

## Isomerization in a batch reactor with Aspen Plus® V8.0

### 1. Lesson Objectives

- Use chemical reaction kinetics to calculate the time required to reach a desired conversion in a batch reactor
- Use Aspen Plus to confirm the analytical solution

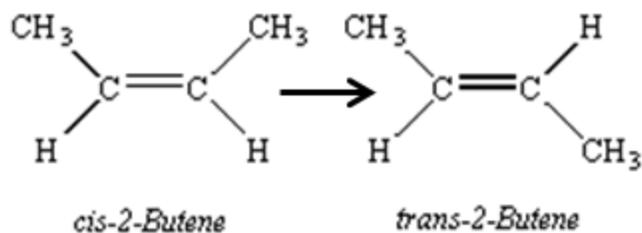
### 2. Prerequisites

- Aspen Plus V8.0
- Basic knowledge of reaction rate laws

### 3. Background

2-Butene is a four carbon alkene that exists as two geometric isomers: *cis*-2-butene and *trans*-2-butene. The irreversible isomerization reaction with 1<sup>st</sup> order reaction kinetics is shown below. It is desired to determine the time required to reach 90% reaction conversion in a batch reactor.

Homogeneous reaction



1<sup>st</sup> order reaction kinetics       $r_A = kC_A, k = 0.23\text{min}^{-1} = 0.003833\text{s}^{-1}$

**The examples presented are solely intended to illustrate specific concepts and principles. They may not reflect an industrial application or real situation.**

## 4. Solution

Analytic Solution:

$$r_A = kC_A = kN_A/V$$

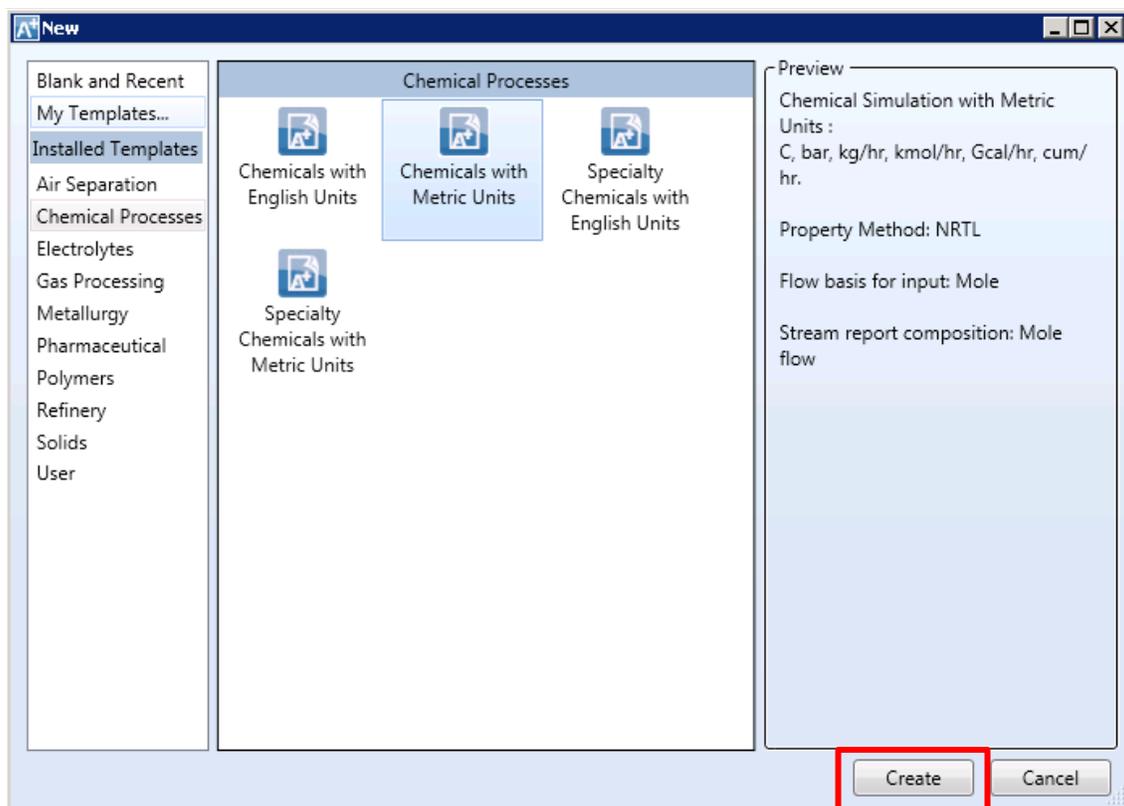
$$\int_0^t dt = - \int_{N_{A0}}^{N_A} \frac{1}{V} \frac{dN_A}{r_A} = - \frac{1}{k} \ln \frac{N_A}{N_{A0}}$$

