

Methanol Synthesis

Objective: To Evaluate Predictions of Alternative Models

In this example, we propose and evaluate Mass Action and Langmuir Hinshelwood (LHHW) models for methanol synthesis from $CO/CO_2/H_2$ gas mixtures over Copper/Zinc-Oxide/Chromia catalyst in a fixed bed reactor. For each model, the kinetic parameters are estimated by reconciling experimental data from [1]. You may <u>download</u> the zip file containing the experimental data and the rex files.

Features Illustrated

- Modelling with Equilibrated Reactions
- Using Derived Quantities to calculate and report Auxiliary Variables.
- Building Mass Action and LHHW Models
- Basics of Reaction Traffic charting capabilities
- Use of Compare Projects tool to quantify the difference between projects

Starting Point: Reaction Network and Experimental Data

The principal reactions that occurs in the synthesis of methanol from $CO/CO_2/H_2$ mixtures are the following:

CO-to-Methanol:	CO + 2H ₂	₹	CH₃OH
CO2-to-Methanol:	$CO_2 + 3H_2$	₹	$CH_3OH + H_2O$
Water Gas Shift Reaction:	$H_2O + CO$	₹	$H_2 + CO_2$

Of those reactions, water gas shift can be assumed to be equilibrated. Formation of higher alcohols is not considered.

Available experimental data from [1] are shown in columns A to L of the *Methanol-Synthesis.xlsx* file contained in the zipped file. The specifications of the experiments are summarized below :

- → Total Molar Flow in Feed: From 0.9 to 3.4 mol/h
- \rightarrow Feed Molar Fractions:
 - H_2 from 22 to 58% CO from 16 to 66% CO₂ from 0 to 33% Ar from 2.7 to 14% Methanol from 0% in most sets, up to 5.3%
- \rightarrow Pressure: from 50 to 100 atm
- \rightarrow Outlet Molar Fractions:
 - Methanol
 - Higher Alcohols
- \rightarrow Temperature: 285C for all sets
- $\rightarrow\,$ Catalyst Mass: basically constant, from 1.56 to 1.57 gr

Feed molar fractions are converted to inflow moles in columns O to S of the excel file in accordance with \underline{REX} format requirements. Methanol production is given as a molar fraction of the outflow.

Enforcing Equilibrium for Water Gas Shift (WGS) Reaction

After defining the compounds and reactions, we specify the WGS reaction to be at equilibrium:

Project Explorer <	Re	Reactions							
- Projects »	Dra	rag a column header here to group by that column							
Project: Methanol_MassAction-1 »		Include	Reaction	Equation	Quasi Equilibrium				
🔺 🗛 Chemistry »		V	CO-to-Methanol	CO + 2 H2 <> CH30H					
Units Configuration		V	CO2-to-Methanol	CO2 + 3 H2 <> CH3OH + H2O					
A Compounds »	►		WaterGasShift	CO + H2O <-eq-> CO2 + H2					
A Pseudo-Compounds »	*								
$\triangleright \rightarrow \text{Reactions } \ast$									

By selecting as equilibrated, the model assumes that forward and reverse rates are instantaneous and:

$$r_{WGS,Forw} = r_{WGS,Rev}$$

We explain below how the equilibrium constant is enforced in the model.

For this example, we define in the Units Configurations node that Partial Pressure is to be used as the unit for Concentration. Also, we set compound orders for both directions of the WGS reaction to be same as stoichiometric molecularities. Thus, the previous constraint can be rewritten as:

$$k_{WGS,Forw}P_{CO}P_{H_2O} = k_{WGS,Rev}P_{CO_2}P_{H_2}$$

Rearranging, the equilibrium constant is obtained:

$$\frac{k_{WGS,Forw}}{k_{WGS,Rev}} = \frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} = K_p$$

Now we enforce relationship between equilibrium constant and kinetic parameters such as Preexponential and Activation Energy for both directions of WGS reaction. From the Van't Hoff equation, we can express the equilibrium constant as a function of Temperature by:



$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = K_0 \ e^{[(-\Delta H/R)(1/T - 1/T_0)]}$$

where ΔH represents the heat of reaction, K_0 is the equilibrium constant at temperature T_0 , and K_p is the equilibrium constant at Temperature T. Knowing the equilibrium constant K_0 at T_0 , we can rearrange the previous to:

$$\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} = K_0 e^{[+\Delta H/(RT_0)]} e^{[-\Delta H/(RT)]} = K^* e^{[-\Delta H/(RT)]}$$

Where K^{*} is a value that can be calculated from known values of equilibrium constant K_{0} at some temperature T_{0} .

