Polymers Plus®

POLYMER PROCESS MODELING

Version 3

With Aspen Plus® 10

Examples and Applications

AspenTech®

CASE BOOK

Use of Aspen Plus and This Manual

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PREFACE

ABOUT THE EXAMPLES AND APPLICATIONS CASE BOOK

This book is a compilation of simulation examples and steady-state and dynamic applications. The examples section provides step-by-step directions for performing simulations. Most of the steady-state and dynamic applications describe how to simulate the reactor section of a specific polymer production process. A few describe a complete plant flowsheet, and others focus on physical property representation.

Some of the simulations require Fortran files. These are found in the same location as the simulation files (\xmp or \app sub-directory of the GUI installation directory. You must compile the accompanying Fortran before running the files.

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Comments and Suggestions

Our goal is to provide you with Polymers Plus documentation that meets your information needs. To help us reach this goal, forward your comments and suggestions to

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For your convenience, a Comments form is included at the end of the Case Book.

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1 CREATING A SIMULATION MODEL

SUMMARY

This example describes how to construct a polymer simulation model.

The steps covered include:

- Drawing the Simulation Flowsheet
- Specifying Setup and Global Options
- Specifying Components
- Characterizing Polymers
- Specifying Physical Properties
- Specifying Feed Streams
- Specifying Kinetics
- Defining the Unit Operation Block
- Running the Simulation
- Plotting Distributions
- Creating Live Distribution Plots
- Pasting and Linking Between Polymers Plus and Excel
- Saving the Run and Exiting

This example uses a process containing two CSTR reactors and a mixer. Free-radical kinetics take place in the reactors. The purpose is to provide you an overview of Polymers Plus.

SETUP INSTRUCTIONS

The step-by-step instructions to construct the simulation model are given below.

First you will need to start Polymers Plus. To do this:

➤Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with Metric Units** as your template. The default **Run type**, Flowsheet, is appropriate for this example. Click **OK**.

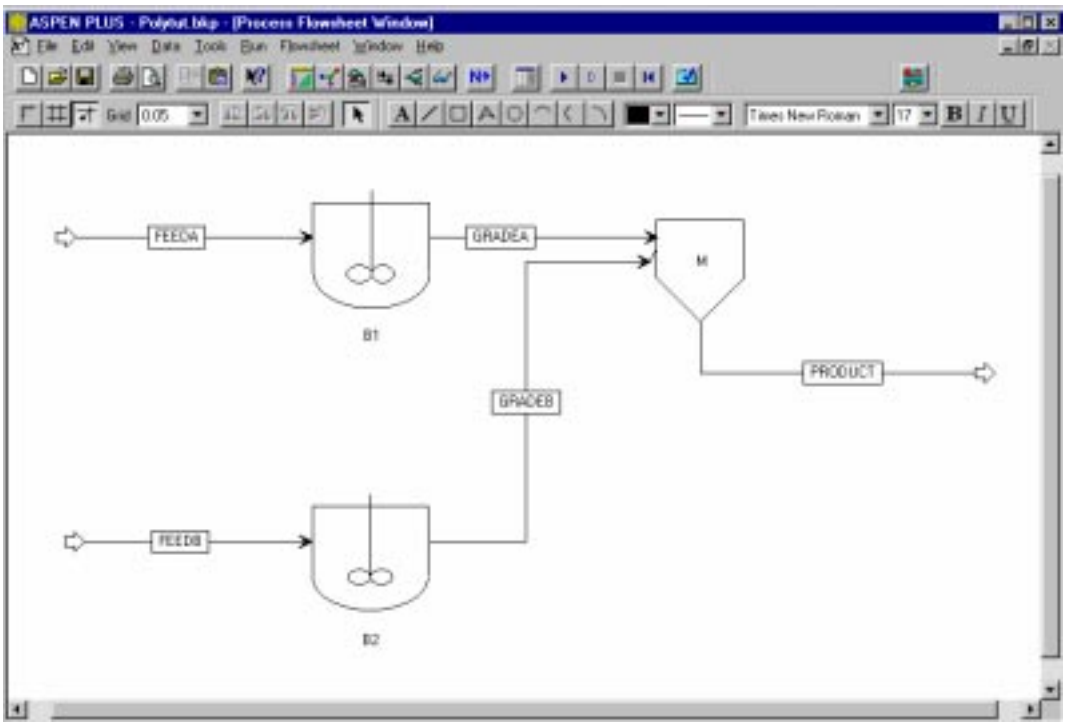
The Aspen Plus main window is now active.

Drawing the Simulation Flowsheet

The process flowsheet for this example is shown below.

In a flowsheet you can:

- Place blocks
- Place streams
- Rename blocks and streams



To place unit operation blocks:

1. Click on the **Reactors** tab in the model library and click on the **RCSTR** icon.

   Available model icons are displayed by clicking on the down-arrow of the RCSTR icon.

2. Move the "+" cursor to the process flowsheet window, and click to place the block B1.
3. Repeat the same procedure to place the second RCSTR block B2.
4. Click on the **Mixers/Splitters** tab in the Model Library and select a **Mixer** icon from the menu list.

   Move the "+" cursor to the process flowsheet window, and click to place block B3.

To place streams:

1. Click on the **Material STREAMS** icon and move the mouse to the process flowsheet window.

   Red and blue arrows on unit operation blocks will appear. These arrows indicate the location of the required (red) and optional (blue) stream connection ports.
2. Place the "+" cursor on the red feed arrow of B1 and click to make the connection. Move the mouse away from the block and click again to place stream 1.
3. Place the "+" cursor on the red product arrow of B1 and click to make the connection. Move the mouse to the red feed arrow of B3 and click again to connect two blocks.
4. Repeat the above procedure to create a feed stream for B2, connect B2 and B3, and create a product stream for B3.
5. After the placing all blocks and streams, turn off the insert mode by clicking on the arrow button that appears to the top left of the **Material STREAMS** icon .

To rename blocks and streams:

1. Click on the block to be renamed, such as B3, and click on the right mouse button to display the pop-up menu.
2. Select **Rename Block** from the pop-up menu.
3. Enter the Block ID as "M" and click **OK**.
4. Select the stream to be renamed, such as 1, and click on the right mouse button to bring up the pop-up menu.
5. Select **Rename Stream** from the pop-up menu.
6. Enter the Stream ID as "FEEDA" and click **OK**.
7. Repeat the above procedure to rename other streams.

You will now enter input data for your simulation.

Specifying Setup and Global Options

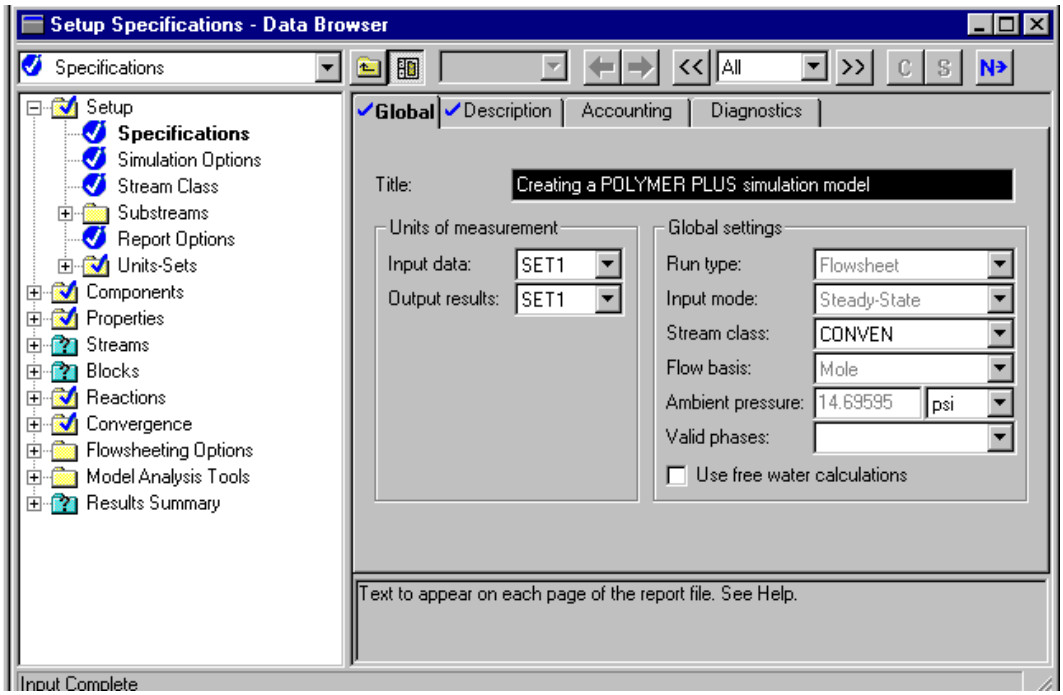
To enter process and model specifications into Polymers Plus, you can use the Expert guidance system (Next button ), or use the Data Browser navigation tree. In this example, we will enter the data using the Aspen Plus Data Browser navigation tree.

You will use the **Setup** folder in the Data Browser to give your simulation a title, define your units-sets and review the global options that were set when you selected the **Polymers with Metric Units** simulation template.

To specify a title:

1. Open the Data Browser by clicking on the Data Browser button  in the Aspen Plus main window toolbar.

2. Double click on the **Setup** folder, and click on **Specifications**.
3. On the **Global** tab sheet, type the title of your simulation run as "Creating a Polymers Plus Simulation Model".



This example requires a user defined units-set for input data and output results.

To define a unit-set:

1. In the Data Browser tree view, double click on the **Units Sets** sub-folder to bring up the Units-Sets Object manager.
2. Click **New** to create a new set.

   Enter an ID (e.g. SET1) for the new units-set and click **OK**.
3. On the Aspen Plus dialog box that appears requesting approval to make SET1 the global unit set, click **Yes**.
4. A **Setup Units Sets** form appears.

   Use SI units as the basis for your new set by selecting SI from the **Copy from** drop down list.
5. Enter user defined units as:

   - Mass Flow = kg/hr
   - Mole Flow = kmol/hr
   - Pressure = atm
   - Temperature = C

A Description sheet is available to enter a more detailed description of the simulation.

To enter the description for this example:

1. From the Data Browser, click on the **Specifications** form.
2. On the **Specifications** form, click on the **Description** tab.

   Type in the following information: “This example describes how to put together a polymer simulation model”.

Since you chose the **Polymers with Metric Units** simulation template when you started this example, Aspen Plus has set the following defaults for calculating and reporting stream properties:

- No mole flow
- Mass flow

A user defined stream report format is entered as follows:

1. From the Data Browser, click on the **Report Options** form.
2. On the **Report Options** form, click on the **Stream** tab.
3. In addition to the default options selected, click **Mole** in the **Flow basis** frame and **Mass** in the **Fraction basis** frame. **POLY_M** is defined for **Stream format** which is appropriate for this example.

Other simulation options can be entered as follows:

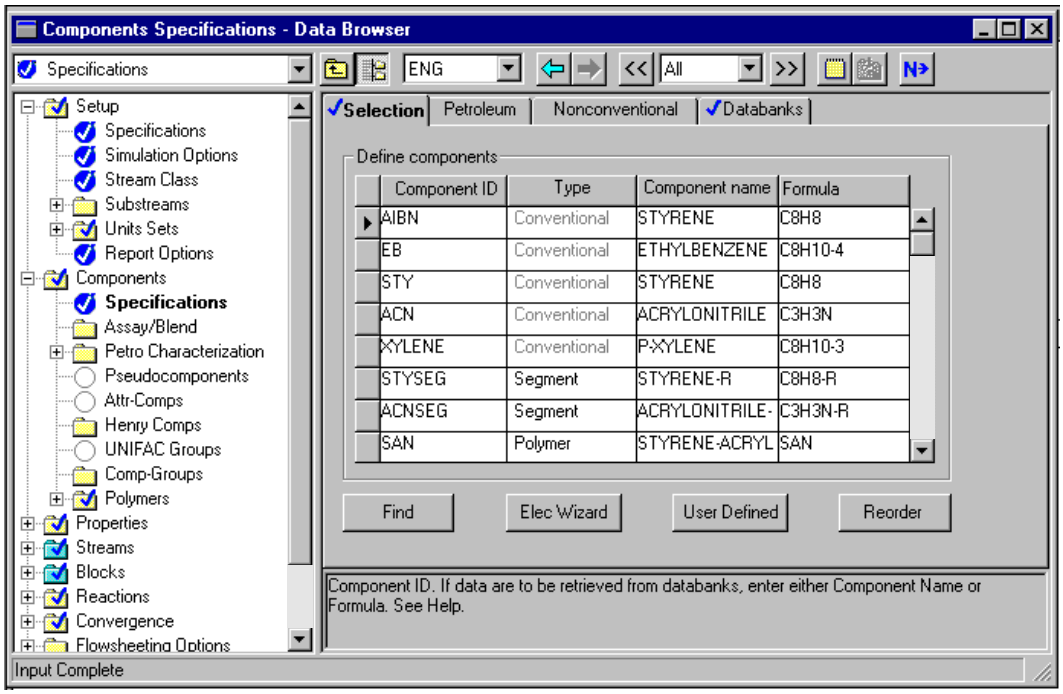
1. From the Data Browser, click on the **Simulation Options** form.
2. On the **Simulation Options** form, click on the **Limits** tab.
3. Enter 1000 in the **Simulation time limit in CPU seconds** field.
4. Click on the **System** tab, and click on the **Print Fortran tracebacks when a Fortran error occurs** option.

Specifying Components

You can use **Components** forms to select chemical components for your simulation and specify component types (e.g. conventional, solid, assay, blend, polymer, segment, oligomer, and pseudocomponent).

To select components:

1. From the Data Browser, double click on the **Components** folder.
2. From the **Components** folder, click on the **Specifications** form.
3. On the **Selection** tab sheet, enter the components as shown below:



Characterizing Polymers

You must enter additional characterization information for segments, polymers, oligomers and site-based species. You must define the type of segments present. Segments may be repeat units, end groups or branch points attached to three or four branches.

To define the segments:

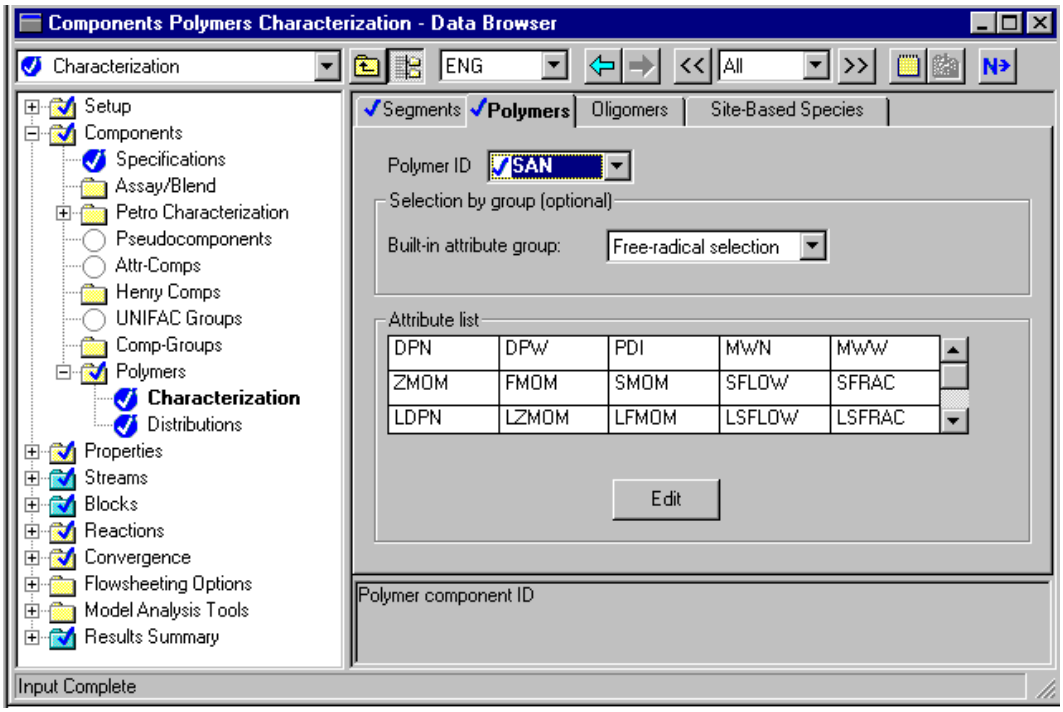
1. From the Data Browser, double click on the **Polymers** sub-folder.
2. From the **Polymers** sub-folder, click on the **Characterization** form.
3. On the **Segments** tab sheet, assign type REPEAT to segments STYSEG and ACNSEG.

For each polymer you must define the component attributes to be tracked. All components specified as type **Polymer** in the **Specifying Components** section require component attributes.

To specify component attributes for the polymers:

1. Click on the **Polymers** tab.
2. Select the desired polymer SAN from the **Polymer ID** drop down list.
3. In the **Built-in attribute group** field, select **Free-radical selection** as the attribute group.

   The attribute summary table, **Attribute list**, is automatically filled out. You can click on the attribute list table or click **Edit** to change the selections.



In order to track distributions in your simulation and later generate plots or table, you need to specify the type of distribution, the polymer, and the display characteristics for the generated distribution data.

To request a distribution:

1. From the Data Browser, click on the **Distributions** form.
2. On the **Selection** tab sheet, select the desired polymer SAN from the **Polymer ID** drop down list.
3. Click **Chain-size** for **Distribution type** and enter **No. points** = 100, **Upper** = 10000 for **Plot characteristics**.

Specifying Physical Properties

To define global physical property methods:

1. In the Data Browser, double click on the **Properties** folder.
2. From the **Properties** folder, click on **Specifications**.
3. On the **Global** tab sheet, select POLYNRTL as the **Base method**.

User defined property parameters such as molecular weight for polymers are defined in the **Properties** folder:

1. From the Data Browser, double click on the **Parameters** sub-folder.
2. In the **Parameters** sub-folder, double click on the **Pure Component** folder.
3. In the **Object manager**, click **New** to bring up a **New Pure Component Parameters** pop-up window.
4. Enter DATA1 as new name for parameter. Click **OK** to accept the default **Scalar** option.
5. Select **MW** from the **Parameters** drop down list.
6. Enter the molecular weights for the components: **AIBN**=164.0 and **SAN**=104.150.

Specifying Feed Streams

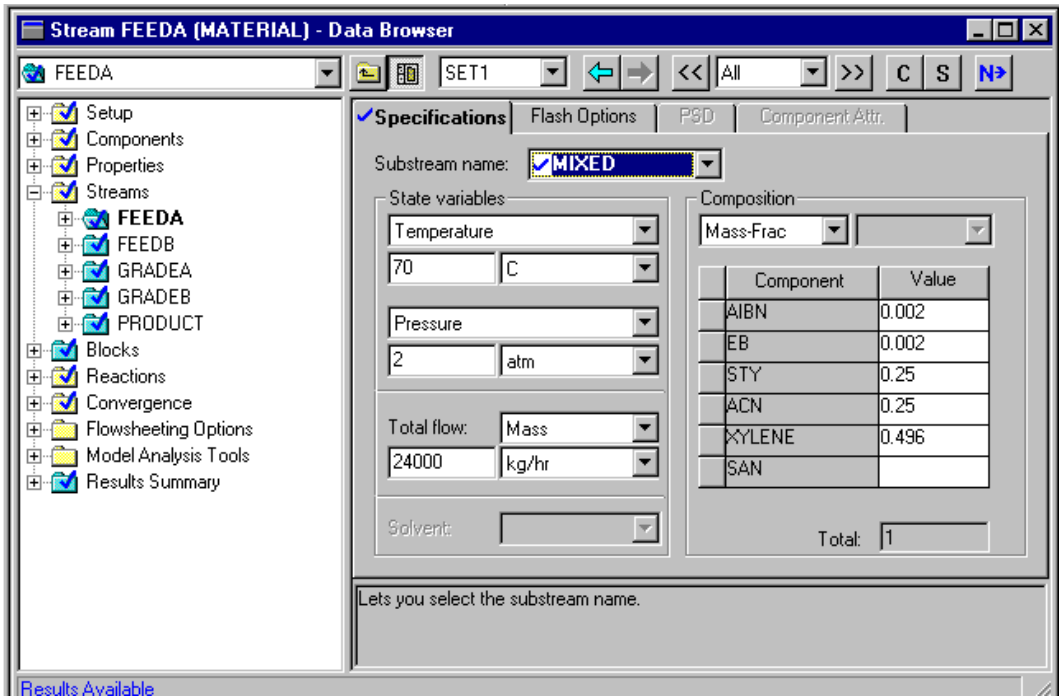
To enter stream specifications, you either open input forms from the Data Browser navigation tree, or select a stream on the process flowsheet window and right mouse click to bring up a pop-up menu where you select Input to open the input form. Here, we will use the Data Browser navigation tree.

To enter feed stream specifications:

1. From the Data Browser, double click on the **Streams** folder.
2. From the **Streams** folder, double click on the **FEEDA** sub-folder.
3. From the **FEEDA** sub-folder, click on **Input**.

   On the **Specifications** tab sheet, enter:

   - Temperature =70 C
   - Pressure =2 atm
   - Total Flow (Mass) = 24000 kg/hr
   - Composition = Mass Frac
     - AIBN = 0.002
     - EB = 0.002
     - STY = 0.25
     - ACN = 0.25
     - XYLENE = 0.496



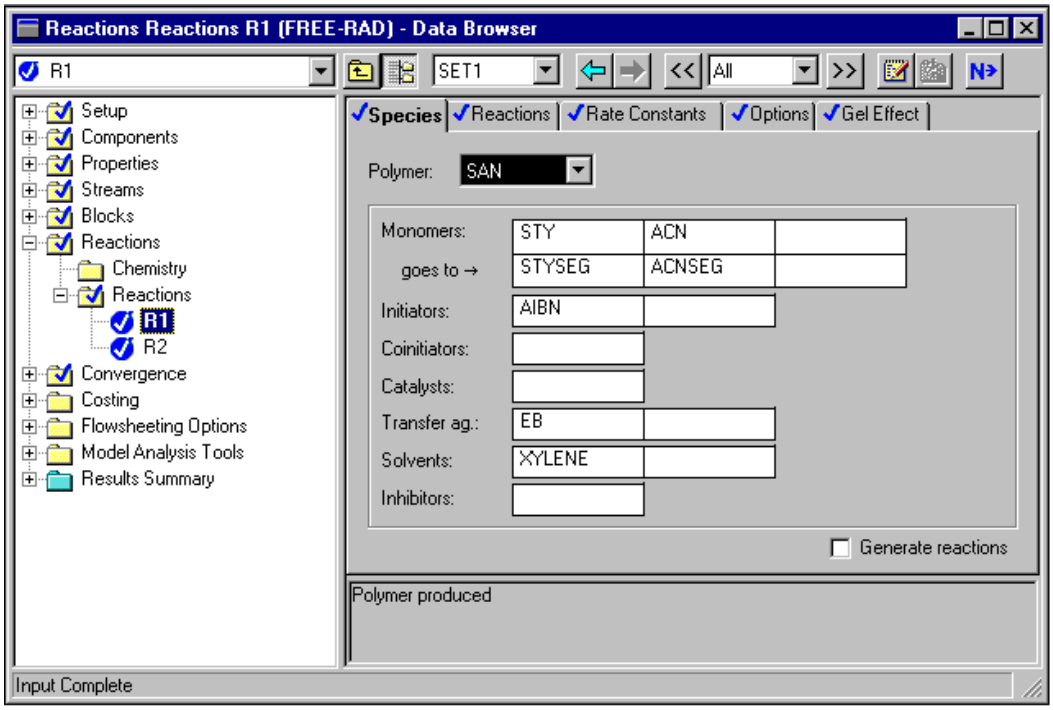
4. From the Data Browser, double click on the **FEEDB** sub-folder. Click on **Input**.
5. On the **Specifications** tab sheet, enter the same temperature, pressure, and total flow rate as FEEDA, and specify mass fractions:
   - AIBN = 0.004
   - STY = 0.1
   - ACN = 0.4
   - XYLENE = 0.496

Specifying Kinetics

Kinetic inputs are specified in the **Reactions** folder. This example uses the free-radical kinetics model.

To specify the free-radical polymerization inputs:

1. From the Data Browser, double click on the **Reactions** folder.
2. From the **Reactions** folder, double click on the **Reactions** sub-folder.
3. In the **Object manager**, click **New** to create a new reaction R1 and select **FREE-RAD** as the reaction type. Click **OK**.
4. On the **Species** tab sheet, enter components as follows:



5. Click on the comment icon  to add the description "Grade A SAN polymerization kinetics". Click **OK**.
6. Click the **Generate Reactions** option to generate reactions automatically from the list of reacting species.
7. Click on the **Reactions** tab.

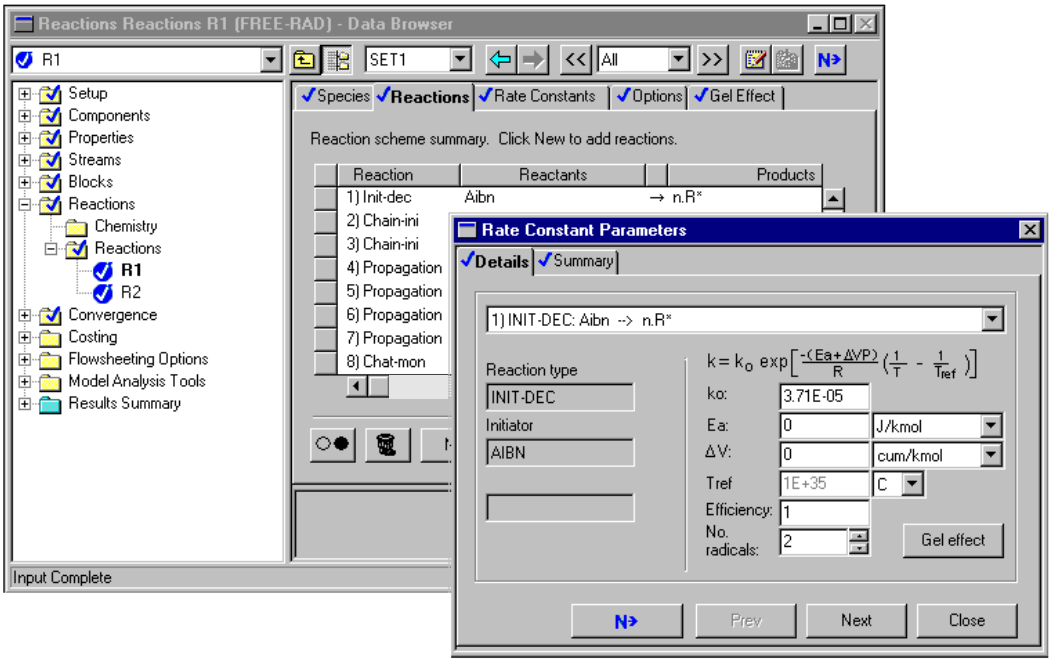
   An **Auto Generation** dialog box appears, click **Yes** to turn off reaction generation.

   On the **Reactions** tab sheet, review the automatically generated reactions and delete any unnecessary equations by selecting them in the table and clicking the **Delete** button  . For this example, you can delete the reactions for: chat-agent, chat-sol and term-dis.

8. Click on the **Rate Constants** button to open the **Rate Constant Parameters** pop-up form for each reaction. Click on the **Summary** tab and enter reaction rate constants.