$$t = - \frac{1}{k} \ln(1 - x_A); \quad x_A = 1 - \frac{N_A}{N_{A0}}$$

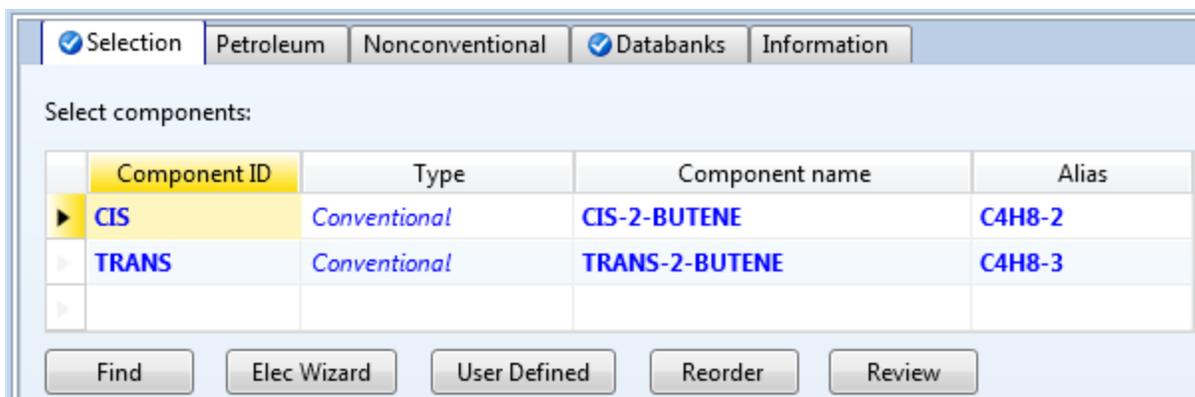
$$\therefore t = - \frac{1}{0.23 \text{ min}^{-1}} \ln(1 - 0.9) = 10.01 \text{ min}$$

Aspen Plus Solution:

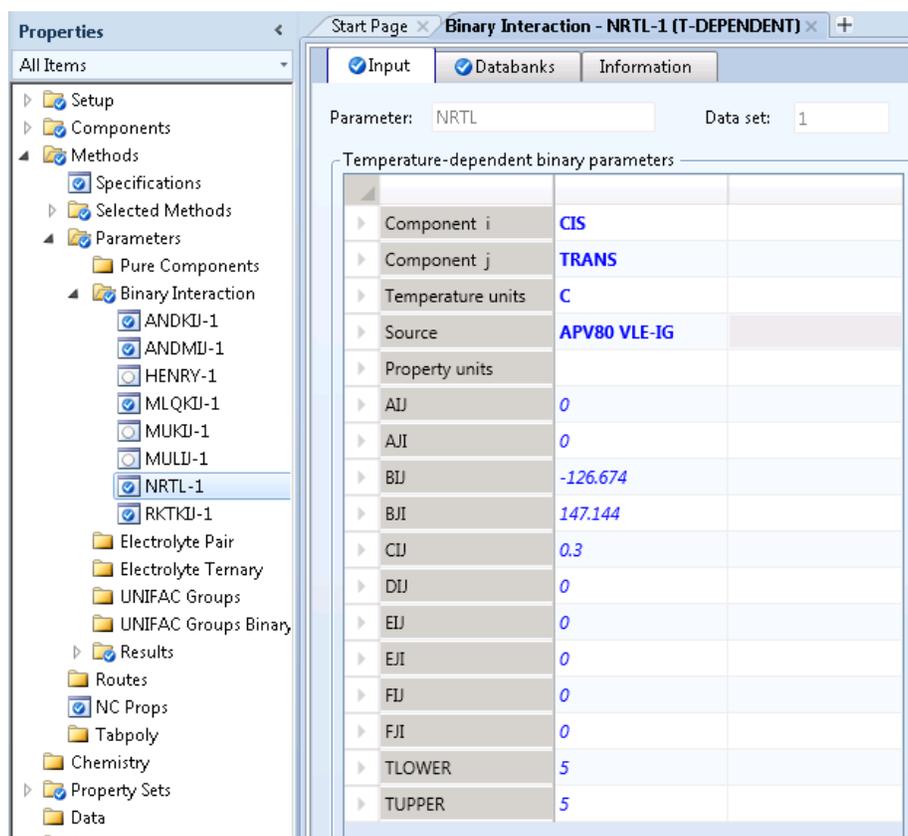
- 4.01. Start **Aspen Plus V8.0**. Create a new simulation by clicking **New** on the **Start Page**. Select the template by clicking **Chemical Processes | Chemicals with Metric Units**. Click **Create** to begin.