For example, we can obtain the equilibrium constant at T_0 =298.15K by using the standard Gibbs energy change of reaction:

$$\Delta G^0 = -RT_0 \ln K_0$$

Given that $\Delta G^{\circ} = -28.6$ kJ/mol, then $K_0 = 1.024$ E+5.

Using the standard heat of reaction $\Delta H^{\circ} = -41.2$ kJ/mol, we obtain $K^{*} = 0.0062$.

Replacing the numerical values into the equilibrium constant, we have:

$$\frac{k_{WGS,Forw}}{k_{WGS,Rev}} = 0.0062e^{\left[-(-41.2)/RT\right]} = 0.0062e^{\left[+41.2/(RT)\right]}$$

Substituting the Pre-exponentials and Activation Energies in the rate constant, we have:

$$\frac{A_{WGS,Forw} e^{[-E_{WGS,Forw}/(RT)]}}{A_{WGS,Rev} e^{[-E_{WGS,Rev}/(RT)]}} = 0.0062 e^{[+41.2/(RT)]}$$

From here, we get relationships for the Pre-exponentials and Activation Energies:

$$\frac{A_{WGS,Forw}}{A_{WGS,Rev}} = 0.0062$$



$E_{WGS,Forw} - E_{WGS,Rev} = -41.2 \ kJ/mol$

These relationships are held in <u>REX</u> by fixing the following parameters to these values:

 $A_{WGS,Forw} = 0.0062$ $A_{WGS,Rev} = 1$ $E_{WGS,Forw} = 0$ $E_{WGS,Rev} = 41.2$

Please note that the pair of values entered for Pre-exponentials and Activation Energy are not unique. Any set of values that satisfy the constraints will give the same results in <u>REX</u>, provided that the reaction is set as equilibrated. We fix these parameter values by turning off the Estimation flag for the WGS reaction in the Estimation node:



Setting up the REX Project

Having defined the equilibrated reaction, we now set the reaction orders for the methanol producing reactions.

For CO + $2H_2 \rightleftharpoons CH_3OH$ reaction, we set order 1 for CO and H_2 in the forward direction, reverse direction is order 1 for CH₃OH. Similarly for CO₂ + $3H_2 \rightleftharpoons CH_3OH + H_2O$, we set order 1 for CO₂ and H_2 for the forward direction, and the reverse direction order is 1 for both CH₃OH and H₂O. These orders are fixed by keeping their bounds closed in the Estimation \rightarrow Parameters node:



Project Explorer <	Read	leaction Parameters - Initial Estimates [Rate Units: gmol/(gram - hour)]							
> Projects »		Reaction	PreExponential Min	PreExponential	PreExponential Max	Activation Min	Activation Energy [kJ/mol]	Activation Max	
Project: Methanol_MassAction-1 »	-			Direction :	Forward				
> ^A > _B Chemistry »	•	CO-to-Methanol	1.00E-05	4.10E-05	1.00E+00	0.00	0.00	0.00	
✓ ₩ Estimation »		CO2-to-Methanol	1.00E-05	5.76E-05	1.00E+00	0.00	0.00	0.00	
> (P) Parameters »		WaterGasShift	0.00E+00	6.62E-02	1.00E+03	0.00	0.00	0.00	
> 👌 Reactor	-			Direction :	Reverse				
> 🕂 Experiments »		CO-to-Methanol	1.00E-05	6.61E-03	1.00E+00	0.00	0.00	0.00	
> TA Weights ¬		CO2-to-Methanol	1.00E-05	1.00E-05	1.00E+00	0.00	0.00	0.00	
Y Yield Calculations		WaterGasShift	1.00E+00	1.00E+00	1.00E+00	41.20	41.20	41.20	
> 🎝 Run Estimation	CO-t	o-Methanol							
 R Results & Reaction Traffic » 		Component	t [Atm]	Order Min	Order	Order Ma	x		
- 00	► C	0		1	1		1		
	H	2		1	1		1		
🔍 🗄 😫 🔺	k ₪	lass Action 🛓 🖥 Rat	e Bounds						

Since the experimental data are all at constant temperature, the Activation Energies are kept fixed at zero. Only the pre-exponentials factors for the two reactions that produce methanol will be estimated.