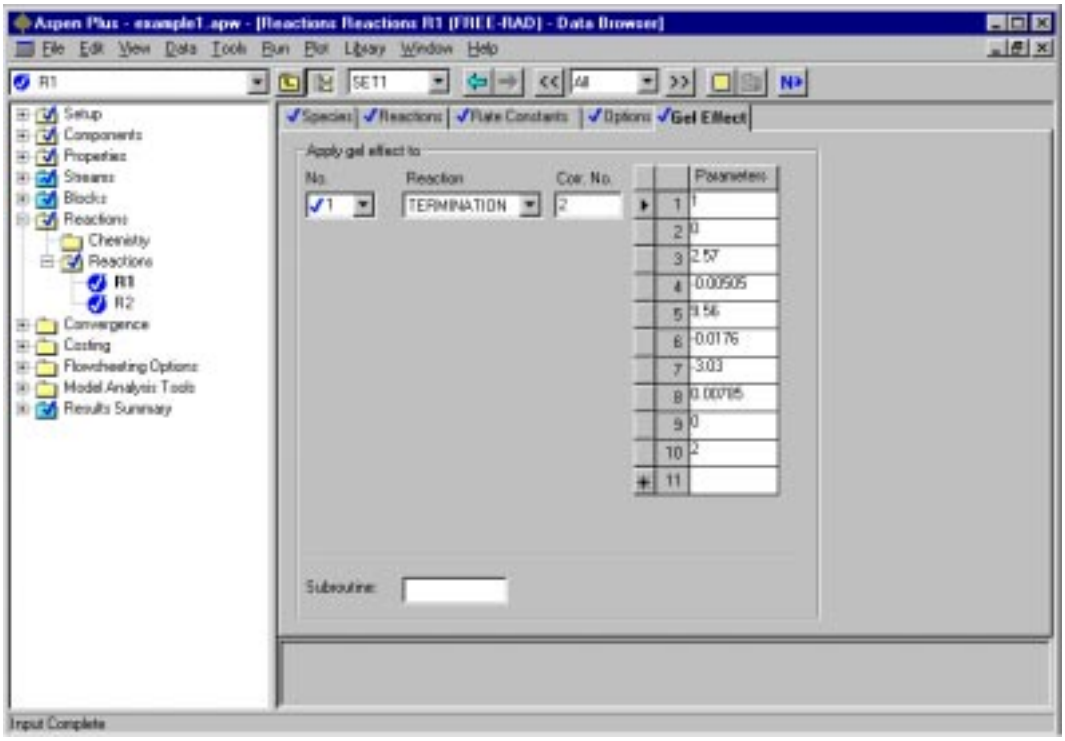
   Refer to the REACTIONS paragraph in Figure 1.1 for the rate constants of R1. After entering the data, click on **Close**.

   The **Reactions** and the **Rate Constant Parameters** sheets are shown below:



9. Click on the **Options** tab to specify additional simulation options for the model. Select **Gel effect** for R1.

10. Click on the **Gel Effect** tab and enter, reaction number, reaction type, and gel effect correlation number. To input in the **No.** field you need to right click on the field and select **Create** from the pop-up menu. Parameters for the gel effect correlation are specified as shown below:



Follow the same procedure and reference the REACTIONS paragraph for R2 in Figure 1.1 to define species, rate constants and gel-effect for R2.

Defining the Unit Operation Block

You must define the operating conditions for unit operations.

To enter block specifications for the CSTR reactors:

1. From the Data Browser, double click on the **Blocks** folder.
2. From the **Blocks** folder, double click on the **B1** sub-folder.
3. Click on **Setup**, and on the **Specifications** tab sheet enter:
   - Pressure =2 atm
   - Temperature =70 C
   - Valid Phases = Liquid-Only
   - Reactor Volume = 10 cum
4. Click on the **Reactions** tab.

   Select R1 as the **Reaction Set** that describes the chemical reactions occurring in B1 by clicking on the > button.
5. Click on the **Component Attr.** tab and set:
   - Substream ID = MIXED

- Component ID = SAN

6. Enter a series of **Attribute ID** and **Component Attribute** values as below:

- Attribute ID = LPFRAC, Component Attribute value = 1E-005
- Attribute ID = LEFRAC, Component Attribute values = 0.5, 0.5
- Attribute ID = LSFRAC, Component Attribute values = 0.5, 0.5
- Attribute ID = LDPN, Component Attribute value = 500
- Attribute ID = SFRAC, Component Attribute values = 0.5, 0.5
- Attribute ID = PDI, Component Attribute value = 1.5
- Attribute ID = DPN, Component Attribute value = 1000

On the **Convergence** form, you specify estimates for the component flow rates in the outlet stream to improve convergence. To do this:

1. From the Data Browser, click on the **Convergence** form in the **B1** sub-folder.
2. On the **Estimates** tab sheet enter the following component values on a mole basis:

- STY = 30 kmol/hr
- ACN = 60 kmol/hr
- SAN =50 kmol/hr
- AIBN = 0.2 kmol/hr

You also select the solution algorithm to converge the mass balance equations and specify user required convergence parameters and error tolerance for mass balance calculations. To do this:

1. Click on the **Parameters** tab and enter:
   - Max iterations = 500
   - Error tolerance =1E-05
2. Click the **Initialize using integration** option.

   When this option is checked, CSTR uses an integrator to provide an initial guess to the simultaneous equation solver.

Block Options forms can be used to override global values for physical properties, simulation options, diagnostic message levels and report options. For B1 the control panel diagnostic message level is set higher than the global default value 4. To override values:

1. From the Data Browser, click on the **Block Options** form in the **B1** sub-folder.
2. Click on the **Diagnostics** tab, set the **On screen** slider bar to level 7.

Repeat the above procedures to define the unit operation block B2. Refer to the BLOCKS B2 paragraph in Figure 1.1 for B2 specifications.

To enter Mixer specifications:

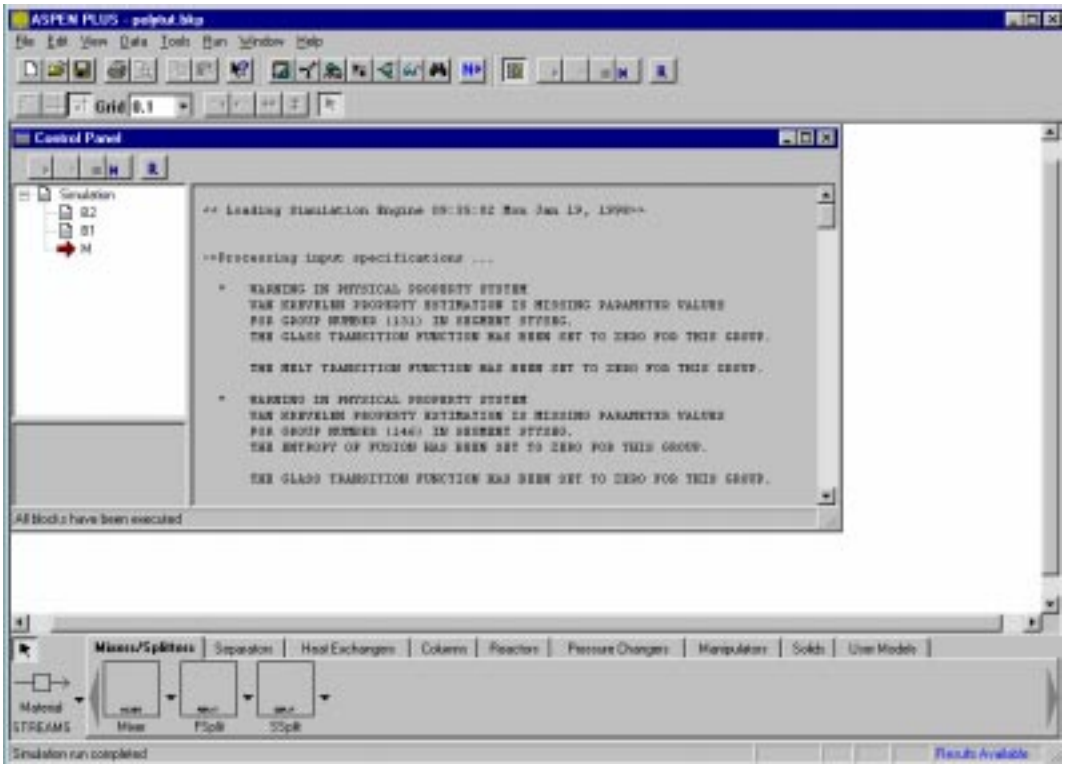
1. From the Data Browser, double click on the **M** sub-folder.
2. From the **M** sub-folder, click on **Input**.
3. On the **Flash Options** tab sheet enter:
   - Pressure = 1 atm
   - Valid phases = Liquid-Only

RUNNING THE SIMULATION

To run a simulation:

1. Click on the Aspen Plus expert system, Next button  , to confirm that you have finished entering all required input. The Required Input Complete dialog box appears.
2. Click OK to open a Control Panel and run the simulation.
3. You can also open a control panel and start a run by clicking on Run control panel button  and Start button  in the Aspen Plus main window toolbar.

As the run proceeds status messages appear in the Control Panel. When the calculations are complete, the message **Results Available** appears in the status bar at the right bottom corner of the Aspen Plus main window.



EXAMINING SIMULATION RESULTS

When the message **Results Available** appears in the status bar you can examine your simulation results.

To examine the results:

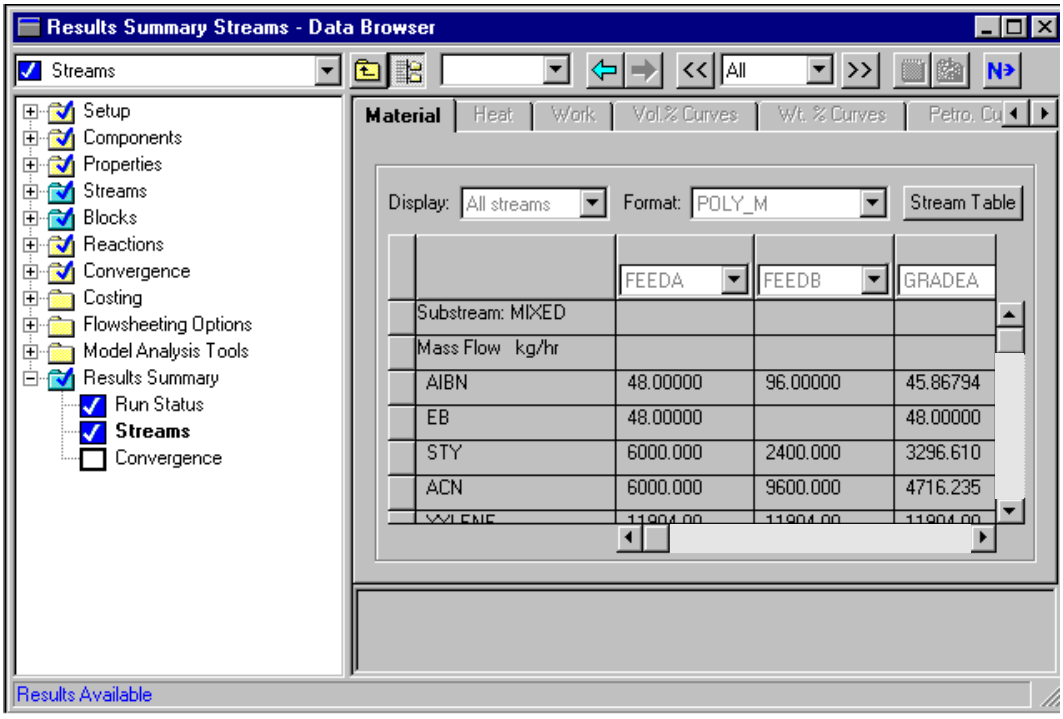
1. From the Data Browser, double click on the **Results Summary** folder.
2. In the **Results Summary** folder, click on **Run Status**.

   The **Summary** sheet appears.

   The Aspen Plus version, run starting time and run status are summarized on this sheet.
3. From the **Results Summary** folder, click on **Streams**.

   The **Material** sheet appears with the stream results.

Since you selected the **Polymers with Metric Units** Simulation Template, POLY_M is used as the stream result format and reports stream Temperature, Pressure, Average MW, and other results. Mass Flow, and Mass Fraction are reported based on the selections made in the Specifying Setup and Global Options section. Since the **Material** sheet contains a scrolling table, you can click the scroll bar to review the stream results that are off the screen.



You select **Results** from the drop down list between the << and >> buttons and use the browser forward button >> to navigate to the next form with results.

1. After reviewing the **Material** sheet, click the >> button.

   The **Poly. Curves** sheet appears. You can review the polymer structural property distribution results for the streams.

2. Click the >> button.

   The **Stream FEEDA Results** form appears.

3. Repeat steps 1 and 2 to review the rest of your results.

Plotting Distributions

You can display and plot the distribution data for a polymerization reactor or you can display a distribution table for a stream or for the entire flowsheet.

To display and plot the distribution data for a polymerization reactor:

1. From the Data Browser, click on the **Results** form in the **Blocks** folder **B1** sub-folder.
2. Click on the **Distributions** tab.
3. Select **Plot Wizard** from the **Plot** pull-down menu on the menu bar.
4. Click **Next**, then select **Chain Size Distr.** as the plot type by clicking on the appropriate button.
5. Click **Next** to review your plot options.

   You can click **Next** again to review further plot options

   – or –

   Click **Finish** to display the plot.

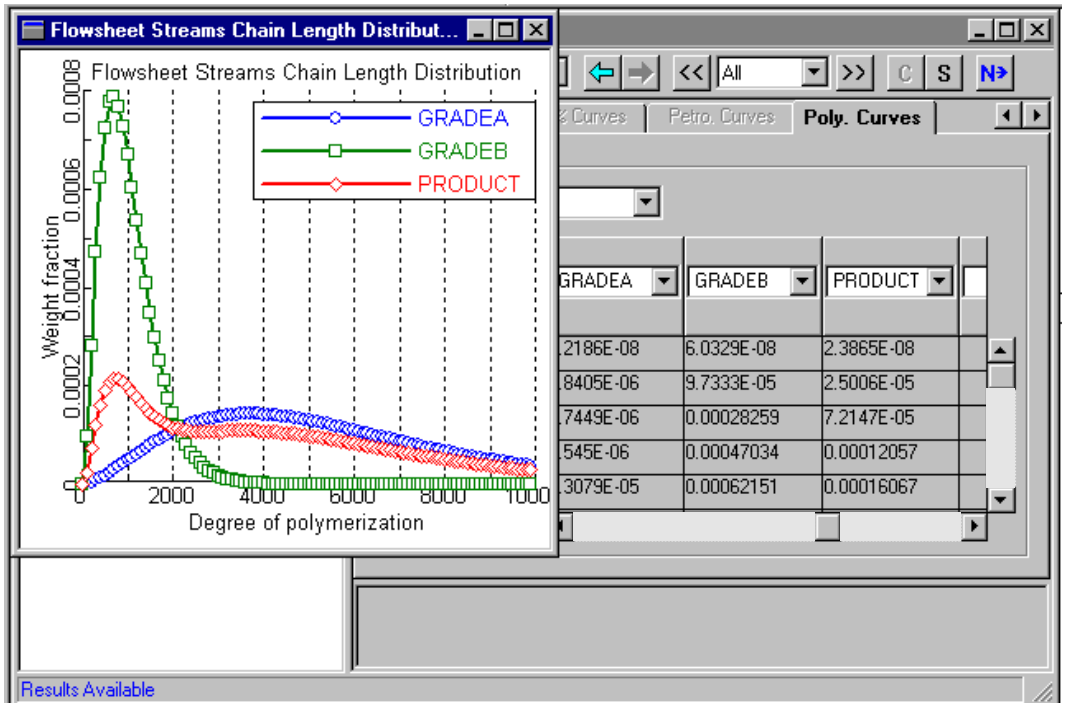
   You can modify the plot by right mouse clicking on the objects in the plot window and selecting **Edit**, **Properties** and **Modify** from the pop-up menu.

To display a distribution table for a stream or for the entire flowsheet:

1. From the Data Browser, click on the **Streams** form in the **Results Summary** folder
2. On the **Streams** tab sheet, click on the **Poly. Curves** tab.
3. Select **Plot Wizard** from the **Plot** pull-down menu on the menu bar.
4. Click **Next**, then select **Chain Size Distr.** as plot type by clicking on the CSD curve button.
5. Click **Next**, highlight the stream(s) you want to plot from the **Available** box and click the > button to select each stream you want to plot. In this example all streams are selected.
6. Click **Next** to review your plot options.

   – or –

   Click **Finish** to display the plot.



Creating Live Distribution Plots

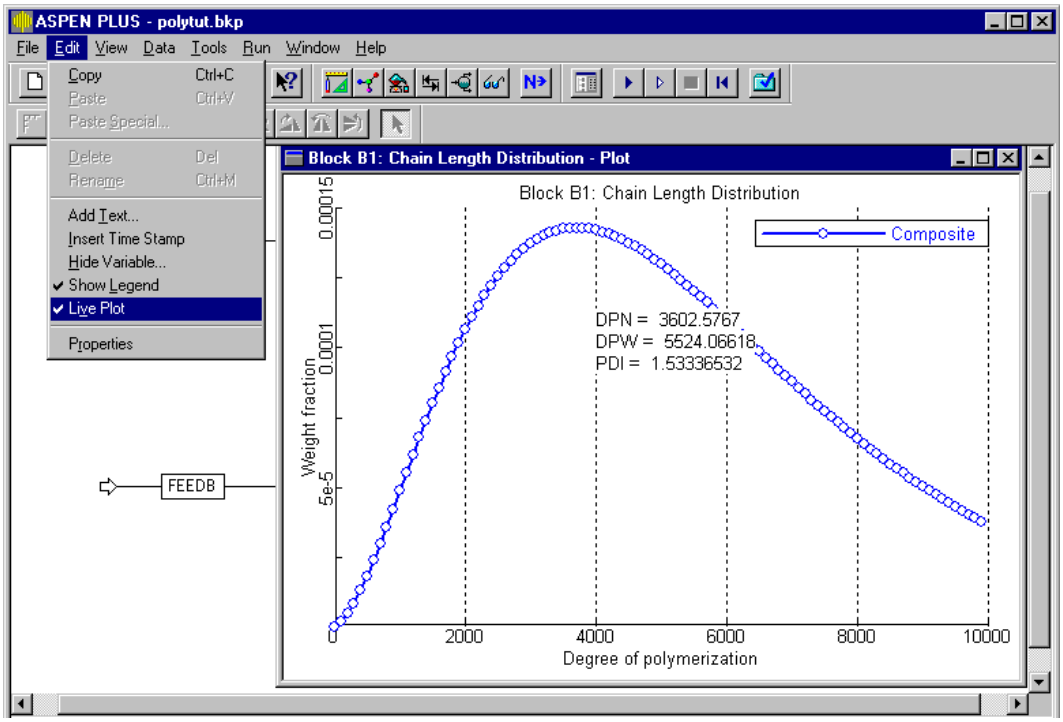
The distribution plotting capability allows you to create live plots which are automatically refreshed when you rerun the simulation.

To create a live distribution plot for a reactor:

1. From the Data Browser, click on the **Results** form in the **Blocks** folder **B1** sub-folder.
2. Click on the **Distributions** tab.

3. Select **Plot Wizard** from the **Plot** pull-down menu on the menu bar.
4. Click on **Next** then select **Chain Size Distr.** as the plot type by clicking on the appropriate button.
5. Click on **Next** to set the plot style. Make sure the **Show average properties** option is checked.
6. Click on **Next** to set more plot styles. In the frame asking if you would like to update the plot when new results are available, choose **Yes**.
7. Click **Finish** to display the plot.

If you did not choose the right option for refreshing the plot in step 6. You can still do this. With the plot window active, click on **Edit** in the menu bar. Select **Live Plot** from the **Edit** pull-down menu.

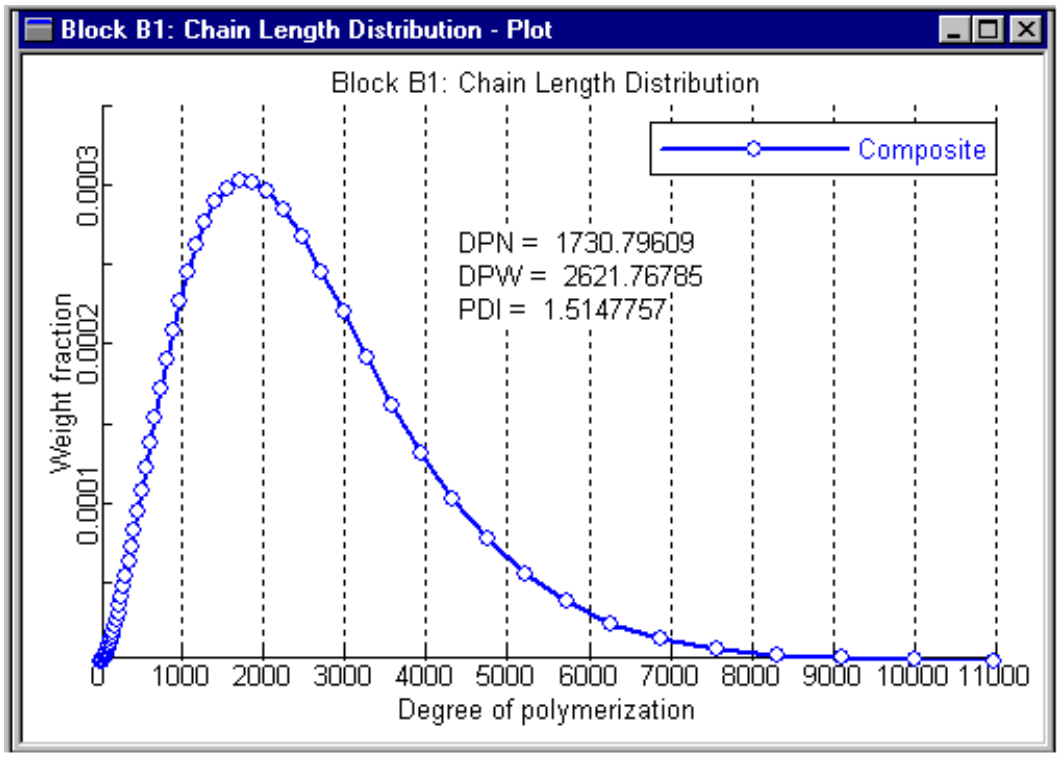


You are now ready to make another simulation and see the plot change.

To change the specifications for B1:

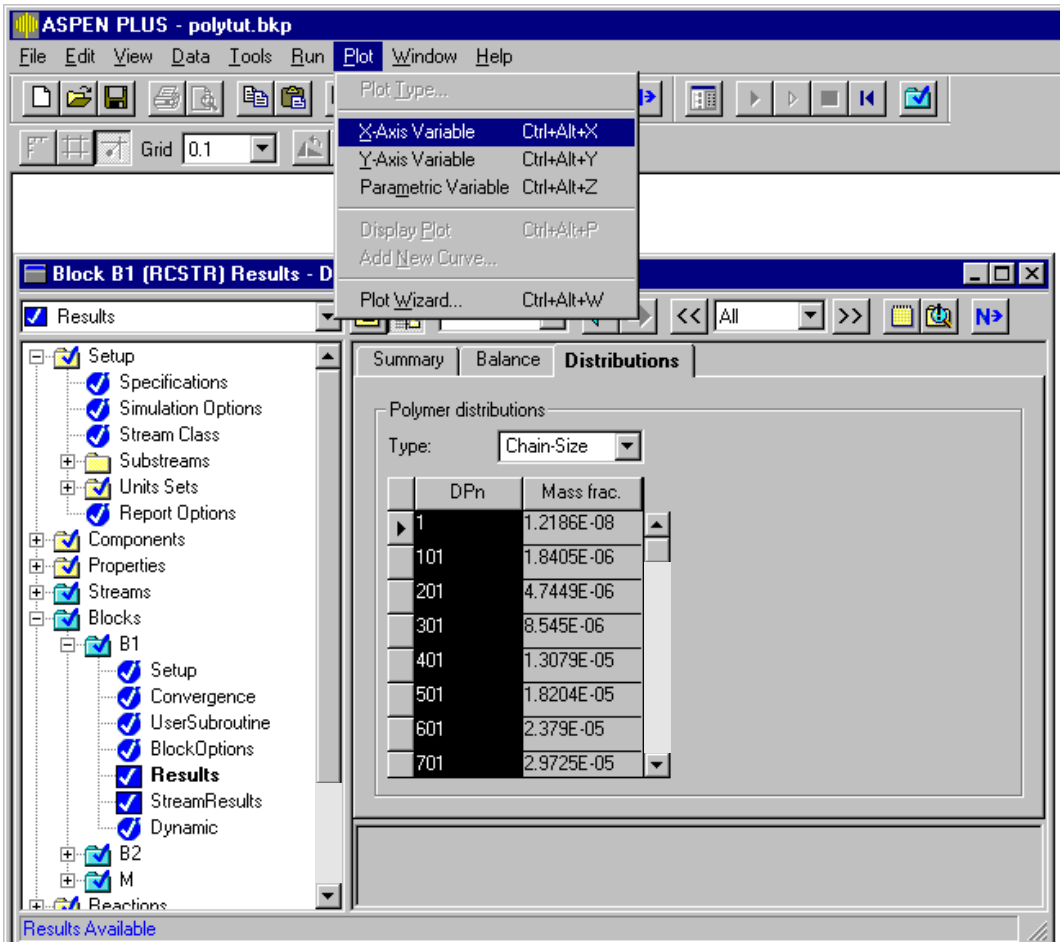
1. Keeping the plot window on your screen, from the Data Browser, click on the **Setup** form in the **Blocks** folder **B1** sub-folder.
2. On the **Specifications** tab sheet change temperature to 5°C and reactor volume to 70 cum.
3. Run the simulation by clicking on the **Start** button in the control panel or on the toolbar.

Watch the distribution curve and average properties change in the plot window.



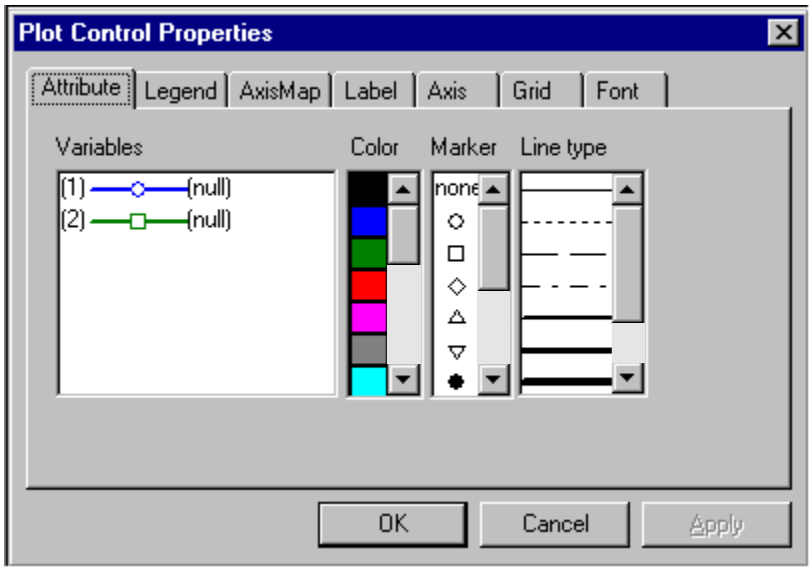
To manually superimpose distribution plots for several simulations:

1. Make the plot window active. From the **Edit** pull-down menu, turn off the **Live Plot** option.
2. Select the average property text on the plot, right mouse click and **Delete**.
3. From the Data Browser, click on the **Setup** form in the **Blocks** folder **B1** sub-folder.
4. On the **Specifications** tab sheet change temperature back to 70°C and reactor volume to 10 cum.
5. Run the simulation by clicking on the **Start** button in the control panel or on the toolbar. This time the plot does not change.
6. From the Data Browser, click on the **Results** form in the **Blocks** folder **B1** sub-folder.
7. Click on the **Distributions** tab. You are going to select manually the x-axis values and y-axis values for the new plot.
8. Click on **DPn** to select the degree of polymerization column as the x-axis. That column changes color, an indication that it is selected.
9. From the **Plot** pull-down menu, select **X-Axis Variable** to set DPn as the x-axis.