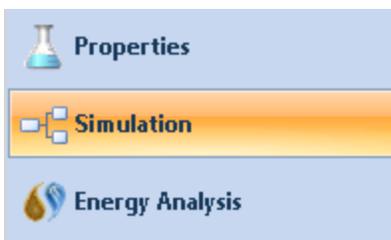
- 4.02. Define components. After creating a new simulation, Aspen Plus should open to the **Components | Specifications** form. To define components enter **CIS-2-BUTENE** and **TRANS-2-BUTENE** for **Component name** and enter **CIS** and **TRANS** as **Component ID's**. A warning message will appear saying that this change will cause the parameters to be updated. Click **Yes**.



- 4.03. Populate the binary interaction parameters. Since a template was chosen to create the simulation, the property method is already chosen, in this case NRTL. However, since components have been added, the binary interaction parameters must be populated. Go to **Methods | Parameters | Binary Interaction | NRTL-1**.

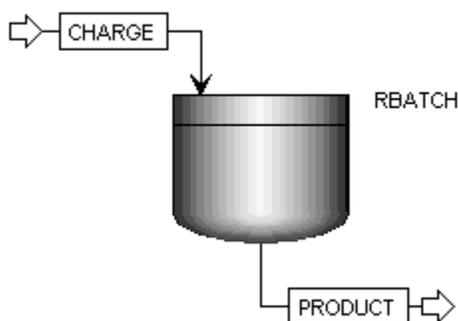


- 4.04. We are now ready to create the flowsheet. Move to the simulation environment by clicking the **Simulation** button at the bottom left of the screen.



- 4.05. In the simulation environment add an **RBatch** reactor model to the main flowsheet. Go to the **Reactors** tab of the **Model Palette**, select **RBatch** and drop it to the flowsheet. Connect two **Material streams** for batch charge and reactor product. You can rename the streams and the reactor block by using **Ctrl+M**.

*Note: The RBatch block models a specified reaction using the kinetic data and specified residence time. However, it is still a steady state model, and so a realization of the model would require many batch reactors in parallel with staggered start and end times.*



- 4.06. Define Reaction. In the navigation pane go to **Reactions | New**. Select **GENERAL** for reaction type. By default, reaction ID **R-1** will be created or you can create a new ID. Click **OK**.



- 4.07. Go to **Reactions | R-1** and click **New**. Enter **RXN1** as the reaction name. Select **CIS** for the reactant component and **TRANS** for the product component, as well as the reactant and product stoichiometric coefficients (both **1** in this case). Notice that the coefficient for the reactants automatically becomes negative. Click **Close** when complete.

**Edit Stoichiometry**

No:  Reaction class: *POWERLAW*

Name:  Status: *On*

Reaction is reversible

Reactants	
Component	Coefficient
CIS	-1

Products	
Component	Coefficient
TRANS	1

- 4.08. Define reaction kinetics. In Reaction group R-1, go to the **Kinetic** tab. Enter **k = 0.003833** and enter **E = 0** (as this is isothermal). Note that the default units for rate constant are inverse seconds.

