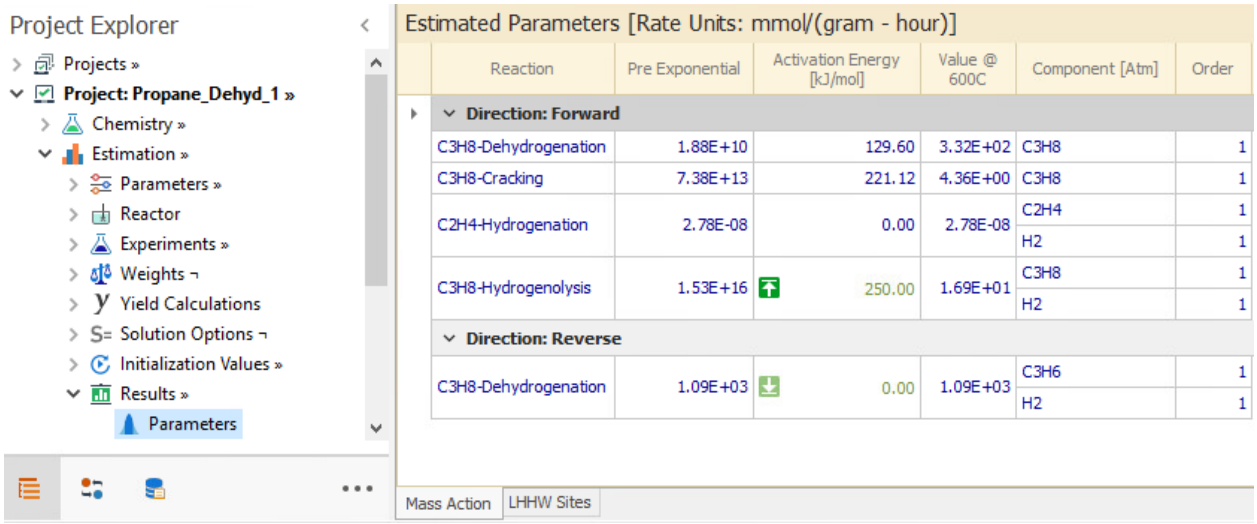
In the Estimation node, all reactions and the LHHW site are selected for estimation. Bounds are open for pre-exponentials and activation energies of all reactions in Estimation→Parameters node. In the Weights node, we select the compounds to be reconciled, and hybrid weights are generated for them:

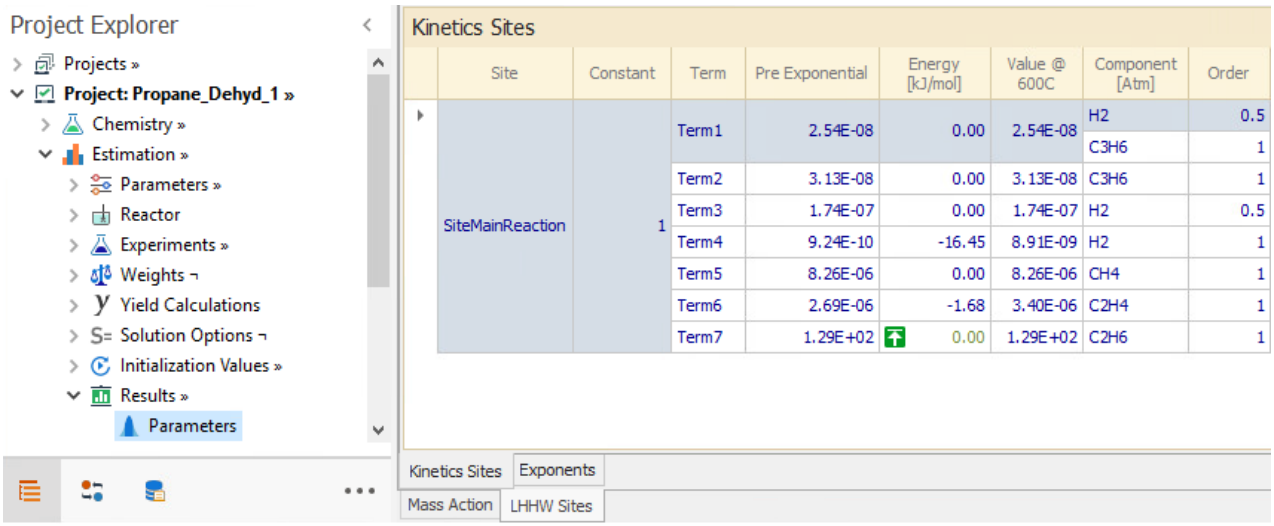


Finally, we select “Kinetics Parameters = Estimate” in the Run→Solution Options node. The kinetic parameters are estimated by minimizing the weighted least squares prediction error of the reconciled compounds.

