



KAMAL I.M. AL-MALAH

# ASPEN PLUS®

CHEMICAL ENGINEERING  
APPLICATIONS



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## Chemical Engineering Applications

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*To my creator who taught humans things they did not know before;  
To the last prophet Mohammad and to the preceding prophets, peace be upon all of them;  
To my first lovely teachers in this life: mom and dad;  
To my wife (Fadia), daughters (Anwar and Lama), and sons (Abdallah and Mohammad);  
To my biological brothers and sisters;  
To my first class teacher (Mr Raslan Al-Malah), mercy be upon him;  
To my succeeding teachers and professors between the first class and until I got my Ph.D.  
degree;  
To my last professor (my Ph.D. supervisor, Dr Joe McGuire);  
To my Chemical Engineering students at different universities;  
To AspenTech, Inc., who sponsored this work;  
To John Wiley & Sons, Inc. book editorial staff; and  
To SPi Global, book production team.  
Finally to my brothers and sisters in humanity worldwide;  
To the first, I say: I owe you everything and you are the first and last.  
To the rest, I say: my sincere and warm greetings to all of you.*

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# 6

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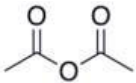
## REACTORS WITH SIMPLE REACTION KINETIC FORMS

### 6.1 PROBLEM DESCRIPTION

This chapter deals with chemical reactor design. The problem was taken from Fogler [1]. The problem was stated and solved in Example 8.5, under two reactor conditions: an adiabatic plug-flow reactor (PFR) and a PFR with a constant cooling temperature.

**NOTE #1:** *This chapter only covers reactions with simple kinetics (i.e., what is called “POWERLAW” type reaction in Aspen Plus terminology). Complex kinetics type of reactions (i.e., what is called “LHHW” type reaction in Aspen Plus terminology) will be the battlefield of CHAPTER 7. I split Aspen Plus reaction engineering applications into two chapters so that the student does not get overwhelmed or clotted by the versatile features of Aspen Plus being applied to chemical reaction engineering (or reactor design).*

### 6.2 DEFINING REACTION RATE CONSTANT TO ASPEN PLUS® ENVIRONMENT

In a treatment of the design of an acetic anhydride (  ) manufacturing facility, it is stated that one of the key steps is the vapor-phase cracking of acetone to ketene and methane:



It is further stated that this reaction is first order with respect to acetone and that the specific reaction rate can be expressed by

$$\ln k = 34.34 - 34,222 / T \quad (6.2)$$

In this design, it is desired to feed 7850 kg of acetone per hour to a tubular reactor. If the reactor is adiabatic, the feed is pure acetone, the inlet temperature is 1035 K, and the pressure is 162 kPa (1.6 atm), what will be the tubular reactor volume needed to achieve 20% conversion?

Acetic anhydride is prepared by the reaction of ethenone (ketene) with acetic acid at 45–55°C and low pressure (0.05–0.2 bar).



There are two different ways by which we can define the reaction rate constant to Aspen Plus environment. We arrange Equation 6.2 in these two forms: one form contains a reference temperature,  $T_0$ , and another does not. However, both forms are equivalent. Take the exponent value for both sides of Equation 6.2 and we have

$$k = e^{34.34 - \frac{34,222}{T}} = e^{34.34} e^{-\frac{34,222}{T}} = e^{34.34} \times e^{-\frac{34,222 \times R}{R \times T}} = 8.1973 \times 10^{14} \times e^{-\frac{284,521.7}{R \times T}} \quad (6.4)$$

Alternatively,  $T_0$  can be arbitrarily chosen and  $k^*$  will be calculated accordingly. Let us use  $T_0 = 1000 \text{ K}$ . We have

$$k = k^* e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)} = k^* e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{1000} \right)} = k^* \times e^{-\frac{E}{R} \left( \frac{1}{T} \right)} \times e^{\frac{E}{R} \left( \frac{1}{1000} \right)} \quad (6.5)$$

Equate both expressions of  $k$ , we have

$$k = e^{34.34} e^{-\frac{34,222}{T}} = k^* e^{-\frac{E}{R} \left( \frac{1}{T} \right)} e^{\frac{E}{R} \left( \frac{1}{1000} \right)} \quad (6.6)$$

First, equate the exponent terms, on both sides, which contain  $1/T$  term to calculate  $E$ :

$$\begin{aligned} -\frac{34,222}{T} &= -\frac{E}{R} \left( \frac{1}{T} \right) \Rightarrow \frac{E}{R} = 34,222 \Rightarrow E = R \times 34,222 = 8.314 \times 34,222 \\ &= 284,521.7 \text{ J/mol} \end{aligned} \quad (6.7)$$

Notice that  $E$  is the same as that in Equation 6.4. Second, substitute the value of  $E$  from Equation 6.7 into Equation 6.6 and equate constants on both sides of Equation 6.6.

$$e^{34.34} = k^* e^{\frac{E}{R} \left( \frac{1}{1000} \right)} = k^* e^{\frac{284,521.7}{8.314} \left( \frac{1}{1000} \right)} = k^* e^{34.222} \Rightarrow k^* = e^{34.34 - 34.222} = e^{0.118} = 1.125 \quad (6.8)$$

Notice that  $k^*$  is calculated in terms of  $T_0 = 1000 \text{ K}$ . However,  $E$  is fixed for a given reaction and does not depend on  $T_0$ .

Equation 6.5 becomes

$$k = k^* e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)} = 1.125 e^{-\frac{284,521.7}{R} \left( \frac{1}{T} - \frac{1}{1000} \right)} \quad (6.9)$$

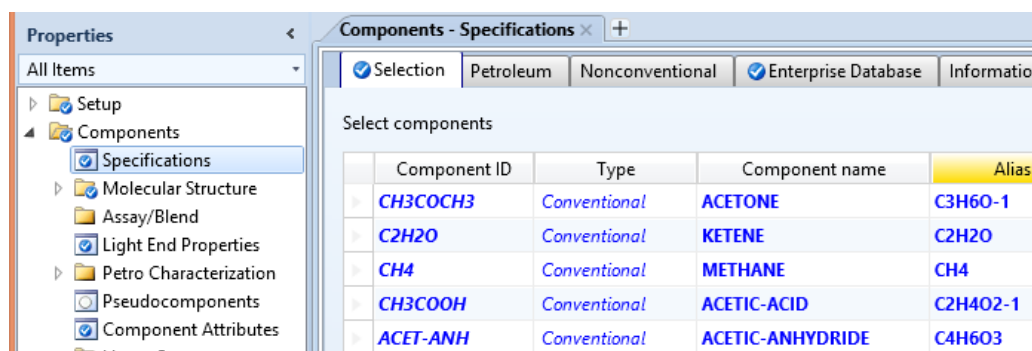
where  $k$  is in reciprocal seconds (for a 1<sup>st</sup>-order reaction) and  $T$  is in Kelvin.

In general, the rate constant  $k$  can be expressed in either form, Equation 6.4 or 6.9, depending on the chemical reaction engineering textbook being used.

### 6.3 ENTERING COMPONENTS AND METHOD OF PROPERTY

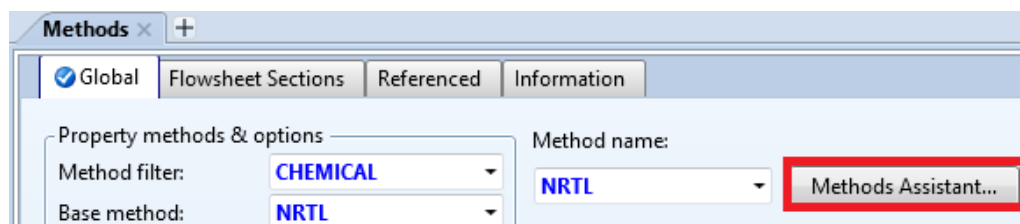
Using “**Specialty Chemicals with Metric Units**” template, create an Aspen Plus project. Under “**Properties**” environment, in “**Navigation**” pane, go to “**Setup**” | “**Global**” sheet and enter the title: “*Production of Acetic Anhydride*”.

In “**Navigation**” pane, click on “**Components**” folder, and you will be faced by “**Selection**” tab window. Use “**Find**” button, shown at the bottom of “**Selection**” tab window, to search for components by name or chemical formula. Add the following components: ACETONE ( $\text{CH}_3\text{COCH}_3$ ), KETENE ( $\text{C}_2\text{H}_2\text{O}$ ), METHANE ( $\text{CH}_4$ ), ACETIC-ACID ( $\text{CH}_3\text{COOH}$ ), and ACETIC-ANHYDRIDE (ACET-ANH) as shown in Figure 6.1.



**Figure 6.1** Entering reactants and products of the reactions involved in the synthesis of acetic anhydride.

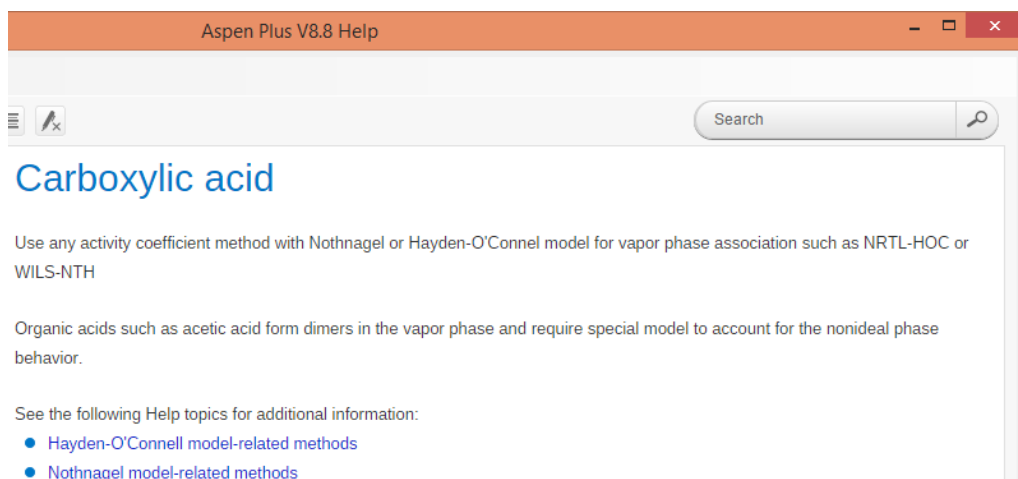
Go to “**Methods**” folder | “**Global**” sheet and use the “**Property Method Selection Assistant**” wizard by clicking on the “**Methods Assistant ...**” button shown in Figure 6.2.



**Figure 6.2** Clicking on the “**Methods Assistant ...**” button, will invoke the “**Property Method Selection Assistant**” wizard.

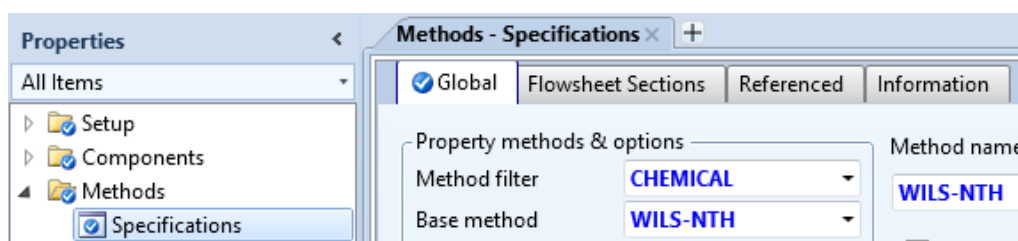
Select “**Specify process type**”; followed by selecting the type of process to be “**Chemical**”; and finally clicking “**Carboxylic acids**” as a subset of “**Chemical**” processes. This will guide you to either “**NRTL-HOC**” or “**WILS-NTH**” as shown in Figure 6.3.





**Figure 6.3** The property method selection assistant will recommend either “NRTL-HOC” or “WILS-NTH” for the subcategory: “Chemical” | “Carboxylic acids”.

You can choose either one; so, in “Global” tab window, from the “Method name” pull-down menu select “WILS-NTH” as shown in Figure 6.4.



**Figure 6.4** Following the recommendation by the “Property Method Selection Assistant” wizard, the property method is set to “WILS-NTH”.

Under “Methods” | “Parameters” | “Binary Interaction” | “WILSON-1” sheet be sure that the “*Estimate missing parameters by UNIFAC*” option is checked. Click “Reset” followed by “Next” button to run the simulation and assure that properties analysis completed successfully.