Another issue is that the methanol measurement in the reactor effluent is provided as a molar fraction. To reconcile this measurement, we need to first define an auxiliary variables in the Reactor \rightarrow Derived Quantities node. First, we add a linear variable that adds all compounds moles:

Project Explorer <	Derived Quantities Defin	ition							
> Projects »	Drag a column header here to	group by that column							
Project: Methanol_MassAction-1 »	Derived Quantity	Туре	Constant Term	Units					
> ^A » _B Chemistry »	Sum(Moles)	Linear Sum	Linear Sum 0 gmol/hour						
 Istimation » Parameters » 	$Sum(Moles) = [Ar_{TM}] + [CH30H_{TM}] + [CO_{TM}] + [CO2_{TM}] + [H2_{TM}] + [H2O_{TM}]$								
 d Reactor Derived Quantities » 	Terms in Sum(Moles)								
> 📥 Experiments »	Diag a columniteader nere to	group by that column	Constrained U.Co.						
> 🖾 Weights ¬	Compound	value	Coemcient/Ex	ponent					
> Y Yield Calculations	Ar	 Total Moles 		1					
> 🅼 Run Estimation	CH3OH	Total Moles		1					
> R Results	CO	Total Moles		1					
8 Reaction Traffic »	C02	Total Moles							
0.0	H2	Total Moles		1					
	H20	Total Moles		1					

Then the methanol fraction is defined as a nonlinear derived quantity:



Derived Quanti	ity	Туре		Constant Term			
▶ xMeOH		Nonlinear Proc	duct	1			
xMeOH = ([CH3OH _{TM}]) / ([Sum(Moles)])							
Terms in xMeOH							
Compound Value Coefficient/Exponen							
CH3OH 🗸	Total M	oles		1			

In the reactor node, a PFR reactor is selected with Pressure as Interpolated from Data and Flow as *Float for Pressure control.* Thus, the gas flow will be automatically calculated to keep the pressure fixed to the experimental values entered for the PFR entry.

In the Experiments \rightarrow Measurements node, the auxiliary variable for methanol fraction is selected as measured so that these values can be entered in the Measurements \rightarrow Sets nodes. Finally, in the Weights node, we select the methanol fraction as the only variable to reconcile, and their weights are generated with the Hybrid assumption.

Mass Action Model

We start by estimating the Pre-Exponentials for the Mass Action Model, as shown in the <u>Methanol MassAction-1.rex</u> file. For this model, the Weighted Least Square Error is 0.14228 as shown in Results node; the pre-exponential values are provided in Results→Parameters node:

Project Explorer <	Sho	w: <u>All Parameters</u> <u>C</u>	only PreExponential	And Activation Ener	rav	
> Projects »	Esti	mated Parameter	rs [Rate Units:	gmol/(gram - ho	ur)]	
Project: Methanol_MassAction-1 » A. Chemistry »		Reaction	PreExponential	Activation Energy [kJ/mol]	Component [Atm]	Order
V M Estimation »		-	Direction	: Forward		
Darameters »	•	CO-to-Methanol	4.10E-05	0.00	CO	1
> d Peactor					H2	1
Experiments »		CO2-to-Methanol	5.76E-05	0.00	CO2 H2	1
> 🖾 Weights ¬		WaterGasShift	6.62E-02	0.00	CO	1
Y Vield Calculations					H2O	1
> 纋 Run Estimation		-	Direction	: Reverse		
✓ R Results		CO-to-Methanol	6.61E-03	0.00	СНЗОН	1
Parameters		CO2-to-Methanol	1.00E-05	0.00	СНЗОН	1
😡 Rate Equations					H2O	1
🔪 Marginal Values		WaterGasShift	1.00E+00	41.20	CO2	1
🁆 Model-Data Comparison »					H2	1
🌾 Yield - Conversion » 🗸 🗸						
🙀 🗄 😫 🔺	k	Mass Action				



The green arrow indicates that the pre-exponential solution value is at its lower bound and in general, relaxing the bound should improve the model prediction. However, we would first like to check whether the reverse direction of CO2-to-Methanol reaction is significant and if it were negligibly small, we could eliminate it from the model.

We do that by looking at the carbon traffic in Reaction Traffic node. In order to see the Carbon traffic we need to fill the carbon atom count for every compound in Chemistry \rightarrow Compounds \rightarrow Formula node. Then in Reaction Traffic \rightarrow Options node we choose Carbon traffic for both directions:

Project Explorer <	General
 Projects » ✓ Project: Methanol_MassAction : ▷ ^A_{vB} Chemistry » ▷ ▲ Estimation » ▲ A Reaction Traffic » 	Graph Options Graph Direction: Top -> Bottom Graph Direction: Top -> Bottom Graph Direction: Top -> Bottom
00 冒炎 Options ¬	Highlight Pathway Show Compounds by: Compound Show Reactions by: Reaction Display Pathway Traffic for Variable
	Variable: Carbon Moles Directions Shown: Both Max Arrow Width: 15 Min Arrow Width: 0.5 Traffic Display Range: 100% to 3.33% of Max Traffic. If Traffic less than 3.33% : Use Min Width