**Simulation** | Start Page | Main Flowsheet | **R-1 (GENERAL)**

Configuration |  **Kinetic** | Equilibrium | Activity | GLHHW Adsorption | Information

1) CIS(MXED) --> TRANS(MXED)

Reaction class: *POWERLAW* | Reacting phase: *Liquid*

Powerlaw kinetic expression:  $r = [\text{Kinetic factor}][\text{Driving force}]$

[Ci] basis: *Molarity* | [Ci] units: *kmol/cum* | Rate basis: *Reac (vol)* | Rate units: *kmol/cum-s*

Kinetic factor

If  $T_0$  is specified: Kinetic factor =  $k(T/T_0)^n e^{-(E/R)[1/T-1/T_0]}$

If  $T_0$  is not specified: Kinetic factor =  $k T^n e^{-E/RT}$

k:  | n:  | E:  *kcal/mol* |  $T_0$ :

- 4.09. Hovering the mouse over an input field will show hover text giving information about it. Clicking into the field and pressing **F1** brings up the **Aspen Plus Help** page on the topic. Doing this in the field for **k** shows the help page about the pre-exponential factor which shows the equation in which it is used.

**Aspen Plus Help**

Hide Back Forward Home Print Options

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**General Input Kinetic Sheet**

Use this sheet to specify reacting phase, solids options, and kinetic parameters for rate-controlled reactions of the power-law, LHHW, and GLHHW classes. For power-law and LHHW reactions, this sheet is similar to the **Kinetic** sheet of Power Law and LHHW reaction sets. For GLHHW reactions, this sheet is similar to the **LHHW | Kinetic** sheet but the shared adsorption parameters are specified on the **GLHHW Adsorption** sheet. See the help on the [Power Law | Input | Kinetic](#) sheet and [LHHW | Input | Kinetic](#) sheet for details.

In addition to the features of those other Kinetic sheets, you can specify rate units for power law, LHHW, and GLHHW reactions in General reaction sets. You can also specify the concentration units when the concentration basis is partial pressure. On the Driving Force dialog box, you can specify whether the reaction is reversible, and whether to specify the rate constants and concentration exponents.

The pre-exponential factor K has units given by:

$$\frac{(\text{Rate units})}{(T_o \text{ units})^n ([C_i] \text{ units})^{DFCE}}$$

Where  $n$  is the temperature exponent specified on this sheet,  $T_o$  units are the absolute temperature units for the units shown on this sheet, Rate units and  $[C_i]$  units are shown or specified on this sheet, and  $DFCE$  (driving force concentration exponent) is the sum of the concentration exponents in the forward term of the driving force expression for all components in the reaction.

Click the **Solids**, **Driving Force**, and **Adsorption** buttons to enter parameters of these types for appropriate reactions. Click the **Summary** button to see a summary of the kinetic parameters in a grid format. Click **Specifications** to enter parameters for individual reactions, including the solids, driving force, and adsorption parameters.

The rate constants in the driving force expression and the adsorption constants, which may represent ratios of kinetic constants, can be temperature-dependent instead of constant. This temperature dependency is written as:

$$\ln(K) = A + \frac{B}{T} + C \times \ln(T) + D \times T$$

Where:

- 4.10. Next, select the **Driving Force** button. Enter **1** as the exponent for cis-2-butene. Click **Close** when complete.

Start Page x Main Flowsheet x R-1 (GENERAL) x +

Configuration Kinetic Equilibrium Activity GLHHW Adsorption Information

1) CIS(MIXED) --> TRANS(MIXED)

Reaction class: POWERLAW Reacting phase: Liquid

Powerlaw kinetic expression  
 $r = [\text{Kinetic factor}][\text{Driving force}]$

[Ci] basis: Molarity  
 [Ci] units: kmol/cum  
 Rate basis: Reac (vol)  
 Rate units: kmol/cum-s

Kinetic factor  
 If To is specified: Kinetic factor =  $k(T/T_0)^n e^{-(E/R)(1/T-1/T_0)}$   
 If To is not specified: Kinetic factor =  $kT^n e^{-E/RT}$

k: 0.003833  
 n: 0  
 E: 0 kcal/mol  
 To: C

Solids  
 Driving Force  
 Adsorption

Specifications Summary

Driving Force Expression

1) CIS(MIXED) --> TRANS(MIXED)  Reaction is reversible

Reacting phase: Liquid [C] basis: Molarity

Reverse rate calculation option  
 Compute reverse rate using microscopic reversibility  
 Specify rate const. and conc. exponents for forward and reverse reactions

Concentration exponents  
 Specify parameters for forward reaction rate

Reactants	Exponent	Products	Exponent
CIS	1	TRANS	

Coefficients for driving force constant  
 A: B: C: D:

Close

- 4.11. Define reactor feed stream. In the navigation pane go to **Streams | CHARGE | Input**. Enter **25°C** for **Temperature**, **1 bar** for **Pressure**, and a **Mole-Flow** of **1 kmol/hr** for component **CIS**.