**NOTE #2:** “Control Panel” shows a warning as follows:

\* WARNING IN PHYSICAL PROPERTY SYSTEM  
 PROP-NAME WILSON FOR COMPONENT PAIR  $\text{CH}_3\text{COCH}_3$  AND  $\text{C}_2\text{H}_2\text{O}$   
 CANNOT BE ESTIMATED USING THE UNIFAC METHOD AS SPECIFIED  
 BECAUSE OF MISSING INPUT PARAMETERS:  
 STRUCTUR, GMUFR, GMUFQ

Such a warning can be ignored given the fact that the pairwise interaction parameters are already calculated by UNIFAC method and are shown in “Parameters” | “Binary Interaction” | “WILSON-1” sheet with the source as R-PCES. Moreover, even

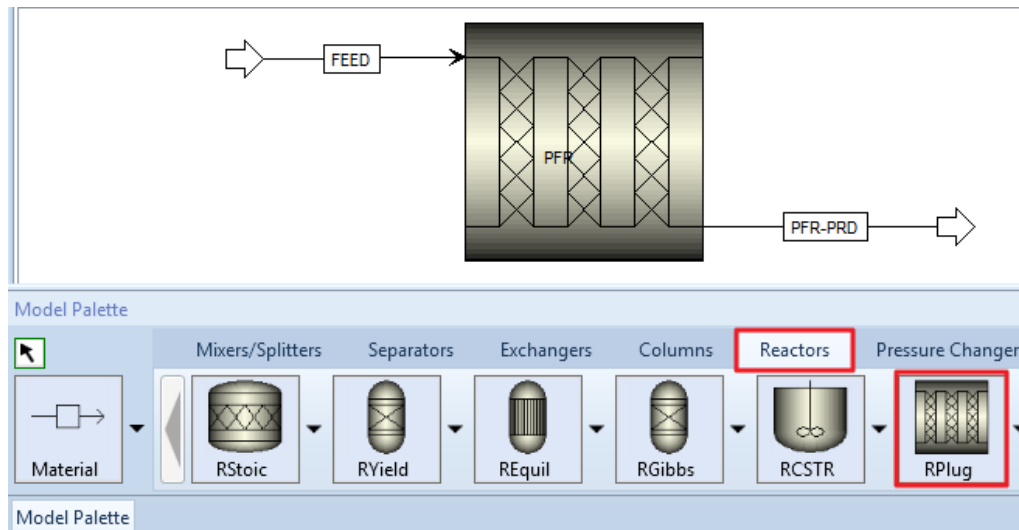
if we define the structure of ketene under “**Components**” | “**Molecular Structure**” via the built-in Aspen Plus Molecule Editor, the warning will persist.

To remove this persisting warning to propagate to “Simulation” environment, deselect the option “Estimate missing parameters by UNIFAC” after the pairwise interaction parameters are all calculated and are shown in “**Parameters**” | “**Binary Interaction**” | “**WILSON-1**” sheet, and rerun the simulation under “**Properties**” environment for the second time you will notice that the nagging warning will disappear and the “**Properties Analysis/Setup Complete**” pop-up window will tell the user that properties analysis successfully completed. Nevertheless, a warning like this can be ignored

```
WARNING IN PHYSICAL PROPERTY SYSTEM
  FUNCTIONAL GROUP GENERATION FOR THE UNIFAC METHOD CANNOT BE COM-
  PLETED
  FOR COMPONENT C2H2O.  THE FOLLOWING ATOMS WERE NOT MATCHED:
  C 1  C 2  O 3
```

## 6.4 THE RIGOROUS PLUG-FLOW REACTOR (RPLUG)

At the start, the flowsheet consists of one inlet stream, a plug-flow reactor (“**PFR**”), and one product stream. It should resemble Figure 6.5. This can be done by adding the “**RPlug**” reactor found under “**Reactors**” tab in “**Model Palette**”.



**Figure 6.5** The addition of “**PFR**” block to the flowsheet using the “**RPlug**” reactor under “**Reactors**” tab in “**Model Palette**”.

Table 6.1 shows a brief description about each reactor model found under “**Reactors**” tab.

**TABLE 6.1** Different reactor models are found in Aspen Plus under “Reactors” tab in “Model Palette”.

Model	Description	Purpose	Use
Rstoic	Stoichiometric reactor	Stoichiometric reactor with specified reaction extent or conversion	Reaction kinetics is unknown or unimportant but its stoichiometry and extent are given
RYield	Yield reactor	Reactor with specified yield	Reaction stoichiometry and kinetics are unknown or unimportant but yield distribution is known
REquil	Equilibrium reactor	Chemical and phase equilibrium by stoichiometric calculations	Single- and two-phase chemical equilibrium and simultaneous phase equilibrium. The user must specify the reaction stoichiometry and the reactor conditions. If no additional specifications are given, “ <b>REquil</b> ” model will assume that the reactions will reach equilibrium
RGibbs	Equilibrium reactor	Chemical and phase equilibrium by Gibbs free energy minimization, subject to atom balance constraints	Chemical and/or simultaneous phase and chemical equilibrium. Solid phase equilibrium may be included. This model does not require reaction stoichiometry; however, the user must specify the reactor temperature and pressure, or pressure and enthalpy. See Homework/Classwork 9.4 (The Selectivity of Parallel Reactions)
RCSTR	Continuous stirred-tank reactor	Continuous stirred-tank reactor	One-, two-, or three-phase stirred-tank reactor with reaction taking place in the vapor or liquid
RPlug	Plug-flow reactor	Plug-flow reactor	One-, two-, or three-phase plug-flow reactor with reaction taking place in the vapor or liquid
RBatch	Batch reactor	Batch or semi-batch reactor	Batch and semibatch reactor with known reaction kinetics

Click on “**Next**” button, and Aspen Plus will bring the user to entering feed stream properties

**Temperature:** 1035 K (change units if necessary)

**Pressure:** 1.6 atm (change units if necessary)

**Total flow:** Change to Mass kg/h

For the total mass flow rate of “**FEED**” stream, type 7850. Leave ketene and methane at zero (no mass flow in the feed stream). For “**Composition**” drop-down menu, use “*Mass-Frac*” and enter 1.0 for acetone ( $\text{CH}_3\text{COCH}_3$ ). See Figure 6.6.

Main Flowsheet ☒ FEED (MATERIAL) - Input ☐ +

☒ Mixed ☐ CI Solid ☐ NC Solid ☐ Flash Options ☐ EO Options ☐ Costing ☐ Information

Specifications

Flash Type: Temperature Pressure

State variables:
   
 Temperature:  K
  
 Pressure:  atm
  
 Vapor fraction: 
  
 Total flow basis: Mass
  
 Total flow rate:  kg/hr
  
 Solvent:

Composition: Mass-Frac

Component	Value
CH3COCH3	1
C2H2O	
CH4	
CH3COOH	
ACET-ANH	

**Figure 6.6** Entering feed stream properties in terms of flow,  $P$ ,  $T$ , and composition.

Click on “Next” button.

## 6.5 REACTOR AND REACTION SPECIFICATIONS FOR RPLUG (PFR)

“Reactor type”: “*Adiabatic reactor*”, as shown in Figure 6.7.

Main Flowsheet ☒ PFR (RPlug) ☐ +

☒ Specifications ☒ Configuration ☐ Streams ☒ Reactions ☒ Pressure

Reactor type: Adiabatic reactor

Operating conditions:
   
 No additional specifications

Reactor type options:
   
 Reactor with specified temperature
   
 Adiabatic reactor
   
 Reactor with constant thermal fluid temperature
   
 Reactor with co-current thermal fluid
   
 Reactor with counter-current thermal fluid
   
 Reactor with specified thermal fluid temperature profile
   
 Reactor with specified external heat flux profile

**Figure 6.7** Under “Specifications” tab, choose the type of plug-flow reactor (PFR).

Move to “Configuration” tab and enter specifications as shown in Figure 6.8.

Main Flowsheet × PFR (RPlug) - Setup +

Specifications Configuration Streams Reactions Pressure

☐ Multitube reactor      Number of tubes

☐ Diameter varies along the length of the reactor

Reactor dimensions

Length  meter

Diameter  meter

Elevation

☒ Reactor rise  meter

☐ Reactor angle  deg

Valid phases

Process stream

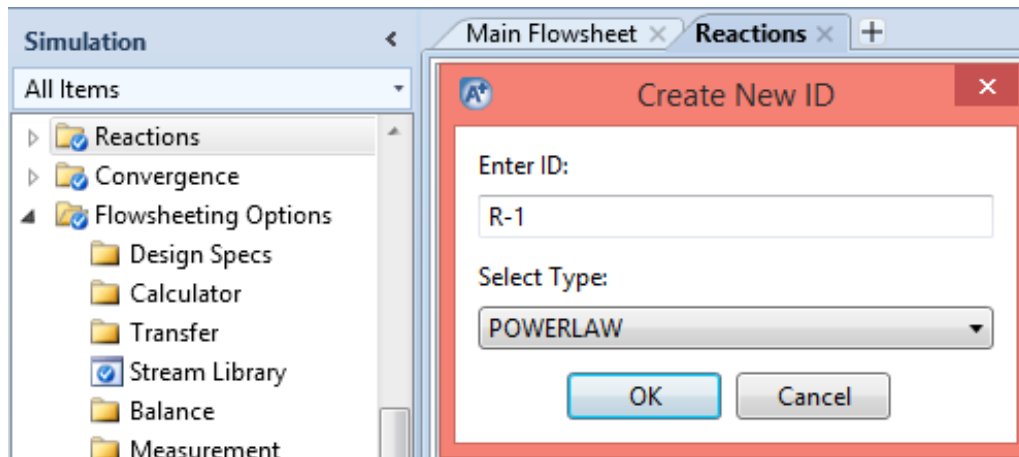
**Figure 6.8** “PFR” is chosen as a single-tube reactor (*i.e.* a cylinder with length 3.0 and diameter 1 m). The “Process stream” is “Vapor-Only” based on the given pressure and temperature.

On the other hand, the user may choose, however, a multitube reactor, for instance, 1000 tubes of length 2.5 meters and inside diameter (ID) of 0.9 inches.

**NOTE #3:** If the inlet pressure value is left “0”, under the “Pressure” tab shown in Figure 6.8, then we will instruct Aspen Plus to let the inlet pressure be equal to the feed stream pressure.

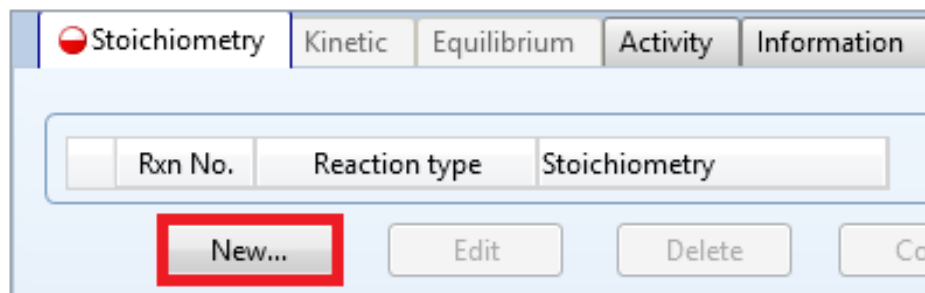
If you click on “Reactions” tab, you will notice that you need to associate a reaction set to “PFR” block; however, since we did not define any reaction yet, the available reaction sets side will be empty.

Click on “Next” button to create the reaction set as shown in Figure 6.9, which will be added later to the “Reactions” tab here. Figure 6.9 shows that we created “R-1” reaction set with “POWERLAW” type. The reason for describing “R-1” as a reaction set is simply because it may contain more than one reaction. Here, we have only one reaction as given by Equation 6.1.



**Figure 6.9** The reaction type is “POWERLAW” with an ID: “R-1”.

Figure 6.10 shows the “Stoichiometry” tab window where we need to define the reaction stoichiometry.



**Figure 6.10** The reaction set “R-1” is still undefined for Aspen Plus.

Click on “New ...” button and the “Edit Reaction” window will pop up where the user will be required to define the reaction equation, its type whether kinetic or equilibrium, and the reaction order (*i.e.*, exponent) if it is of kinetic type, as shown in Figure 6.11.

Rxn No.	Reaction type	Stoichiometry
1	Kinetic	CH <sub>3</sub> COCH <sub>3</sub> --> C <sub>2</sub> H <sub>2</sub> O + CH <sub>4</sub>

Reaction No. 1

Reaction type Kinetic

**Reactants**

Component	Coefficient	Exponent
CH <sub>3</sub> COCH <sub>3</sub>	-1	1

**Products**

Component	Coefficient	Exponent
C <sub>2</sub> H <sub>2</sub> O	1	
CH <sub>4</sub>	1	

Next

Close

**Figure 6.11** The “Edit Reaction” window where the user defines the reaction equation and whether or not it is of “Kinetic” type. Here, it means that the reaction is first order with respect to acetone (CH<sub>3</sub>COCH<sub>3</sub>).

Under “**Reaction type**”, select “Kinetic”.

Under “**Reactants**”, select acetone (CH<sub>3</sub>COCH<sub>3</sub>) from the components pull-down menu and set the “**Coefficient**” to  $-1$  and the “**Exponent**” to  $1$ .

Under “**Products**”, select ketene and methane and set both coefficients to  $1$ .

Click on “Next” button or “Close” button shown at the bottom of the “Edit Reaction” window.

Figure 6.12 shows that the reaction stoichiometry is defined; however, the kinetic parameters are not yet defined.

Main Flowsheet
R-1 (POWERLAW)

☒ Stoichiometry
☐ Kinetic
☐ Equilibrium
☐ Activity
☐ Information

Rxn No.	Reaction type	Stoichiometry
1	Kinetic	CH <sub>3</sub> COCH <sub>3</sub> (MIXED) --> C <sub>2</sub> H <sub>2</sub> O(MIXED) + CH <sub>4</sub> (MIXED)

New...