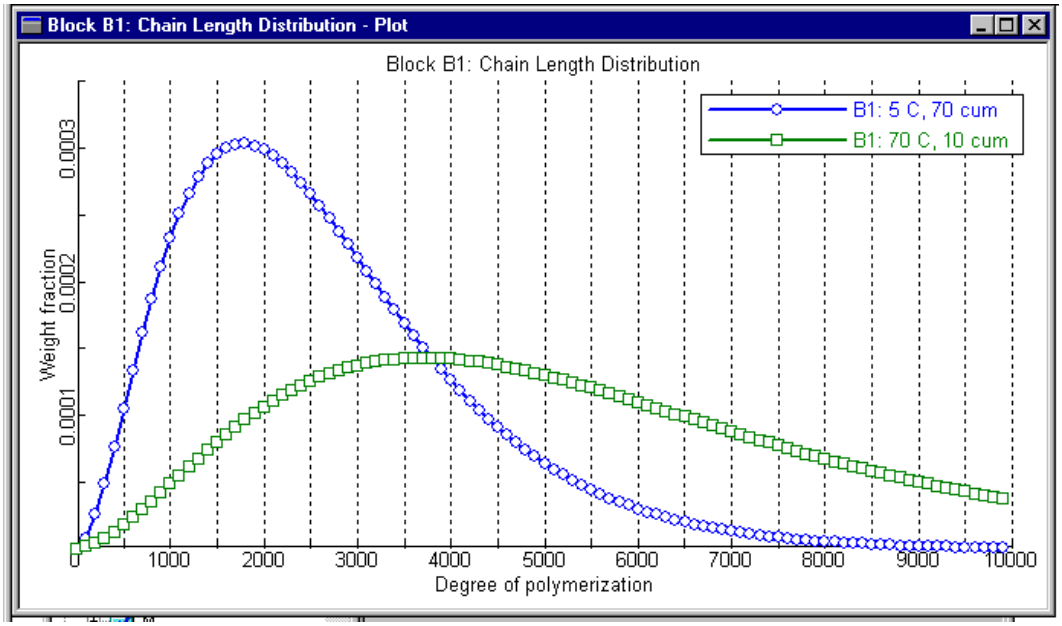


10. Go back to the **Distributions** tab sheet, click on **Mass frac.** to select the mass fraction column as the y-axis.
11. From the **Plot** pull-down menu, select **Y-Axis Variable** to set mass fraction as the y-axis.
12. From the **Plot** pull-down menu, select **Add New Curve** to superimpose this new data on the previous plot.
13. In the **Plot Window List** window, select **B1: Chain Length Distribution** as the plot on which the new curve should be superimposed. Click **OK**.

14. The plot window now has two superimposed curves with each having a separate y-axis. To use a single y-axis, click on the curve line, right mouse click and select **Properties** to go to the plot properties.



15. Click on the **AxisMap** tab. Click the **All in One** button. Then click on **Apply** to update the plot. You can also change the legend for the new plot to define the reactor conditions.



Pasting and Linking Between Polymers Plus and Excel

You use OLE linking to establish connections between Aspen Plus and other applications.

To paste and link the distribution table of B1 to an Excel application:

1. From the Data Browser, open the **Blocks** folder.
2. Open the **B1** sub-folder, click on **Results**.
3. Click on the **Distributions** tab, select the entire DPn column by clicking on the column selector, then right mouse click to bring up pop-up menu and select **Copy**.
4. Open an Excel work sheet and enter DPn as the title of the first column.

   Place the mouse on the second row, right mouse click to bring up the pop-up menu and select **Paste Special**.
5. Select **Paste Link** and **Text** in the **Paste Special** pop-up form then click **OK.**
6. Repeat the same procedure for **Mass frac.** column.

The distribution table is generated in Excel and will be updated when the simulation results change in Aspen Plus.

To obtain reaction rate constants from Excel:

1. Open an Excel file containing the reaction rate constant parameters.
2. Select a column of reaction constants, such as Pre-Exp (ko), right mouse click and select **Copy** from the pop-up menu.
3. In Aspen Plus, from the Data Browser, open the **Reactions** folder.
4. From the **Reactions** folder, click **R1** and click the **Reactions** tab.
5. Click **Parameters** and click on the **Summary** tab of the **Rate Constant Parameters** pop-up form.
6. Place the cursor in the top cell on the **Pre-Exp** column and right mouse click to select **Paste Special**.

   Click the **Paste Link** option and select the **Text** option.

The reaction constants will be copied to Aspen Plus and will be updated when changes are made in Excel.

Saving the Run and Exiting

Before you exit Aspen Plus, save the run as a Backup file (*.bkp) or a Quick Restart file (*.apw). It is recommended that you use the backup file format to save disk space and for future version compatibility.

To save an .apw and a .bkp file:

1. Select **Save As** from File pull-down menu.
2. Enter a file name, then select .apw or .bkp in the **Save as type** field. Click **Save** to apply.

To exit Aspen Plus:

➢ Select **Exit** from the File pull-down menu.

When the dialog box appears asking if you want to save the run, select **Yes** if you have not saved the run.

Congratulations! You have just built and run a complete polymerization example using Polymers Plus.

Figure 1.1 Input Summary

```
TITLE 'Creating a Polymers Plus Simulation Model'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm  &
        TEMPERATURE=C PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=1000.0

DESCRIPTION "
        This example describes how to put together a polymer simulation model."

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    AIBN C8H8 AIBN /
    EB C8H10-4 EB /
    STY C8H8 STY /
    ACN C3H3N ACN /
    XYLENE C8H10-3 XYLENE /
    STYSEG C8H8-R STYSEG /
    ACNSEG C3H3N-R ACNSEG /
    SAN SAN SAN

FLOWSHEET
    BLOCK B1 IN=FEEDA OUT=GRADEA
    BLOCK B2 IN=FEEDB OUT=GRADEB
    BLOCK M IN=GRADEA GRADEB OUT=PRODUCT

PROPERTIES POLYNRTL

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST MW
    PVAL AIBN 164.0
    PVAL SAN 104.150

POLYMERS
    SEGMENTS STYSEG REPEAT / ACNSEG REPEAT
    POLYMERS SAN
    ATTRIBUTES SAN DPN DPW PDI MWN MWW ZMOM FMOM SMOM SFLOW  &
        SFRAC LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW LEFRAC  &
        LPFRAC
    DISTRIBUTION SAN CHAIN-SIZE NPOINTS=100 UPPER=10000.

STREAM FEEDA
    SUBSTREAM MIXED TEMP=70.0 PRES=2.0 MASS-FLOW=24000.0
    MASS-FRAC AIBN .0020 / EB .0020 / STY .250 / ACN .250  &
        / XYLENE .4960
```

Figure 1.1 Input Summary (cont.)

```
STREAM FEEDB
    SUBSTREAM MIXED TEMP=70.0 PRES=2.0 MASS-FLOW=24000.0
    MASS-FRAC AIBN .0040 / STY .10 / ACN .40 / XYLENE  &
        .4960

BLOCK M MIXER
    PARAM PRES=1.0 NPHASE=1 PHASE=L

BLOCK B1 RCSTR
    PARAM VOL=10. TEMP=70.0 PRES=2.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=500 MB-TOL=.000010 TRACE=1.0000E-08  &
        ALGORITHM=INTEGRATOR MAX-NSTEP=100
    MOLE-FLOW MIXED STY 30.0
    MOLE-FLOW MIXED ACN 60.0
    MOLE-FLOW MIXED SAN 50.0
    MOLE-FLOW MIXED AIBN .20
    COMP-ATTR MIXED SAN LPFRAC ( .000010 )
    COMP-ATTR MIXED SAN LEFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN LSFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN LDPN ( 500.0 )
    COMP-ATTR MIXED SAN SFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN DPN ( 1000.0 )
    COMP-ATTR MIXED SAN PDI ( 1.50 )
    BLOCK-OPTION TERM-LEVEL=7
    REACTIONS RXN-IDS=R1

BLOCK B2 RCSTR
    PARAM VOL=10. TEMP=70.0 PRES=2.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=500 MB-TOL=.000010 ALGORITHM=INTEGER
    MOLE-FLOW MIXED STY 10.0
    MOLE-FLOW MIXED ACN 100.0
    MOLE-FLOW MIXED SAN 50.0
    MOLE-FLOW MIXED AIBN .20
    COMP-ATTR MIXED SAN LPFRAC ( .000010 )
    COMP-ATTR MIXED SAN LEFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN LSFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN LDPN ( 500.0 )
    COMP-ATTR MIXED SAN SFRAC ( .50 .50 )
    COMP-ATTR MIXED SAN DPN ( 1000.0 )
    COMP-ATTR MIXED SAN PDI ( 1.50 )
    BLOCK-OPTION TERM-LEVEL=7
    REACTIONS RXN-IDS=R2

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

REACTIONS R1 FREE-RAD
    DESCRIPTION "GRADE A SAN POLYMERIZATION KINETICS"
    PARAM
    SPECIES INITIATOR=AIBN MONOMER=STY ACN CHAINTAG=EB  &
        SOLVENT=XYLENE POLYMER=SAN
    MON-RSEG STY STYSEG / ACN ACNSEG
    INIT-DEC AIBN .00003710 0.0 0.0 EFFIC=1.0 NRADS=2
    CHAIN-INI STY 4820.0 0.0 0.0
    CHAIN-INI ACN 225.0 0.0 0.0
```

Figure 1.1 Input Summary (cont.)

```
    PROPAGATION STY STY 4820. 0.0 0.0
    PROPAGATION STY ACN 10277. 0.0 0.0
    PROPAGATION ACN STY 7165.6 0.0 0.0
    PROPAGATION ACN ACN 225. 0.0 0.0
    CHAT-MON STY STY 0.289 0.0 0.0
    CHAT-MON STY ACN 0.289 0.0 0.0
    CHAT-MON ACN STY .0060 0.0 0.0
    CHAT-MON ACN ACN .0060 0.0 0.0
    TERM-COMB STY STY 13900000. 0.0 0.0
    TERM-COMB STY ACN 358000000. 0.0 0.0
    TERM-COMB ACN STY 358000000. 0.0 0.0
    TERM-COMB ACN ACN 10200000. 0.0 0.0
    GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1.0 0.0  &
        2.570 -.005050 9.560 -.01760 -3.030 .007850 0.0 2.0

REACTIONS R2 FREE-RAD
    DESCRIPTION "GRADE B SAN POLYMERIZATION KINETICS"
    PARAM
    SPECIES INITIATOR=AIBN MONOMER=STY ACN CHAINTAG=EB  &
        SOLVENT=XYLENE POLYMER=SAN
    MON-RSEG STY STYSEG / ACN ACNSEG
    INIT-DEC AIBN 3.71E-005 0.0 0.0 EFFIC=1.0 NRADS=2
    CHAIN-INI STY 4820.0 0.0 0.0
    CHAIN-INI ACN 225.0 0.0 0.0
    PROPAGATION STY STY 4820.0 0.0 0.0
    PROPAGATION STY ACN 10277.0 0.0 0.0
    PROPAGATION ACN STY 7165.60 0.0 0.0
    PROPAGATION ACN ACN 225.0 0.0 0.0
    CHAT-MON STY STY .2890 0.0 0.0
    CHAT-MON STY ACN .2890 0.0 0.0
    CHAT-MON ACN STY .0060 0.0 0.0
    CHAT-MON ACN ACN .0060 0.0 0.0
    TERM-COMB STY STY 1.3900E+08 0.0 0.0
    TERM-COMB STY ACN 3.5800E+09 0.0 0.0
    TERM-COMB ACN STY 3.5800E+09 0.0 0.0
    TERM-COMB ACN ACN 1.0200E+08 0.0 0.0
    GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1.0 0.0  &
        2.570 -.005050 9.560 -.01760 -3.030 .007850 0.0 2.0
```

2 PREDICTING PHYSICAL PROPERTIES

SUMMARY

This example demonstrates how to use Polymers Plus to predict pure component properties of polymers using the Van Krevelen group contribution method.

The steps covered include:

- Drawing the Simulation Flowsheet
- Specifying Setup and Global Options
- Specifying and Characterizing Components
- Specifying Physical Properties
- Supplying Process Information
- Defining Molecular Structure
- Creating Property Sets
- Creating Property Tables
- Running the Simulation and Examining the Results

The Van Krevelen method is based on the chemical structure of the polymers (Van Krevelen, 1990). It uses additive molar functions based on group contribution. Using this technique a variety of polymer properties can be predicted. In Polymers Plus the Van Krevelen method is used to estimate heat capacity of both liquid and solid polymers, liquid viscosity for both polymer melt and polymer solution, and density. In this example heat capacity, enthalpy and density are predicted at atmospheric pressure in the temperature range of 500 to 600 K for a liquid copolymer of polystyrene with n-butyl-acrylate.

A convenient approach is to use the Flowsheet option of Polymers Plus. Therefore, in the following example, a feed stream containing the copolymer, with a degree of polymerization of 1000 and consisting of fifty percent by weight polystyrene and fifty percent by poly(butyl-acrylate) is flashed at 500 K and 1 bar.

The copolymer considered in this example is not available in the Polymers Plus databanks, hence the generic polymer component is used to describe it. In addition, for demonstration purposes, it is assumed that the properties of n-butyl-acrylate segment are not available and they are estimated using Van Krevelen group contribution method, by providing the groups constituting this segment.

Property tables and property sets are used to tabulate liquid heat capacity, enthalpy and density of the copolymer.

SETUP INSTRUCTIONS

In this example you will create a Polymers Plus flowsheet, run the simulation and examine the results.

In the flowsheet, there is a single feed stream containing equal amounts of styrene and n-butyl-acrylate monomers and styrene-butyl-acrylate copolymer. Components considered in the simulation are summarized as:

Component	Name	Type	Databank
n-butyl acrylate	BA	Conventional	PURECOMP
Styrene	STYRENE	Conventional	PURECOMP
Copolymer	SBA	Polymer	POLYMER
b-butyl-acrylate	BA-R	Segment	SEGMENT
Styrene-R	Sty-R	Segment	SEGMENT

The feed stream consists of 1 kg/hr of styrene, 1 kg/hr of n-butyl-acrylate and 1 kg/hr of the copolymer at one atmosphere pressure and 500 K. The feed is flashed at 500 K and 1 atm.

The step-by-step instructions to construct a simulation model are given below.

➤ Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with Metric Units** as your template. The default **Run type**, Flowsheet, is appropriate for this example. Click **OK**.

The Aspen Plus main window is now active.

Drawing the Simulation Flowsheet

To place unit operation blocks:

1. On the model library palette, click on the **Separators** tab. The icons in the separator category are displayed in the model menu.
2. Click on the **Flash2** icon. Move the cursor to the process flowsheet window and click at the desired location.

   The Flash2 block will appear on the flowsheet window.

To place streams:

1. Click on the **Material STREAMS** icon and move the mouse to the process flowsheet window.

   Red and blue arrows will appear. These arrows indicate the location of required (red) and optional (blue) stream connection ports to the inlet port of FLASH2.

2. Click on the red feed arrow, drag the mouse to a proper location and click again. Repeat the procedure to create two product streams.
3. Click on the arrow symbol that appears to the top left of the **Material STREAMS** icon to switch the mouse out of the insert mode.

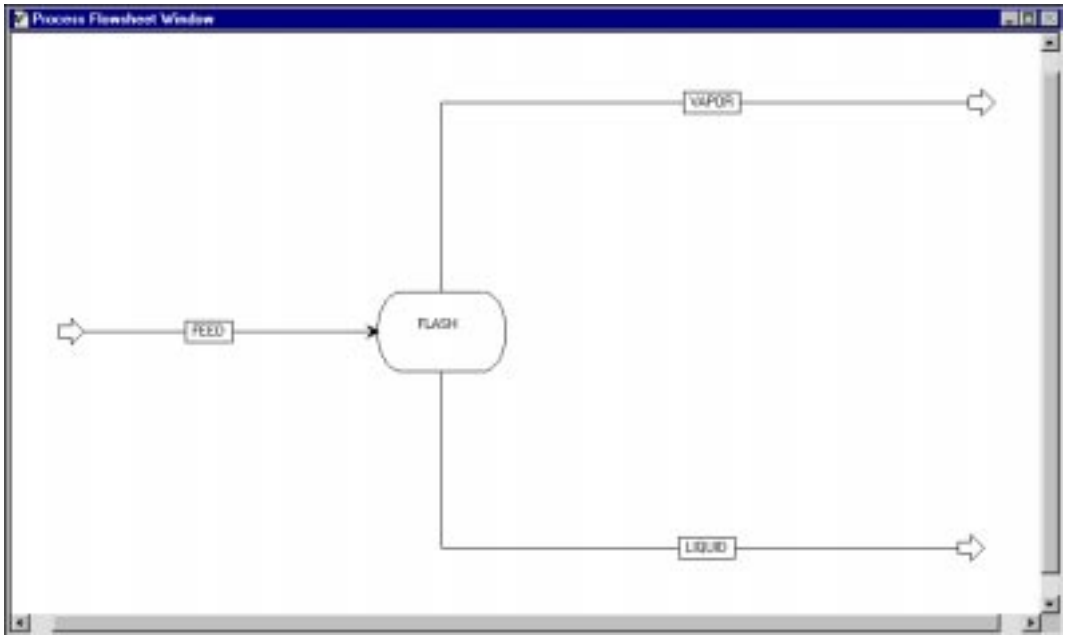
   If the mouse is showing cross-hair, +, it means the mouse is still in the insert mode.

To rename streams:

1. Click on the name box of the stream to be renamed.
2. Click the *right* mouse button and select **Rename Stream** from the pop-up menu.

   Insert a proper name for each stream by repeating the procedure.

Your flow diagram should look like this:



Specifying Setup and Global Options

In this example you will use the Expert guidance system (Next button) rather than the Data Browser navigation tree to enter process and model specifications in Polymers Plus.

To specify setup and global options:

1. Click on the **Setup** button on the toolbar.

   The **Specifications** form is displayed. The cursor will appear in the title space of the **Global** tab sheet.

   Type the title of your run as “Van Krevelen predictions for Cp, H and Rho for Copolymers”.

   Make sure that the **Run type** is specified as Flowsheet.

2. Click on the **Description** tab.

   Type the following information: “The objective of this example is to demonstrate how to use Polymers Plus to predict pure component properties of polymers using the Van Krevelen group contribution method”.

3. Click on the **Next** button .

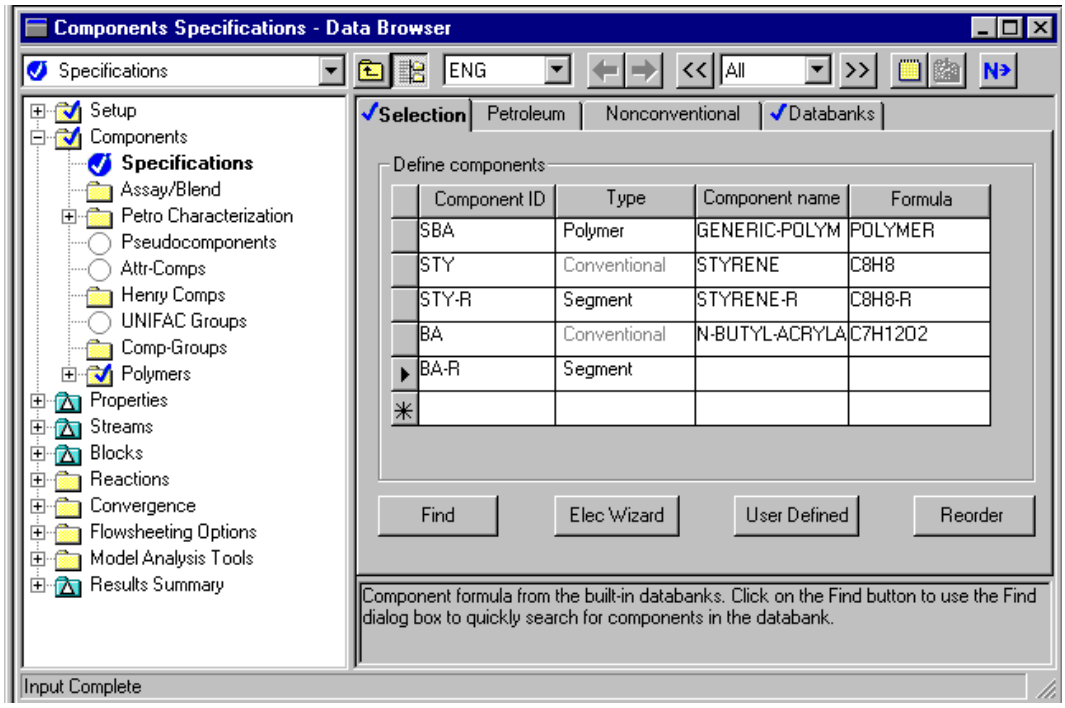
   A **Components Specifications** form appears.

Specifying and Characterizing Components

To specify and characterize components:

1. On the **Selection** tab sheet, enter the **Component ID**, **Type**, **Component name**, and **Formula** for monomers, segments and copolymer.

   Your form should look like this:



For the segment BA-R, the name and formula slots are left empty because as part of this exercise you will provide molecular structure for this segment. Also, for the polymer the generic polymer component is selected since this copolymer is not in the databank

2. Click on the **Next** button  .

   A **Components Polymers Characterization** form appears.

3. In the **Segments** tab sheet, select REPEAT from the **Type** drop down list to define STY-R and BA-R as the repeat segments.

4. Click on the **Polymers** tab.

   For polymer SBA, select **Properties selection** as the **Built-in attribute group** from the drop down list.

Specifying Physical Properties

To specify physical properties:

1. Click on the **Next** button .

   A **Properties Specifications** form is displayed.

2. On the **Global** tab sheet, select POLYNRTL from the **Base method** drop down list.

3. Click on the **Next** button .

   A **Required Properties Input Complete** pop-up form appears.

4. Click **OK** to **Go to Next required input step**.

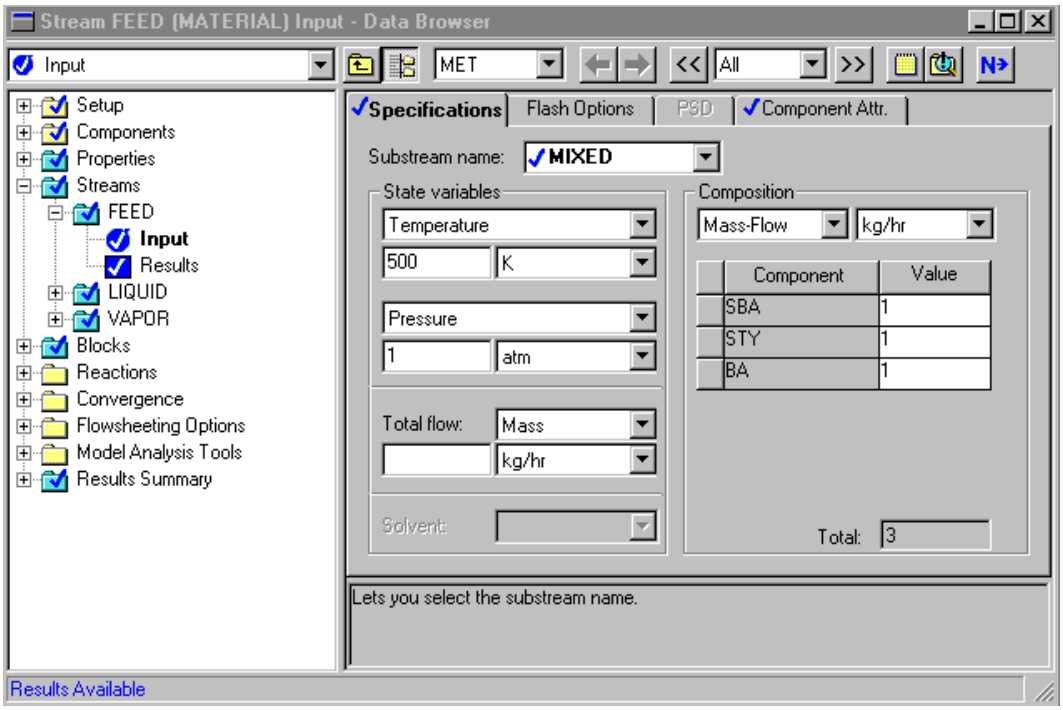
Supplying Process Information

To supply process information:

1. The **Stream FEED Input** form is displayed.

2. Enter 500K for Temperature, 1 atm for Pressure and 1 kg/hr for the Mass-Flow rate for each component.

   Your form should look like this:



3. Click on the **Component Attr.** tab.

   From the **Attribute ID** drop down list, select DPN and enter 1000 in the **Value** cell.

   From the **Attribute ID** drop down list, select SFLOW and enter 1 in the **Value** cell for STY-R and BA-R.

4. Click on the **Next** button .

   The **FLASH Input** form is displayed.

5. In the **Specifications** tab sheet, enter 500K for **Temperature** and 1 atm for **Pressure**.

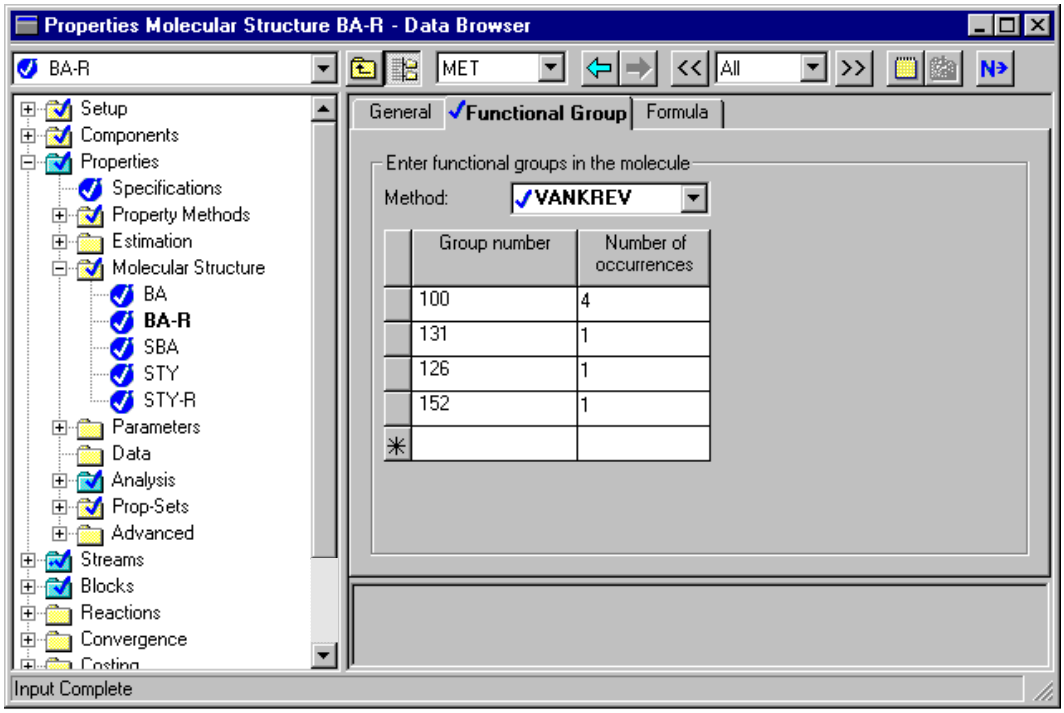
Defining Molecular Structure

To define the molecular structure for the segment BA-R:

1. From the Data Browser **Properties** folder, click on the **Molecular Structure** sub-folder.
2. In the **Object manager**, click on the name **BA-R** and click **Edit**.
3. Click on the **Functional Group** tab.

   From the **Method** drop down list select the **VANKREV** (Van Krevelen) method.

4. Enter the **Group number** and **Number of occurrences** as shown:



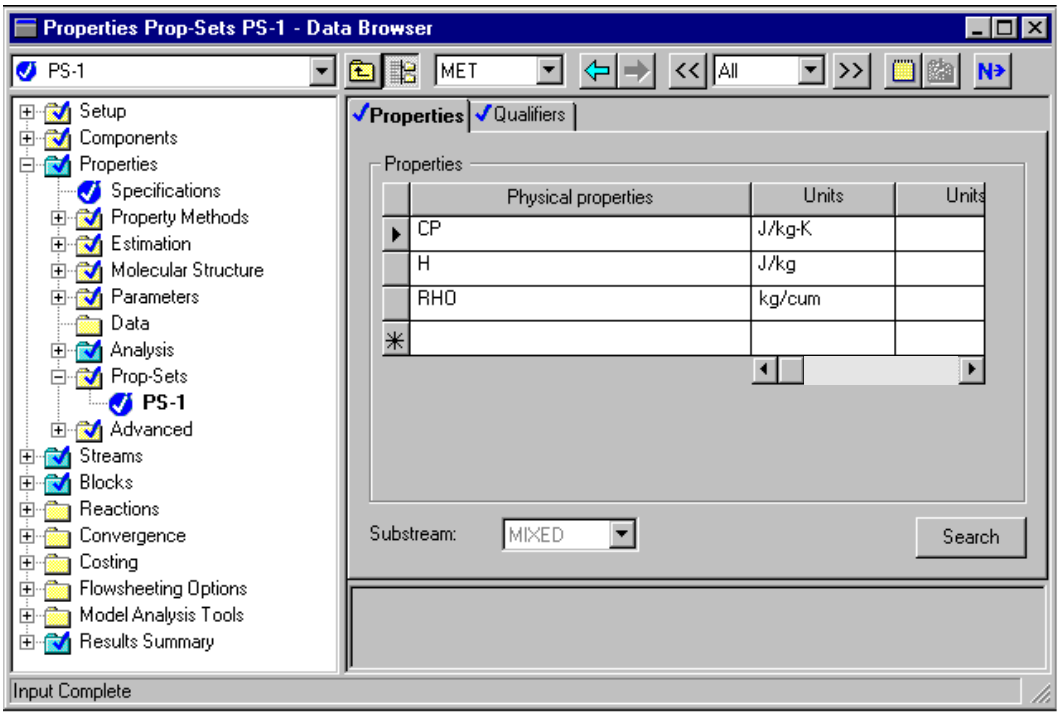
Creating Property Sets

To be able to list desired polymer properties, you need to create property sets and property tables. To do this:

1. In the Data Browser **Properties** folder, click on the **Prop-Sets** sub-folder.
2. In the **Object manager**, click **New**.