*Note: If you enter a flow into the composition section, you are not required to enter any additional flow data.*

The screenshot shows the Aspen Plus software interface for defining reactor feed stream specifications. The 'Specifications' section is expanded, showing the following fields:

- Flash Type: Temperature (dropdown), Pressure (dropdown)
- State variables:
  - Temperature: 25 (input), C (dropdown)
  - Pressure: 1 (input), bar (dropdown)
  - Vapor fraction: (empty input)
  - Total flow basis: Mole (dropdown)
  - Total flow rate: (empty input), kmol/hr (dropdown)
  - Solvent: (empty dropdown)

The 'Composition' section is also expanded, showing a table with the following data:

Component	Value
CIS	1
TRANS	

Below the table, the 'Total' flow rate is shown as 1 (input).

*(FAQ) Useful Option To Know: Modeling batch reactors in steady state simulations*

Aspen Plus models batch reactors in steady state, so a real-world plant running batch reactors would need several reactors in parallel with staggered start and end times to approximate steady state operation.

- 4.12. Specify reactor conditions. Go to **Blocks | RBATCH | Setup**. In the **Reactor operating specification** field select **Constant temperature** and enter a temperature of **25°C**. Note that this is not a realistic reactor temperature; however, since our kinetics are not temperature dependent it is acceptable for this simplified example. Next, enter the reactor operating pressure. You may enter the operating pressure by entering a pressure greater than zero, or you can specify the pressure drop through the reactor by entering a number less than or equal to zero. In this case enter **0** for **Reactor pressure**, which means that this reactor will not experience any pressure losses and will operate at the given feed pressure of 1 bar.

Specifications Reactions Stop Criteria Operation Times Continuous F

Reactor operating specification

Constant temperature

Temperature: 25 C

Pressure specification

Specify reactor pressure

Reactor pressure: 0 bar

Catalyst loading: 0 kg

- 4.13. Choose the reaction set. In the **Reactions** tab, specify **R-1** as the selected reaction set.

Specifications Reactions Stop Criteria Operation Times Continuous Feeds

Reactive system

Select reaction set(s) to be included in the model

Available reaction sets

Selected reaction sets

R-1

>

>>

<

<<

New

- 4.14. Specify Stop Criteria in order to stop Aspen Plus computation when the conversion reaches a designated number. In this case, when the mole fraction of trans-2-butene in the reactor reaches 0.9, Aspen Plus will stop reactor computations and the product stream will represent the composition of the reactor at this designated stop time. In the **Stop Criteria** tab, complete the input fields as shown below.

Stop criteria		
Criterion no.	1	
Location	Reactor	
Variable type	Mole fraction	
Stop value	0.9	
Unit		
Component	TRANS	
Substream	MIXED	
Property set ID		
Approach from	Below	

- 4.15. Define Operation Times in order to create result tables and plots. Complete the input fields in the **Operation Times** tab as shown below.

Batch cycle time		
<input checked="" type="radio"/> Total cycle time:	1	hr
<input type="radio"/> Batch feed time:		hr
Down time:	0	hr