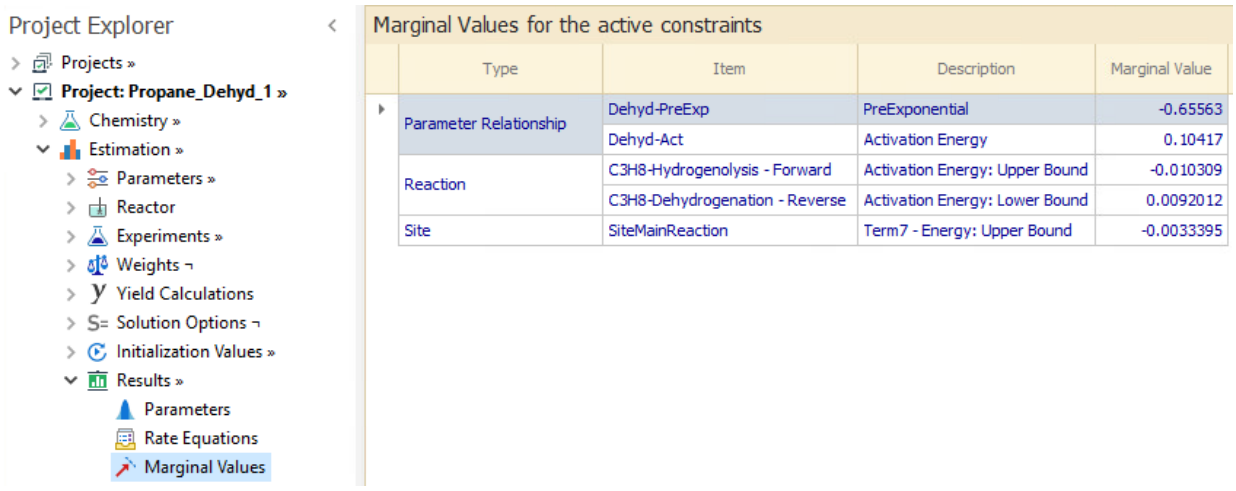
Model 1: Results

After running the model in Propane_Dehyd_1.rex, we see the optimal parameter values in the Results→Parameters node:



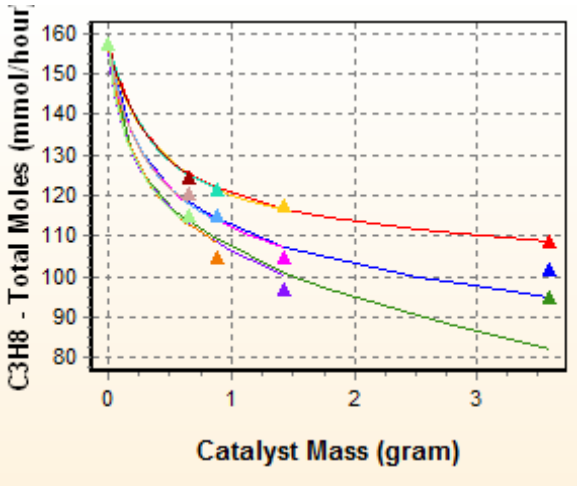


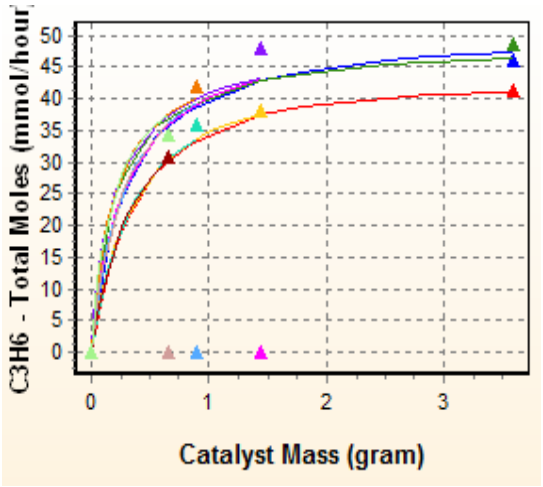
A parameter whose solution value lies at one of the bounds is indicated with a green arrow. Arrows pointing up indicate that the parameter reached its upper bound; downward arrows indicate the lower bound. The same can be seen in the Estimation→Parameters node if a parameter is at a bound. Relaxing the 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:

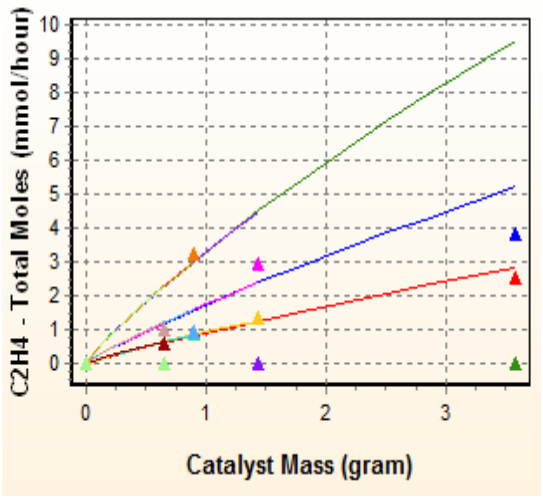


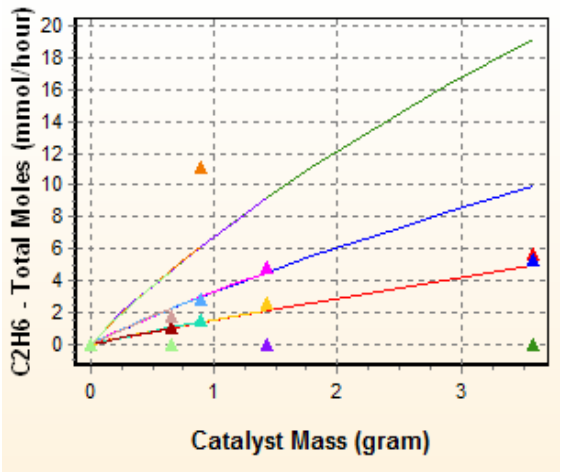
The small marginal value indicates that the reduction in the weighted least square error would be small if the upper bound is increased. Thus we keep the bounds unchanged.

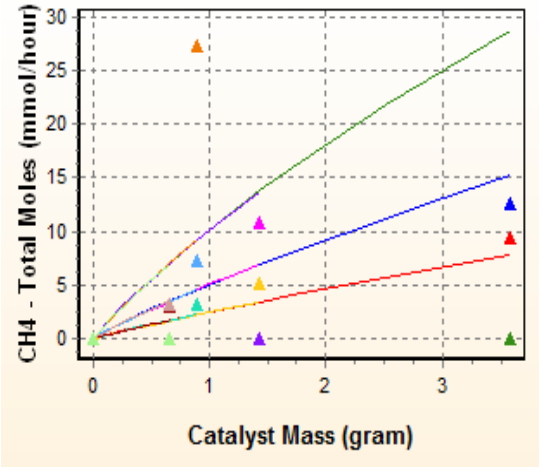
Now we inspect the model predictions to data in the *Model-Data Comparison* node.
The compounds profiles for the reactant and products are shown below:

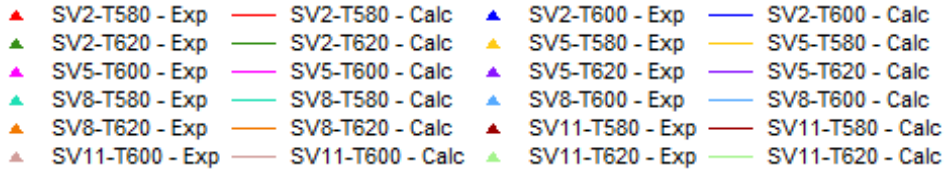

C3H8 - Total Moles (mmol/hour)
160
150
140
130
120
110
100
90
80
0
1
2
3
Catalyst Mass (gram)


C3H6 - Total Moles (mmol/hour)
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
Catalyst Mass (gram)


C2H4 - Total Moles (mmol/hour)
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
Catalyst Mass (gram)

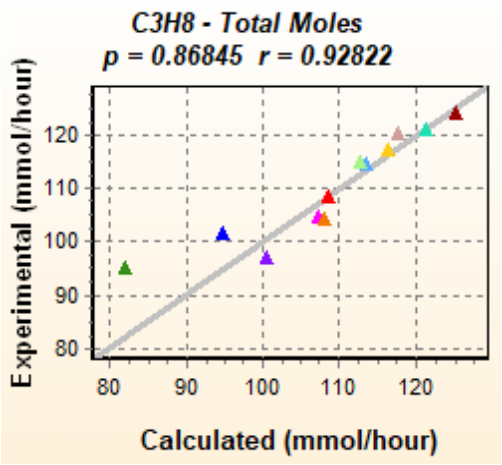

C2H6 - Total Moles (mmol/hour)
20
18
16
14
12
10
8
6
4
2
0
0
1
2
3
Catalyst Mass (gram)

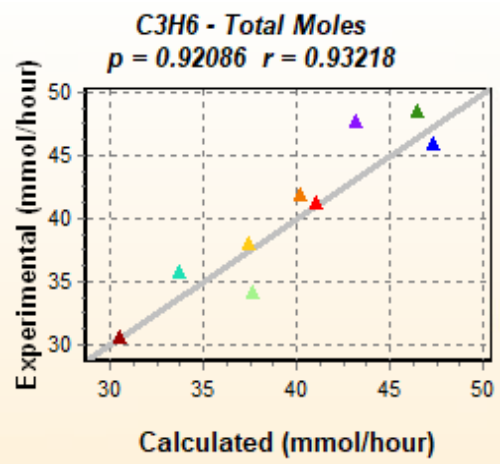

CH4 - Total Moles (mmol/hour)
30
25
20
15
10
5
0
0
1
2
3
Catalyst Mass (gram)

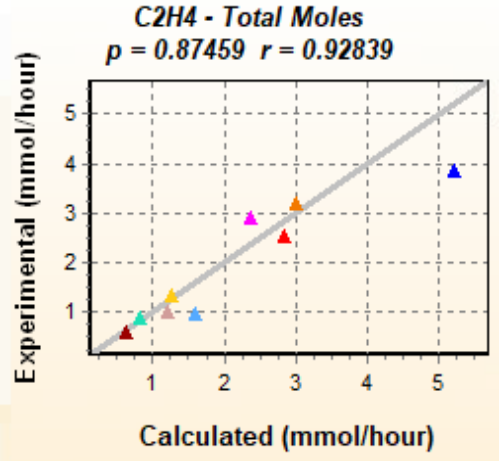

SV2-T580 - Exp
SV2-T580 - Calc
SV2-T600 - Exp
SV2-T600 - Calc
SV2-T620 - Exp
SV2-T620 - Calc
SV5-T580 - Exp
SV5-T580 - Calc
SV5-T600 - Exp
SV5-T600 - Calc
SV5-T620 - Exp
SV5-T620 - Calc
SV8-T580 - Exp
SV8-T580 - Calc
SV8-T600 - Exp
SV8-T600 - Calc
SV8-T620 - Exp
SV8-T620 - Calc
SV11-T580 - Exp
SV11-T580 - Calc
SV11-T600 - Exp
SV11-T600 - Calc
SV11-T620 - Exp
SV11-T620 - Calc

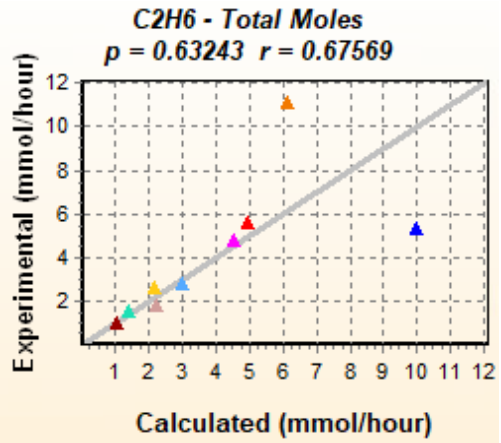
In the above charts, some of the experimental points (labeled) are not consistent with the experimental trends and are likely to be outliers. For example, C_2H_4 data increases with temperature, with the only exception of SV2-T600 where less C_2H_4 is produced than the SV2-T580 set.