Edit

Delete

Copy

Paste

**Figure 6.12** The reaction stoichiometry (*i.e.*, equation) is already defined but the kinetic parameters are not.

**NOTE #4:** Based on Aspen Plus built-in help, here is how to enter kinetic parameters for a reaction:

If  $T_o$  is specified, then the general law expression will be

$$r = k(T/T_o)^n e^{(-E/R)\left[\frac{1}{T} - \frac{1}{T_o}\right]} \prod_{i=1}^N C_i^{\alpha_i} \quad (6.10)$$

On the other hand if  $T_o$  is not specified, the general law expression will reduce to

$$r = k(T)^n e^{(-E/R)\left[\frac{1}{T}\right]} \prod_{i=1}^N C_i^{\alpha_i} \quad (6.11)$$

The rate is expressed in  $\text{kmol}/(\text{s} \cdot \text{basis})$  where the basis is either  $\text{m}^3$  for “**Rate Basis:** Reac (vol)”, or kilogram catalyst for “**Rate Basis:** Cat (wt)”.

The reactor volume or catalyst weight is determined by specifications in the reactor where the reaction is used.

Next, click on the “**Kinetic**” tab where the user needs to input the kinetic parameters. Change “**Reacting phase**” to “Vapor”. The “**Rate basis**” will be left as “Reac(vol)”. Enter 1.125 for  $k$  (i.e.,  $k^*$  in Eq. 6.9). Enter 1000 K for  $T_o$ . Enter the activation energy  $E$  of the Arrhenius equation,  $E = 284,521.7 \text{ J/mol}$  (Eq. 6.4 or Eq. 6.7). Notice  $E$  is also equal to 284,521.7 kJ/kmol. Figure 6.13 shows the “**Kinetic**” tab window, after inputting the required data.

The screenshot shows the 'Kinetic' tab in Aspen Plus. At the top, there are tabs for 'Stoichiometry', 'Kinetic' (selected), 'Equilibrium', 'Activity', and 'Information'. Below the tabs, the reaction is listed as '1) CH3COCH3 --> C2H2O + CH4'. The 'Reacting phase' is set to 'Vapor' and the 'Rate basis' is 'Reac (vol)'. The 'Power Law kinetic expression' section is expanded, showing the kinetic factor as  $k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$ . The input fields are:  $k = 1.125$ ,  $n = 0$ ,  $E = 284522$  kJ/kmol,  $T_o = 1000$  K, and '[Ci] basis' is 'Molarity'.

**Figure 6.13** The reaction phase and the kinetic parameters are defined in “**Kinetic**” tab window, based on Equation 6.9 and in light of Equation 6.10.



Alternatively, the user may attempt to enter the kinetic data based on Equation 6.4, as shown in Figure 6.14.

1) CH<sub>3</sub>COCH<sub>3</sub> --> C<sub>2</sub>H<sub>2</sub>O + CH<sub>4</sub>

Reacting phase: Vapor      Rate basis: Reac (vol)

Power Law kinetic expression

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

If To is not specified      Kinetic factor       $= kT^n e^{-E/RT}$

k: 8.19733e+14

n: 0

E: 284522      kJ/kmol

To:      K

[Ci] basis: Molarity

**Figure 6.14** The reaction phase and the kinetic parameters are defined in “Kinetic” tab window, based on Equation 6.4 and in light of Equation 6.11.

Notice that in Figure 6.8 “PFR” block still lacks some information (*i.e.*, a half-filled red circle).

Click on “Next” button and Aspen Plus will move to the “Setup” window of “PFR” block as shown in Figure 6.15.

Blocks

- CMRSSR
- DSTL
- PFR
  - Setup
  - Convergence
  - Report
  - User Subroutine
  - Dynamic
  - Block Options
  - EO Modeling

Specifications      Configuration      Streams      Reactions

☒ Reactive system

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

Available reaction sets: R-1

Selected reaction sets:

>

>>

**Figure 6.15** The user needs to highlight “R-1” set on the left side and then to move it to the right side *via* the first top arrow.

## 6.6 RUNNING THE SIMULATION (PFR ONLY)

Click on “Next” and “OK” buttons. When the simulation is complete, go to “Blocks” | “PFR” | “Stream Results”. Figure 6.16 shows the stream properties from and to “PFR” block.

	FEED	PFR-PRD
Temperature C	761.9	641.2
Pressure bar	1.621	1.621
Vapor Frac	1	1
Mole Flow kmol/hr	135.158	163.05
Mass Flow kg/hr	7850	7850
Mole Flow kmol/hr		
CH <sub>3</sub> COCH <sub>3</sub>	135.158	107.267
C <sub>2</sub> H <sub>2</sub> O		27.891
CH <sub>4</sub>		27.891

**Figure 6.16** The stream results of PFR. The conversion,  $X$ , can be calculated as  $(27.89)/135.16 = 0.206$ .

Check the conversion ( $X = \text{moles reacted}/\text{moles fed}$ ). Does  $X = 20\%$ ? If  $X < 20\%$ , you must increase the length of “PFR”. If  $X > 20\%$ , you must decrease the length of “PFR”. For our case, it is found that  $X = (27.89)/135.16 = 0.206$  (20.6%). Luckily, the tube length is satisfactory.

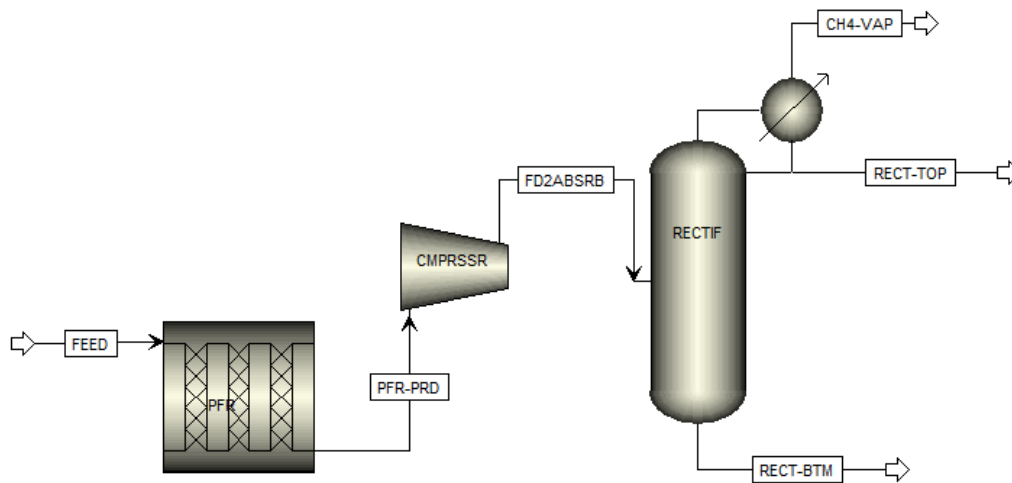
### EXERCISE 6.1

Utilizing the results shown in Figure 6.16, answer the following questions:

- Given that the PFR is adiabatically operated and the product stream temperature (641.2°C) is less than that of the feed stream (761.9°C), what will be the heat of reaction, endothermic or exothermic?
- Unlike the total mass flow rate (7850 kg/h) that remains unchanged, why is the total molar flow rate of the product stream (163.05 kmol/h) is greater than that of the feed stream (135.158 kmol/h)?
- What is the molecular weight of the pure feed stream?
- What is the average molecular weight of the product stream?

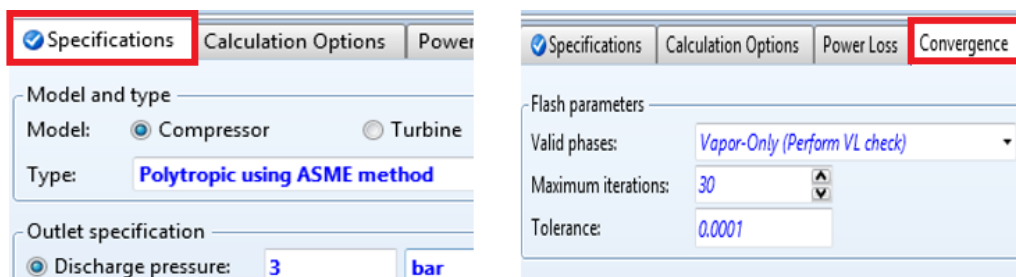
## 6.7 COMPRESSOR (CMRSSR) AND RADFRAC RECTIFYING COLUMN (RECTIF)

On the other hand, if we look at the outlet composition of the reactor product stream (**PFR-PRD**), we will find that it contains an excessive amount of acetone, which means that we need to separate acetone from the products ketene and methane prior to sending ketene to the second reactor that will be installed later. So, we have to add an absorption tower that will basically split acetone from ketene and methane. Figure 6.17 shows the addition of two pieces of equipment: the first is the gas compressor and the second is “**RadFrac**” type absorption tower (rectifier). The rectifier is basically the upper half of a distillation tower with a condenser and no reboiler.



**Figure 6.17** For the sake of purification, a compressor and absorption tower (rectifier) will be installed prior to introducing the product stream to the second reactor that will be installed at a later stage.

Figure 6.18 shows that the discharge pressure for the compressor is 3 bar and the convergence condition is such that we have vapor only while performing vapor–liquid (VL) check. Of course, an error will be issued if a two-phase system coexists within the compressor.



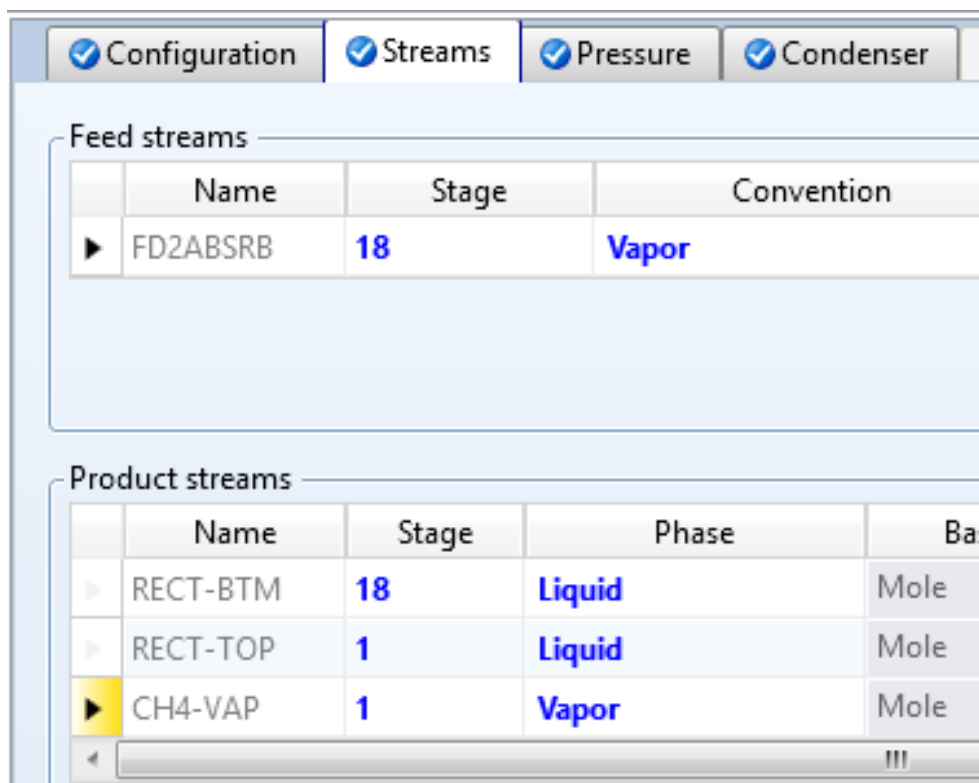
**Figure 6.18** Specifications for the compressor; “**Polytropic using ASME method**” type is chosen and a discharge pressure of 3 bar is assigned (*left*) and a restriction for the presence of vapor phase only (*right*).

On the other hand, Figure 6.19 shows “RECTIF” | “Specifications” | “Setup” | “Configuration” tab window. The user must specify the number of stages, reboiler type (if any), condenser type, and one of “Operating specifications”, such as “Bottoms rate”. It is to be mentioned here that a bottoms mass flow rate of 6250 kg/h is a matter of trial-and-error approach because it affects the composition of both the top and bottom streams. Obviously, the value has to be somewhere between zero and that of the feed stream entering the tower.

The screenshot shows the 'RECTIF Specifications' window with the 'Configuration' tab selected. The window has several tabs: 'Configuration', 'Streams', 'Pressure', 'Condenser', 'Reboiler', '3-Phase', and 'Info'. The 'Configuration' tab is active, showing 'Setup options' and 'Operating specifications'. In the 'Setup options' section, the following values are set: Calculation type: Equilibrium; Number of stages: 18; Condenser: Partial-Vapor-Liquid; Reboiler: None; Valid phases: Vapor-Liquid; Convergence: Standard. In the 'Operating specifications' section, 'Bottoms rate' is selected with a value of 6250 kg/hr.

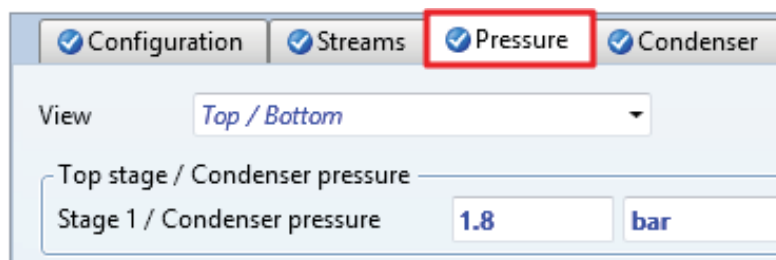
**Figure 6.19** The “Configuration” tab window for the “Setup” sheet for the absorption column named “RECTIF”. The number of stages; condenser type; reboiler type (if any); and one of “Operating specifications”, such as “Bottoms rate”, are to be entered here.