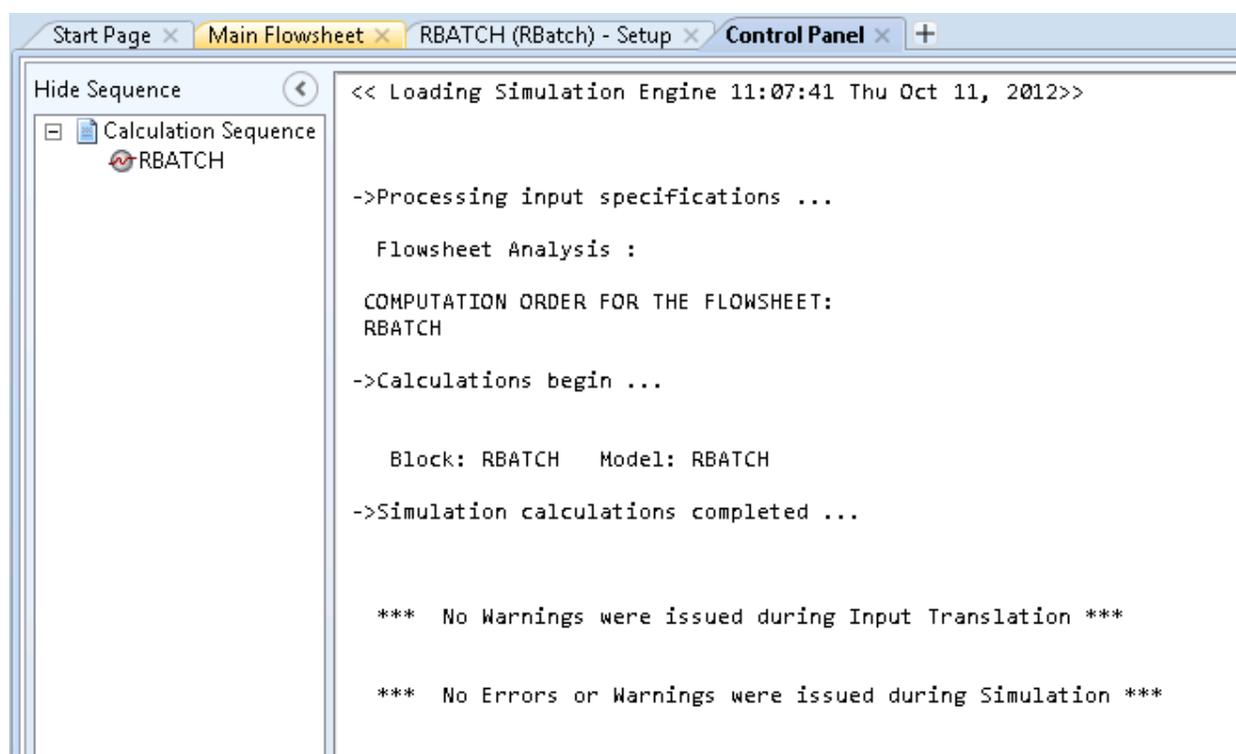
  

Profile result time		
Maximum calculation time:	1	hr
Time interval between profile points:	10	sec
Maximum number of profile points:	1000	

- 4.16. Save your Aspen Plus simulation file (use .bkp format, for example **Reactor\_Batch\_CIStoTRANS.bkp**)
- 4.17. All the input required to run the simulation has been entered. On the **Home** tab of the ribbon, click the **Control Panel** button. It is a good habit to open the control panel before running the simulation.



4.18. Run the simulation (**F5**). The simulation should run to completion with no errors or warnings.



4.19. Check the result table. Go to the **Blocks | RBATCH | Profiles | Compositions** tab. The computed time at which the TRANS mole fraction is 0.9 is **10.01 min.**, which is identical to the analytic solution.