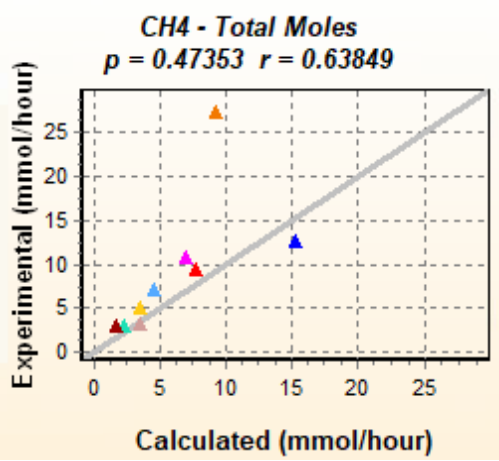
Parity Charts are an alternative way of displaying the experimental and predicted values. Points on the 45 degree mean exact model match to data, while overpredicted values are located to the right of that line and underprediction to the left:











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-exponentials terms in the LHHW site to zero. The results of this study are summarized below:

Run Trial	Weighted LSQ
All Terms estimated (Model 1)	*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

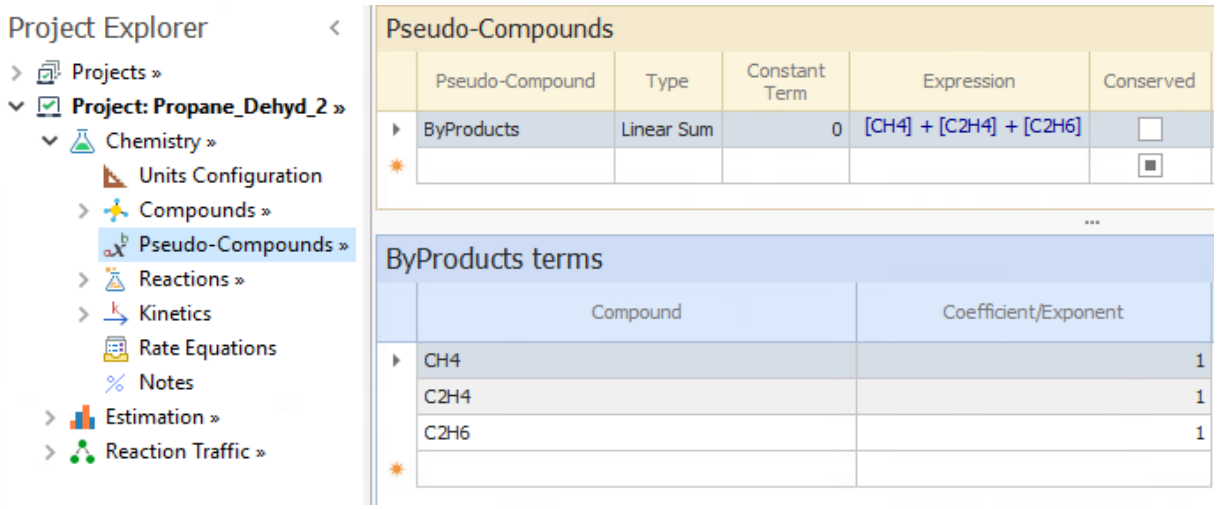
From these runs, it can be seen that the solution with all the terms optimized has nearly the same prediction error (Weighted LSQ) as the last three runs. We may draw two conclusions from these runs:

- 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.

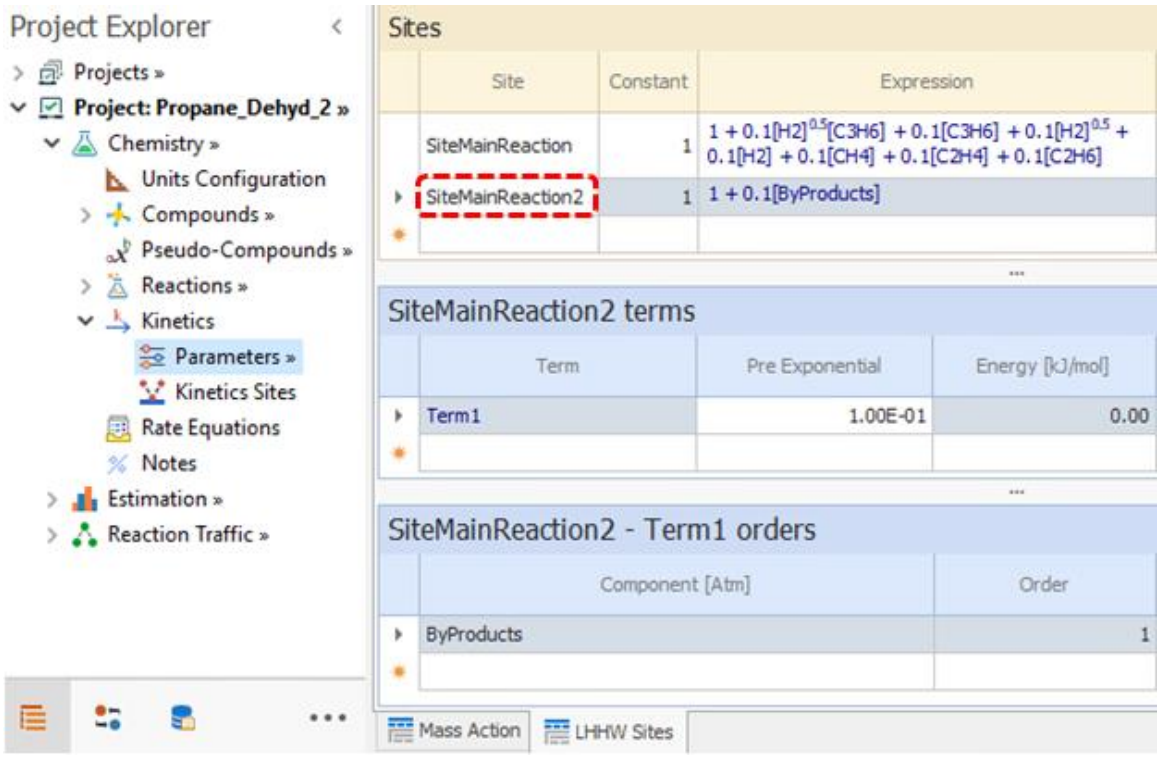
In next section, we proceed with model improvements based on this analysis.