   A **Create new ID** pop-up form appears, click **OK** to accept the name PS-1.
3. On the **Properties** tab sheet, select **CP** (in J/kg-K), **H** (in J/kg) and **RHO** (in kg/cum) from the **Physical properties** drop down list.

   Your form should look like this:



4. Click on the **Qualifiers** tab.

   Select **Liquid** in the **Phase** drop down list and enter SBA, STY, and BA in the **Component** row.

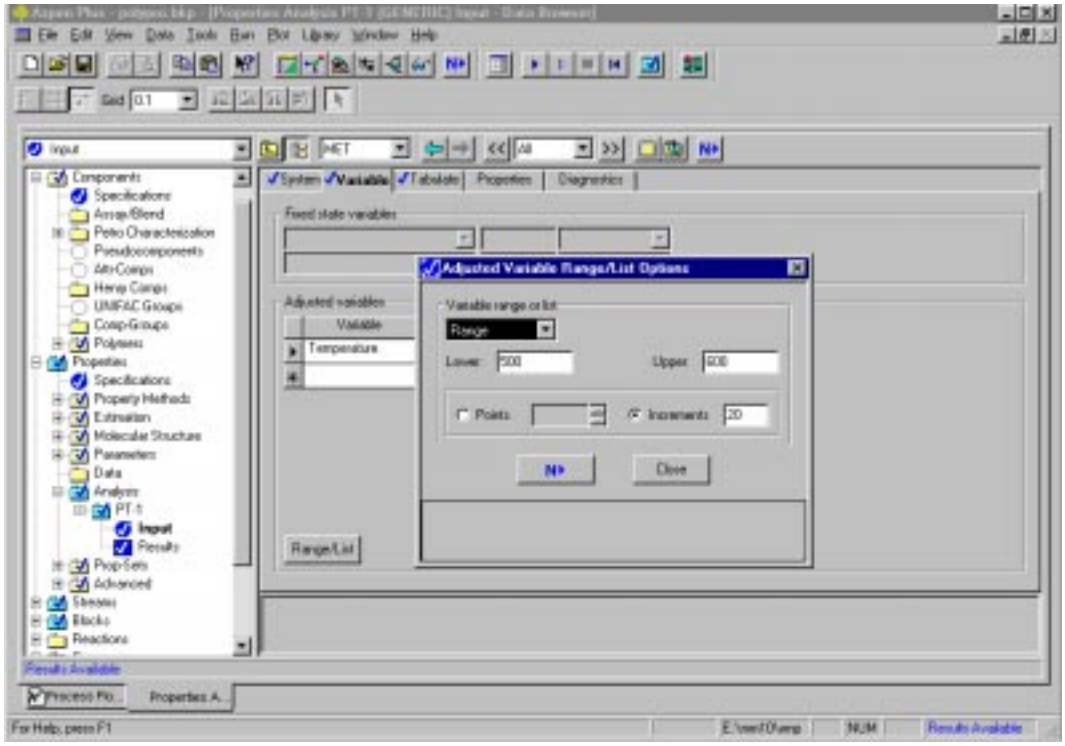
Creating Property Tables

To create property tables:

1. In the Data Browser, click on the **Analysis** sub-folder.
2. In the **Object manager**, click **New**.

   The **Create new ID** pop-up form appears.
3. Select **GENERIC** from the **Select type** drop down list and accept PT-1 by clicking on **OK**.
4. On the **System** tab sheet, click to select **Reference flowsheet stream**.
5. Select stream **FEED** from the **Stream ID** drop down list and select **Temperature & pressure** for the **Flash type**.
6. Click on the **Variable** tab and select **Temperature** as the adjusted variable from the drop down list.
7. Click on the **Range/List** button.

   On the **Adjusted Variable Range/List Options** pop-up form select **Range** from the drop down list and enter 500K to 600K with Increments of 20. Click **Close**.



8. Click on the **Tabulate** tab, and select Prop-Set **PS-1** by clicking on the > button.

Your simulation is now complete.

RUNNING THE SIMULATION AND EXAMINING THE RESULTS

To run the simulation:

1. In the Aspen Plus main window toolbar, click on the **Run Control Panel** button to open the **Control Panel**.
2. Click on the Start button to run the simulation.

To examine the results:

The results can be checked by selecting the **Results** option from the drop down list between the << and >> buttons and using the browser forward button >> to navigate to the next form with results.

The input summary is shown in Figure 2.1.

Figure 2.1 Input Summary

```
TITLE 'Van Krevelen Predictions for Cp, H and Rho for Copolymers'

IN-UNITS MET

DEF-STREAMS CONVEN ALL

DESCRIPTION "
        The objective of this example is to demonstrate how to use
        Polymers Plus to predict pure component properties of polymers using
        the Van Krevelen group contribution method. "

DATABANKS POLYMER  / SEGMENT  / PURE93  / NOASPENPCD

PROP-SOURCES POLYMER  / SEGMENT  / PURE93

COMPONENTS
    SBA POLYMER SBA /
    STY C8H8 STY /
    STY-R C8H8-R STY-R /
    BA C7H12O2-D1 BA /
    BA-R * BA-R

FLOWSHEET
    BLOCK FLASH IN=FEED OUT=VAPOR LIQUID

PROPERTIES POLYNRTL

STRUCTURES
    VANKREV BA-R 100 4 / 131 1 / 126 1 / 152 1

POLYMERS
    SEGMENTS STY-R REPEAT / BA-R REPEAT
    POLYMERS SBA
    ATTRIBUTES SBA SFRAC SFLOW DPN ZMOM FMOM

PROP-SET PS-1 CP H RHO UNITS='J/kg-K' 'J/kg' 'kg/cum'  &
        SUBSTREAM=MIXED COMPS=SBA STY BA PHASE=L

STREAM FEED
    SUBSTREAM MIXED TEMP=500. <K> PRES=1.
    MASS-FLOW SBA 1. / STY 1. / BA 1.
    COMP-ATTR SBA SFLOW ( 1. 1. )
    COMP-ATTR SBA DPN ( 1000. )

BLOCK FLASH FLASH2
    PARAM TEMP=500. <K> PRES=1.

STREAM-REPOR NOMOLEFLOW MASSFLOW

PROP-TABLE PT-1 FLASHCURVE
    STREAM FEED FLASH-CODE=TP
    VARY TEMP
    RANGE LOWER=500. UPPER=600. INCR=20.
    TABULATE PROPERTIES=PS-1
```

REFERENCES

Van Krevelen, D. W., Properties of Polymers, 3rd Ed., Elsevier, Amsterdam (1990).

3 REGRESSING PROPERTY PARAMETERS

SUMMARY

This example demonstrates how to use the data regression (DRS) capabilities to fit the mixture parameters of an equation of state (EOS) model to binary vapor-liquid equilibrium (VLE) data.

The steps covered include:

- Specifying Setup and Global Options
- Specifying and Characterizing Components
- Specifying Physical Property Method
- Entering Experimental Data
- Specifying a Regression Case
- Specifying Physical Property Parameters
- Running the Simulation and Examining the Results

Correlative models that are used to describe thermodynamic properties of mixtures often contain binary interaction parameters. These parameters account for mixture non-idealities, and are necessary for accurate representation of the mixture behavior. For each constituent pair of a multicomponent mixture, these parameters are obtained by regressing some form of binary experimental information.

In this example, binary VLE data of ethylene-polyethylene mixture are regressed to obtain the two binary interaction parameters of the Sanchez-Lacombe EOS, k_{ij} and η_{ij}. You can find the details of this model in Section 3.9 of the *Polymers Plus User Guide*. Ethylene-polyethylene binary mixture is encountered in polyolefin production, and at high pressures the thermodynamic behavior of this mixture can be described by an EOS such as the Sanchez-Lacombe model.

In this example you will create a Polymers Plus data regression (DRS) session, run the DRS, and examine the results.

SETUP INSTRUCTIONS

The step-by-step instructions to define the simulation model are given below.

➤Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with Metric Units** as your template. Select **Data Regression** as the **Run type**. Click **OK**.

The Aspen Plus main window is now active.

Specifying Setup and Global Options

In this example you will use the Expert guidance system (Next Button ) rather than the Data Browser navigation tree to enter process and model specifications in Polymers Plus.

To specify setup and global options:

1. Click on the **Setup** button  on the toolbar.

   A **Specifications** form is displayed. The cursor will appear in the title space of the **Global** tab sheet.

   Type title of your run as “Regression of binary parameters for the POLYSL model”.

2. Select the **Run type** as **Data Regression** (DRS), in the **Units of measurement** frame, select SI for **Input data** and **Output results**.

3. Click on the **Description** tab.

   Type the following information: “The objective of this example is to demonstrate how to use the data regression capabilities to fit the mixture parameters of an EOS model to binary VLE data”.

4. From the Data Browser, click on the **Units Sets** sub-folder and click **New**.

   Click **OK** to accept US-1 as the Unit set ID.

   A dialog box appears requesting approval to make US-1 the global unit set, click **No**.

5. On the **Standard** tab sheet, select **Eng** from the **Copy from** drop down list.
6. Change the following units to:

   Pressure = bar
   Temperature = K
7. Click on the **Transport** tab and set Density=kg/cum.
8. Refer to steps 4-7 to create unit set US-3 in which **Copy from**=SI, Pressure=bar, Delta P=bar.
9. Click on the **Next** button  .

   The **Components Specifications** form is displayed.

Specifying and Characterizing Components

The component information necessary for this DRS run is:

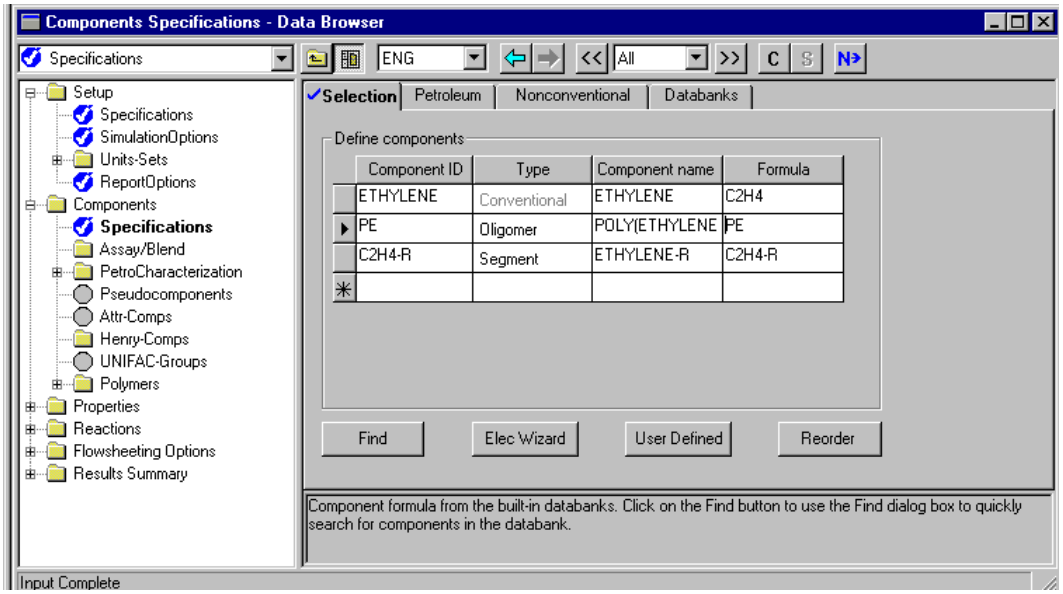
Component ID	Type	Component Name	Formula
PE	Oligomer	POLY(ETHYLENE)	PE
ETHYLENE	Conventional	ETHYLENE	C2H4
C2H4-R	Segment	ETHYLENE-R	C2H4-R

In this example the polymer is identified as oligomer. This is because no chemical reaction or any other unit operation involving the polymer is present. Consequently, you do not need to specify any polymer attributes. By defining the polymer as an oligomer, the need to enter any attribute information is eliminated. However, you need to supply the true molecular weight of the oligomer as described in Specifying Physical Property Parameters below. The results of the DRS run are not be affected by this choice. (Currently DRS runs can be accomplished only for oligomers, but not for polymers).

To supply the information given above:

1. On the **Selection** tab sheet displayed, enter the **Component ID**, **Component name**, and **Formula** for ethylene, polyethylene and ethylene segment.

   At the end of this procedure, your form should look like this:



2. From the Data Browser, double click on the **Polymers** sub-folder, and click on **Characterization**.
3. On the **Segments** tab sheet, select REPEAT from the **Type** drop down list for segment C2H4-R.
4. Click on the **Oligomers** tab, select C2H4-R as the segment and enter 1132 for PE in the oligomer row.
5. Click on the **Next** button .

   The **Properties Specifications** form is displayed.

Specifying Physical Property Method

The Sanchez-Lacombe model physical property method (POLYSL) is used in this example. To choose this method:

1. On the **Global** tab sheet already displayed, select POLYSL from the **Base method** drop down list**.**
2. Click on the **Next** button .
3. In the **Enter the sets of data to be regressed** dialog box that appears, click **OK**.

   The **Properties Data** form is displayed

Entering Experimental Data

The experimental data to be used in this DRS run are from Hao, and they are presented in Table 3.1 (Hao, et al, 1992). To enter the data:

1. In the **Object manager**, click **New**.

   Enter ID as C2PE399 (for data at 399K), and select **MIXTURE** from the drop down list. Click **OK**.

   A **Properties Data** data browser for **C2PE399** appears.

2. From the drop down lists, select **Phase equilibrium** as the **Category** and TPXY as the **Data type**.

   A **Change Data Type** dialog box appears. Click **OK** to continue.

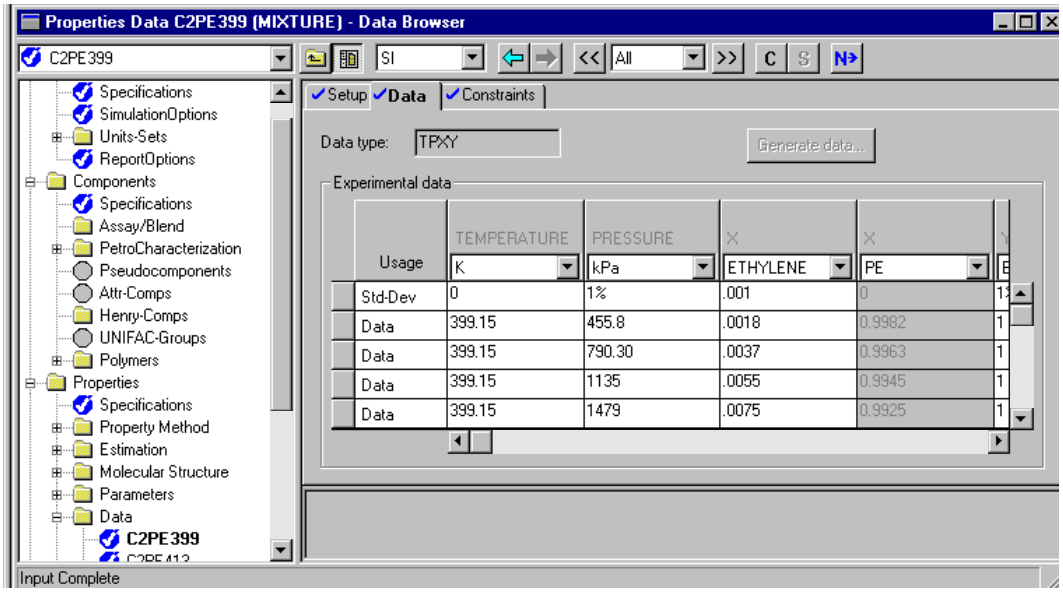
   From the **Available Components** frame, select ETHYLENE and PE by using the > button.

3. Click on the **Constraints** tab, you need to delete PE from the **Component** column since PE is considered involatile in this example.

   This is done by clicking the right mouse button while the cursor is on PE, and choosing **Clear** from the pop-up menu.

4. Click on the **Data** tab, from the drop down lists, select K for **Temperature** and kPa for **Pressure**. In the table enter the data at 399.15K given in Table 3.1.

After the first four entries, your data sheet should look like this:



5. From the Data Browser, click on the **Data** folder and repeat the steps for data entry at 413.15K and 428.15K.

In the first row, standard deviation for the data type in each column is shown. The standard deviation gives an estimate for the magnitude of random error in a particular piece of data. The default inserts can be overwritten if necessary. For example, here you need to enter zero for temperature, one percent for pressure and 0.001 for mole fraction. Complete data entry by entering all data points given in Table 3.1.

Table 3.1 Binary VLE Data of Ethylene+Polyethylene (MWn=31700)

Data Type TPXY				
Composition Basis MASS-FRAC				
Usage	**Temp., K**	**Pressure, KPA**	**X, Ethylene**	**X, PE**
STD-DEV	0	1%	.001	0
DATA	399.15	455.8	.0018	0.9982
DATA	399.15	790.30	.0037	0.9963
DATA	399.15	1135	.0055	0.9945
DATA	399.15	1479	.0075	0.9925
DATA	399.15	1824	.0107	0.9893
DATA	399.15	2168	.0136	0.9864
DATA	399.15	2513	.0158	0.9842
DATA	399.15	2857	.0175	0.9825
DATA	399.15	3202	.0198	0.9802
DATA	399.15	3546	.0221	0.9779
DATA	399.15	3891	.0242	0.9758
DATA	399.15	4235	.0255	0.9745
DATA	399.15	4580	.0285	0.9715
DATA	399.15	4924	.0305	0.9695
DATA	399.15	5269	.0330	0.967
DATA	399.15	5613	.0359	0.9641
DATA	413.15	455.8	.0015	0.9985
DATA	413.15	790.30	.0034	0.9966
DATA	413.15	1135	.0048	0.9952
DATA	413.15	1479	.0068	0.9932
DATA	413.15	1824	.0087	0.9913
DATA	413.15	2168	.0112	0.9888
DATA	413.15	2513	.0131	0.9869
DATA	413.15	2857	.0151	0.9849
DATA	413.15	4580	.0250	0.975
DATA	413.15	4924	.0277	0.9723
DATA	413.15	5269	.0296	0.9704
DATA	413.15	5613	.0328	0.9672
DATA	428.15	455.8	.0013	0.9987

continued

Table 3.1 Binary VLE Data of Ethylene+Polyethylene (MWn=31700) (cont.)

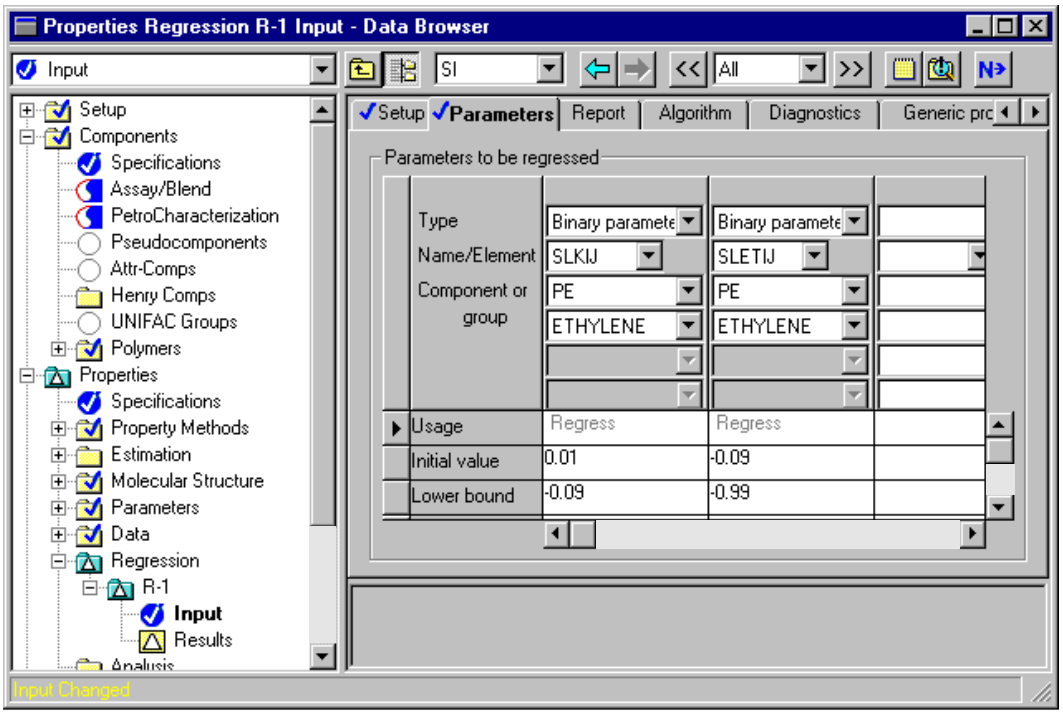
Usage	Temp., K	Pressure, KPA	X, Ethylene	X, PE
DATA	428.15	790.30	.0029	0.9971
DATA	428.15	1135	.0039	0.9961
DATA	428.15	1479	.0055	0.9945
DATA	428.15	1824	.0074	0.9926
DATA	428.15	2168	.0090	0.991
DATA	428.15	2513	.0105	0.9895
DATA	428.15	2857	.012	0.988
DATA	428.15	3202	.0146	0.9854
DATA	428.15	3546	.0164	0.9836
DATA	428.15	3891	.0178	0.9822
DATA	428.15	4235	.0207	0.9793
DATA	428.15	4580	.0222	0.9778
DATA	428.15	4924	.0242	0.9758
DATA	428.15	5269	.0265	0.9735
DATA	428.15	5613	.0286	0.9714

Specifying a Regression Case

After data entry, click on the **Next** button . A **Regression Cases Incomplete** pop-up form appears.

To specify a regression case:

1. Select the **Specify the data regression cases** option. Click **OK**.
2. Click **New** in the **Object manager**. Click **OK** to accept R-1.
3. Click on the **Parameters** tab, refer to the form below to enter the **Initial value** and **Lower bound** values, also select the drop down list options as shown:



Note that unlike the unary parameters, the binary parameters are specified for the oligomer-conventional species pair, not for the segment-conventional species pair.

Specifying Physical Property Parameters

To specify physical property parameters:

1. Click on the **Next** button N>.

   A **Required Properties Input Complete** pop-up form appears.

2. Click to select the **Enter property parameters** option. Click **OK**.

   An **Additional property parameters** pop-up form appears.

3. Accept the **Pure component parameters** option. Click **OK**.

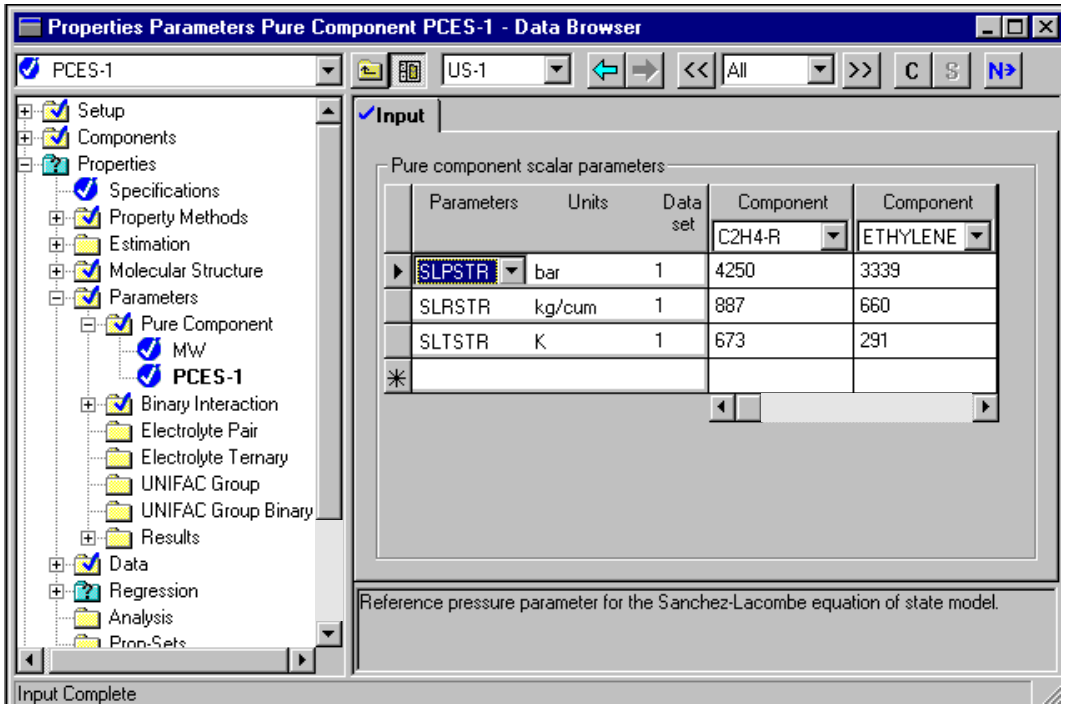
In the Sanchez-Lacombe model, for each component, three pure component constants, T^*, P^*, and ρ^* are needed.

To enter these pure component constants:

1. In the **Pure Component** form displayed, click **New**.

   Enter PCES-1 for the new name. Click **OK** to accept the **Scalar** option and PCES-1.

2. On the **Input** tab sheet enter three Sanchez-Lacombe constants for ethylene and segment of PE and for the local unit sets select **US-1** from the data browser menu bar drop down list as shown.



   These constants are reported in Appendix F of the *Polymers Plus User Guide*. Note that unary parameters are entered for segment of the polymer, rather than the polymer itself.

3. From the Data Browser, click on the **Pure-Component** sub-folder.

4. In the **Object manager**, click **New**.

   Enter MW for the new name. Click **OK** to accept the **Scalar** option.

5. On the **Input** tab sheet, select MW from the **Parameter** drop down list and PE from the **Component** drop down list.

   Enter 31756.85 in the PE cell.

   This is necessary when the oligomer option is used to identify a polymeric molecule.

6. Select the local unit set as US-3 from the data browser menu bar drop down list.

RUNNING THE SIMULATION AND EXAMINING THE RESULTS

To run the simulation:

1. Click on the **Next** button  .

   A **Required Properties Input Complete** pop-up form appears.

2. Click **OK** to accept the default selected.

   A **Required Data Regression Input Complete** dialog box appears.

3. Click **OK**.

   A **Data Regression Run Selection** pop-up form appears.

4. Click **OK** to accept R-1 as the run selection.

   The **Control Panel** window appears.

The simulation starts running and diagnostic messages appear in the control panel. When you see the message **Data Regression completed**, the results are present.

To examine the results:

Select **Results** from the drop down list between the  and  buttons and use the browser forward button  to navigate to the next form with results.

The input summary is given in Figure 3.1.