The carbon traffic is then shown as below:





In that chart, the arrow width represents the total carbon moles that reacts (averaged among sets) for every reaction and direction. Please note that the reverse of CO2-to-Methanol is very thin compared to other reactions. Thus, we may eliminate that direction by unincluding it in the Chemistry \rightarrow Kinetics node and rerun the parameter estimation. This is done in file <u>Methanol MassAction-2.rex</u>. The solution has the same weighted LSQ of 0.14228 obtained before, thus confirming that the removal of that direction does not affect the model predictions.

The parity plots for the experimental methanol fractions is shown below:



LHHW Model

Now we would like to see if further improvements can be obtained by using Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. A list of candidate LHHW models for methanol synthesis is reported in [2]. Here, we use a simple site formulation accounting for potential surface inhibition by reactants or products:

$$Site = 1 + K_1 P_{H_2O} + K_2 P_{CO} + K_3 P_{CO_2} + K_4 P_{H_2} + K_5 P_{CH_3OH}$$

In Chemistry→Kinetics→Parameters node, we define the LHHW site and their terms:



Project Explorer <	Sites		
 Projects » Project: Methanol_LH-1 » A_{xB} Chemistry » 	Site1	Site	Constant 1
 Units Configuration A_B Compounds » A_B Pseudo-Compounds » 	Site1 = 1 + 1[H20] + 1 Terms: Site1	L[CO] + 1[CO2] + 1	[H2] + 1[CH3OH]
 Keactions » Kinetics 	Term	PreExponential	Energy [kJ/mol]
 Parameters » Kinetics Sites Rate Equations Notes Estimation » Reaction Traffic » 	 Term1 Term2 Term3 Term4 Term5 * 	1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00	0.00 0.00 0.00 0.00 0.00
	Orders: Site1 - Term1 Compor	nent [Atm]	Order ▼ 1
🔍 影 😫 🔹	k Mass Action k LHHW Sites	5	

The site is assigned to all LHHW reactions:

Project Explorer <		Kir	netics - Sites		
> 📑 Projects »	~	Dra	g a column heade	r here to group	by that colur
✓ I Project: Methanol_LH-1 »			Reaction	Direction	Site1
✓ ^A _{>B} Chemistry »		►	CO-to-Methanol	Forward	•
🛃 Units Configuration			CO2-to-Methanol	Forward	N
> AB Compounds »			WaterGasShift	Forward	
A Pseudo-Compound			CO-to-Methanol	Reverse	N
$\rightarrow \rightarrow$ Reactions »			WaterGasShift	Reverse	
$\checkmark \stackrel{k}{\longrightarrow}$ Kinetics					
Parameters »					
Kinetics Sites					
💊 Rate Equations	,				
< >					
R 🗄 😫 🔺		.	, Kinetics Sites k	Exponent	



In the Estimation—Parameters node, we allow the pre-exponentials for Site terms to vary between 10^{-7} and 10^{6} . After running the project (<u>Methanol_LH-1.rex</u>), we find that some inhibition terms are very small:

Project Explorer	<	S	how: <u>All Par</u>	ameters Only	PreExpone	ential And Activation	Energy		
> Projects »	^	Ki	netics Sit	es					
✓ 1 Project: Methanol_LH-1 »			Site	Constant	Term	PreExponential	Energy	Component	Order
> 🗛 Chemistry »			Und	Conortaint			[kJ/mol]	[Atm]	0.00.
In Estimation »		►	Site1	1	Term1	3.47E+03	0	H2O	1
>					Term2	2.82E-02	0	CO	1
> 🖻 Reactor					Term3	3.98E+00	0	CO2	1
) 八 Experiments »					Term4	1.00E-07	0	H2	1
> XX Weights ¬					Term5	5.41E-07	0	СНЗОН	1
Y Yield Calculations									
> 🧔 Run Estimation									
✓ R Results									
Parameters	¥	Ki	netics Sites	Exponents					
🔍 🗄 😫	*	k	Mass Actio	n k+1 LHHW:	Sites				

We can compare the magnitude of the site terms by generating the Excel report for the Chemistry Information:

Project Explorer		
	`	Report Options
> Y Yield Calculations	^	
> 🧔 Run Estimation		Path:
✓ R Results		
Parameters		Chemistry Information
😵 Rate Equations		Trends Information
🔪 Marginal Values		Profiles Information
🁆 Model-Data Comparison »		
🌿 Yield - Conversion »		Generate Report Open Report
🕮 Custom View ¬		
> 🏹 Profiles »		
🖪 Report ¬		
$> \mathcal{C}_{0}^{\mathcal{R}}$ Reaction Traffic $>$	¥	