Model 2 : Simplified LHHW Inhibition for Main Reaction

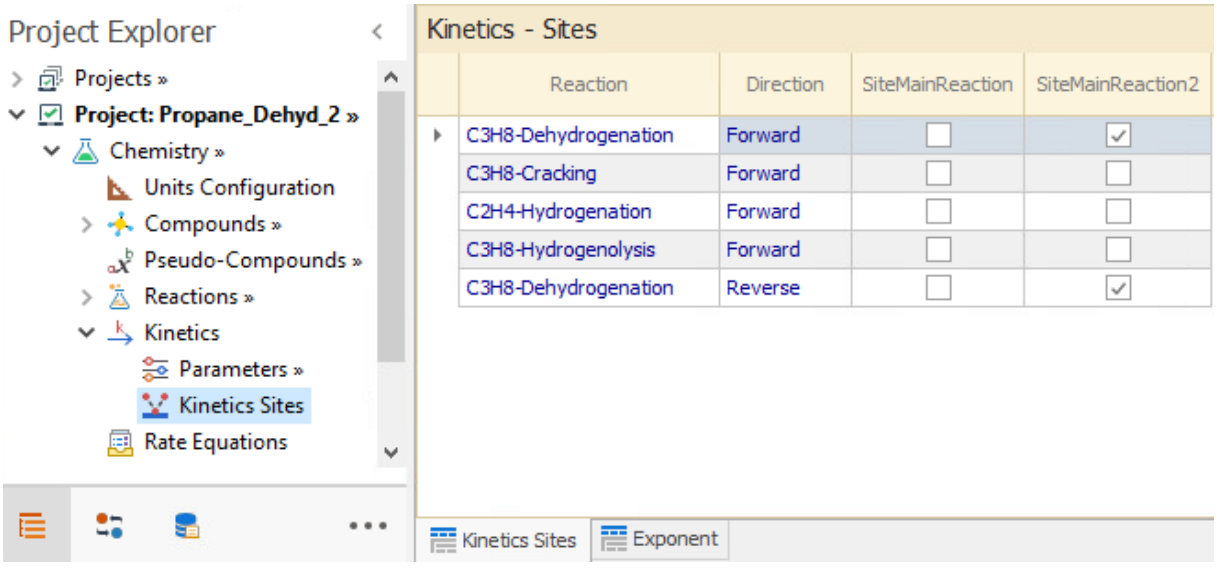
First, we ignore the effect of the outlier experimental points on the parameter estimation. This can be manually done in the Weights→Sets node, where the weights are set to zero for these outlier points. Then, we modify the LHHW Site definition in order to consider only one combined inhibition term for CH_4, C_2H_4 and C_2H_6. To do this, in the pseudo-compounds node, the *ByProducts* variable is created as the sum of the above compounds:



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

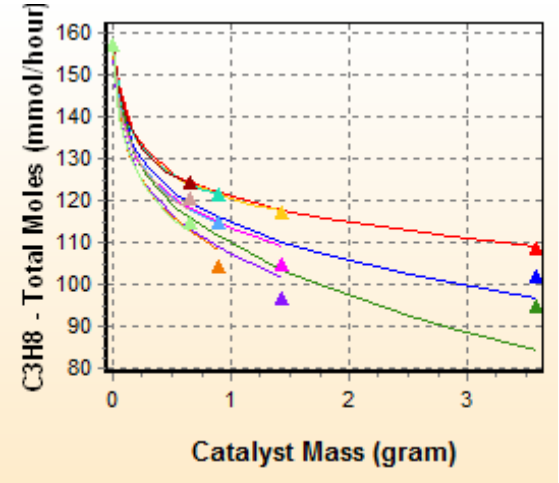


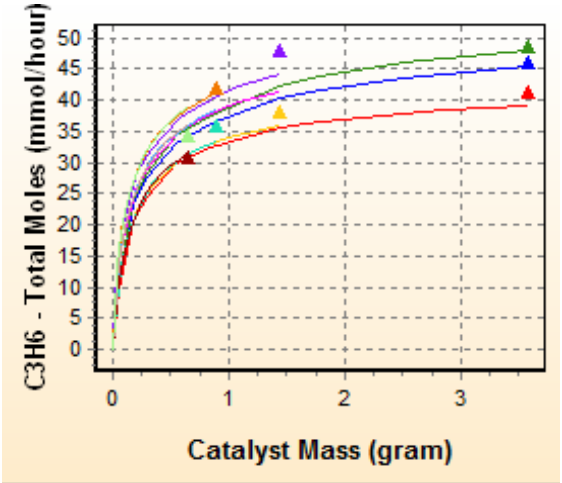
We can delete the older site (SiteMainReaction), or we can keep it without assigning it to any reaction: that way the old site will not be used in the model. The new site is selected for the main reaction:

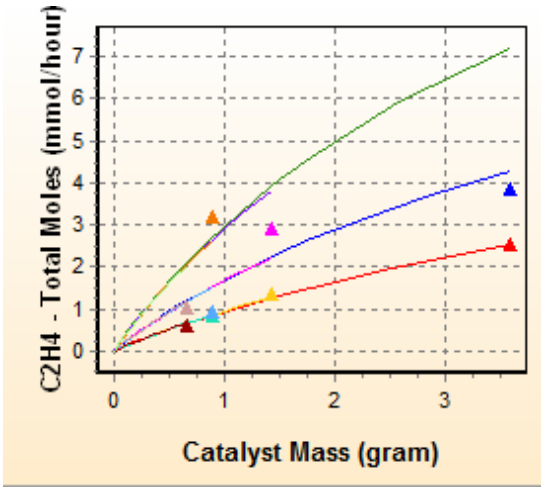


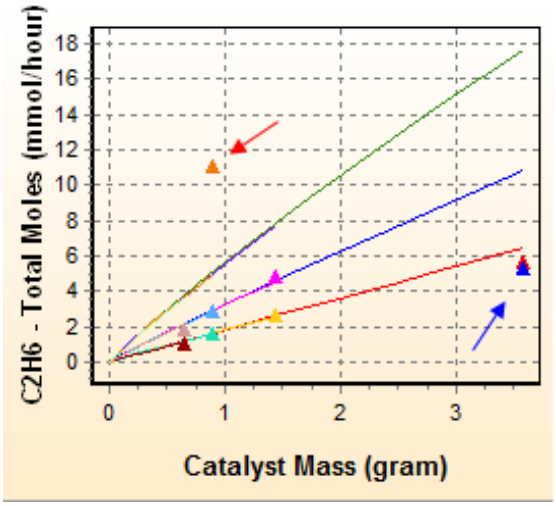
We assign an exponent of 1 for this site in the Exponent tab.