Figure 3.1 Input Summary for DRS Run

```
TITLE 'Regression of binary parameters for the POLYSL model'

IN-UNITS SI

DESCRIPTION "
        The objective of this example is to demonstrate how to use the
        data regression capabilities to fit the mixture parameters of
        an EOS model to binary VLE data. "

DATABANKS POLYMER  / SEGMENT  / PURE93  / NOASPENPCD

PROP-SOURCES POLYMER  / SEGMENT  / PURE93

COMPONENTS
    ETHYLENE C2H4 ETHYLENE /
    PE PE PE /
    C2H4-R C2H4-R C2H4-R

PROPERTIES POLYSL

PROP-DATA MW
    IN-UNITS SI PRESSURE=bar PDROP=bar
    PROP-LIST MW
    PVAL PE 31756.8563

PROP-DATA PCES-1
    IN-UNITS ENG DENSITY='kg/cum' PRESSURE=bar TEMPERATURE=K  &
        PDROP=psi
    PROP-LIST SLPSTR / SLRSTR / SLTSTR
    PVAL C2H4-R 4250 / 887 / 673
    PVAL ETHYLENE 3339 / 660 / 291

PROP-DATA SLETIJ-1
    IN-UNITS SI PRESSURE=bar PDROP=bar
    PROP-LIST SLETIJ
    BPVAL PE ETHYLENE -.4040175320
    BPVAL ETHYLENE PE -.4040175320

PROP-DATA SLKIJ-1
    IN-UNITS SI PRESSURE=bar PDROP=bar
    PROP-LIST SLKIJ
    BPVAL PE ETHYLENE -.0900000000
    BPVAL ETHYLENE PE -.0900000000

PARAMETERS
    BIPARAMETER 1 SLKIJ PE ETHYLENE 1 1.00000000E-02  &
        -9.00000000E-02 1.10000000E-01 1.00000000E+00
    BIPARAMETER 2 SLETIJ PE ETHYLENE 1 -9.00000000E-02  &
        -9.90000000E-01 8.10000000E-01 1.00000000E+00

CASE R-1
    DATA-GROUPS C2PE399 CONSISTENCY=YES / C2PE413  &
        CONSISTENCY=YES / C2PE428 CONSISTENCY=YES
    PARAMETERS BINARY=1 2

DATA-GROUP C2PE399
    IN-UNITS SI PRESSURE=kPa PDROP=atm
    SYSTEM-DEF TPXY ETHYLENE PE COMPOSITION=MASS-FRAC
    PHASE-EQ VL ETHYLENE
    DATA 1 399.15 455.8 .0018 1 /
         2 399.15 790.30 .0037 1 /
         3 399.15 1135 .0055 1 /
         4 399.15 1479 .0075 1 /
```

Figure 3.1 Input Summary for DRS Run (cont.)

```
         5 399.15 1824 .0107 1 /
         6 399.15 2168 .0136 1 /
         7 399.15 2513 .0158 1 /
         8 399.15 2857 .0175 1 /
         9 399.15 3202 .0198 1 /
         10 399.15 3546 .0221 1 /
         11 399.15 3891 .0242 1 /
         12 399.15 4235 .0255 1 /
         13 399.15 4580 .0285 1 /
         14 399.15 4924 .0305 1 /
         15 399.15 5269 .0330 1 /
         16 399.15 5613 .0359 1
    STD-DEV 1 0 -1 .001 -1

DATA-GROUP C2PE413
    IN-UNITS SI PRESSURE=kPa PDROP=atm
    SYSTEM-DEF TPXY ETHYLENE PE COMPOSITION=MASS-FRAC
    PHASE-EQ VL ETHYLENE
    DATA 1 413.15 455.8 .0015 1 /
         2 413.15 790.30 .0034 1 /
         3 413.15 1135 .0048 1 /
         4 413.15 1479 .0068 1 /
         5 413.15 1824 .0087 1 /
         6 413.15 2168 .0112 1 /
         7 413.15 2513 .0131 1 /
         8 413.15 2857 .0151 1 /
         9 413.15 3202 .0166 1 /
         10 413.15 3546 .0189 1 /
         11 413.15 3891 .0208 1 /
         12 413.15 4235 .0235 1 /
         13 413.15 4580 .0250 1 /
         14 413.15 4924 .0277 1 /
         15 413.15 5269 .0296 1 /
         16 413.15 5613 .0328 1
    STD-DEV 1 0 -1 .001 -1

DATA-GROUP C2PE428
    IN-UNITS SI PRESSURE=kPa PDROP=atm
    SYSTEM-DEF TPXY ETHYLENE PE COMPOSITION=MASS-FRAC
    PHASE-EQ VL ETHYLENE
    DATA 1 428.15 455.8 .0013 1 /
         2 428.15 790.30 .0029 1 /
         3 428.15 1135 .0039 1 /
         4 428.15 1479 .0055 1 /
         5 428.15 1824 .0074 1 /
         6 428.15 2168 .0090 1 /
         7 428.15 2513 .0105 1 /
         8 428.15 2857 .012 1 /
         9 428.15 3202 .0146 1 /
         10 428.15 3546 .0164 1 /
         11 428.15 3891 .0178 1 /
         12 428.15 4235 .0207 1 /
         13 428.15 4580 .0222 1 /
         14 428.15 4924 .0242 1 /
         15 428.15 5269 .0265 1 /
         16 428.15 5613 .0286 1
    STD-DEV 1 0 -1 .001 -1

POLYMERS
    SEGMENTS C2H4-R REPEAT
    OLIGOMERS PE C2H4-R 1132

PROPERTY-REP NOPCES PROP-DATA DFMS
```

REFERENCES

Hao, W., Elbro, H. S. and Alessi, P. "*Polymer Solution Data Collection*", Chemistry Data Series, Vol. XIV, Part 1, DECHEMA (1992).

4 FITTING KINETIC PARAMETERS

SUMMARY

The objective of this example is to demonstrate how to fit kinetic rate constant parameters to available data for a single reactor flowsheet. This example describes the basic procedure for setting up a simulation to fit kinetic parameters. The Styrene Ethyl Acrylate process in the Steady-State Applications section provides strategies for fitting parameters for complex systems.

The steps covered include:

- Drawing the Simulation Flowsheet
- Specifying Setup and Global Options
- Specifying and Characterizing Components
- Specifying Physical Properties
- Specifying Polymerization Kinetics
- Supplying Process Information
- Specifying Data Regression
- Running the Simulation and Examining the Results

In this process, vinyl acetate is polymerized in solution in a batch reactor with methanol as a solvent and methyl peroxide as the initiator. The reactor is operated isothermally with the polymerization temperature maintained at the boiling point of methanol, 64.7°C, 1 atm.

The reactor is considered liquid filled. Therefore, vapor-liquid equilibrium calculations will not be accounted for in this simulation. In practice, there is usually some vapor space in the reactor and reflux condenser. This has some effect on the concentration in the liquid phase, however, the effect is not considered significant for this homopolymerization example. The simulation can be easily modified to include VLE calculations if necessary.

The component information is summarized below:

Component ID	Type	Component Name	Formula
MPO	Conventional	VINYL-ACETATE	C4H6O2-1
VAC	Conventional	VINYL-ACETATE	C4H6O2-1
MEOH	Conventional	METHANOL	CH4O
POLY	Polymer	POLY(VINYL-ACETATE)	PVAC
VAC-SEG	Segment	VINYL-ACETATE-R	C4H6O2-R-3

The feed stream consists of 100 kg/hr of vinyl acetate, 80 kg/hr of methanol, 0.0258 kg/hr of initiator at one atmosphere and 64.7°C. The initial charge is determined by multiplying the flowrates by the cycle time needed to prepare the charge.

SETUP INSTRUCTIONS

The step-by-step instructions for setting up the simulation are given below.

➤Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with Metric Units** as your template. The default **Run type**, Flowsheet, is appropriate for this example. Click **OK**.

The Aspen Plus main window is now active.

Drawing the Simulation Flowsheet

To place unit operation blocks:

1. On the model library palette, click on the **Reactors** tab.

   The models in the reactors category are displayed in the model menu.

2. Click on the **RBatch** icon. Move the cursor to the process flowsheet window and click at the desired location.

   The **RBatch** block will appear on the flowsheet window.

To place streams:

1. Click on the **Material STREAMS** icon and move the mouse to the process flowsheet window.

   Red and blue arrows will appear. These arrows indicate the location of required (red) and option (blue) stream connection ports to the inlet port of batch reactor.

2. Click on the red feed arrow, drag the mouse to a proper location and click again. Repeat the procedure to create one feed stream and one product stream.

3. Click on the arrow symbol that appears on the top left of the **Material STREAMS** icon to switch the mouse out of the insert mode.

   If the mouse is showing a "+" it means the mouse is still in the insert mode.

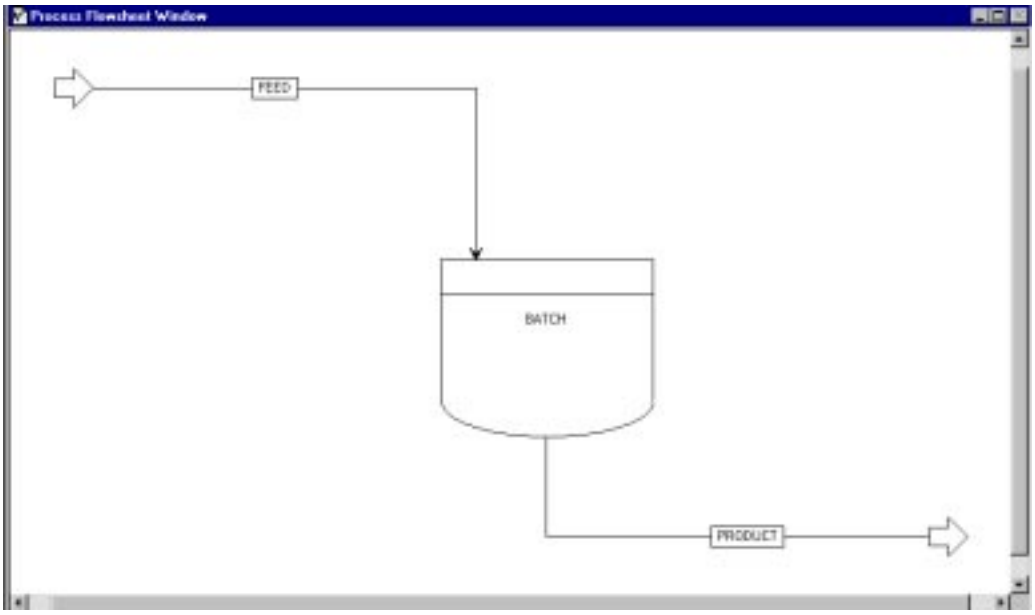
To rename streams:

1. Click on the name box of the stream to be renamed.

2. Click the *right* mouse button and select **Rename Stream** from the pop-up menu.

   Insert a proper name for each stream by repeating the procedure.

Your flow diagram should look like this:



Specifying Setup and Global Options

In this example you will use the Expert guidance system (Next Button) rather than the Data Browser navigation tree to enter process and model specifications in Polymers Plus.

To specify setup and global options:

1. Click on the **Setup** button on the toolbar.

   The **Specifications** form is displayed. The cursor will appear in the title space of the **Global** tab sheet.

   Type the title of your run as "Free-Radical Kinetics Parameter Fitting."

   Make sure that the **Run type** is specified as Flowsheet.

2. Click on the **Description** tab.

   Type in the following information: “This example illustrates how to fit kinetic rate constant parameters in Polymers Plus”.

To specify simulation options:

1. In the Data Browser, click on the **Simulation Options** form.
2. Click on the **System** tab and select **Print Fortran tracebacks when a Fortran error occurs**.
3. Click on the **Limits** tab and enter 10000 for the **Simulation time limit in CPU seconds**.

To define a unit-set:

1. In the Data Browser tree view, double click on the **Units Sets** sub-folder to bring up the Units-Sets Object manager.
2. Click **New** to create a new set.

   Enter an ID (e.g. SET1) for the new units-set and click **OK**.

3. On the Aspen Plus dialog box that appears requesting approval to make SET1 the global unit set, click **Yes**.
4. A **Setup Units Sets** form appears.

   Use SI units as the basis for your new set by selecting SI from the **Copy from** drop down list.

5. Enter user defined units as:
   - Mass Flow = kg/hr
   - Mole Flow = kmol/hr
   - Pressure = atm
   - Temperature = C
6. Click on the **Next** button .

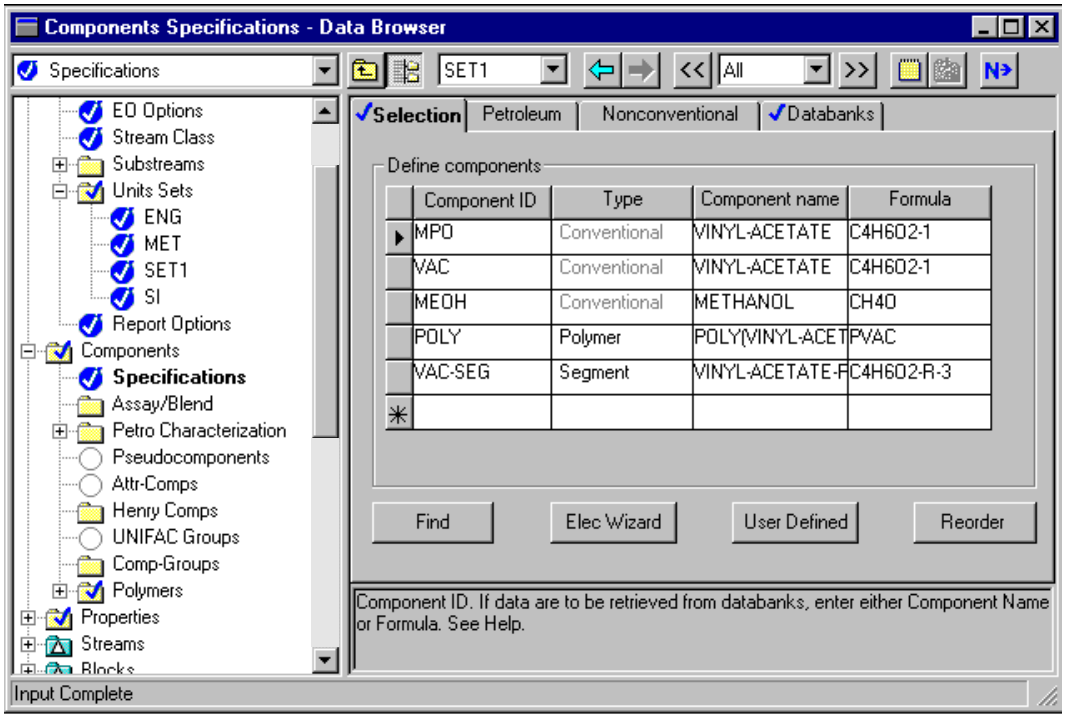
   A **Components Specifications** form appears.

Specifying and Characterizing Components

To specify and characterize components:

1. On the **Selection** tab sheet, enter the **Component ID**, **Component name**, and **Formula** for monomers, segments and copolymer.

   Your form should look like this:



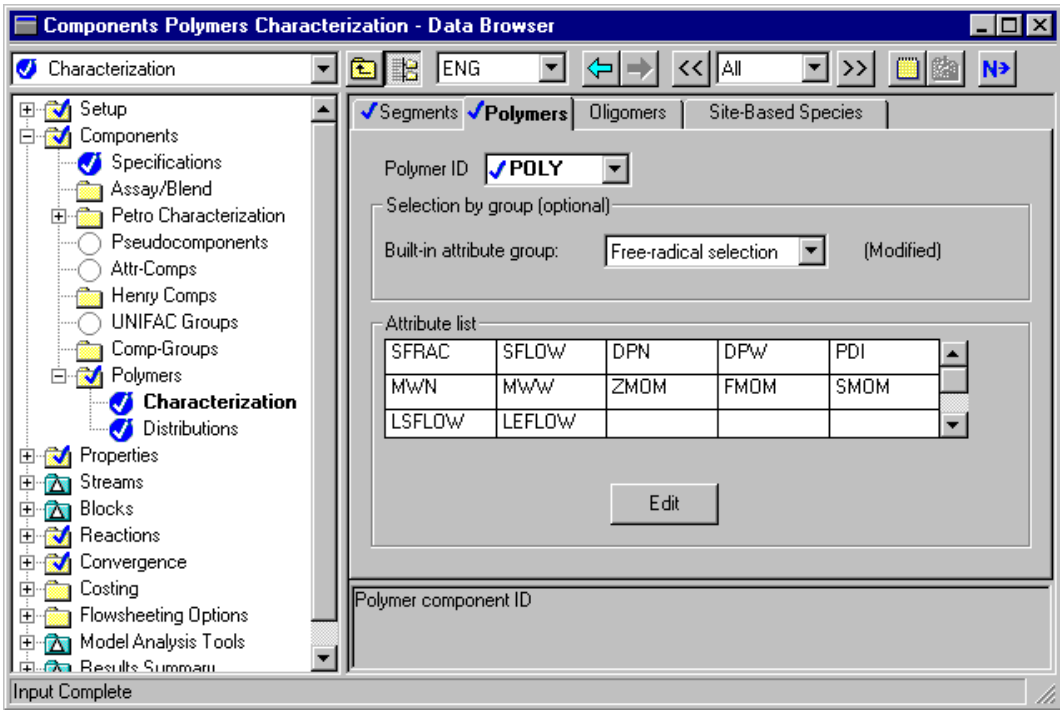
2. Click on the **Next** button N>.

   A **Components Polymers Characterization** form appears.

3. In the **Segments** tab sheet, select REPEAT from the **Type** drop down list to define VAC-SEG as a repeat segment .

4. Click on the **Polymers** tab, select **Free-radical selection** from the **Built-in attribute group** drop down list and click on **Edit** to modify the attribute group in the **Polymer Attributes** pop-up form.

The modified attribute group is shown below, deselect the attributes which do not appear here:



Specifying Physical Properties

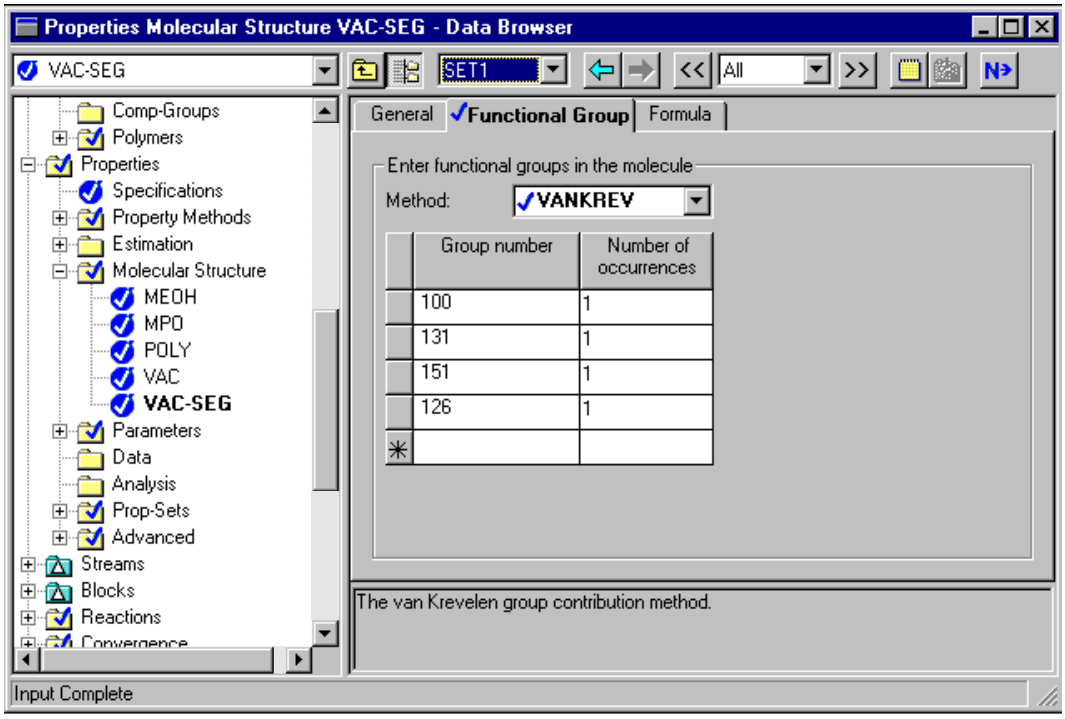
To specify physical properties:

1. Click on the **Next** button .

   A **Properties Specifications** form is displayed.

2. Select POLYNRTL from the **Base method** drop down list.
3. From the Data Browser, double click on the **Molecular Structure** sub-folder.
4. From the **Molecular Structure** sub-folder, click on **VAC-SEG**.
5. Click on the **Functional Group** tab and choose the VANKREV (Van Krevelen) from the **Method** drop down list.

   Enter the groups and occurrences to match the following:



6. From the Data Browser, double click on the **Parameters** sub-folder.

   Click on the **Pure Component** sub-folder.

7. In the **Object manager**, click **New**.

   Enter DATA-1 as the new name of a property, and accept SCALAR as the type.

8. On the **Pure Component** form for **DATA-1**, choose MW from the **Parameters** drop down list.

   For **Component**, enter the data shown below:

Component	MW
MPO	76.050
VAC	86.090
MEOH	32.040
POLY	258270.0
VAC-SEG	86.090

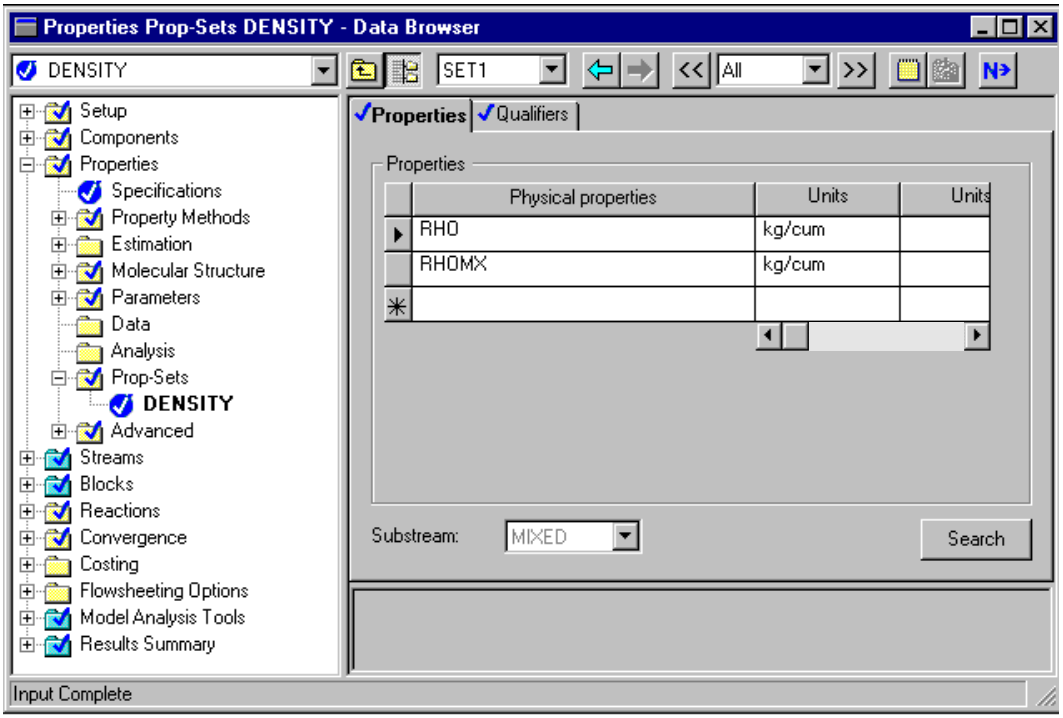
9. From the Data Browser, click on the **Pure Component** sub-folder.

10. In the **Object manager**, click **New**.

    Click to select **T-dependent correlation** and choose DHVLWT-1 from the default name list that appears. Click **OK**.

11. On the **Pure Component** form for **DHVLWT-1**, choose MPO, VAC, POLY and VAC-SEG from the **Components** drop down list and enter for each component:
    - **Temperature units**=K
    - **Property units**=J/kmol
    - Row 1=39556000.0
    - Row 2=180.350
12. From the Data Browser, double click on the **Prop-Sets** sub-folder.
13. In the **Object Manager**, click **New**.

    Enter **DENSITY** as the new name of the property set and select the following physical properties on the **Properties** tab sheet:



14. Click on the **Qualifiers** tab and select **Liquid** from the **Phase** drop down list and VAC, POLY, and MEOH, from the **Component** drop down list.
15. To display the **DENSITY** set in the stream report, on the Data Browser, click on the **Report Options** form in the **Setup** folder and click on the **Stream** tab.

    Click on the **Property Sets** button and select **DENSITY** using the  button. Click **Close**.

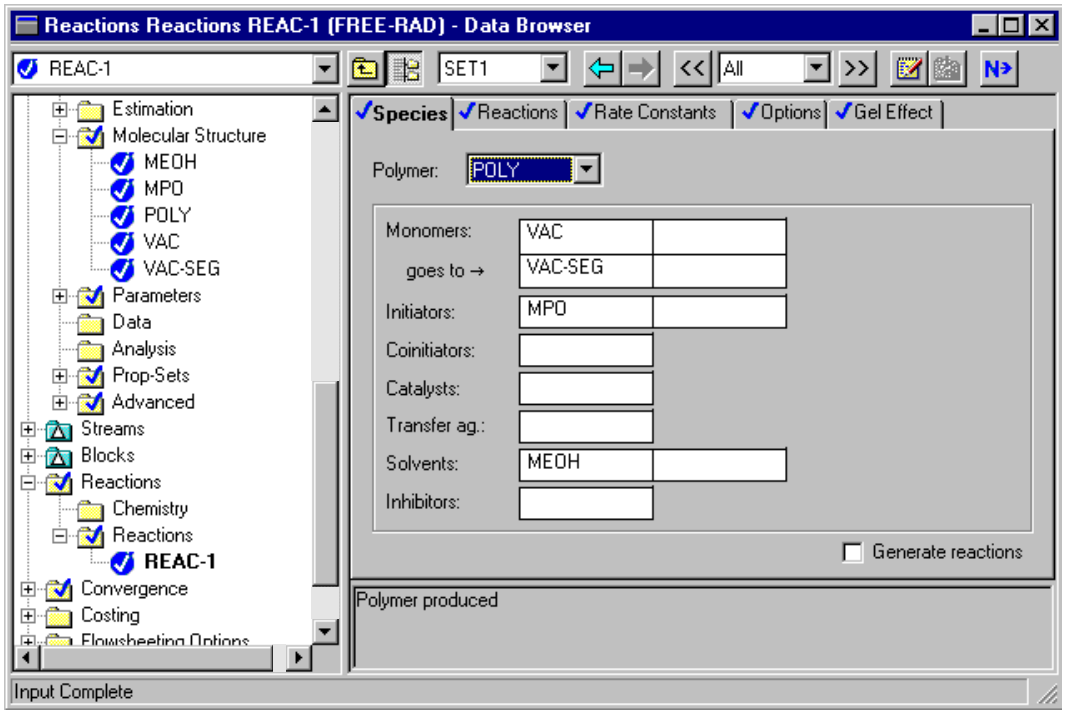
Specifying Polymerization Kinetics

To specify polymerization kinetics:

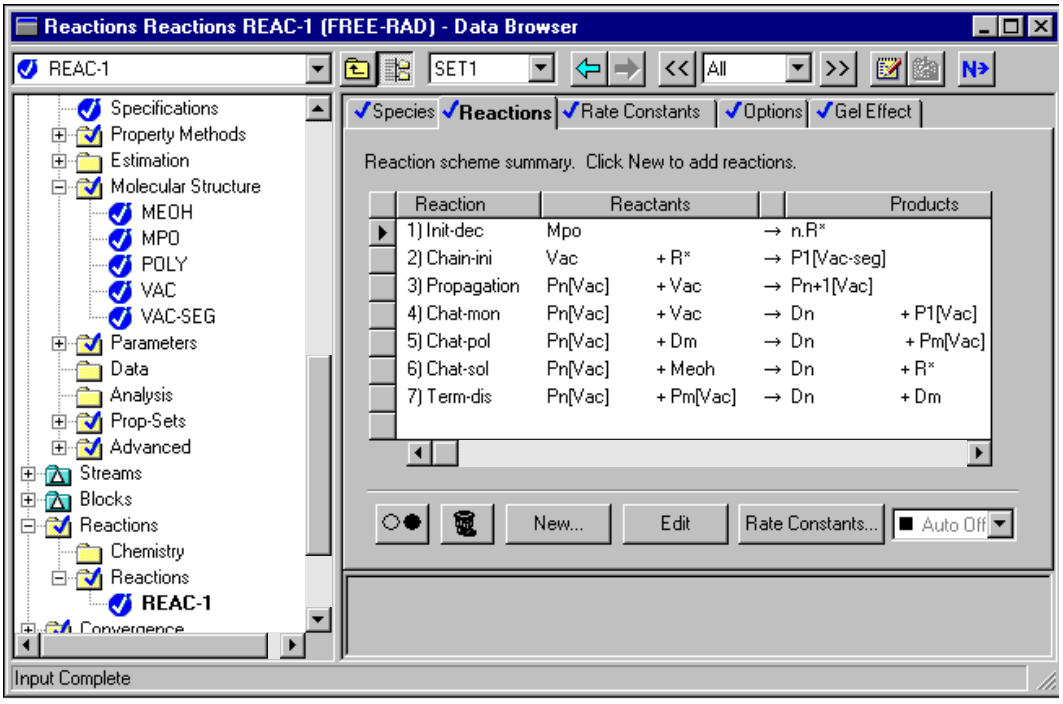
1. From the Data Browser, double click on the **Reactions** folder.
2. From the **Reactions** folder, click on the **Reactions** sub-folder.
3. In the **Object manager**, click **New**.