Click on “Next” button and Aspen Plus will move to the “Streams” tab window as shown in Figure 6.20. Here, the location of the feed stream (or feed tray) must be defined with respect to the top tray (#1). Notice that the location of the feed tray is way down at the bottom of the rectifier. This makes sense as we need not have a reboiler; the feed stream will be available as the vapor phase throughout the entire rectifying column.



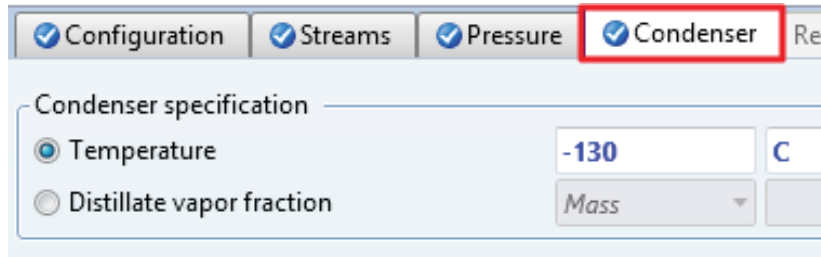
**Figure 6.20** The location of feed tray from the first top tray (#1) is made *via* “Streams” tab window. The vapor feed will be introduced at the bottom; hence, there is no need for reboiler in a rectifying column.

Click on “Next” button and you will be prompted by “Pressure” tab window as shown in Figure 6.21. Here, the pressure at the top stage (condenser stage) must be defined. Enter *1.8 bar* for the condenser pressure.



**Figure 6.21** The “Pressure” tab window is used to define the pressure profile throughout the column.

Click on “Next” button and you will be prompted by “Condenser” tab window as shown in Figure 6.22. Here, the temperature of the condenser must be defined. Alternatively, the distillate vapor fraction can be defined. Enter  $-130^{\circ}\text{C}$  for the condenser temperature.



**Figure 6.22** The “Condenser” tab window is used to define the condenser temperature.

## 6.8 RUNNING THE SIMULATION (PFR + CMPRSSR + RECTIF)

Click on “Reset” followed by “Next” and by “OK” button to allow Aspen Plus to do the calculations on your behalf. Figure 6.23 shows a portion of the results, which pertains to the absorption column. As you can see that the bottom (**RECT-BTM**) stream is 99.7 wt% acetone and the top (**RECT-TOP**) stream is mainly composed of methane and ketene. The acetone stream will be recycled to the inlet of PFR. Moreover, the vapor portion of the top stream is 99.8 wt% methane gas, which can be combined with another stream and be sent to a storage facility for methane. Here, we have a partial condenser (see Figure 6.19), which means not all of the rising vapor up the column will be condensed; a small portion will remain as is and the rest will be condensed and split into the top liquid (distillate) and returning (*i.e.*, reflux) stream.

	FD2ABSRB	RECT-BTM	RECT-TOP	CH4-VAP
Temperature C	692.8	69.8	-130	-130
Pressure bar	3	1.8	1.8	1.8
Vapor Frac	1	0	0	1
Mole Flow kmol/hr	163.05	107.775	37.194	18.081
Mass Flow kg/hr	7850	6250	1309.54	290.458
Volume Flow cum/hr	4371.5	8.535	1.724	116.298
Enthalpy Gcal/hr	-3.691	-6.203	-0.698	-0.345
Mass Frac				
CH <sub>3</sub> COCH <sub>3</sub>	0.794	0.997	trace	trace
C <sub>2</sub> H <sub>2</sub> O	0.149	0.003	0.88	0.002
CH <sub>4</sub>	0.057	142 PPM	0.12	0.998
CH <sub>3</sub> COOH				
ACET-ANH				

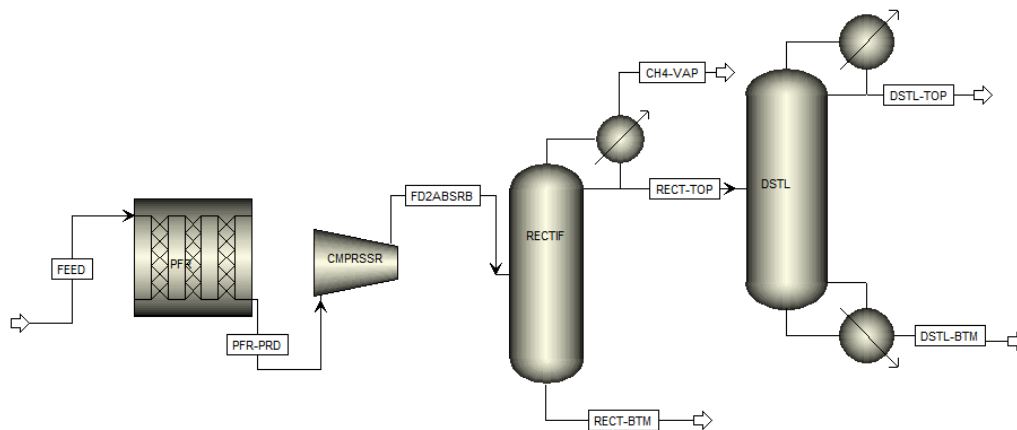
**Figure 6.23** The simulation results indicate that “RECTIF” tower managed to isolate acetone from the other two components methane and ketene.

**EXERCISE 6.2**

Carry out pure component analysis. Under “**Properties**” environment, click on “**Home**” ribbon | “**Analysis**” tab | “**Pure**” button and select the thermodynamic property to be “**PL**”, which represents the vapor pressure of a pure component as a function of temperature. Select the temperature range between 0 and 100°C and the phase to be liquid to analyze the vapor pressure of the three components acetone, ketene, and methane. Sort them in descending order with respect to volatility. Verify that acetone is the least volatile.

**6.9 RadFrac DISTILLATION COLUMN (DSTL)**

As was done in the previous step, the top “**RECT-TOP**” stream will be sent to another “**RadFrac**” type distillation tower where methane will be separated from ketene, as shown in Figure 6.24.



**Figure 6.24** The addition of “**RadFrac**” type distillation tower to separate methane from ketene.

Figures 6.25–6.27 show the specifications of the “**RadFrac**” type distillation column (DSTL).

Control Panel x Main Flowsheet x **DSTL Specifications** +

Configuration Streams Pressure Condenser Reboiler 3-Phase

Setup options

Calculation type: *Equilibrium*

Number of stages: **12** Stage Wiza

Condenser: **Total**

Reboiler: *Kettle*

Valid phases: *Vapor-Liquid*

Convergence: *Standard*

Operating specifications

Distillate rate: *Mass* **150** kg/hr

Reflux ratio: *Mole* **3**

**Figure 6.25** In “Configuration” tab window, condenser and reboiler type, # of stages, and two operating specifications are defined.

Control Panel x Main Flowsheet x **DSTL Specifications** x

Configuration **Streams** Pressure Condenser

Feed streams

	Name	Stage	Convention
▶	RECT-TOP	<b>6</b>	<i>Above-Stage</i>

Product streams

	Name	Stage	Phase	
▶	DSTL-TOP	<b>1</b>	<b>Liquid</b>	M
▶	DSTL-BTM	<b>12</b>	<b>Liquid</b>	M

**Figure 6.26** Location of the feed tray (#6 from the top) for “DSTL” column.



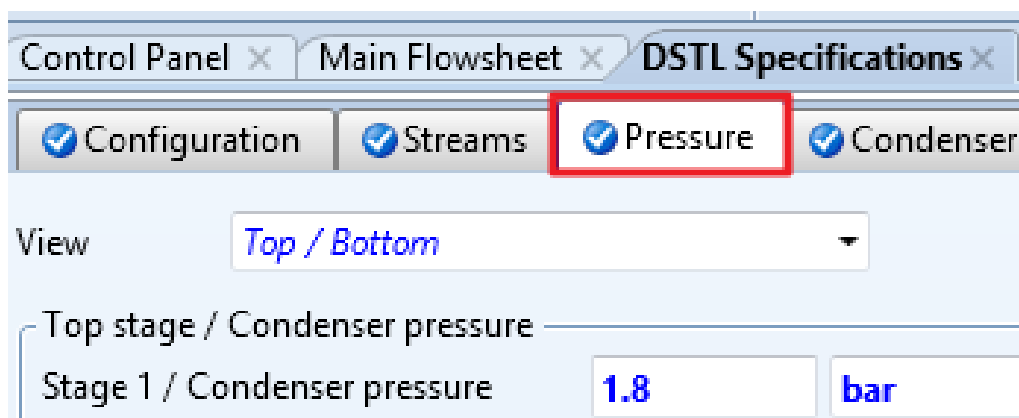


Figure 6.27 Pressure profile of “DSTL” column.

### 6.10 RUNNING THE SIMULATION (PFR + CMPRSSR + RECTIF + DSTL)

Reinitialize, click on “OK” button twice, click on (Next) button, and on “OK” button. See “Control Panel” if there is an error or serious warning regarding the process simulation.

Figure 6.28 shows a portion of the results, which pertains to the recently added piece of equipment (*i.e.*, “DSTL”).

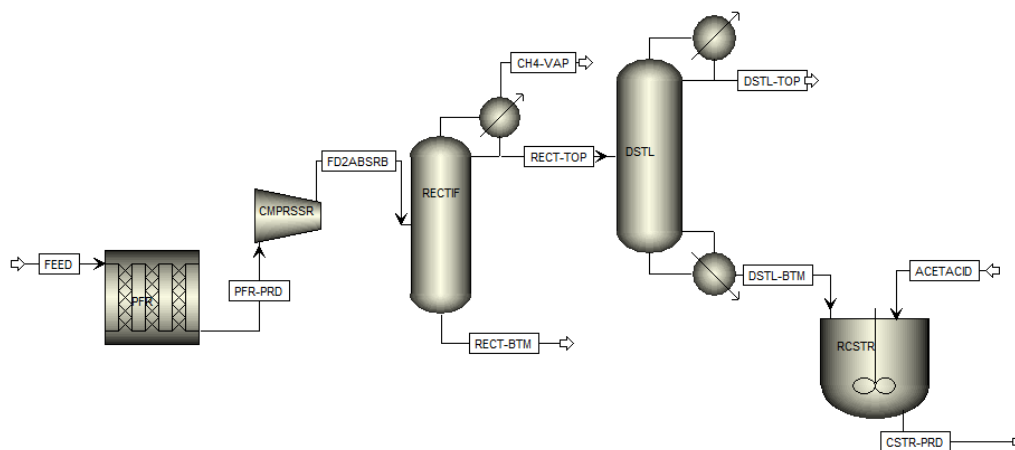
	RECT-TOP ▾	DSTL-TOP ▾	DSTL-BTM
Temperature C	-130	-154	-49.6
Pressure bar	1.8	1.8	1.8
Vapor Frac	0	0	0
Mole Flow kmol/hr	37.194	9.35	27.844
Mass Flow kg/hr	1309.54	150	1159.54
Volume Flow cum/hr	1.724	0.365	1.55
Enthalpy Gcal/hr	-0.698	-0.198	-0.469
Mass Frac			
CH <sub>3</sub> COCH <sub>3</sub>	trace		
C <sub>2</sub> H <sub>2</sub> O	0.88	trace	0.994
CH <sub>4</sub>	0.12	1	0.006
CH <sub>3</sub> COOH			
ACET-ANH			

Figure 6.28 The “RadFrac” type distillation column (“DSTL”) successfully separated the methane/ketene mixture (“RECT-TOP”) into two extra pure streams: “DSTL-TOP” ( $Y_{\text{CH}_4} = 1.0$ ) and “DSTL-BTM” ( $Y_{\text{CH}_2\text{CO}} = 0.994$ ).

Of course, methane can be used either as a precursor for other chemical industries or as a fuel (*i.e.*, source of energy). On the other hand, ketene will be finally sent to the second reactor where it reacts with acetic acid to form acetic anhydride.

## 6.11 REACTOR AND REACTION SPECIFICATIONS FOR RCSTR

Figure 6.29 shows that a rigorous CSTR (“RCSTR”) is added for carrying out the second reaction, that is, reaction of ketene with acetic acid to form acetic anhydride. In addition, acetic acid (“ACETACID”) stream is also added to the inlet of the new reactor.