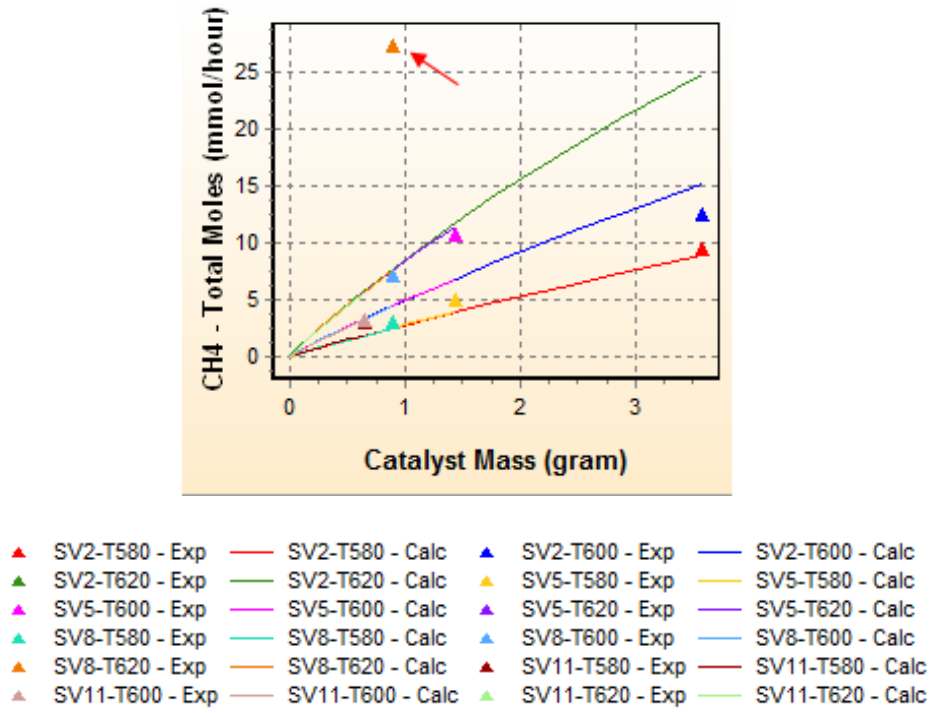
After opening bounds for the new site in the Estimation→Parameters node, we can run this project, as shown in the Propane_Dehyd_2.rex file. The compound profiles are shown below. The outliers that are not reconciled are indicated by arrows:



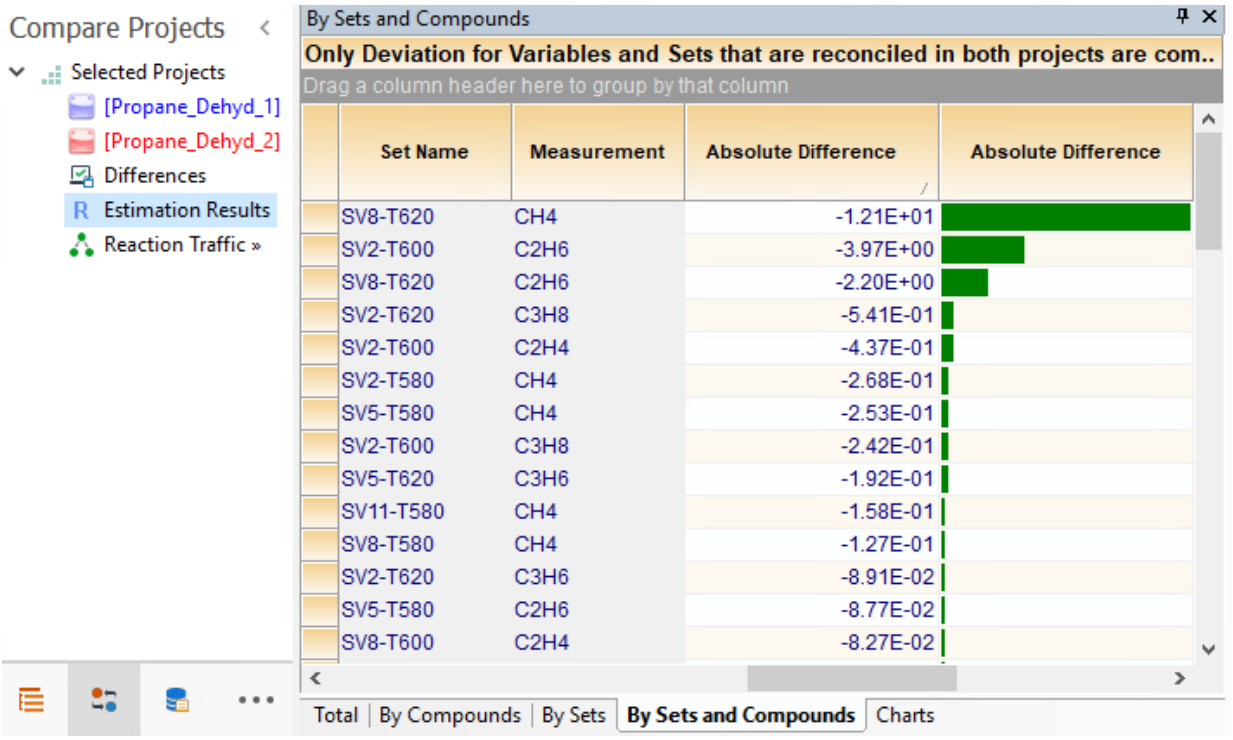








The LSQ decreases from 28.05 in Model 1 to 8.38 in Model 2. 91% of the reduction is due to the zeroing of weights for the outliers. You may use the Compare Projects tool to do further analysis. The basics for using Compare Projects are described in the last section of the Methanol Synthesis example. 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:



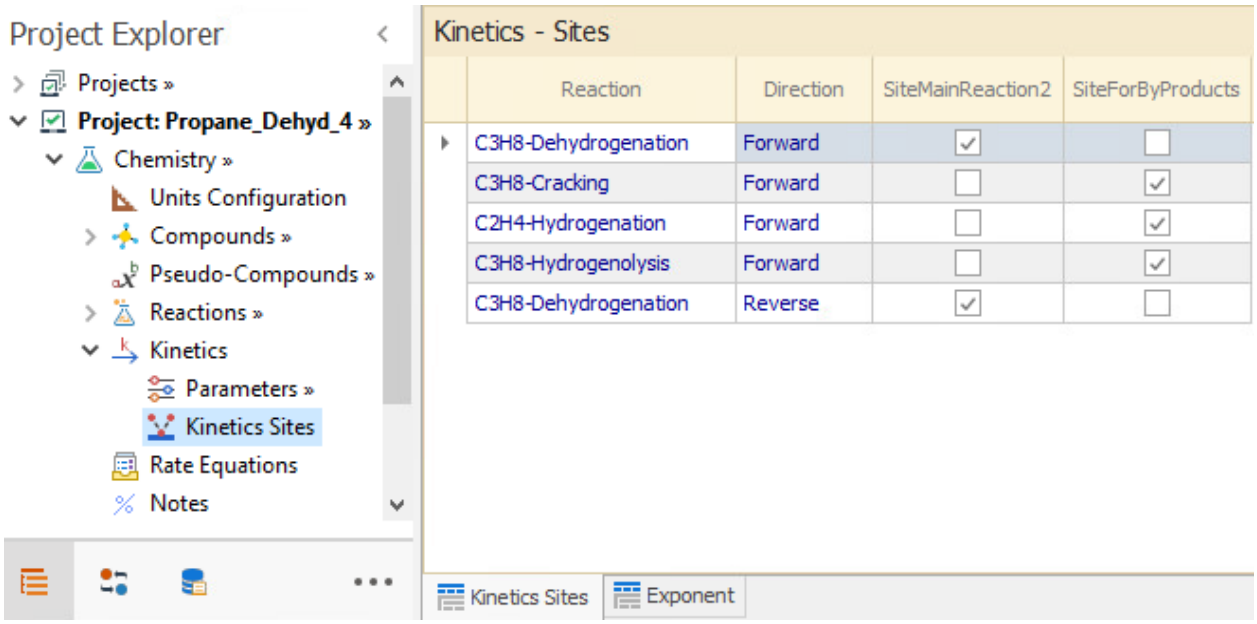
LSQ reductions are indicated with a green bar, while increases are shown in red. If you scroll down, you will see a few measurements whose LSQ worsened from Model 1 to Model 2.

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

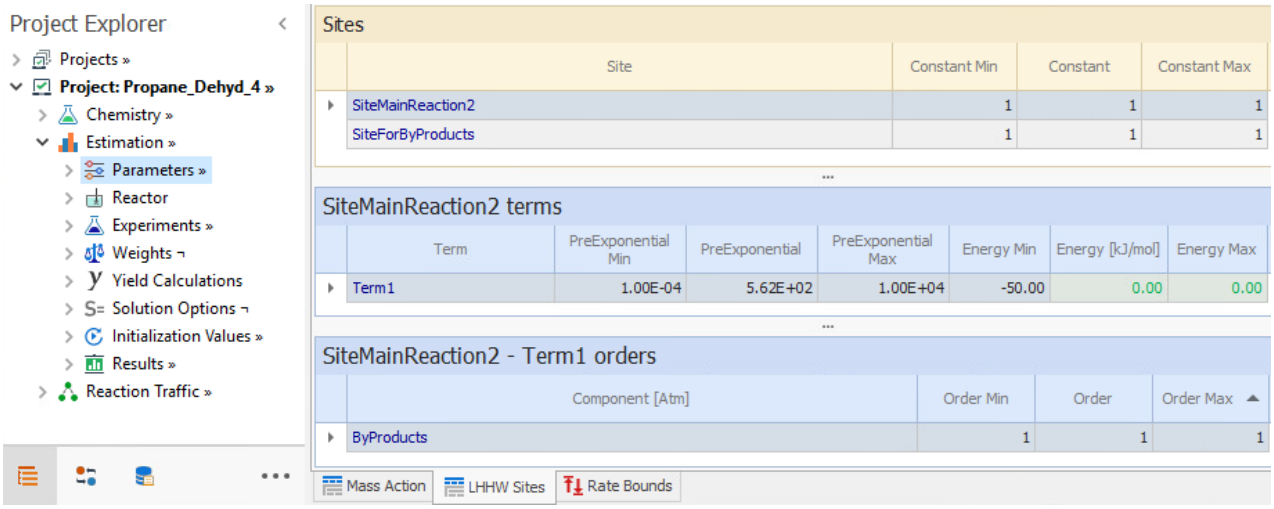
So far we considered Site inhibition for the main reaction only, while the reactions for byproduct formation were modeled without LHHW Sites. A look at the predicted byproduct profiles shows that the increase of CH_4 and C_2H_6 is almost linear with catalyst mass. On the other hand, the data indicates 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_4, C_2H_4 and C_2H_6 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.