   Enter REAC-1 as the new ID name.

   Select FREE-RAD from the **Type** drop down list. Click **OK**.
4. On the **Species** tab sheet enter the data as shown below:



5. Click on the **Reactions** tab. You will need to fill in the sheet so that it looks like:



To do this for the first reaction:

6. Click **New**.

   On the **Add Reaction** pop-up form, select INIT-DEC for the **Reaction type** and MPO for the **Initiator**. Click **Done**.

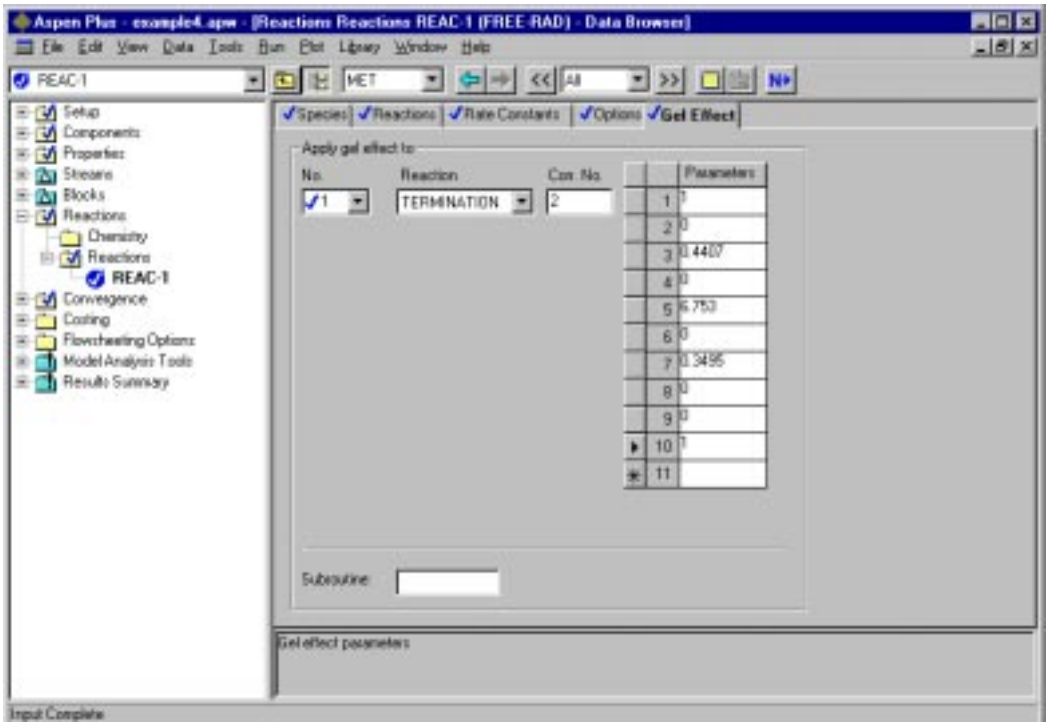
   Repeat this step for the other 6 reactions shown.

7. Click the **Rate Constants** button on the **Reactions** form. Chose the **Summary** tab and fill in the following rate information:

Type	Pre-Exponential (1/s)	Activation Energy (J/kmol)
Initiator Decomposition	5.0E-6	0
Chain Initiation	9500	0
Propagation	1000	0
Chain Transfer to Monomer	2.337	0
Chain Transfer to Polymer	1.235	0
Chain Transfer to Solvent	0.323	0
Termination by disproportionation	1.645E8	0

8. Click **Close**.

9. Click the **Options** tab and click to select the **Gel Effect** option.
10. Click the **Gel Effect** tab and fill in the information as shown:



Supplying Process Information

To enter feed stream information:

1. From the Data Browser, double click on the **Streams** folder.
2. From the **Streams** folder, double click on the **FEED** sub-folder.
3. On the **Specifications** tab sheet, enter the stream conditions as follows:

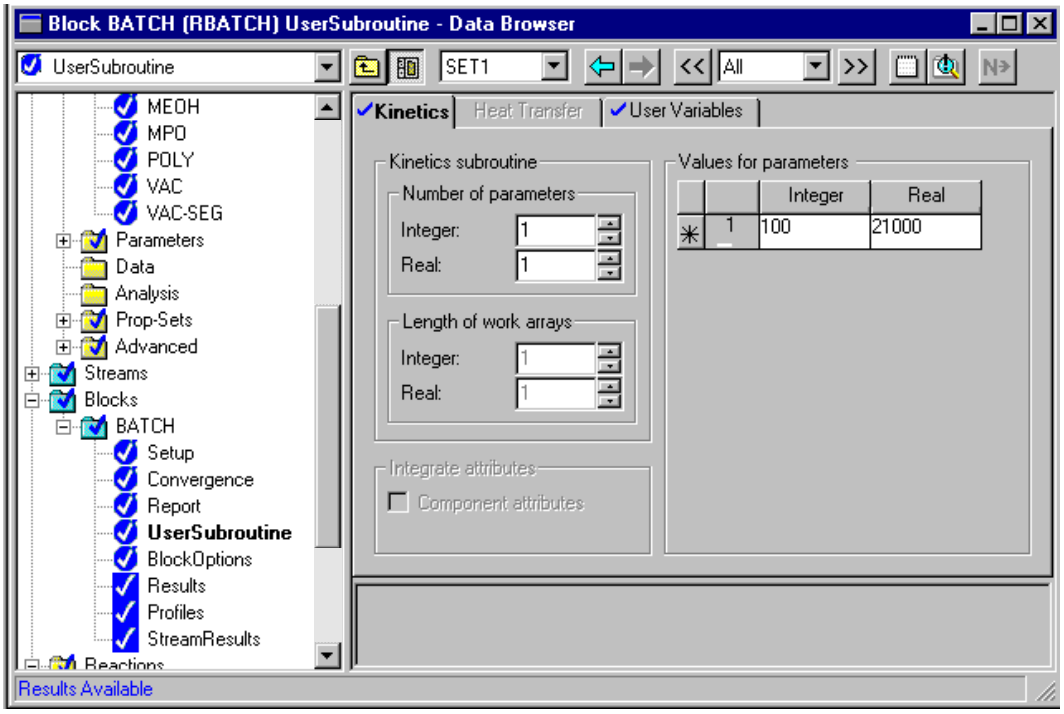
Temperature	64.7°C
Pressure	1 atm
MPO	0.0258 kg/hr
VAC	100 kg/hr
MEOH	80 kg/hr

To enter block information:

1. Click on the **Next** button  .
2. On the **Specifications** tab sheet, select **Constant temperature** from the **Reactor operating specification** drop down list.

Enter a temperature of 64.7°C and pressure of 1 atm, **Liquid-Only** is appropriate for the **Reactor** drop down list selection.

3. Click on the **Reactions** tab and move REAC-1 to the **Selected reaction sets** frame using the  button.
4. Click on the **Stop Criteria** tab, enter:
   - **Criterion No. =**1
   - **Location** = Reactor
   - **Variable type** = Time
   - **Stop value** = 5
5. Click on the **Operation Times** tab, enter:
   - **Total cycle time** =1 hr
   - **Maximum calculation time** = 5 hr.
   - **Time interval between profile points** = 0.5 hr
   - **Maximum number of profile points** = 52
6. From the Data Browser, click on the **Convergence** form in the **BATCH** sub-folder.
7. On the **Flash Options** tab, enter an error tolerance of 0.001.
8. Click on the **Integration Loop** tab and enter:
   - Integration convergence tolerance of 1E-6
   - Initial step size of 1E-7
   - Maximum step size of 0.1 hr.
9. From the Data Browser, click on the **User Subroutine** form in the **BATCH** sub-folder, and fill out the **Kinetics** tab sheet as shown below:



10. Click on the **User Variables** tab and enter 1 for the **Number of user variables**.

Specifying Data Regression

To specify data regression:

1. From the Data Browser, double click on the **Model Analysis Tools** folder.

   Double click on the **Data Fit** folder and the **Data Set** sub-folder.

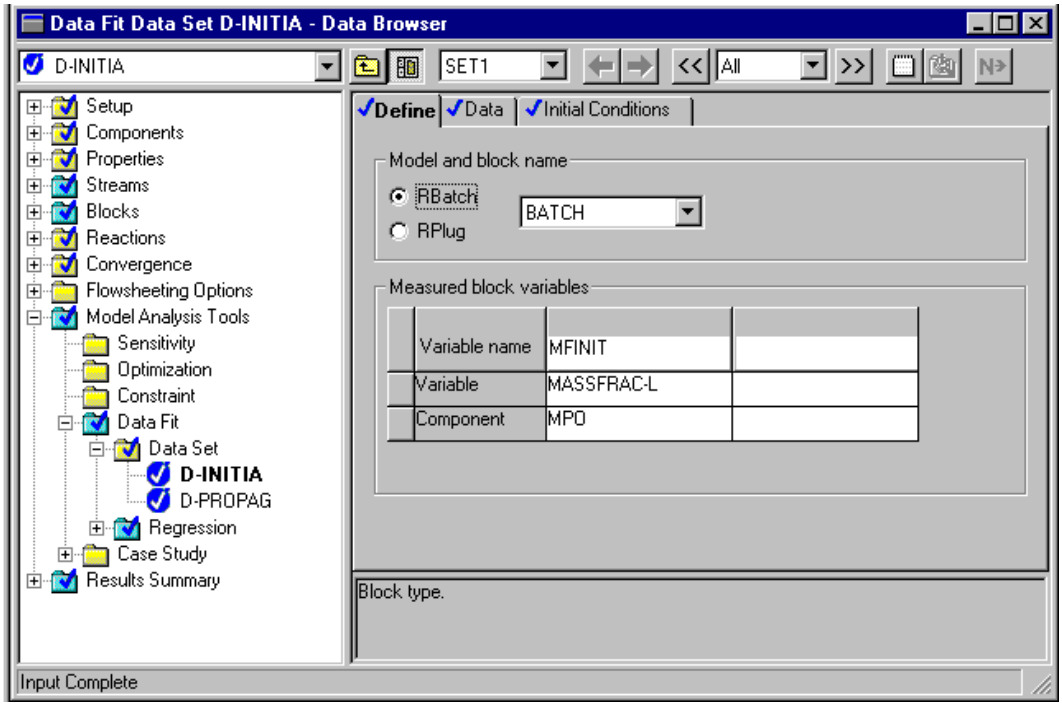
You will need to create two data sets: one named D-INITIA and one named D-PROPAG.

To create the first data set:

1. In the **Object manager**, click **New**.

   Enter the new name as D-INITIA, and select PROFILE-DATA as the type. Click **OK**.

2. On the **Define** tab sheet, enter the data as shown (where MFINIT is the mass fraction of the initiator):



3. Click on the **Data** tab, enter a **Std-Dev** of 1.0%.

   Enter the time and mass fraction data shown in Table 4.1.

4. Click on the **Initial Conditions** tab, enter the temperature as 65°C, and the pressure as 1 atm. The reactor type and block name are already displayed as RBATCH and BATCH respectively.

To create the second data set:

1. From the Data Browser, double click on the **Data Set** sub-folder.
2. In the **Object manager**, click **New**.

   Enter the new name as D-PROPAG, and select PROFILE-DATA as the type. Click **OK**.

3. On the **Define** tab sheet, enter DUTY as the **Variable name** and **Variable**, the block name as already displayed as RBATCH. Make sure that BATCH is selected from the drop down list.
4. Click on the **Data** tab, enter a **Std-Dev** of 5.0%.

   Enter the time and heat release data shown in Table 4.1.

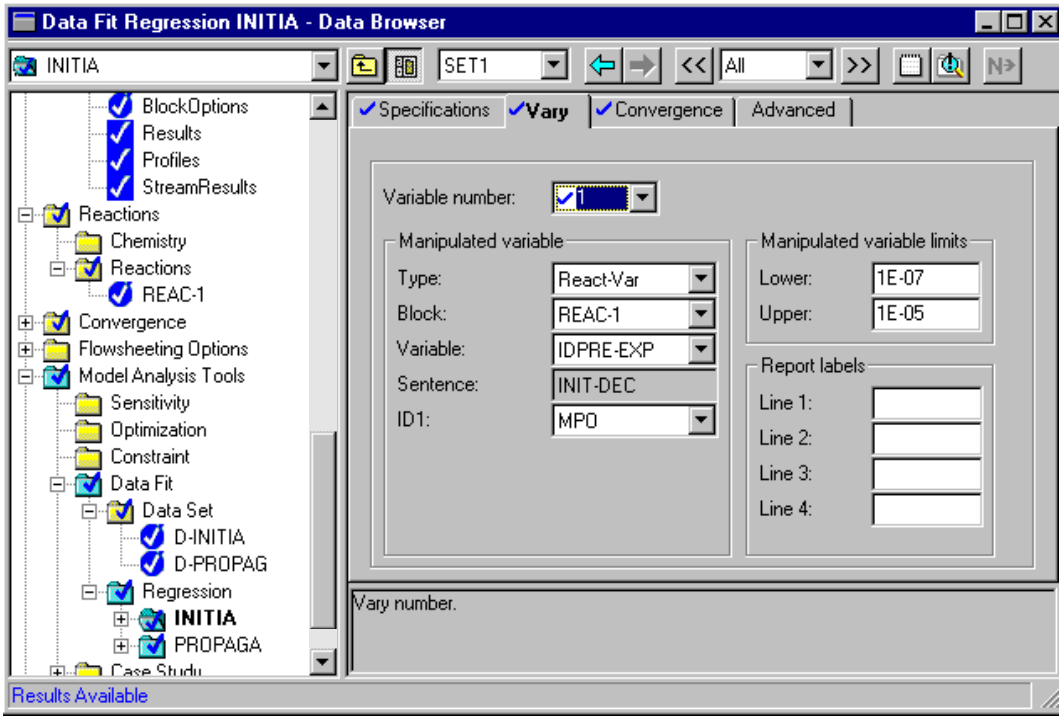
5. Click on the **Initial Conditions** tab, and enter the temperature as 64.5°C, and the pressure as 1 atm. The reactor type and block name are already displayed as RBATCH and BATCH respectively.

Table 4.1 PVAC Regression Data

Data Point	Time (hr)	Mass Fraction of Initiator	Instantaneous Heat Release (Watt)
1	0.0	1.554E-4	-3750.0
2	0.5	1.551E-4	-3700.0
3	1.0	1.546E-4	-3300.0
4	1.5	1.542E-4	-3250.0
5	2.0	1.538E-4	-3100.0
6	2.5	1.532E-4	-3000.0
7	3.0	1.526E-4	-2800.0
8	3.5	1.522E-4	-2650.0
9	4.0	1.518E-4	-2350.0
10	4.5	1.513E-4	-2150.0
11	5.0	1.509E-4	-3750.0

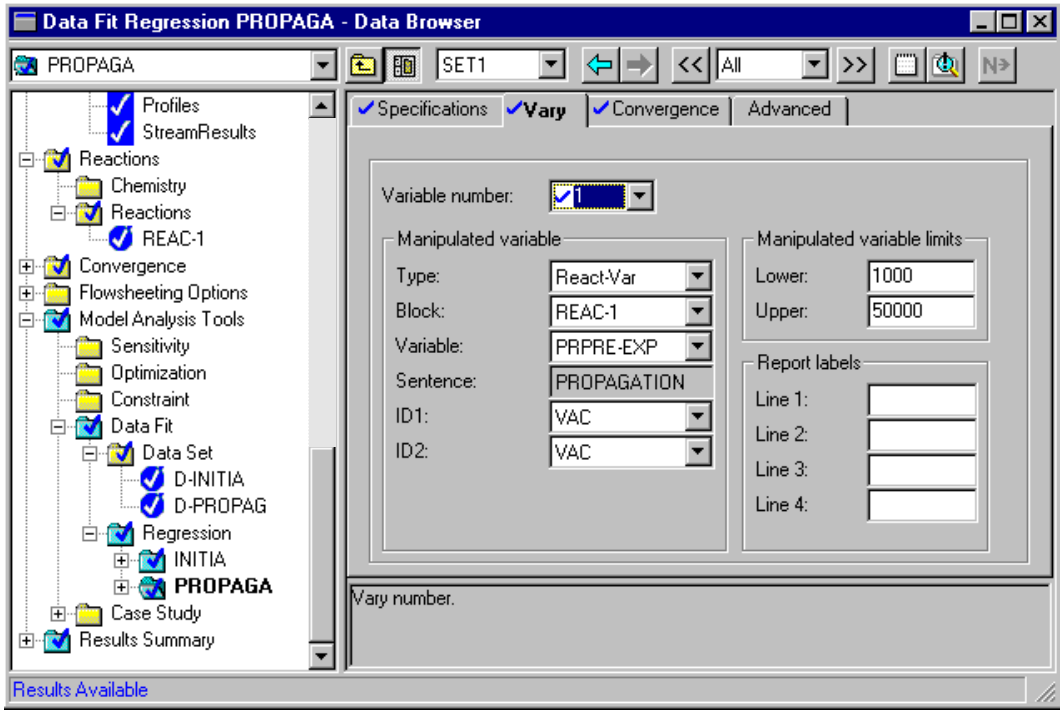
To define the regression cases:

1. Click on the **Next** button, on the **Data-Fit Regression Cases Incomplete** pop-up form, click to select **Specify Data-Fit Regression Cases**. Click **OK**.
2. In the **Object manager**, click **New**, enter INITIA as the name and click **OK**.
3. On the **Specifications** tab sheet, select D-INITIA from the **Data set** drop down list and accept 1 as the weight.
4. Click on the **Vary** tab and enter the data as shown below:



Note that to enter 1 as the **Variable number** you need to right mouse click in the cell and select **Create** from the pop-up menu, or by selecting **<New>** from the drop down list.

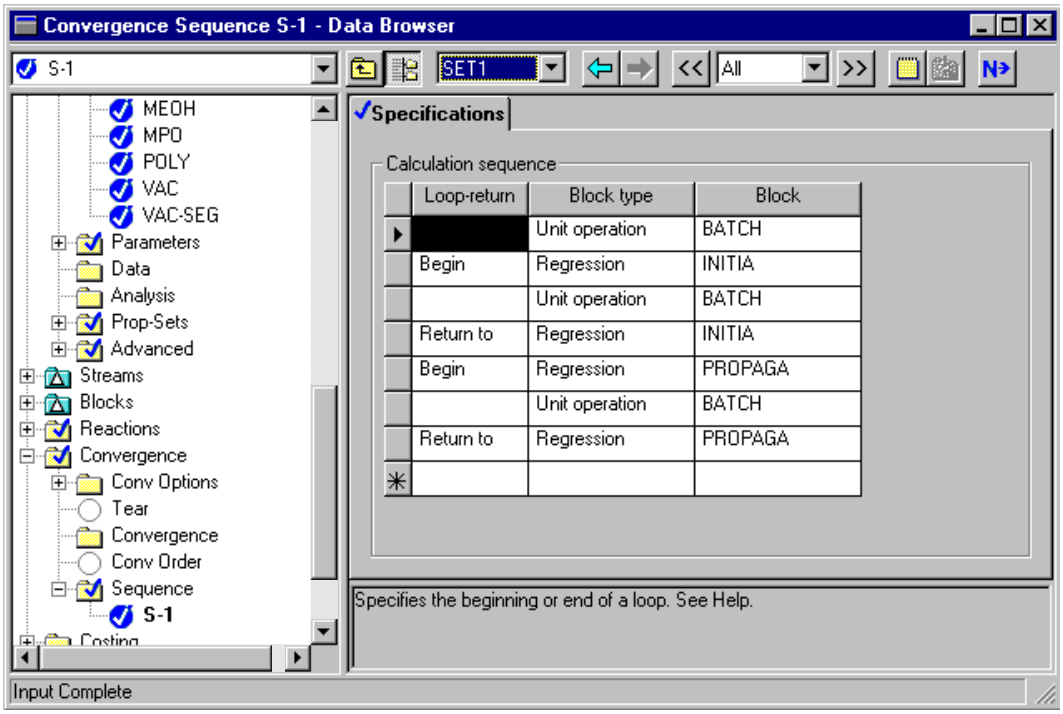
5. From the Data Browser, double click on the **Regression** sub-folder.
6. In the **Object manager**, click **New**, enter PROPAGA as the name and click **OK**.
7. On the **Specifications** tab sheet, select D-PROPAG from the **Data set** drop down list and accept 1 as the weight.
8. Click on the **Vary** tab and enter the data as shown below:



9. Click on the **Convergence** tab, and enter an **Absolute function tolerance** of 1.0.

Block Convergence

1. From the Data Browser, double click on the **Convergence** folder.
2. From the Convergence folder, click on the **Sequence** sub-folder.
3. Click **New** in the **Object manager**, accept S-1 as the sequence name. Click **OK**.
4. Fill in **Specifications** tab sheet as shown:



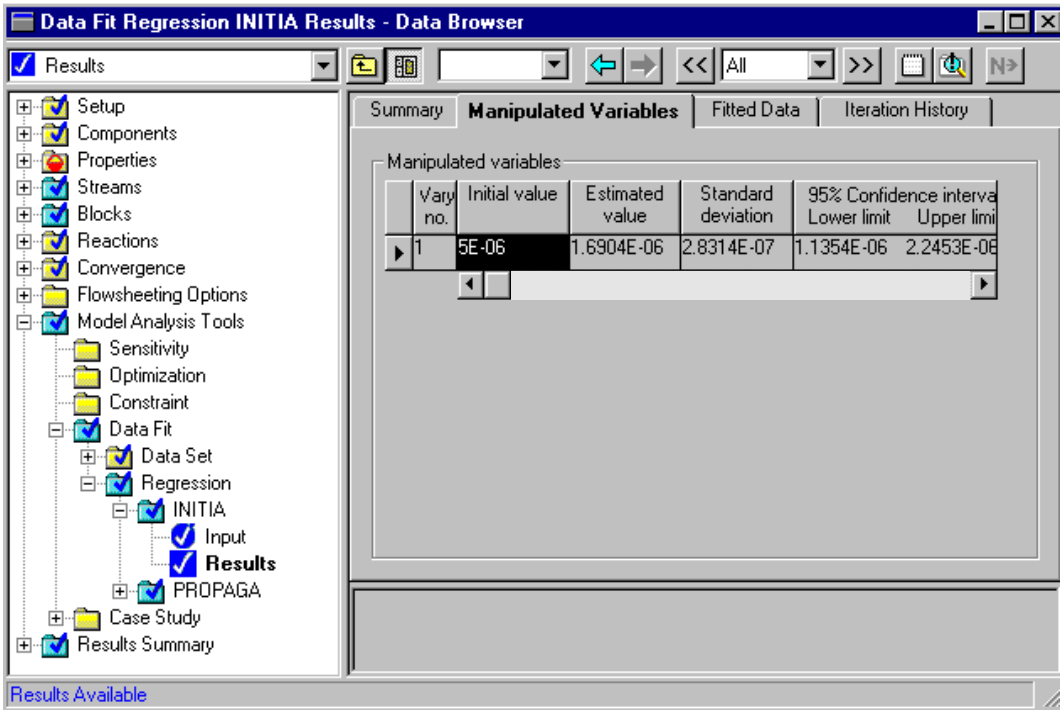
RUNNING THE SIMULATION AND EXAMINING THE RESULTS

To run the simulation:

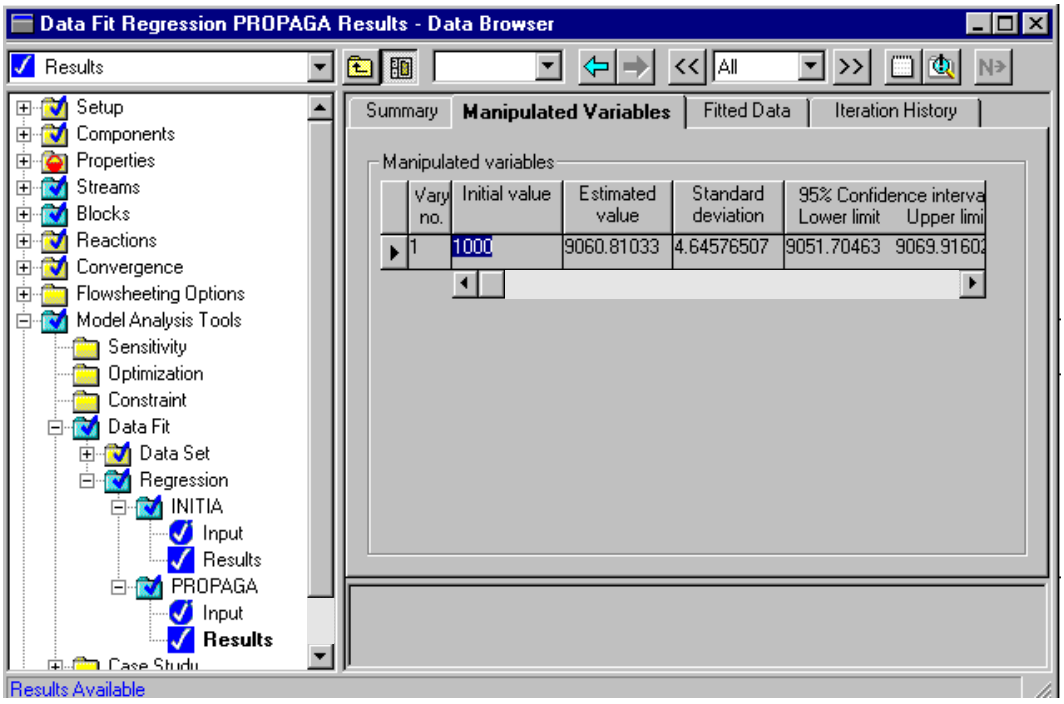
1. In the Aspen Plus main window toolbar, click on the **Run Control Panel** button to open the **Control Panel**.
2. Click on the Start button to run the simulation.

To examine the results:

The results can be checked by selecting the **Results** option from the drop down list between the << and >> buttons and using the browser forward button >> to navigate to the next form with results. The results for initiation are:



The results for propagation are:



The input summary is given in Figure 4.1.