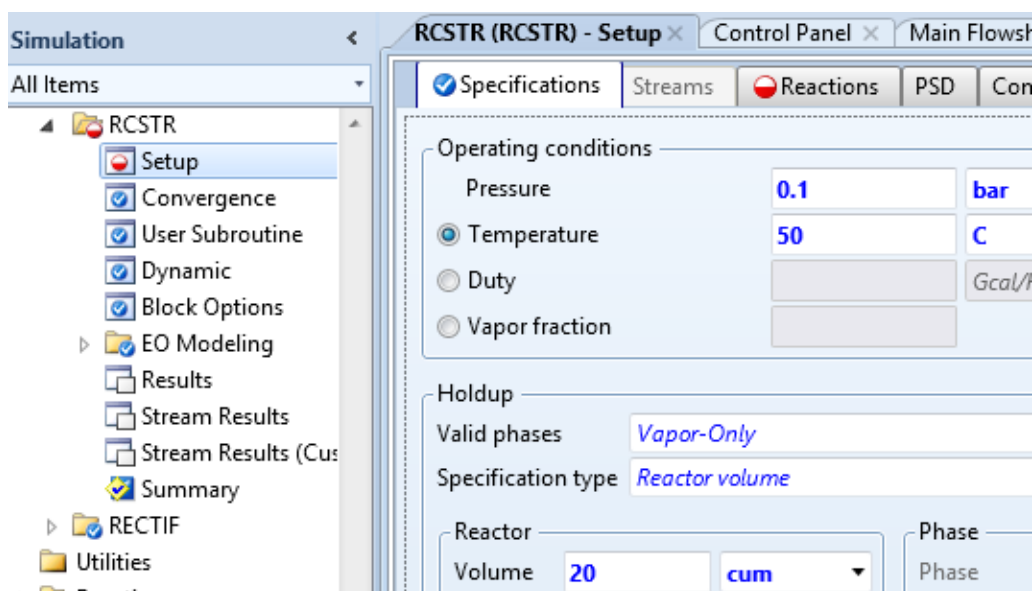
**Figure 6.29** Addition of a Rigorous CSTR (“RCSTR”) for the sake of carrying out the second reaction, that is, reaction of ketene with acetic acid to form acetic anhydride.

Click on “NEXT” button and Aspen Plus will bring you to the input form of “ACETACID” stream. Here, the molar flow rate (kmol/h) of acetic acid will be equal to that of ketene present in “DST-BTM” stream. Figure 6.30 shows the “Mixed” tab input form of “ACETACID” stream.

Component	Mole-Flow (kmol/hr)
CH3COCH3	
C2H2O	
CH4	
CH3COOH	27.44

**Figure 6.30** Entering stream properties via “Mixed” tab window under “Input” sheet of “ACETACID” stream.

Click on “Next” button and Aspen Plus will bring you to “RCSTR” | “Setup” window. Figure 6.31 shows that a temperature of 50°C and a pressure of 0.1 bar were entered for the reactor condition. As a result of very low pressure, the reaction will be carried out in vapor phase (see Exercise 6.3). Twenty cubic meter is assumed as the reactor volume.

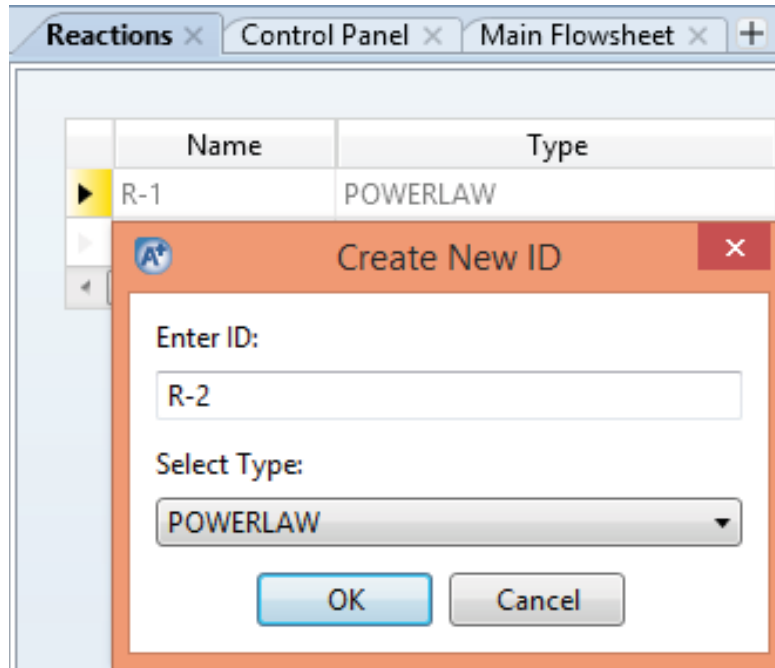


**Figure 6.31** The reactor conditions in terms of pressure, temperature, reaction phase, and reactor volume.

Now, it is time for defining the type of reaction in this reactor. Since we do not have the reaction kinetics (the rate constant, activation energy, and reaction order), then we will assume that the reaction attains equilibrium. If the reaction kinetic data is available, then the reaction type must be converted from equilibrium to kinetic so that reaction products will be better estimated.

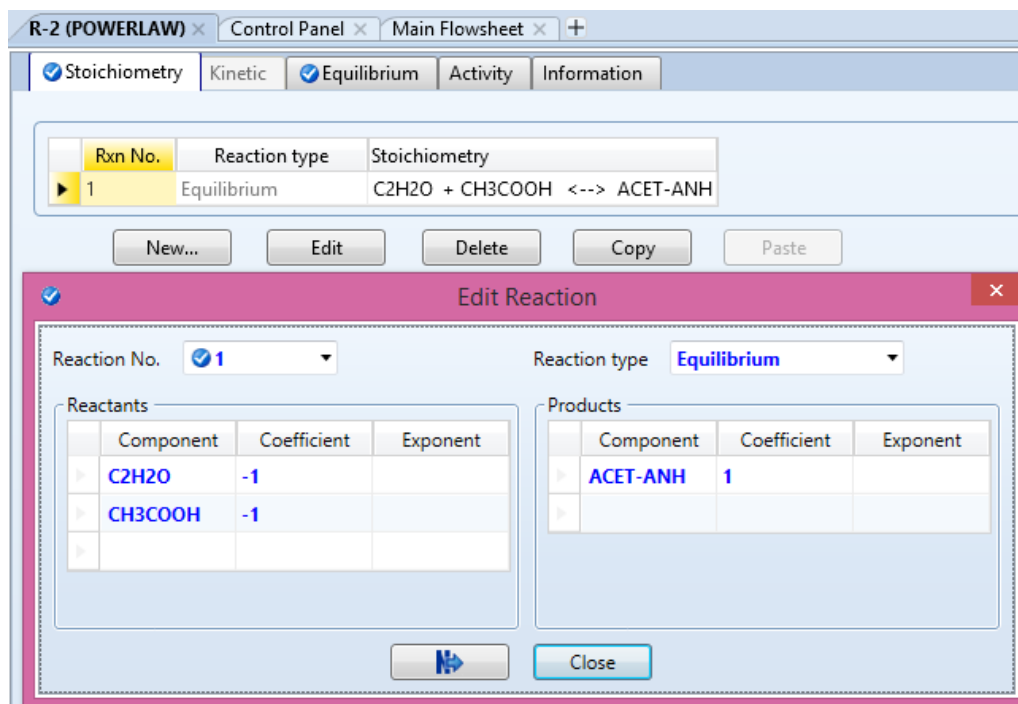
For equilibrium reactions, ASPEN can predict or calculate equilibrium data. Let us go and define the reaction first, and then get back to “Reactions” tab under “RCSTR” | “Setup” window (shown as a half-filled red circle in Figure 6.31). Go to “Reactions” folder in “Navigation” pane so that we can define a new reaction that will account for the conversion of acetic acid and ketene into acetic anhydride. The “Reactions” window has already “R-1” reaction set.

As we have dealt with the previous reaction “R-1” set, click on the “New ...” button and you will be prompted by a window similar to that shown in Figure 6.32.



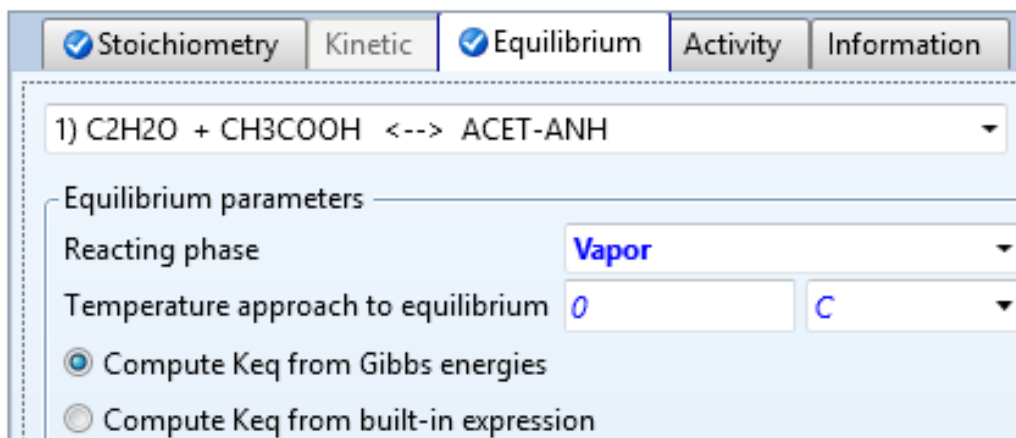
**Figure 6.32** The new reaction is given the ID of “R-2” and it is of type “POWERLAW”.


Click on “OK” button shown in Figure 6.32 and Aspen Plus will revert to “Stoichiometry” tab window where we need to define the stoichiometry of the equilibrium reaction. Click on “New ...” button at the bottom of the “Stoichiometry” tab window, the “Edit Reaction” window will pop-up as shown in Figure 6.33, where we enter the stoichiometry of each reacting species, whether it is reactant or product, and the reaction type.



**Figure 6.33** Enter  $-1$  for reactant coefficient and  $+1$  for product coefficient and choose “Reaction type” as “Equilibrium”.

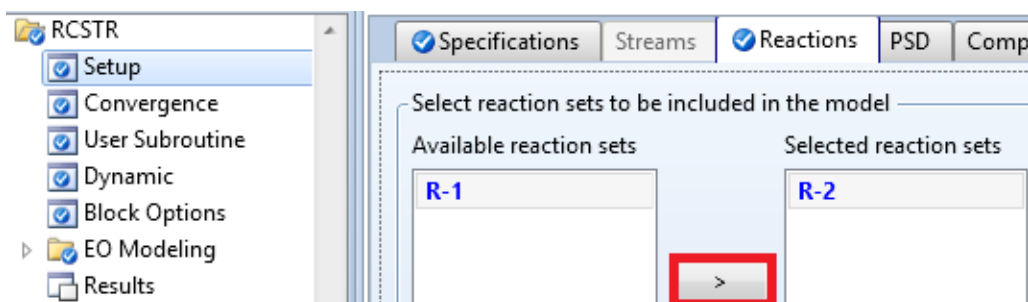
Click on “N→” button at the bottom of the “**Edit Reaction**” window and Aspen Plus will bring you back to reaction **R-2** window. Click on “**Equilibrium**” tab and its window will show up as in Figure 6.34. Select the reacting phase as vapor and select the first choice. If  $K_{eq} = f(T)$  is given, then you may go with the second option.



**Figure 6.34** In “**Equilibrium**” tab window, choose the reaction phase to be “*Vapor*” and select the first choice (i.e.,  Compute Keq from Gibbs energies).

You will notice that everything is now defined for Aspen Plus except for “**RCSTR**” block where we need to associate “**R-2**” reaction set with “**RCSTR**” block.

Click on “**Next→**” button and Aspen Plus will bring you to “**RCSTR**” block as shown in Figure 6.35. Highlight **R-2** from the “**Available reaction sets**” and move it to the “**Selected reaction sets**” side.



**Figure 6.35** Association of “**RCSTR**” with “**R-2**” reaction set.

After selecting “**R-2**” reaction set, the blue checkmark will replace the half-filled red circle.

## 6.12 RUNNING THE SIMULATION (PFR + CMPRSSR + RECTIF + DSTL + RCSTR)

Aspen Plus is ready to start the simulation. Click on “**Reset**” followed by “**Next→**” button and Aspen Plus will start the process of simultaneously solving the set of steady-state total mass-balance, component mass-balance, and energy-balance equations around each block, augmented by all thermodynamic and equation of state relationships.

Check “**Control Panel**” to see if there is any error or serious warning.

Figures 6.36 and 6.37 show the simulation results pertaining to “**RCSTR**” block.

RCSTR (RCSTR) - Results		
Control Panel		
Main Flowsh		
Summary	Balance	Utility Usage
Distributions	Polym	
▶ Outlet temperature	50	C
▶ Outlet pressure	0.1	bar
▶ Outlet vapor fraction	1	
▶ Heat duty	-144.024	kW
▶ Net heat duty	-144.024	kW
▶ Volume		
▶ Reactor	20	cum
▶ Vapor phase	20	cum
▶ Liquid phase		
▶ Liquid 1 phase		
▶ Salt phase		
▶ Condensed phase		
▶ Residence time		
▶ Reactor	9.70341	sec
▶ Vapor phase	9.70341	sec


**Figure 6.36** The heat duty, the reactor volume, and the residence time for “**RCSTR**” block. A reactor volume of 20 m<sup>3</sup> is needed with a residence time of 9.7 s and the heat of reaction is exothermic.

	DSTL-BTM	ACETACID	CSTR-PRD
Temperature C	-49.6	25	50
Pressure bar	1.8	1	0.1
Vapor Frac	0	0	1
Mole Flow kmol/hr	27.844	27.44	27.865
Mass Flow kg/hr	1159.54	1647.84	2807.38
Volume Flow cum/hr	1.55	1.536	7420.07
Enthalpy Gcal/hr	-0.469	-3.168	-3.761
Mass Frac			
CH <sub>3</sub> COCH <sub>3</sub>			
C <sub>2</sub> H <sub>2</sub> O	0.994		56 PPM
CH <sub>4</sub>	0.006		0.002
CH <sub>3</sub> COOH		1	443 PPM
ACET-ANH			0.997

**Figure 6.37** The inlet and outlet streams of “RCSTR” block plus their properties in terms of flow rate,  $P$ ,  $T$ , and composition.