The average value for the site and for each terms are reported, confirming that the contribution of the H_2 and CH_3OH inhibition terms to total site is negligible. Also we see that Term1 for water has the most impact on site inhibition followed by CO_2 , and a smaller CO inhibition:

Site	Average Value	Term	Average Value
Site1	51.735	Term1	37.939
		Term2	1.0339
		Term3	11.762
		Term4	2.7804E-06
		Term5	8.1625E-07

Next, we delete the last two terms and rerun the model. The weighted LSQ error from the new model in <u>Methanol LH-2.rex</u> file is the same, confirming that the removed terms have no effect on the model predictions.

Comparing Mass Action vs LHHW Model

In this example we have only one measurement that is reconciled: Methanol molar fraction. Its weighted LSQ decreased roughly by half from 0.142 for Mass Action model to 0.068 when considering H2O, CO_2 and CO inhibition. We can compare their parity charts:



Further comparison can be done in *Compare Projects* tool. In the navigation bar, *Project Explorer* is selected by default:





You may switch to *Compare Projects*, and then choose the projects to be compared in the grid on the right hand side.

To compare Estimation results the proper box must be checked. After pressing the *Apply* button, the tree on the left hand grid shows all nodes where differences between the project have been found, followed by the *Estimation Results* node where LSQ is compared:

Compare Projects <	Ontions	Projects To Compare			
 Selected Projects [Methanol_MassAction-2] 	Model Comparison Options: Show:	Projects To Compare			
		Drag a column header here to group by that colur			
[Methanol_LH-2]	Differences		Project	Name	
✓ ☐ Differences	O Identicals	Proj	ect A	Methanol_MassAction-2	
Parameters	Nodes:	Proj	ect B	Methanol_LH-2	
$\frac{k}{k+1}$ LHHW Sites $\frac{k}{k+1}$ LHHW Sites-Orders $\frac{k}{k+1}$ LHHW Sites-Bounds	Chemistry Estimation Optimization				
R Estimation Results	Show Only Nodes with results				
< >	Compare Also:				
R Project Explorer	Reaction Traffic				
⊟∛ Compare Projects	Apply				
Parations					



Selecting the Estimation Results node, there are several options for values comparison:

 \rightarrow Weighted or Unweighted Least Square Errors (LSQ)

 \rightarrow Numerical columns for the LSQ, with an optional display of column bars

 \rightarrow LSQ comparison between the projects for total LSQ, or discriminated between Sets and/or Measurements

By clicking in any column header, the rows are sorted automatically. For example if you wish to see the sets in which the predictions have improved the most by the LHHW model, you can go to the *By Sets* tab and click the header of the first (numeric) *Absolute Difference* column:

Set Name	Absolute Dif	fference	Absolute Diffe	erence
M24		-1.23E-02		
M52		-1.10E-02		
M48		-7.66E-03		
M46		-6.74E-03		
M54		-5.64E-03		
M41		-4.56E-03		
M25		-3.59E-03		
M56		-3.55E-03		
M38		-3.41E-03		
M62		-3.08E-03		
M61		-2.86E-03		
M43		-2.77E-03		
F11		-2.30E-03		
M60		-1.78E-03		
P19A		-1.62E-03		
M55		-1.61E-03		
M14		-1.58E-03		
F15		-1.46E-03		
M21		-1.42E-03		
FA12		-1.29E-03		
P17B		-1.27E-03		
P18B		-1.14E-03		
F16		-1.13E-03		
F12		-9.93E-04		
P18C		-8.56E-04		
MQ1		-8 53E-04		
tal By Compour	nds By Sets	By Sets an	d Compounds	Charts

The bars with green color represent the Sets whose LSQ have a improved from the first to the second project selected. Red bars indicate a worsening of prediction in the second project and can be seen by scrolling down the list.



References

1. Calverley, E.M. (1989) A Study of the Mechanism and Kinetics of the Synthesis of Methanol and Higher Alcohols Over Alkali Promoted Copper/Zinc-oxide/Chromia Catalysts. PhD Thesis, McMaster University.

2. Rahman, D., (2012). Kinetic Modeling of Methanol Synthesis from Carbon Monoxide, Carbon Dioxide and Hydrogen Over a Cu/ZnO/Cr2O3 Catalyst. MS Thesis, San Jose State University. Weblink: http://scholarworks.sjsu.edu/etd_theses/4162/