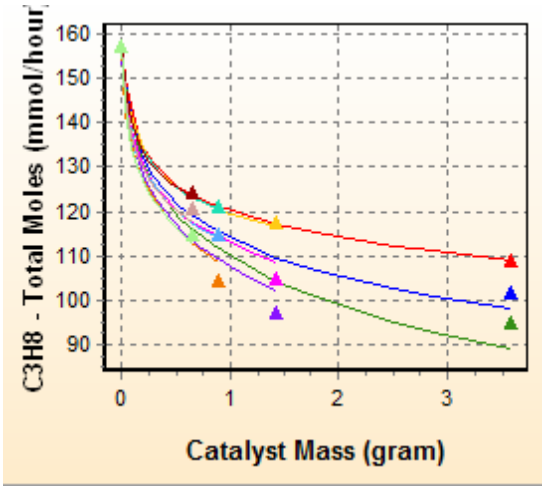
We can define an additional site for byproduct inhibition, to be assigned only for byproduct reactions. This new site also has only one term for the pseudo-compound that adds CH_4, C_2H_4 and C_2H_6. The main reaction will have the original site, as seen in the Kinetics→ Kinetics Sites node of Propane_Dehyd_4.rex file:

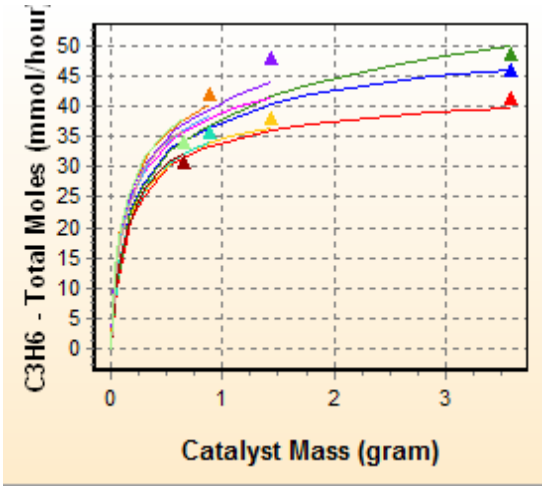


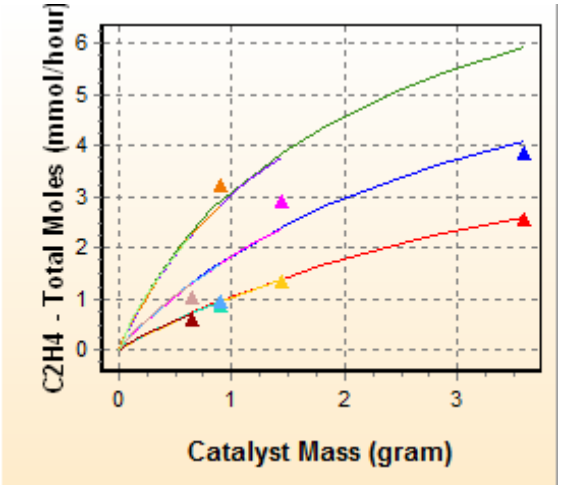
In the Estimation→Parameters node, we open the bounds for the pre-exponential and activation energy in the new site. We also open bounds between one and two for the order of the ByProducts in order to allow for stronger inhibition as byproducts build up:

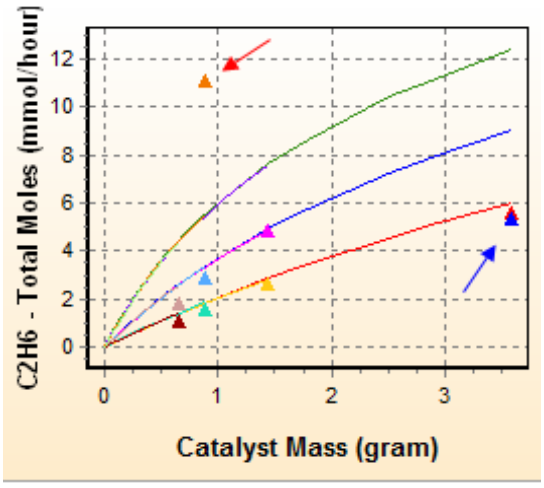


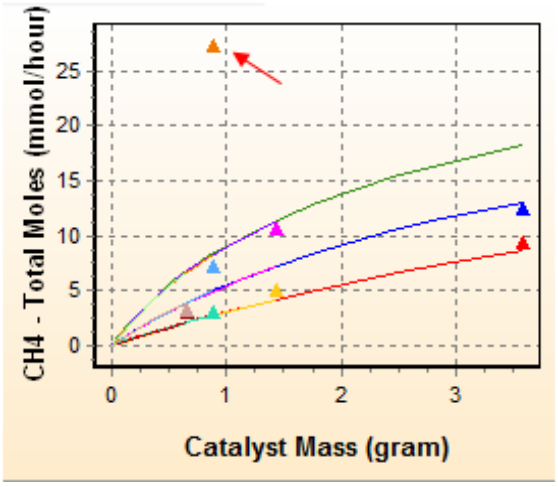
After running the project we now get a 25% reduction of LSQ, from 8.38 (Model 2) to 6.29 in this Model 4.
You can see the more curved profile for the byproduct in the chart below. (Outliers not reconciled are indicated with arrows)

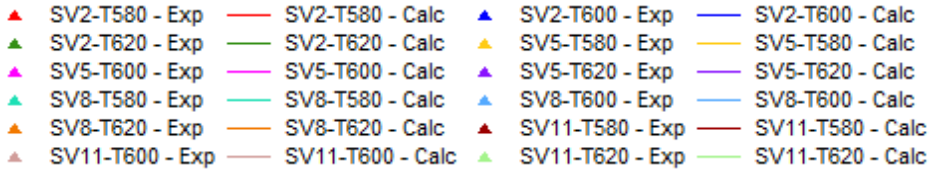

C3H8 - Total Moles (mmol/hour)
160
150
140
130
120
110
100
90
0
1
2
3
Catalyst Mass (gram)


C3H6 - Total Moles (mmol/hour)
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
Catalyst Mass (gram)


C2H4 - Total Moles (mmol/hour)
6
5
4
3
2
1
0
0
1
2
3
Catalyst Mass (gram)


C2H6 - Total Moles (mmol/hour)
12
10
8
6
4
2
0
0
1
2
3
Catalyst Mass (gram)


CH4 - Total Moles (mmol/hour)
25
20
15
10
5
0
0
1
2
3
Catalyst Mass (gram)


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/γ-Al2O3 catalyst". *Scientia Iranica C (2011) 18 (3), 458–464*