Finally, notice that the mass fraction of acetic anhydride in the product stream is 0.997 with trace amounts of other chemical species.

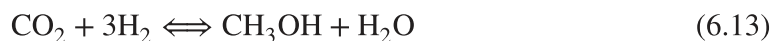
### EXERCISE 6.3

Under “**Properties**” environment, go to “**Home**” ribbon | “**Analysis**” tab | and click on “**Mixture Analysis**” (  ) button and create a mixture analysis case study. Verify that that an equimolar mixture of ketene and acetic acid at 50°C and 0.1 bar (“RCSTR” condition) will be in the vapor phase not in the liquid phase. Use the property set “TXPORT” to tell whether or not we have a vapor mixture at the given conditions of  $P$  and  $T$ .

### 6.13 SENSITIVITY ANALYSIS: THE REACTOR'S OPTIMUM OPERATING CONDITIONS

At the end of this chapter, we show an example to demonstrate the parametric plot for one dependent variable as a function of two independent variables. The advantage is to see how the dependent variable changes as a function of both independent variables; hence, we will have the chance to see the function topology in terms of minimum and maximum points.

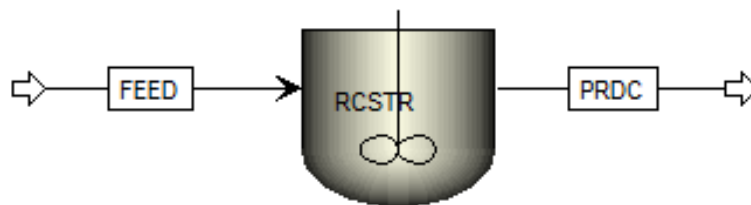
Methanol is widely used as an industrial feedstock and may become an alternative energy resource. It is mainly produced from a mixture of carbon monoxide, carbon dioxide, and hydrogen under high pressure and temperature using Cu/ZnO-based catalysts. Synthesis of methanol involves three main reactions [2]:



We will test the synthesis of methanol under equilibrium conditions using the rigorous CSTR (**RCSTR**) model. The pressure can vary between 15 and 75 bar and temperature between 450 and 550 K.

The feed stream enters the reactor at 500 K and 50 bar with 1/3 mole fraction equally for CO, CO<sub>2</sub>, and H<sub>2</sub>. The total molar flow rate can be set 99 kmol/h. The same reactor conditions are assumed as those of the feed in terms of *P* and *T*. The reactor volume is assumed 5 m<sup>3</sup>. The goal is to maximize the selectivity of methanol production. To achieve this, we will carry out the following steps:

1. Choose “**Chemicals with Metric Units**” template to create a steady-state flowsheet as shown in Figure 6.38. As the pressure is higher than 10 bar, the property model can be “**PSRK**” with “**Free-water method**” set to “**STEAMNBS**”, under “**Methods**” | “**Specifications**” | “**Global**” sheet.



**Figure 6.38** Testing methanol synthesis via the rigorous-CSTR (**RCSTR**) model.



2. Add the five components: CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, and CH<sub>3</sub>OH.
3. Under “**Properties**” environment, go to “**Estimation**” | “**Input**” | “**Setup**” sheet and be sure that the “*Estimate all missing parameters*” option is affirmed. Click “**Reset**” followed by “**Next**” button to run the simulation and assure that properties analysis completed successfully. Switch to “**Simulation**” environment.
4. Define three “**POWERLAW**” type equilibrium reactions as shown in Figure 6.39.

<input checked="" type="checkbox"/> Stoichiometry    Kinetic <input checked="" type="checkbox"/> Equilibrium    Activity    Information			
	Rxn No.	Reaction type	Stoichiometry
	1	Equilibrium	CO + 2 H <sub>2</sub> <--> CH <sub>3</sub> OH
	2	Equilibrium	CO <sub>2</sub> + 3 H <sub>2</sub> <--> CH <sub>3</sub> OH + H <sub>2</sub> O
	3	Equilibrium	CO + H <sub>2</sub> O <--> CO <sub>2</sub> + H <sub>2</sub>

**Figure 6.39** Defining the three equilibrium reactions involved in methanol synthesis.

5. In “**Navigation**” pane and under “**Model Analysis Tools**” folder | “**Sensitivity**” subfolder, create “**S-1**” set. In “**Vary**” tab window, vary both  $T$  and  $P$  as block (“**RCSTR**”) variables between 180 and 280°C with an increment of 20°C for  $T$  and between 15 and 75 bar with an increment of 10 bar for  $P$ , as shown in Figure 6.40 for “**RCSTR**”  $T$  &  $P$  variable. In “**Define**” tab window, define the sensitivity variable as the mole fraction of methanol (**MF METH**) in the product (**PRDC**) stream. In “**Tabulate**” tab window, tabulate “**MF METH**”.

☒ Vary ☒ Define ☒ Tabulate Options Cases Fortran Declarations Information

☒ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

	Variable	Active	Manipulated variable	
▶ 1		<input checked="" type="checkbox"/>	Block-Var Block=RCSTR Variable=TEMP Sentence=PARAM	C
▶ 2		<input checked="" type="checkbox"/>	Block-Var Block=RCSTR Variable=PRES Sentence=PARAM	bar

New... Delete Copy Paste

Edit selected variable

Manipulated variable

Variable: 1

Type: Block-Var

Block: RCSTR

Variable: TEMP

Sentence: PARAM

Units: C

Manipulated variable limits

☒ Specify limits

Lower: 180 C

Upper: 280 C

☐ Number of points: 6

☒ Increment: 20 C

☐ List of values

Manipulated variable

Variable: 2

Type: Block-Var

Block: RCSTR

Variable: PRES

Sentence: PARAM

Units: bar

Manipulated variable limits

☒ Specify limits

Lower: 15 bar

Upper: 75 bar

☐ Number of points: 7

☒ Increment: 10 bar

☐ List of values

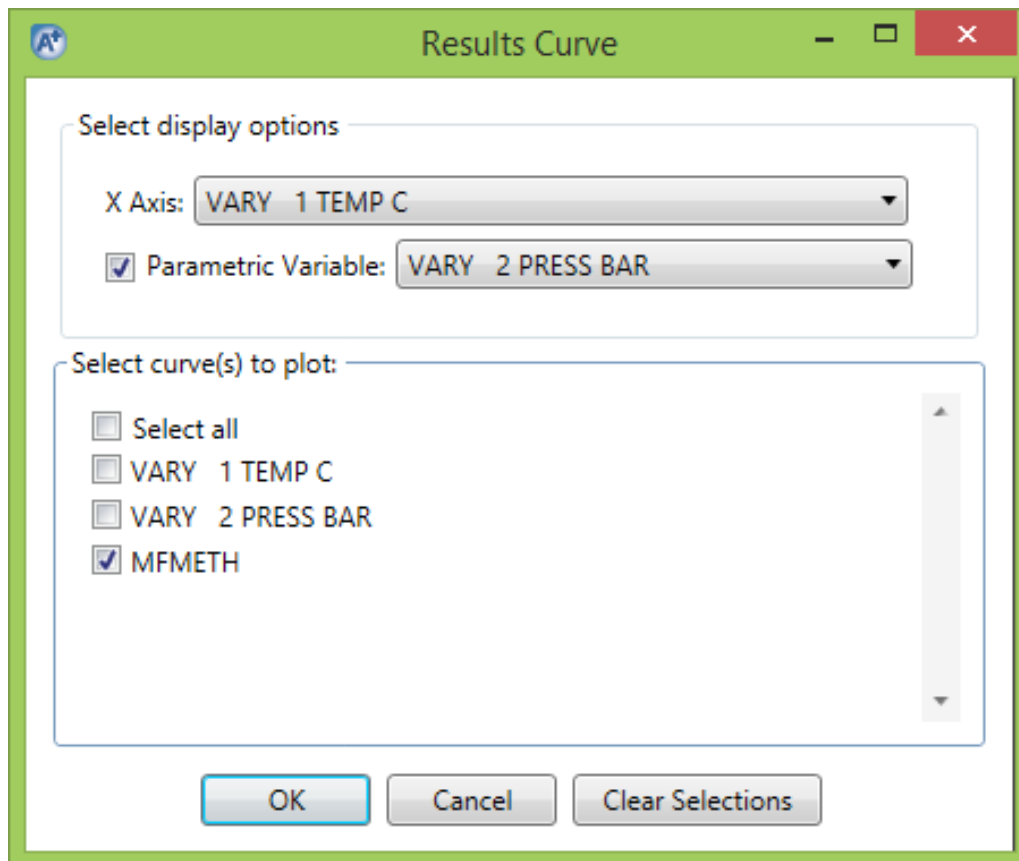
**Figure 6.40** *T & P of the reactor will be varied to see how they affect the reaction performance.*

6. Reinitialize and run the show. The Sensitivity (**S-1**) results are shown in Figure 6.41.

Row/Case	Status	VARY 1 TEMP	VARY 2 PRESS	MF METH
		C	BAR	
1	OK	180	15	0.0532831
2	OK	180	25	0.0832499
3	OK	180	35	0.108987
4	OK	180	45	0.132262
5	OK	180	55	0.15406
6	OK	180	65	0.193963
7	OK	180	75	0.467996
8	OK	200	15	0.0365432
9	OK	200	25	0.0619424
10	OK	200	35	0.0838891

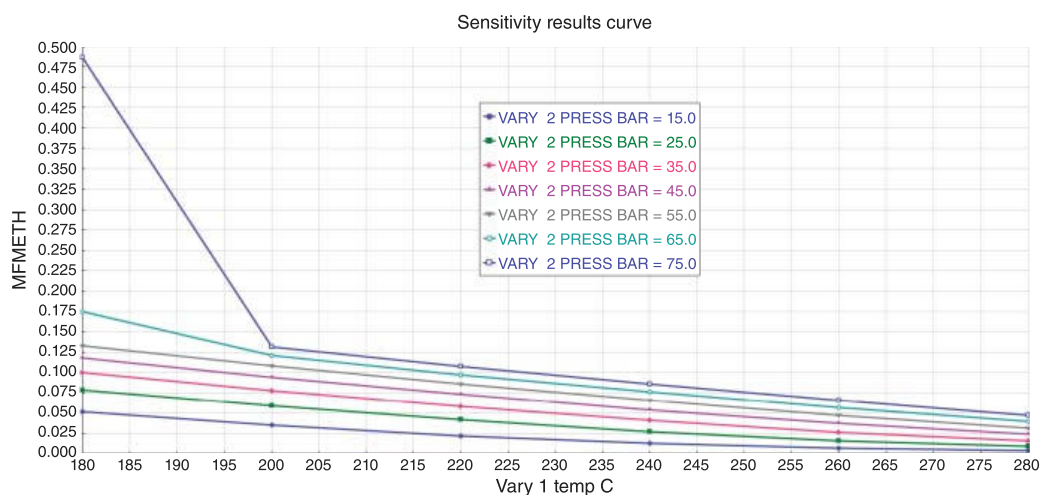
**Figure 6.41** A portion of sensitivity analysis results where both  $T$  and  $P$  are varied to see their effects on **MF METH**.

- While the “S-1” summary of results window (*i.e.*, Figure 6.41) is active, click on “Home” ribbon | “Plot” group | “Results Curve” button and the “Results Curve” window will show up, as shown in Figure 6.42. Select  $T$  as X-Axis,  $P$  as the parametric variable, and **MF METH** as the dependent variable (*i.e.*, Y-Axis).



**Figure 6.42** The “Results Curve” window where the user decides on X, Y, and the parametric variable.

8. Click on “OK” button and finally the “Sensitivity Results Curve” plot will show up as in Figure 6.43, which shows  $\text{MF METH} = f(P, T)$ . **MF METH** is maximum at high  $P$  and low  $T$ .



**Figure 6.43** The effect of **RCSTR** operating conditions  $P$  and  $T$  on **MF METH** (*i.e.*, conversion).

9. Change “**RCSTR**”  $P$  and  $T$  to 75 bar and 180°C (453 K), respectively. In “**Navigation**” pane and under “**Model Analysis Tools**” | “**Sensitivity**” | “**S-1**” sheet, right-click on “**S-1**” and select **Deactivate** command from the shortcut context menu. This means that “**S-1**” analysis will not be included in simulation as we have already made use of it and changed “**RCSTR**” conditions to high  $P$  and low  $T$  to maximize the mole fraction of methanol (**MF METH**) in the product stream.
10. Define a new sensitivity set “**S-2**”. Figure 6.44 shows “**Vary**” tab window. The first variable (Variable no. 1) that accounts for  $H_2$  molar flow rate in **FEED** stream between 1 and 91 kmol/h with an increment of 30 kmol/h. The second variable (Variable no. 2) will be CO molar flow rate in **FEED** stream between 1 and 91 kmol/h with an increment of 30 kmol/h. On the other hand,  $CO_2$  will not be changed as we say here that **MF METH** in **PRDC** stream is a function of four linearly independent variables:  $Y_{CH_3OH} = f(P, T, Y_{H_2}, Y_{CO})$ . We have already found the best values of  $P$  and  $T$  that will maximize  $Y_{CH_3OH}$ .  $Y_{CO_2}$  is dependent on  $Y_{H_2}$  and  $Y_{CO}$ , as the summation adds up to one.