Composition profiles

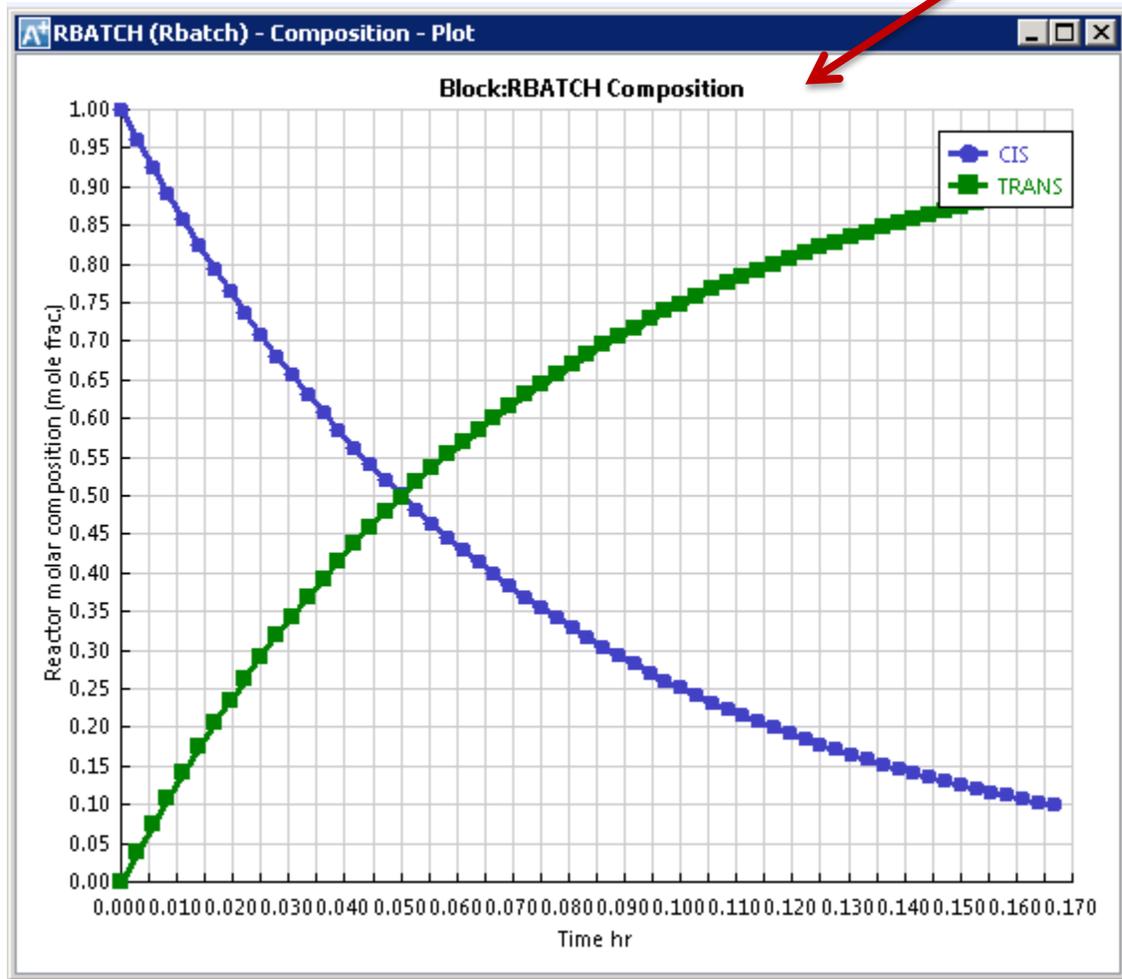
View: Reactor molar composition

Time	CIS	TRANS
7	0.199925	0.800075
7.16667	0.192405	0.807595
7.33333	0.185166	0.814834
7.5	0.1782	0.8218
7.66667	0.171495	0.828505
7.83333	0.165044	0.834956
8	0.158836	0.841164
8.16667	0.15286	0.84714
8.33333	0.147108	0.852892
8.5	0.141573	0.858427
8.66667	0.136246	0.863754
8.83333	0.13112	0.86888
9	0.126188	0.873812
9.16667	0.121439	0.878561
9.33333	0.116869	0.883131
9.5	0.112471	0.887529
9.66667	0.108239	0.891761
9.83333	0.104167	0.895833
10	0.100248	0.899752
10.0107	0.100001	0.899999

You can change the time unit

The required reaction time to reach 90% conversion for component A

4.20. Check the result plot. Select **Composition Plot** in the Ribbon.



4.21. Optional calculation in Aspen Plus

- Increase the Stop value in the Stop Criteria (as shown in Step 9) so that you can see more results for a longer time
- What would happen if you changed the reaction constant  $k$  (e.g.  $k = 0.1$  or  $0.001$  1/s)
- It would be interesting to simulate the batch reactor behavior when the reaction is complex with additional reacting components. As we could imagine, an analytic solution won't be available if the reaction is complex with multi-components, but we can still simulate it in Aspen Plus. You just need to add more components and change reaction data. That is sufficient for any batch reactor simulation.

## 5. Conclusion

Both the analytical solution and stop criteria in Aspen Plus result in a residence time of 10.01 min. for 90% conversion. The ordinary differential equation (ODE) solution yields an exponential function, and the composition plot has an exponential shape. Using RBatch allows for more advanced calculations. It will model complex reaction systems including parallel and series reactions which lead to coupled systems of ODEs.

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