Figure 4.1 Input Summary

```
TITLE 'Free-Radical Kinetics Parameter Fitting'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm  &
        TEMPERATURE=C TIME=hr PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=10000.0

DESCRIPTION "
        This example illustrates how to fit kinetic rate constant parameters
        in Polymers Plus. "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    MPO C4H6O2-1 MPO /
    VAC C4H6O2-1 MONOMER /
    MEOH CH4O METHANOL /
    POLY PVAC POLY /
    VAC-SEG C4H6O2-R-3 SEGMENT

FLOWSHEET
    BLOCK BATCH IN=FEED OUT=PRODUCT

PROPERTIES POLYNRTL

STRUCTURES
    VANKREV VAC-SEG 100 1 / 131 1 / 151 1 / 126 1

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST MW
    PVAL MPO 76.050
    PVAL VAC 86.090
    PVAL MEOH 32.040
    PVAL POLY 258270.0
    PVAL VAC-SEG 86.090

PROP-DATA DHVLWT-1
    IN-UNITS SI
    PROP-LIST DHVLWT
    PVAL MPO 39556000.0 180.350
    PVAL VAC 39556000.0 180.350
    PVAL POLY 39556000.0 180.350
    PVAL VAC-SEG 39556000.0 180.350

POLYMERS
    SEGMENTS VAC-SEG REPEAT
    POLYMERS POLY
    ATTRIBUTES POLY SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM LSFLOW LEFLOW
```

Figure 4.1 Input Summary (cont.)

```
PROP-SET DENSITY RHO RHOMX UNITS='kg/cum' SUBSTREAM=MIXED  &
        COMPS=VAC POLY MEOH PHASE=L

STREAM FEED
    SUBSTREAM MIXED TEMP=64.70 PRES=1.0
    MASS-FLOW MPO .028 / VAC 100 / MEOH 80

BLOCK BATCH RBATCH
    INT VALUE-LIST=100
    REAL VALUE-LIST=21000.0
    PARAM TYPE=T-SPEC PRINT-TIME=.5 CYCLE-TIME=1.0 MAX-TIME=5.0  &
        MAX-NPOINT=52 PRES=1.0 TEMP=64.70 NPHASE=1 PHASE=L  &
        INT-TOL=1.000E-06 HINIT=1.000E-07 FLASH-TOL=1E-3
    INTEG-PARAMS MAXSTEP=.1
    STOP 1 REACTOR TIME 5.0
    REACTIONS RXN-IDS=REAC-1
    REGR-POINTS 1 D-INITIA VALUE-LIST= 0.0 1800.000 3600.000  &
        5400.000 7200.000 9000.000 10800.00 12600.00 14400.00  &
        16200.00 18000.00 / 2 D-PROPAG VALUE-LIST= 1800.000  &
        3600.000 5400.000 7200.000 9000.000 10800.00 12600.00  &
        14400.00 16200.00 18000.00
    REGR-PARAM MAXPOINT= 11

SEQUENCE S-1 BATCH INITIA BATCH (RETURN INITIA) PROPAGA BATCH  &
        (RETURN PROPAGA)

STREAM-REPOR NOZEROFLOW NOMOLEFLOW MASSFLOW PROPERTIES=DENSITY

REACTIONS REAC-1 FREE-RAD
    DESCRIPTION "EXAMPLE FREE-RADICAL INPUT"
    PARAM
    SPECIES INITIATOR=MPO MONOMER=VAC SOLVENT=MEOH POLYMER=POLY
    MON-RSEG VAC VAC-SEG
    INIT-DEC MPO 5E-6 .0 .0
    CHAIN-INI VAC 9500.0 .0 .0
    PROPAGATION VAC VAC 1000.0 .0 .0
    CHAT-MON VAC VAC 2.3370 .0 .0
    CHAT-POL VAC VAC 1.2350 .0 .0
    CHAT-SOL VAC MEOH .3230 .0 .0
    TERM-DIS VAC VAC 1.645E+08 .0 .0
    GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1.0 .0  &
        .44070 .0 6.7530 .0 .34950 .0 .0 1.0

REGRESSION INITIA
    DATA D-INITIA
    VARY REACT-VAR REACTION=REAC-1 VARIABLE=IDPRE-EXP  &
        SENTENCE=INIT-DEC ID1=MPO
    LIMITS 1E-7 1E-5

REGRESSION PROPAGA
    DATA D-PROPAG
    VARY REACT-VAR REACTION=REAC-1 VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=VAC ID2=VAC
    LIMITS 1E3 5E4

PROFILE-DATA D-INITIA
    PARAM BLOCK=BATCH TEMP=65.0 PRES=1 UNITS=hr
    DEFINE ZZTEMP BLOCK-VAR BLOCK=BATCH SENTENCE=PARAM  &
        VARIABLE=TEMP
    DEFINE ZZPRES BLOCK-VAR BLOCK=BATCH SENTENCE=PARAM  &
        VARIABLE=PRES
    VECTOR-DEF MFINIT BLOCK-VEC BLOCK=BATCH SENTENCE=  &
        REGR-C-PROF VARIABLE=MASSFRAC-L ID2=MPO
```

Figure 4.1 Input Summary (cont.)

```
    USE STD-DEV * -1.0 / DATA 0.0 1.554E-4 / DATA 0.5  &
        1.551E-4 / DATA 1.0 1.546E-4 / DATA 1.5 1.542E-4 /  &
        DATA 2.0 1.538E-4 / DATA 2.5 1.532E-4 / DATA 3.0  &
        1.526E-4 / DATA 3.5 1.522E-4 / DATA 4.0 1.518E-4 /  &
        DATA 4.5 1.513E-4 / DATA 5.0 1.509E-4

PROFILE-DATA D-PROPAG

    PARAM BLOCK=BATCH TEMP=64.5 PRES=1 UNITS=hr
    DEFINE ZZTEMP BLOCK-VAR BLOCK=BATCH SENTENCE=PARAM  &
        VARIABLE=TEMP
    DEFINE ZZPRES BLOCK-VAR BLOCK=BATCH SENTENCE=PARAM  &
        VARIABLE=PRES
    VECTOR-DEF DUTY BLOCK-VEC BLOCK=BATCH SENTENCE= REGR-PROF  &
        VARIABLE=DUTY
    USE STD-DEV * 5.0 / DATA 0.5 -3750.0 / DATA 1.0  &
        -3700.0 / DATA 1.5 -3300.0 / DATA 2.0 -3250.0 /  &
        DATA 2.5 -3100.0 / DATA 3.0 -3000.0 / DATA 3.5  &
        -2800.0 / DATA 4.0 -2650.0 / DATA 4.5 -2350.0 /  &
        DATA 5.0 -2150.0
```

5 FRACTIONATING OLIGOMERS

SUMMARY

This example illustrates the use of Polymers Plus for modeling a polymer/oligomer fractionation process.

The steps covered include:

- Drawing the Simulation Flowsheet
- Specifying Setup and Global Options
- Specifying and Characterizing Components
- Specifying Physical Properties
- Supplying Process Information
- Running the Simulation and Examining the Results

One typical fractionation method is to dissolve the polymer in a good solvent and then add small amounts of antisolvent to it. At the phase equilibria, the high-molecular weight polymer precipitates in the solvent phase, while the lower-molecular weight polymer dissolves in the antisolvent phase. By continuing addition of antisolvent, progressively lower molecular-weight polymer precipitates.

The system in this example contains benzene (1, solvent), ethanol (2, antisolvent) and polystyrene (3, polymer). A pseudo-component approach is used to represent the polydispersity of polystyrene. In the pseudo-component approach, a series of oligomers with different degree of polymerization (DP) is defined. The mass distribution of the oligomers in the feed is approximately a Gamma distribution. The Flory-Huggins model of polymer solution is used to calculate the liquid-liquid phase equilibria in this quasi-ternary mixture. The Flory-Huggins binary interaction parameters χ are obtained from Wu and Prausnitz (Wu and Prausnitz, 1990).

SETUP INSTRUCTIONS

In this example you will create a Polymers Plus process model to fractionate polystyrene using benzene and ethanol, run the simulation and examine the results.

The step-by-step instructions to construct a simulation model are given below.

➢ Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with English Units** as your template. The default **Run type**, Flowsheet, is appropriate for this example. Click **OK**.

The Aspen Plus main window is now active.

Drawing the Simulation Flowsheet

To place unit operation blocks:

1. On the model library palette, click on the **Separators** tab.

   The models in the separator category are now displayed in the model menu.

2. Click on the **Flash3** icon. Move the cursor to the process flowsheet window and click at a desired location.

   The Flash3 block will appear on the flowsheet window.

To place streams:

1. Click on the **Material STREAMS** icon and move the mouse to the process flowsheet window.

   Red and blue arrows will appear. These arrows indicate the location of the required (red) and optional (blue) stream connection ports to unit operations.

2. Click on the red arrow, and move the mouse cursor to connect to the inlet port of Flash3. Repeat the procedure to create a second feed stream, one vapor product and two liquid products.

3. Click on the arrow symbol that appears to the top left of the **Material STREAMS** icon to switch the mouse out of the insert mode

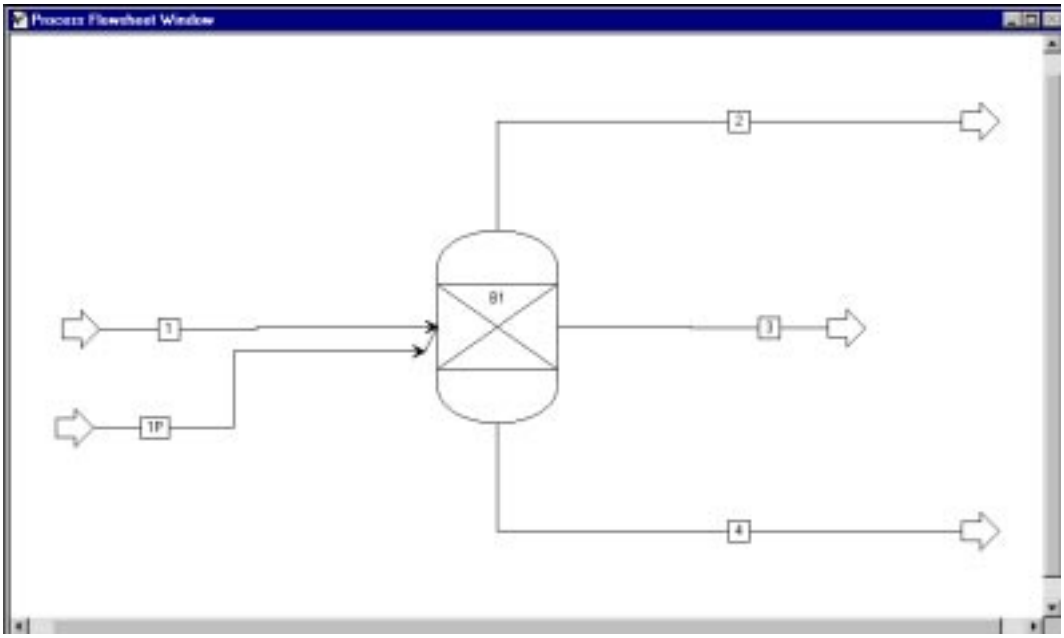
   If the mouse is showing cross-hair, +, it means the mouse is in the insert mode.

To rename streams:

1. Click on the name box of the stream to be renamed.
2. Click the *right* mouse button and select **Rename Stream** from the pop-up menu.

   Name the oligomer stream 1P and the antisolvent stream 1.

The flowsheet you created should look like this:



Specifying Setup and Global Options

In this example you will use the Aspen Plus Data Browser navigation tree rather than the Expert guidance system (Next button N) to enter process and model specifications in Polymers Plus.

To specify global options:

1. Open the Data Browser by clicking on the Data Browser button in the Aspen Plus main window
2. Double click on the **Setup** folder, and click on **Specifications**.

   On the **Global** tab sheet, type the title of your simulation as "Polystyrene Oligomer Fractionation".
3. Click on the **Description** tab.

   Type the following information: “This example illustrates the use of Polymers Plus for modeling polymer/oligomer fractionation process”.

4. From the Data Browser, click on **Report Options**.
5. Click on the **Stream** tab, click to select **Mole** for the **Flow basis** and **Mass** and **Mole** for the **Fraction basis**.
6. From the Data Browser, double click on the **Units Sets** folder.
7. In the **Object manager**, click **New**.

   Enter SET1 as the ID. Click **OK**.

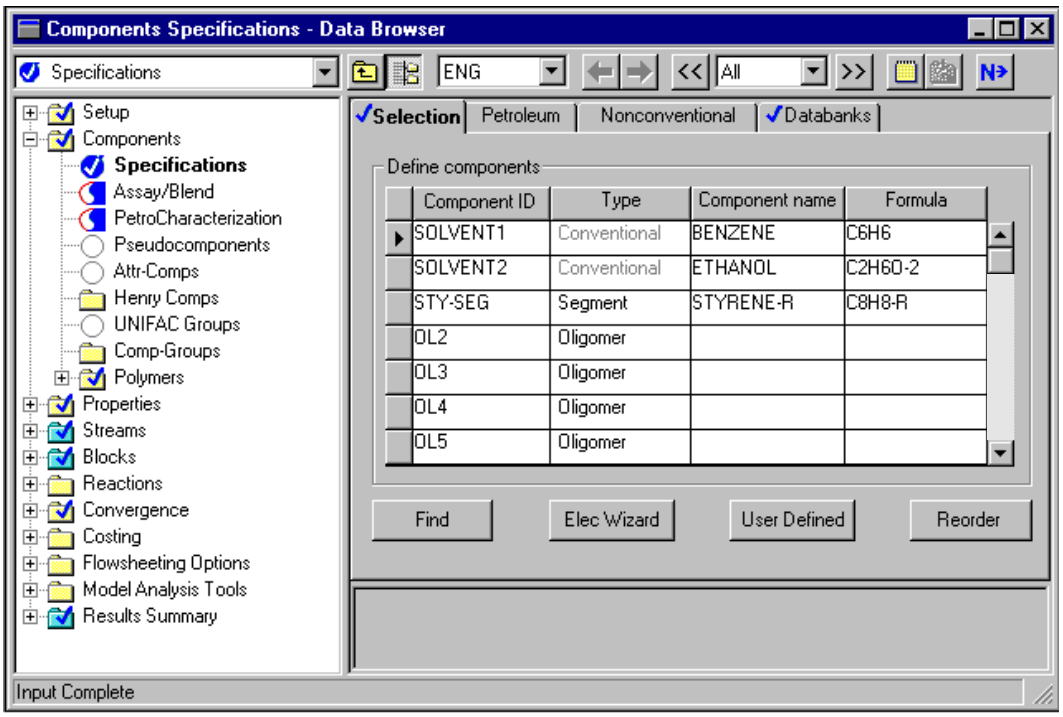
   An Aspen Plus dialog box requesting approval to make SET1 the global unit set appears. Click **No**.
8. On the **Standard** tab sheet, select **Eng** from the **Copy from** drop down list.
9. On the **Standard** tab sheet, select K for **Temperature** and atm for **Pressure**.

Specifying and Characterizing Components

To specify components:

1. From the Data Browser, double click on the **Components** folder.
2. From the **Components** folder, select **Specifications**.
3. On the **Selection** tab sheet, define benzene, ethanol and ten oligomer components (from OL2 to OL11) as shown below.

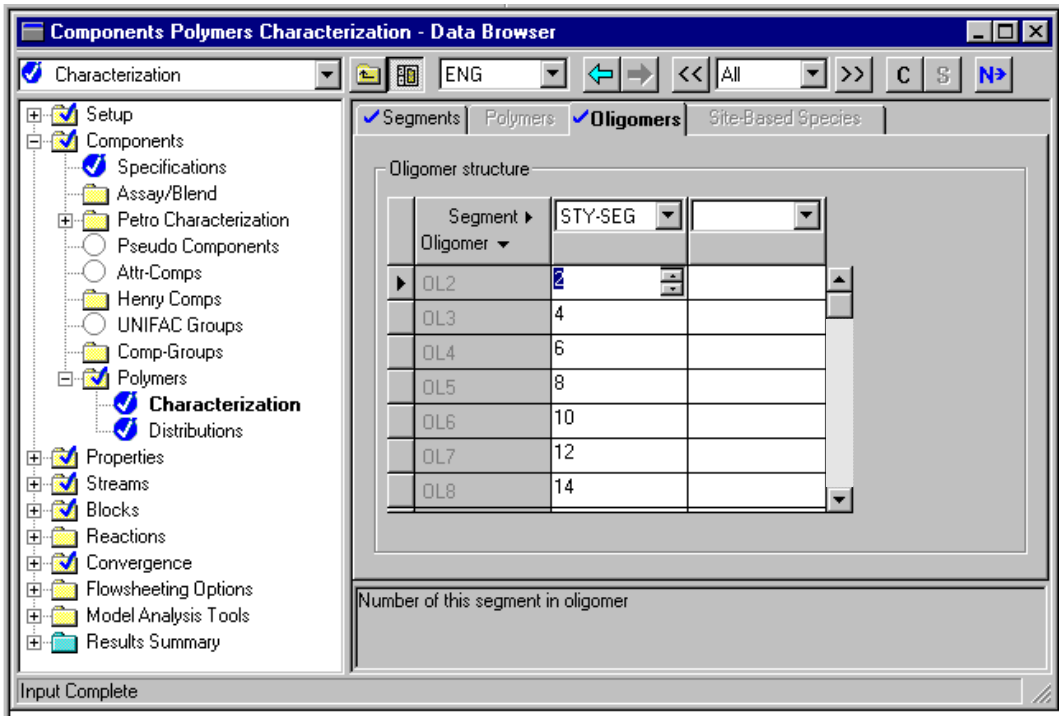
   Styrene segment is needed to define the structure of oligomers.



To characterize components:

1. From the **Data Browser**, double click on the **Polymers** sub-folder.
2. In the **Polymers** sub-folder, click on **Characterization**.
3. On the **Segments** tab sheet, select REPEAT from the **Type** drop down list for segment **STY-SEG**.
4. Click on the **Oligomers** tab.

   You need to provide the number of segments for each oligomer. Enter these as shown below using even numbers from 2-20.



Specifying Physical Properties

A physical property option set is needed for this simulation.

To specify the global physical property method:

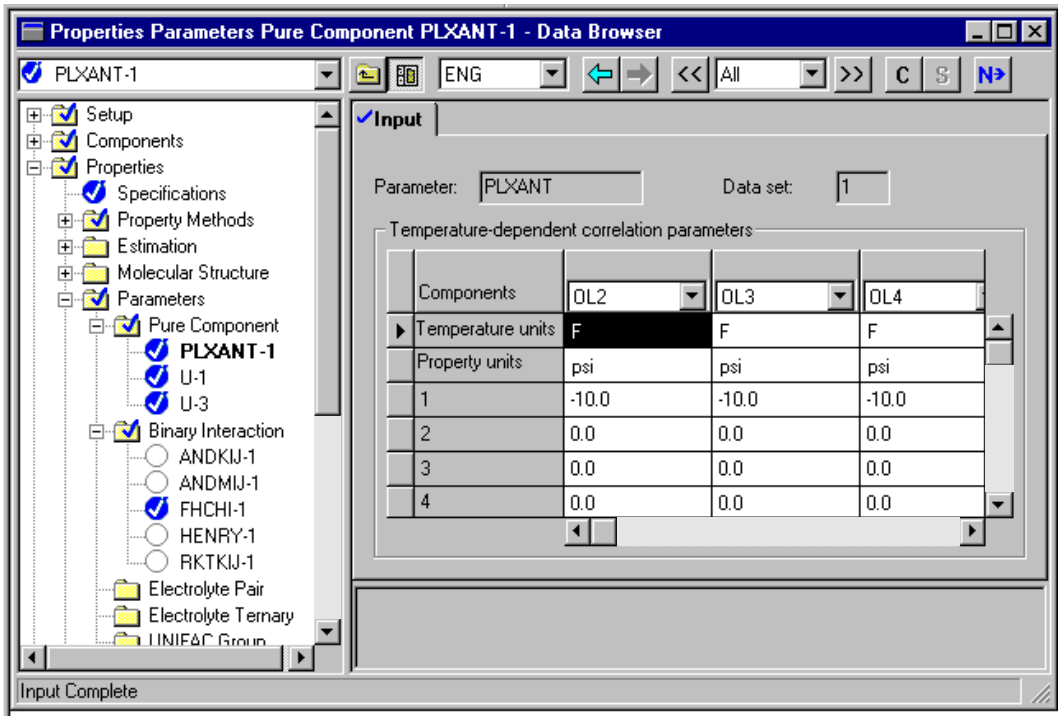
1. From the Data Browser, double click on the **Properties** folder.
2. From the **Properties** folder, click on **Specifications**.
3. On the **Global** tab sheet, select POLYFH from the **Base method** drop down list.

To enter pure component constants:

1. From the Data Browser, double click on the **Parameters** sub-folder.
2. From the **Parameters** sub-folder, click on the **Pure Component** sub-folder.
3. In the **Object manager**, click **New**.

   Click to select **T-dependent Correlation** and PLXANT-1 as the default name. Click **OK**.

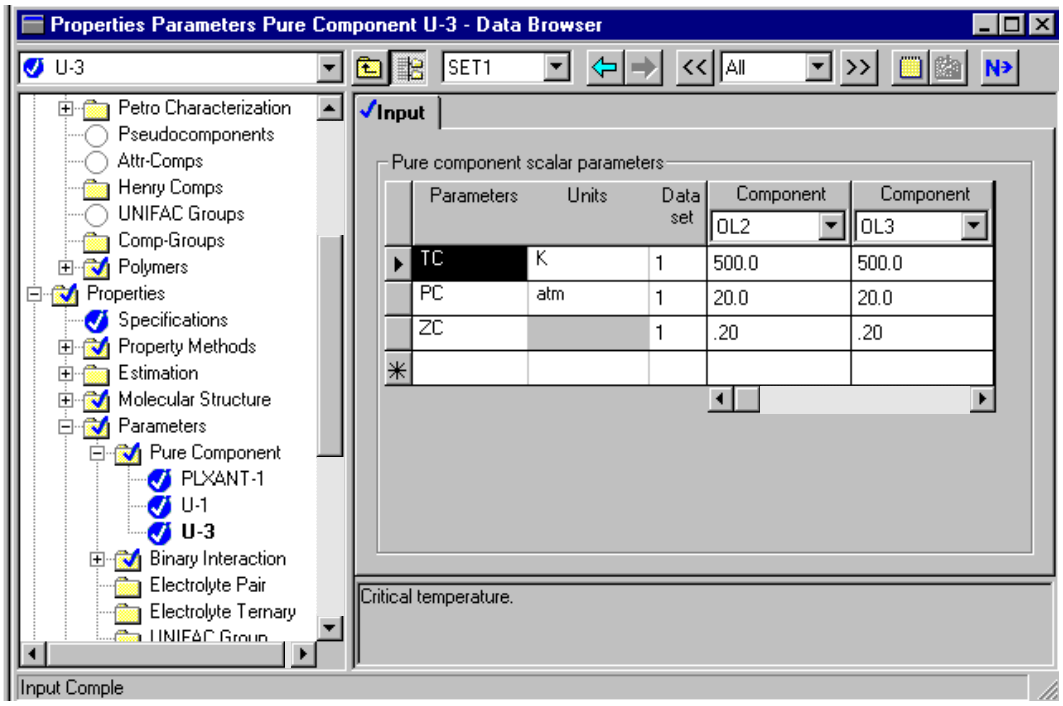
4. Enter **Temperature-dependent correlation parameters** as listed in Figure 5.2 in the PROP-DATA PLXANT-1 paragraph.



5. In the Data Browser, click on the **Pure Component** folder.
6. On the **Object manager**, click **New**.

   Accept the **Scalar** option and enter the new name as **U-3**. Click **OK**.

7. On the **Input** tab sheet, enter the critical constants for oligomers. Refer to the PROP-DATA U-3 paragraph in Figure 5.2 for the values of these constants.
8. Select the User-defined unit-set SET1 from the unit field drop down list on the data browser menu bar.



9. In the Data Browser, click on the **Pure Component** folder.
10. On the **Object manager**, click **New**.

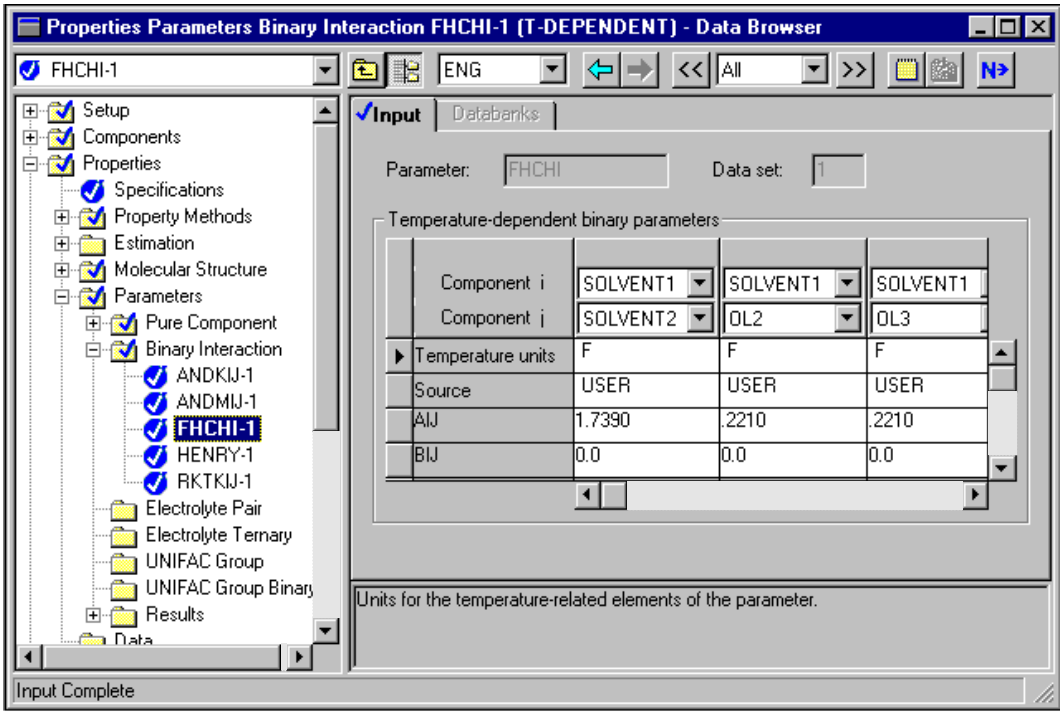
    Accept the **Scalar** option and enter the new name as U-1. Click **OK**.
11. On the **Input** tab sheet, select MW from the **Parameter** drop down list.

    Refer to the PROP-DATA U-1 paragraph in Figure 5.2 to enter the molecular weight values for each component.

To enter binary interaction parameters:

1. From the Data Browser, double click on **Binary Interaction** sub-folder.
2. In the **Binary Interaction** sub-folder, click on **FHCHI-1**.

   Enter values as shown below. Refer to the PROP-DATA FHCHI-1 paragraph in Figure 5.2 for the complete list of parameter values.



To select the properties to be calculated:

1. From the Data Browser, double click on the **Prop-Sets** sub-folder.
2. On the **Object manager**, click **New**. Click **OK** to accept PS-1 as the new name.
3. On the **Properties** tab sheet, select GAMMA for the **Physical property**.
4. Click on the **Qualifiers** tab, select Liquid for the **Phase**.
5. In the Data Browser, click on the **Report Options** form in the **Setup** folder.
6. Click on the **Stream** tab and click **Property Sets**.

   Select PS-1 using the ▸ button and click **Close**.

Supplying Process Information

To specify the stream condition for the oligomer and non-solvent streams:

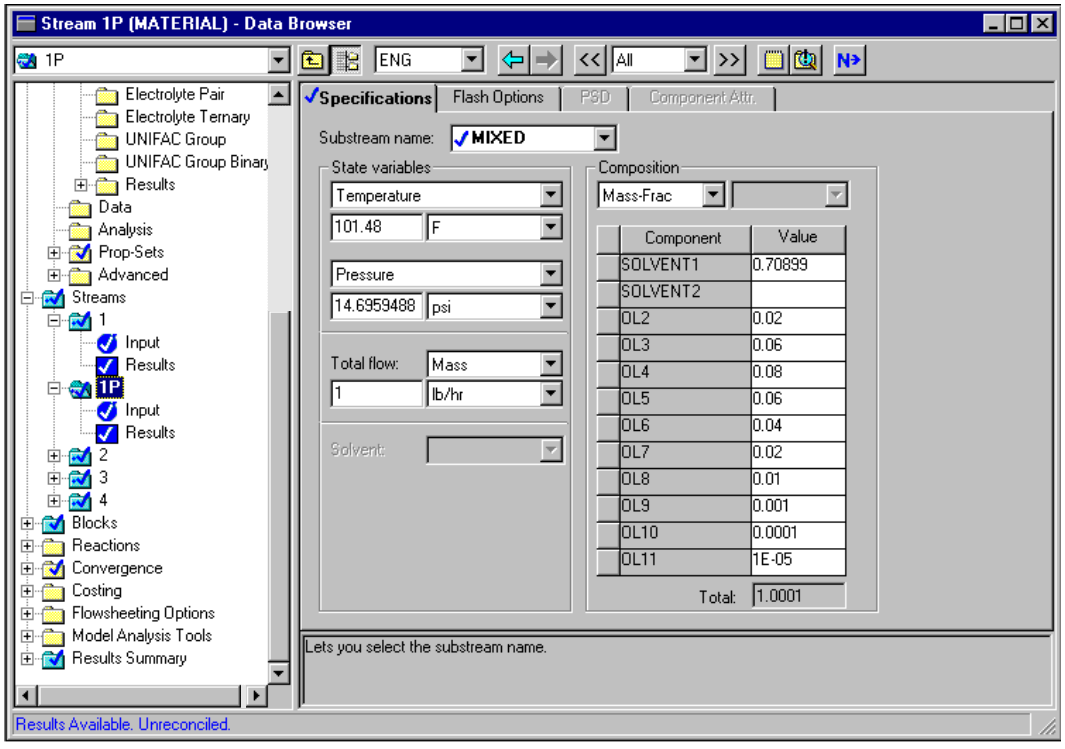
1. From the Data Browser, double click on the **Streams** folder.
2. From the **Streams** folder, double click on the **1** folder.
3. On the **Specifications** tab sheet, enter the mass flow and feed condition as follows:

   Temperature = 101.480003 F

   Pressure = 14.6959488 psi

   Total flow (Mass) = 2.1 lb/hr

   Solvent 2 = 2.1 lb/hr
4. From the Data Browser, double click on the **1P** sub-folder.
5. On the **Specifications** tab sheet enter the data as shown:



To specify the Flash3 block:

1. From the Data Browser, double click on the **Blocks** folder.
2. From the **Blocks** folder, double click on **B1** sub-folder.
3. From the **B1** sub-folder, click on **Input**.
4. On the **Specifications** tab sheet, enter 101.480003 F for **Temperature** and 14.6959488 psi for **Pressure**.
5. Click on the **Key Components** tab, select Solvent 2 from the **Key component in the 2nd liquid phase** drop down list.