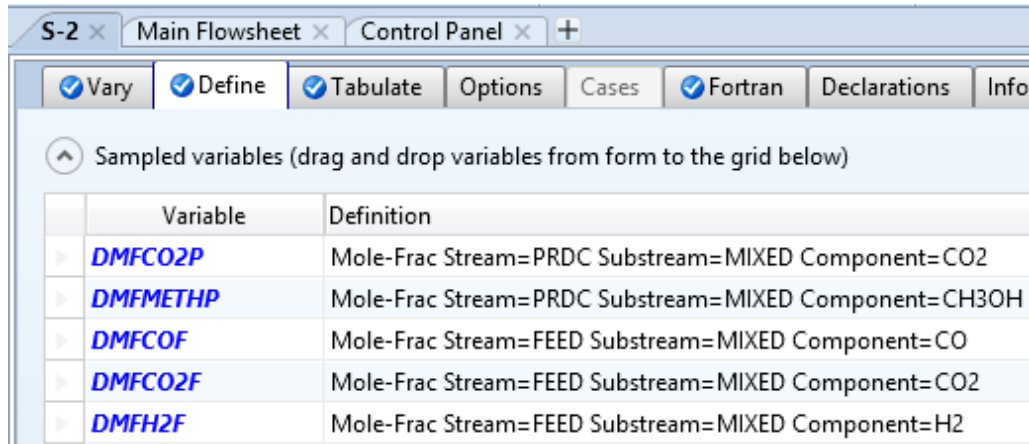
The screenshot shows the 'Vary' tab window in a simulation software. The window is divided into several sections. At the top, there are tabs for 'Vary', 'Define', 'Tabulate', 'Options', 'Cases', 'Fortran', 'Declarations', and 'Information'. Below the tabs, there are checkboxes for 'Active' (checked) and 'Case study' (unchecked). A section titled 'Manipulated variables (drag and drop variables from form to the grid below)' contains a table with two rows:

Variable	Active	Manipulated variable	Units
1	<input checked="" type="checkbox"/>	Mole-Flow Stream=FEED Substream=MIXED Component=H2	kmol/hr
2	<input checked="" type="checkbox"/>	Mole-Flow Stream=FEED Substream=MIXED Component=CO	kmol/hr

Below the table are buttons for 'New...', 'Delete', 'Copy', and 'Paste'. A section titled 'Edit selected variable' contains two panels, one for each variable. Each panel has a 'Manipulated variable' section with dropdowns for 'Variable', 'Type', 'Stream', 'Substream', 'Component', and 'Units'. The 'Manipulated variable limits' section for each variable has radio buttons for 'Specify limits', 'Number of points', 'Increment', and 'List of values'. For both variables, 'Specify limits' is selected, with 'Lower' set to 1 and 'Upper' set to 91 kmol/hr. The 'Increment' is set to 30 kmol/hr.

**Figure 6.44** The feed molar flow rate of  $H_2$  and CO will be varied to see how they affect the reaction performance.

11. Figure 6.45 shows the “**Define**” tab window, which includes the composition of feed and product stream. The variables are prefixed by “**D**”, as in **FORTTRAN** code, to treat all variables as real or double not integer (with prefix “**M**”).



**Figure 6.45** The “**Define**” tab window, which includes the composition of feed and product stream. The variables are prefixed by “**D**”, in compliance with **FORTTRAN** code, to treat all variables as double not integer (prefix “**M**”).

12. Under “**Fortran**” tab, define the following three variables:

$$\mathbf{RCOCO2} = \mathbf{DMFCOF/DMFCO2F}$$

$$\mathbf{RCOH2} = \mathbf{DMFCOF/DMFH2F}$$

$$\mathbf{RMETHCO2} = \mathbf{DMFMETHP/DMFCO2P}$$

The first represents  $(Y_{\text{CO}}/Y_{\text{CO}_2})_{\text{FEED}}$ ; the second  $(Y_{\text{CO}}/Y_{\text{H}_2})_{\text{FEED}}$ ; and the third  $(Y_{\text{CH}_3\text{OH}}/Y_{\text{CO}_2})_{\text{PRDC}}$ . Again, we have only two linearly independent ratios out of three, which describe the composition of **FEED** stream. The higher the value of the third term (**RMETHCO2**), the higher will be the selectivity of  $\text{CH}_3\text{OH}$  over  $\text{CO}_2$  (the undesired side product *via* the third reaction).

13. Under **Tabulate** tab, include the following set of variables:

1. **RCOCO2**
2. **RCOH2**
3. **DMFMETHP**
4. **RMETHCO2**

14. Reinitialize and run the show.

15. Figure 6.46 shows the values of **DMFMETHP** and **RMETHCO2** in **PRD** stream as a function the molar feed ratios **RCOCO2** and **RCOH2**. The maximum yield and selectivity occurs at **RCOCO2** = 0.0303 and **RCOH2** = 0.0105. The feed composition will be

Row/Case	Status	VARY 1 FEED MIXED H <sub>2</sub> MOLEFLOW KMOL/HR	VARY 2 FEED MIXED CO MOLEFLOW KMOL/HR	RCOCO2	RCOH2	DMFMETHP	RMETHCO2
12	OK	61	91	2.75758	1.4918	0.224058	0.867558
13	OK	91	1	0.030303	0.010989	0.433511	5.87755
14	OK	91	31	0.939394	0.340659	0.381014	1.12311
15	OK	91	61	1.84848	0.67033	0.428749	1.29531
16	OK	91	91	2.75758	1	0.334343	1.30584
17	OK	95	1	0.030303	0.0105263	0.467996	11.1451

**Figure 6.46** The sensitivity analysis results showing the best feed molar ratios where both the yield and selectivity are maximum.

$$Y_{H_2} = 95/(95 + 1 + 33) = 0.7364; Y_{CO} = 1/(95 + 1 + 33) = 0.0078;$$

$$Y_{CO_2} = 33/(95 + 1 + 33) = 0.2558$$

Also, from the given molar feed ratios, evaluated at the maximum yield and selectivity

$$\sum_{i=1}^N Y_i = 1 : Y_{CO} + Y_{CO_2} + Y_{H_2} = 1 = Y_{CO} + (1/RCOCO2) \times Y_{CO} + (1/RCOH2) \times Y_{CO}$$

$$= Y_{CO} [1 + (1/33.00) + (95.00)] = 1 \rightarrow Y_{CO} = 1/129 = 0.0078.$$

In doing so, we have optimized the reactor performance in terms of  $P$ ,  $T$  through “S-1” analysis and feed molar composition through “S-2” analysis, where both analyses when combined will give the maximum yield and selectivity. Consequently and based on “S-2” analysis, the best feed molar composition will be 73.64 mol% H<sub>2</sub>; 25.58 mol% CO<sub>2</sub>; and 0.78 mol% CO.

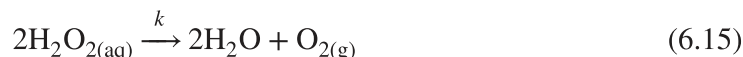
## REFERENCES

- [1] Fogler, H.S. (2006) Elements of Chemical Reaction Engineering, 4th edn, Pearson Education, Inc., New Jersey.
- [2] Lim, H.W., Park, M., Kang, S. *et al.* (2009) Modeling of the kinetics for methanol synthesis using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst: Influence of carbon dioxide during hydrogenation. *Industrial and Engineering Chemistry Research*, **48** (23), 10448–10455.
- [3] Hangx, G., Kwant, G., Maessen, H., *et al.* (2001) Reaction Kinetics of the Esterification of Ethanol and Acetic Acid Towards Ethyl Acetate, Intelligent Column Internals for Reactive Separations (INTINT), Deliverable 22, 2001.

**HOMEWORK/CLASSWORK 6.1 (HYDROGEN PEROXIDE SHELF-LIFE)**

Hydrogen peroxide 3 wt% solution (active ingredient:  $\text{H}_2\text{O}_2$ ) is an antiseptic oral debriding agent, which can be used as a first aid to help prevent the risk of infection in minor cuts, scrapes, and burns. Moreover, it helps in the removal of phlegm, mucus, or other secretions associated with occasional sore mouth; however, it must be externally used.

Consider the decomposition of  $\text{H}_2\text{O}_2$ :



With Arrhenius kinetics:

$$k = 4.80 \times 10^8 e^{(-78,683.7/RT)} \quad (6.16)$$

where  $k$  has unit of  $\text{s}^{-1}$  and the reaction order is one with respect to  $\text{H}_2\text{O}_2$ . Let us analyze how the concentration of  $\text{H}_2\text{O}_2$  will drop with time if we keep the bottle both at room temperature ( $25^\circ\text{C}$ ) and inside the household refrigerator ( $5^\circ\text{C}$ ). To simulate the bottle, we will use **RBATCH** model where we allow the reaction to take place and we will stop the reaction when the conversion reaches 90%, or the mass fraction of  $\text{H}_2\text{O}_2$  drops from 0.03 to 0.003. The time will be reported by Aspen Plus simulator. To achieve this goal, carry out the following steps:

1. Choose “**Specialty Chemicals with Metric Units**” template to create the process flow-sheet. The default property model will be “**NRTL**”.
2. Add the three components:  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}_2$ .
3. In “**Navigation**” pane, select  $\text{O}_2$  as Henry component by creating “**HC-1**” set under “**Components**” | “**Henry Comps**”.
4. Select “**HC-1**” from the drop-down list in “**Methods**” | “**Specifications**” | “**Global**” tab window.
5. Go to “**Methods**” | “**Parameters**” | “**Binary Interaction**” | “**NRTL-1**” sheet and be sure that the “*Estimate missing parameters by UNIFAC*” option is selected. Click “**Reset**” followed by “**Next**” button to run the simulation and assure that properties analysis completed successfully. See NOTE #2 for: *WARNING IN PHYSICAL PROPERTY SYSTEM*.
6. Switch to “**Simulation**” environment.
7. From the “**Model Palette**”, under “**Reactors**” tab, select “**RBATCH**” and add it to your open project. Add two streams one for the batch at time zero and another for the product at the end of the batch time. Your flowsheet should be similar to that shown in Figure 6.47.



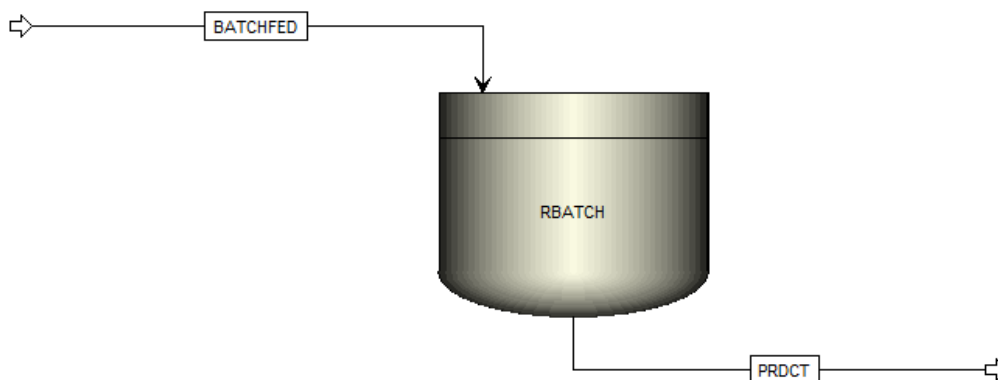


Figure 6.47 Visualization of  $\text{H}_2\text{O}_2$  bottle as “RBATCH” type reactor.

8. The “BATCHFED” stream has 97 kg/h  $\text{H}_2\text{O}$  and 3 kg/h  $\text{H}_2\text{O}_2$  at 1 bar and  $25^\circ\text{C}$ .
9. The simulation will be carried out twice: first, at room temperature ( $25^\circ\text{C}$ ) and 1 bar, and the second, at household refrigerator temperature ( $5^\circ\text{C}$ ) and 1 bar. This will demonstrate the effect of temperature on the shelf-life of the peroxide within the bottle if we keep it outside or inside the refrigerator, respectively.
10. In “Navigation” pane, under “Reactions” folder, define the aforementioned reaction (Eq. 6.15) named **R-1** as kinetic type and enter the kinetic parameters (Eq. 6.16) in “Kinetic” tab window. Notice that the reaction phase is liquid and [Ci] basis is molarity.
11. In “Blocks” | “RBATCH” | “Setup” | “Specifications” tab window, enter the data as shown in Figure 6.48.

Figure 6.48 “RBATCH” reactor specifications (constant  $P$  &  $T$ ).

12. In “Reactions” tab window, associate “R-1” with “RBATCH” reactor.
13. In “Stop Criteria” tab window, enter the data as shown in Figure 6.49.

Stop criteria	
Criterion no.	1
Location	Reactor
Variable type	Conversion
Stop value	0.9
Unit	
Component	H2O2
Substream	MIXED
Property set ID	
Approach from	Below

**Figure 6.49** The stop criteria to stop the reaction and report the batch time whenever  $\text{H}_2\text{O}_2$  conversion of 0.9 is reached.

14. In “**Operation Times**” tab window, enter the data as shown in Figure 6.50.

<input checked="" type="checkbox"/> Specifications <input checked="" type="checkbox"/> Reactions <input checked="" type="checkbox"/> Stop Criteria <input checked="" type="checkbox"/> Operation Times	
Batch cycle time	
<input type="radio"/> Total cycle time:	1 month
<input checked="" type="radio"/> Batch feed time:	1 sec
Down time:	0 hr
Profile result time	
Maximum calculation time:	1 month
Time interval between profile points:	1 day
Maximum number of profile points:	32

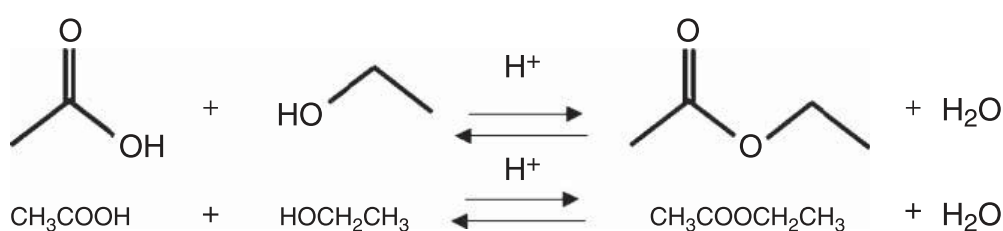
**Figure 6.50** The batch feed time for  $\text{H}_2\text{O}_2$  bottle will be very short and no need for down time, unlike the real batch reactors where they require loading/unloading time.

15. Reinitialize and run the show.
16. Report the reaction time (in hours or days) under “**RBATCH**” | “**Results**” | “**Summary**” tab form until the mass fraction of  $\text{H}_2\text{O}_2$  drops to 0.003 from the initial value 0.03.

17. For the second run, that is, the batch reactor temperature will be 5°C not 25°C. Report the reaction time in hours or days. Compare both values. Do you recommend keeping the bottle of H<sub>2</sub>O<sub>2</sub> solution inside the room (25°C) or inside the refrigerator (5°C)?

### HOMEWORK/CLASSWORK 6.2 (ESTERIFICATION PROCESS)

Consider the reaction between ethanol and acetic acid to produce ethyl acetate and water, or what is called esterification process (Figure 6.51):



**Figure 6.51** A schematic symbolizes the reaction between acetic acid and ethanol to produce ethyl acetate (an ester) and water (the esterification process).

The following kinetic data were quoted from Hangx *et al.* [3]. Purolite CT179 was used as a catalyst, which is a porous cation exchange resin, containing sulfonic acid groups. The particle diameter was 0.6–1.4 mm. The typical porosity is assumed to be 0.5.

Using such a catalyst, it was found that the reaction is first order with respect to ethanol and 1.5<sup>th</sup> order with respect to acetic acid. The reaction rate constant is described by Arrhenius kinetics for both forward and backward directions:

$$r_f = k_1 x_{\text{ETOH}} x_{\text{ACOH}}^{1.5} = \left( 4.24 \times 10^3 (\text{kmol/kg cat} \cdot \text{s}) \times e^{-\frac{48,300}{RT}} \right) x_{\text{ETOH}} x_{\text{ACOH}}^{1.5} \quad (6.18)$$

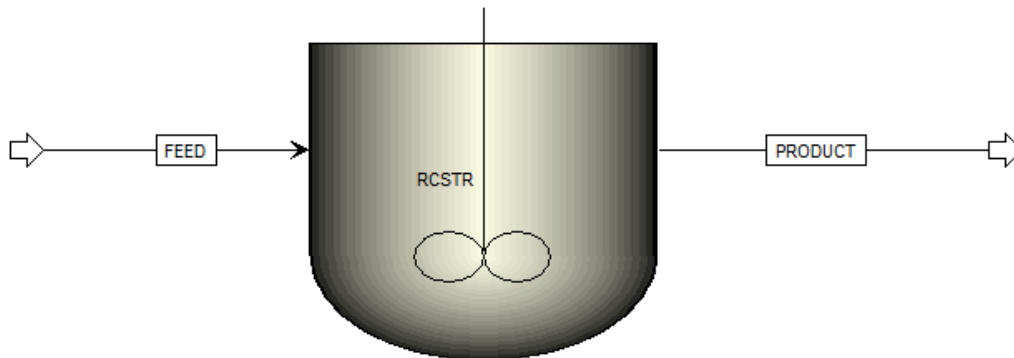
$$r_b = k_2 x_{\text{ETOAC}} x_{\text{H}_2\text{O}} = \left( 4.55 \times 10^5 (\text{kmol/kg cat} \cdot \text{s}) \times e^{-\frac{66,200}{RT}} \right) x_{\text{ETOAC}} x_{\text{H}_2\text{O}} \quad (6.19)$$

where  $x$  represents the mole fraction of a given component. Remember that, according to Aspen Plus built-in help, the reaction rate must be expressed as kmol/kg cat · s (see Eqs. 6.10 and 6.11). The authors reported the value as mol/kg catalyst · s; that is why we have to adjust the basis.

Since the lowest normal boiling point is 77.1°C for ethyl acetate (**ETOAC**), we can run the reaction at 1 atm. and a temperature less than 77.1°C. Alternatively, we can elevate the pressure inside the reactor, which will grant us the luxury to increase the temperature above 77.1°C. Execute the following steps:

1. Choose “**Chemicals with Metric Units**” template to create the process flowsheet. The default property model will be “**NRTL**”.
2. Add the four components, shown in Figure 6.51, to components list.

- Go to “**Methods**” | “**Parameters**” | “**Binary Interaction**” | “**NRTL-1**” sheet and be sure that the “*Estimate missing parameters by UNIFAC*” option is selected. Click “**Reset**” followed by “**Next**” button to run the simulation and assure that properties analysis completed successfully. Switch to “**Simulation**” environment.
- From the “**Model Palette**”, under “**Reactors**” tab, select “**RCSTR**” and add it to your open project. Add two streams one for the feed and another for the product. Your flow-sheet should be similar to that shown in Figure 6.52.



**Figure 6.52** The flowsheet for ethyl acetate production using “RCSTR” type reactor.

- Set the feed stream at 2 atm. and 100°C with a flow rate of 50 kmol/h for each of “ACOH” and “ETOH” reactant.
- Define the forward and backward reactions given by Equations (6.17), (6.18), and (6.19). The type of reaction is “POWERLAW” with “Kinetic” type, as shown in Figure 6.53. Notice that reaction #1 stands for the forward and #2 for the backward direction.

Main Flowsheet

Control Panel

R-1 (POWERLAW)

+

Stoichiometry

Kinetic

Equilibrium

Activity

Information

	Rxn No.	Reaction type	Stoichiometry
▶	1	Kinetic	ACOH + ETOH --> ETOAC + H2O
▶	2	Kinetic	ETOAC + H2O --> ACOH + ETOH

New...

Edit

Delete

Copy

**Figure 6.53** “R-1” reaction set is resolved into two kinetic reactions the forward and backward direction.

7. In **Kinetic** tab window, enter the Arrhenius kinetic parameters, the rate basis (*i.e.*, Cat (wt)), the reacting phase, and [Ci] basis as mole fraction for both the forward and backward reactions.
8. In “**Blocks**” | “**RCSTR**” | “**Setup**” | “**Specifications**” tab window, enter 2 atm for pressure; 100°C for temperature; the valid phase as liquid only; and 1 h as the residence time.
9. In “**Blocks**” | “**RCSTR**” | “**Setup**” | “**Reactions**” tab window, associate “**R-1**” with “**RCSTR**”.
10. In “**Blocks**” | “**RCSTR**” | “**Setup**” | “**Catalyst**” tab window, select the catalyst attributes as shown in Figure 6.54.

**Figure 6.54** Entering catalyst attributes as the reaction rate is expressed per unit mass of a catalyst not volume of a reactor as is the case with homogeneous reactions.

11. Reinitialize and run the show. Check for any simulation errors or warnings. Report the reactor volume for the given residence time and the composition of the product stream.
12. Carry out a sensitivity test via varying the reactor temperature between 50 and 130°C with an increment of 5°C and via defining the dependent variable as the mole fraction of ethyl acetate in the product stream. Plot the mole fraction of ethyl acetate as a function of temperature and see the optimum reactor temperature that gives the maximum amount of ethyl acetate.

### HOMEWORK/CLASSWORK 6.3 (LIQUID-PHASE ISOMERIZATION OF *n*-BUTANE)

Normal butane,  $n\text{-C}_4\text{H}_{10}$ , is to be reversibly isomerized to isobutane,  $i\text{-C}_4\text{H}_{10}$ , in a plug-flow reactor (PFR). Isobutane is a valuable product that is used in the manufacture of gasoline additives. The reaction is to be carried out adiabatically in the liquid phase under high pressure ( $P = 20$  bar) using essentially trace amounts of a liquid catalyst. Calculate the PFR and CSTR volumes necessary to process 163 kmol/h at 70% conversion of a feed mixture made of 90 mol% *n*-butane and 10 mol% *i*-pentane (2-methyl-butane), which is considered an inert. The feed enters at 330 K and 20 bar.

The kinetic data were quoted from Fogler [1] and were modified to suit Aspen Plus basis for entering the kinetic parameters and concentration.



Equation 6.20 can be resolved into forward and backward steps:



$$-r_{n\text{-C}_4} = k_1 C_{n\text{-C}_4} \quad (6.22)$$

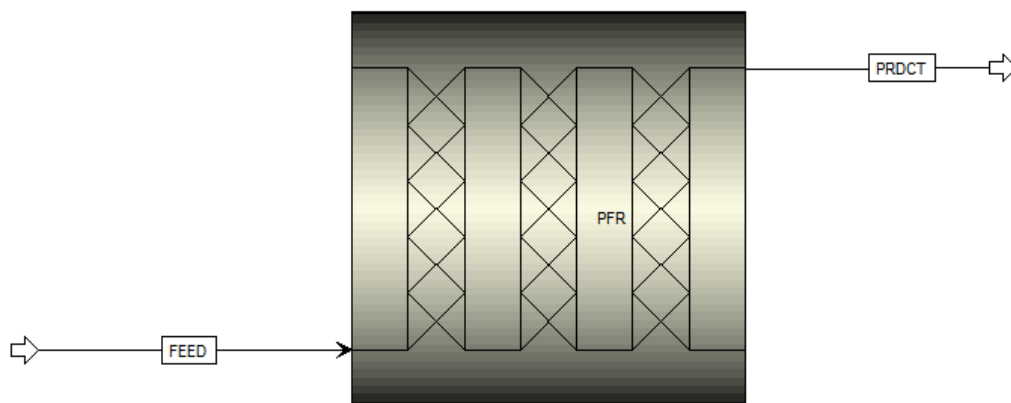
$$k_1 = 2.94 \times 10^7 (\text{s}^{-1}) \times e^{\left(-\frac{65,300}{8.314 \times T}\right)} \quad (6.23)$$



$$-r_{i\text{-C}_4} = k_2 C_{i\text{-C}_4} \quad (6.25)$$

$$k_2 = 1.176 \times 10^8 (\text{s}^{-1}) \times e^{\left(-\frac{72,200}{8.314 \times T}\right)} \quad (6.26)$$

1. Choose “**Chemicals with Metric Units**” template to create the process flowsheet. Set the default property model to be “**PENG-ROB**” for having a hydrocarbon system.
2. Add the three components – *n*-butane, isobutene, and 2-methyl-butane – to components list.
3. Click on “**Reset**” followed by “**Next**” button to run the simulation and assure that properties analysis completed successfully. Switch to “**Simulation**” environment.
4. From the “**Model Palette**”, under “**Reactors**” tab, select “**RPlug**” and add it to your open project. Add two streams one for the feed and another for the product. Your flow-sheet should be similar to that shown in Figure 6.55.



**Figure 6.55** The flowsheet for *n*-butane isomerization using “**RPlug**” type reactor.

5. Enter the feed stream properties as indicated in the problem statement.
6. For the reactor volume requirement, enter 3 m for length and 1.1 m for diameter, which will give a 2.6 m<sup>3</sup> single cylindrical tube, and select *Liquid-only* for “Valid phases”.
7. Define two “POWERLAW” reaction sets that represent the set of equations given by Equations 6.21–6.26. Assure that the reaction medium is liquid; the rate basis is reactor volume; and concentration basis is molarity.
8. Associate the reaction set, which contains both reactions, to “PFR” block.
9. Reset, run the show, and check for error or serious warning *via* “Control Panel”.
10. Report the conversion of *n*-C<sub>4</sub> into *i*-C<sub>4</sub>. Is the number close to 0.7 as reported by Fogler [1] for a PFR with a volume of 2.6 m<sup>3</sup>?
11. Repeat the previous steps but this time for “RCSTR” block. For the same volume requirement (*i.e.*, reactor volume = 2.6 m<sup>3</sup>), calculate the conversion at the exit of such a CSTR.
12. What will be the CSTR volume (expressed in m<sup>3</sup>) needed to achieve 70% conversion?
13. Which reactor type do you recommend for the liquid-phase *n*-C<sub>4</sub> isomerization?