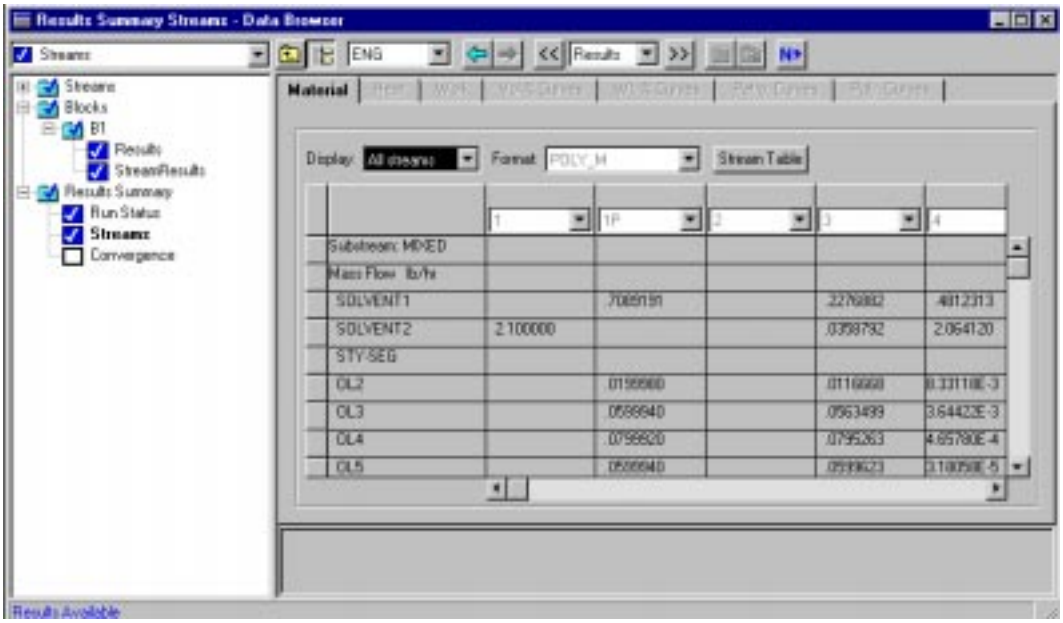
RUNNING THE SIMULATION AND EXAMINING THE RESULTS

To run the simulation:

1. In the Aspen Plus main window toolbar, click on the **Run Control Panel** button to open the **Control Panel**.
2. Click on the Start button to run the simulation.

To examine the results:

The results can be checked by selecting the **Results** option from the drop down list between the << and >> buttons and using the browser forward button >> to navigate to the next form with results.



After flashing, the quasi-ternary mixture separates into two liquid phases: a solvent rich phase and an antisolvent rich phase. Using the Flory-Huggins model, the equilibria compositions in solvent and antisolvent phases are computed. The Flory-Huggins predictions for liquid-liquid equilibria of polystyrene/Benzene/Ethanol system are shown in Figure 5.1. The solid line is the mass distribution of polystyrene oligomer for the feed stream 1P, dashed lines are for the product streams.

Figure 5.2 shows that when ethanol is added to the polystyrene/benzene mixture, the majority of high molecular weight PS remain in the solvent rich stream while most of the low molecular weight ones dissolve into the antisolvent stream.

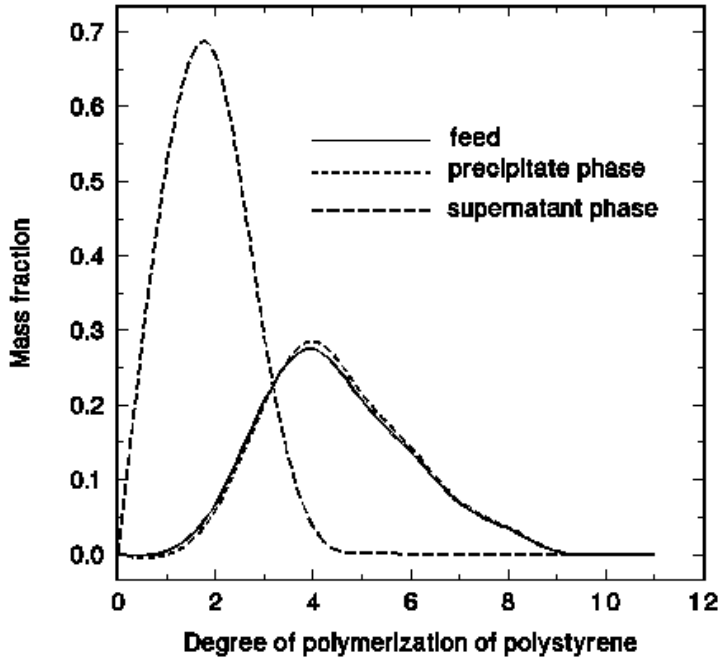


Figure 5.1 *Mass Distribution of Polystyrene*

Figure 5.2 Input Summary for Polystyrene Fractionation

```
TITLE 'Polystyrene Oligomer Fractionation'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

DESCRIPTION "
        This example illustrates the use of Polymers Plus for modeling
        polymer/oligomer fractionation process. "

DATABANKS PURE93  / SEGMENT  / POLYMER  / NOASPENPCD

PROP-SOURCES PURE93  / SEGMENT  / POLYMER

COMPONENTS
    SOLVENT1 C6H6 SOLVENT1 /
    SOLVENT2 C2H6O-2 SOLVENT2 /
    STY-SEG C8H8-R STY-SEG /
    OL2 * OL2 /
    OL3 * OL3 /
    OL4 * OL4 /
    OL5 * OL5 /
    OL6 * OL6 /
    OL7 * OL7 /
    OL8 * OL8 /
    OL9 * OL9 /
    OL10 * OL10 /
    OL11 * OL11

FLOWSHEET
    BLOCK B1 IN=1 1P OUT=2 3 4

PROPERTIES POLYFH

PROP-DATA U-1
    IN-UNITS ENG
    PROP-LIST MW
    PVAL STY-SEG 100.0
    PVAL OL2 200.0
    PVAL OL3 400.0
    PVAL OL4 600.0
    PVAL OL5 800.0
    PVAL OL6 1000.0
    PVAL OL7 1200.0
    PVAL OL8 1400.0
    PVAL OL9 1600.0
    PVAL OL10 1800.0
    PVAL OL11 2000.0

PROP-DATA U-3
    IN-UNITS ENG PRESSURE=atm TEMPERATURE=K PDROP=psi
    PROP-LIST TC / PC / ZC
    PVAL OL2 500.0 / 20.0 / .20
    PVAL OL3 500.0 / 20.0 / .20
    PVAL OL4 500.0 / 20.0 / .20
    PVAL OL5 600.0 / 20.0 / .20
    PVAL OL6 700.0 / 20.0 / .20
    PVAL OL7 800.0 / 20.0 / .20
    PVAL OL8 850.0 / 20.0 / .20
    PVAL OL9 900.0 / 20.0 / .20
    PVAL OL10 1000.0 / 20.0 / .20
    PVAL OL11 1100.0 / 20.0 / .20

PROP-DATA PLXANT-1
    IN-UNITS ENG
    PROP-LIST PLXANT
```

Figure 5.2 Input Summary for Polystyrene Fractionation (cont.)

```
    PVAL OL2 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL3 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL4 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL5 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL6 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL7 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL8 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL9 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL10 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL OL11 -10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PROP-DATA FHCHI-1
    IN-UNITS ENG
    PROP-LIST FHCHI
    BPVAL SOLVENT1 SOLVENT2 1.7390 0.0
    BPVAL SOLVENT1 OL2 .2210 0.0
    BPVAL SOLVENT1 OL3 .2210 0.0
    BPVAL SOLVENT1 OL4 .2210 0.0
    BPVAL SOLVENT1 OL5 .2210 0.0
    BPVAL SOLVENT1 OL6 .2210 0.0
    BPVAL SOLVENT1 OL7 .2210 0.0
    BPVAL SOLVENT1 OL8 .2210 0.0
    BPVAL SOLVENT1 OL9 .2210 0.0
    BPVAL SOLVENT1 OL10 .2210 0.0
    BPVAL SOLVENT1 OL11 .2210 0.0
    BPVAL SOLVENT2 OL2 1.4510 0.0
    BPVAL SOLVENT2 OL3 1.4510 0.0
    BPVAL SOLVENT2 OL4 1.4510 0.0
    BPVAL SOLVENT2 OL5 1.4510 0.0
    BPVAL SOLVENT2 OL6 1.4510 0.0
    BPVAL SOLVENT2 OL7 1.4510 0.0
    BPVAL SOLVENT2 OL8 1.4510 0.0
    BPVAL SOLVENT2 OL9 1.4510 0.0
    BPVAL SOLVENT2 OL10 1.4510 0.0
    BPVAL SOLVENT2 OL11 1.4510 0.0

POLYMERS
    SEGMENTS STY-SEG REPEAT
    OLIGOMERS OL2 STY-SEG 2 / OL3 STY-SEG 4 / OL4 STY-SEG  &
        6 / OL5 STY-SEG 8 / OL6 STY-SEG 10 / OL7 STY-SEG  &
        12 / OL8 STY-SEG 14 / OL9 STY-SEG 16 / OL10  &
        STY-SEG 18 / OL11 STY-SEG 20

PROP-SET PS-1 GAMMA SUBSTREAM=MIXED PHASE=L

STREAM 1
    SUBSTREAM MIXED TEMP=101.480003 PRES=14.6959488  &
        MASS-FLOW=2.10
    MASS-FLOW SOLVENT2 2.10

STREAM 1P
    SUBSTREAM MIXED TEMP=101.480 PRES=14.6959488 MASS-FLOW=1.0
    MASS-FRAC SOLVENT1 .708990 / OL2 .020 / OL3 .060 / OL4  &
        .080 / OL5 .060 / OL6 .040 / OL7 .020 / OL8 .010  &
        / OL9 .0010 / OL10 .00010 / OL11 .000010

BLOCK B1 FLASH3
    PARAM TEMP=101.480003 PRES=14.6959488 L2-COMP=SOLVENT2

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC PROPERTIES=PS-1
```

REFERENCES

Wu, A. H., and J. M. Prausnitz, *J. Appl. Pol. Sci.*, **39**, 629-637 (1990).

6 CALCULATING END-USE PROPERTIES

SUMMARY

This example demonstrates how to use Polymers Plus to predict important end-use properties including melt-index, intrinsic viscosity and zero-shear viscosity for high-density polyethylene and other polyolefins using user-defined Prop-Set.

The steps covered include:

- Drawing the Simulation Flowsheet
- Specifying Setup and Global Options
- Specifying and Characterizing Components
- Specifying Physical Properties
- Supplying Process Information
- Creating a Sensitivity Table
- Running the Simulation and Examining the Results

There are a number of empirical correlative models used in the industry to predict melt index of polyethylene product. End-use properties such as melt index are best implemented as a property set (Prop-Set). A number of built-in Prop-Sets are available in Aspen Plus. In addition, Prop-Sets allow the specification of a property set with add-on user correlations. When doing so, a user-supplied Fortran subroutine is required to perform the calculations.

Polymers Plus supplies a user Prop-Set and the corresponding Fortran subroutine for melt index based on the correlations of Karol et al and Sinclair et al (See Section 2.4 of the *Polymers Plus User Guide*) as well as the intrinsic and zero-shear viscosities (Karol et al., 1973; Sinclair et al., 1983).

SETUP INSTRUCTIONS

The step-by-step instructions to construct a simulation model are given below.

➤Start Aspen Plus from the Start Menu or by double clicking the Aspen Plus icon on your desktop.

The Aspen Plus main window appears.

To create a new simulation:

1. On the Aspen Plus startup dialog box, click on the **Template** option. Click **OK**.

   The **New** template window appears. You can use this window to specify the **Simulation** template and **Run Type** for the new run. Aspen Plus uses the Simulation Template you choose to automatically set various defaults appropriate to your application.

2. Select **Polymers with Metric Units** as your template. The default **Run type**, Flowsheet, is appropriate for this example. Click **OK**.

The Aspen Plus main window is now active.

Drawing the Simulation Flowsheet

To place unit operation blocks:

1. On the model library palette, click on the **Heat Exchangers** tab.

   The models in the heat exchanger category are displayed in the model menu.

2. Select **Heater** by clicking on the icon. Move the cursor to the process flowsheet window and click at the desired location.

   The **Heater** block will appear on the flowsheet window.

To place streams:

1. Click on the **Material STREAMS** icon. Move the mouse to the process flowsheet window.

   Red and blue arrows will appear. These arrows indicate the location of required (red) and option (blue) stream connection ports to the inlet port of **Heater**.

2. Click on the red feed arrow and drag the mouse to a proper location and click again. Repeat the procedure to create one feed stream and one product stream.

3. Click on the arrow symbol that appears to the top left of the **Material STREAMS** icon to switch the mouse out of the insert mode.

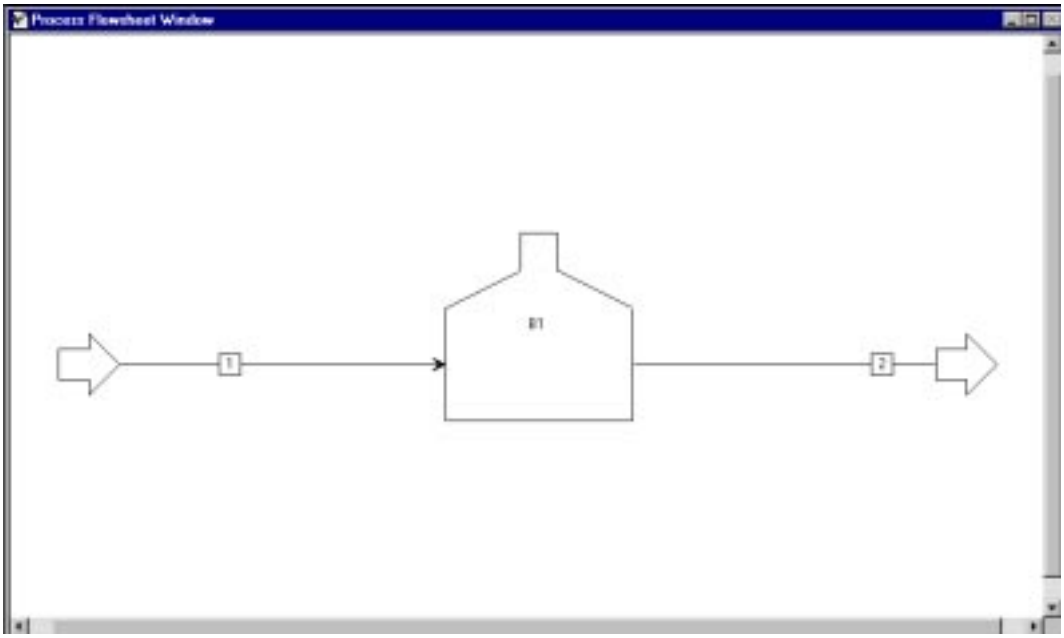
   If the mouse is showing "+" it means the mouse is still in the insert mode.

To rename streams:

4. Click on the name box of the stream to be renamed.
5. Click the right mouse button and select **Rename Stream** from the pop-up menu.

   Insert a proper name for each stream by repeating the procedure.

Your flow diagram should look like this:



Specifying Setup and Global Options

In this example you will use the Expert guidance system (Next Button ) rather than the Data Browser navigation tree to enter process and model specifications in Polymers Plus.

To specify setup and global options:

1. Click on the **Setup** button  on the toolbar.

   The **Specifications** form is displayed. The cursor will appear in the title space of the **Global** tab sheet.

   Type the title of your run as “An example illustrating end-use property calculations”.

   Make sure that the **Run type** is specified as Flowsheet.

2. Click on the **Description** tab.

Type the following information: “The objective of this example is to demonstrate how to use Polymers Plus to predict important end-use properties including melt-index, intrinsic viscosity, and zero-shear viscosity for high-density polyethylene and other polyolefins using user-defined Prop-Sets. This example requires a user Fortran subroutine USRPRP.F. Please copy USRPRP.F from the example directory and compile it in your local directory”.

3. Click on the **Next** button .

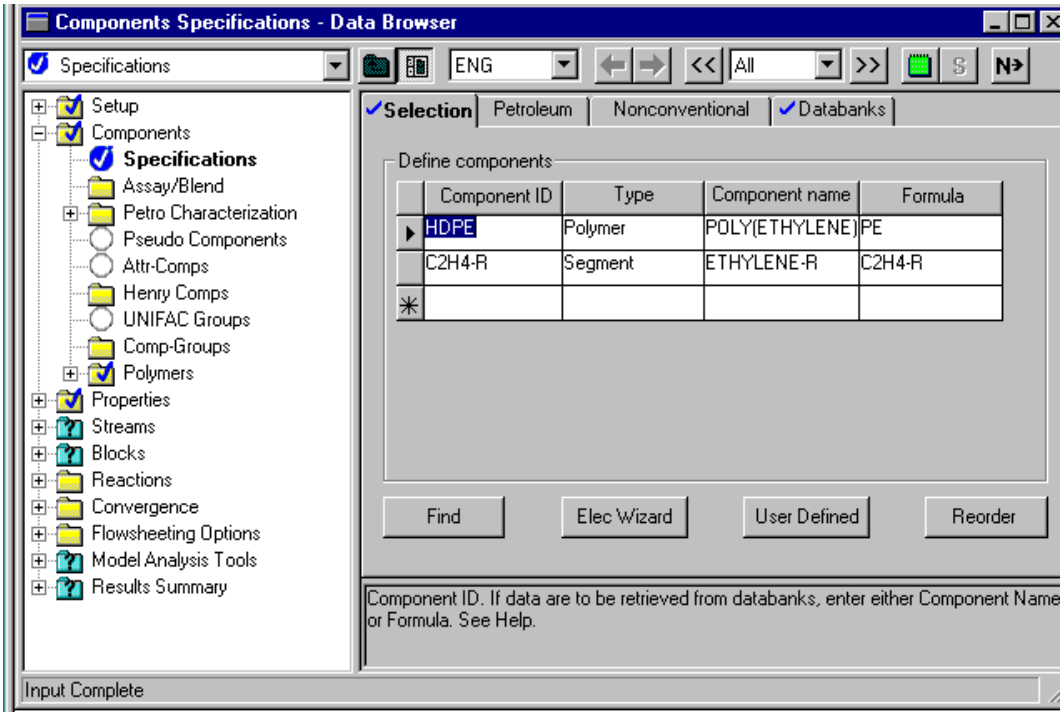
   A **Components Specifications** form appears.

Specifying and Characterizing Components

To specify and characterize components:

1. In the **Selection** tab sheet enter the **Component ID**, **Component name**, and **Formula** for the segment and polymer.

   Your form should look like this:



2. Click on the **Next** button .

   A **Components Polymers Characterization** form appears.

3. In the **Segments** tab sheet, select REPEAT using the **Type** drop down menu.

4. Click on the **Polymers** tab, select **Properties selection** from the **Built-in attribute group** drop down menu.
5. Click **Edit** and click to add MWN, MWW, DPW, PDI and SMOM to your attribute-group check list. Click **Close**.

Specifying Physical Properties

To specify physical properties:

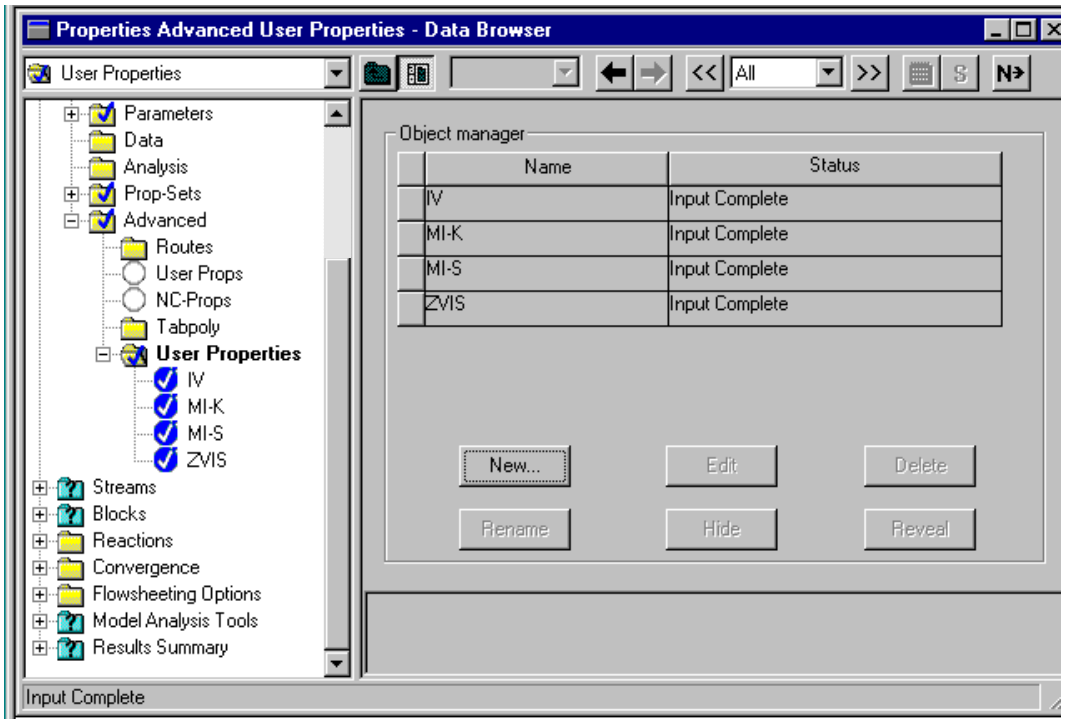
1. Click on the **Next** button  .

   A **Properties Specifications** form is displayed.

2. In the **Global** tab sheet select POLYFH from the **Base method** drop down menu.
3. In the Data Browser, open the **Advanced** sub-folder under the **Properties** folder.
4. Click on the **User Properties** folder
5. In the **Object manager**, click **New** and enter IV as the ID. Click **OK**.

   Enter USRPRP in the **User subroutine name** box.

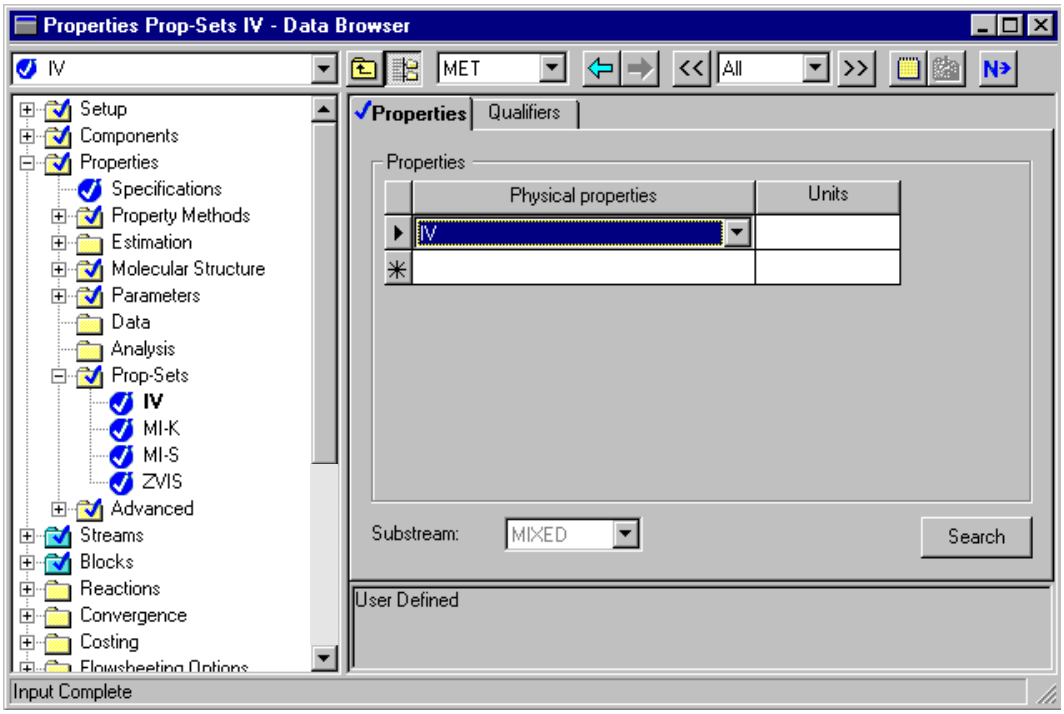
6. Repeat the steps 4 and 5 to enter the properties as shown below:



To be able to list desired polymer properties, you need to create property sets and property tables, to do this:

1. In the Data Browser, click on the **Prop-Sets** sub-folder.
2. In the **Object manager**, click **New** and enter IV as the ID. Click **OK**.
3. In the **Properties** tab sheet, select the user property created in the User Properties sub-folder from the **Physical properties** drop down list.

   Your form should look like this:



4. Repeat the steps to create Prop-Sets for MI-K, MI-S and ZVIS.

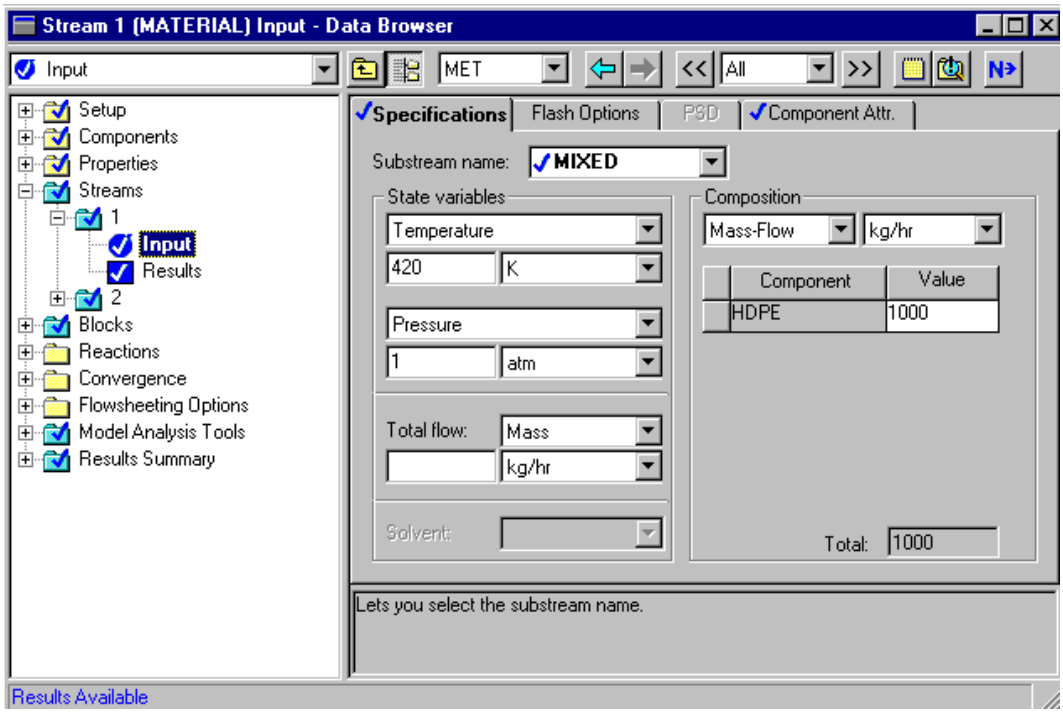
Supplying Process Information

To supply process information:

1. Click on the **Next** button .
2. On the **Required Properties Input Complete** pop-up form, click **OK** to **Go to Next required input step**.

   The **Stream 1 Input** form is displayed.
3. Enter temperature (420 K), pressure (1 atm) and mass flow rate for HPDE (1000 kg/h).

   Your form should look like this:



4. Click on the **Next** button to move to the **Component Attr.** tab sheet.
5. From the **Attribute ID** drop down menu, select DPN and enter 1000 in the **Value** cell.
6. From the **Attribute ID** drop down menu, select SFRAC and enter 1 in the **Value** cell for C2H4-R.
7. From the **Attribute ID** drop down menu, select PDI and enter 3.61 in the **Value** cell .
8. Click on the **Next** button .

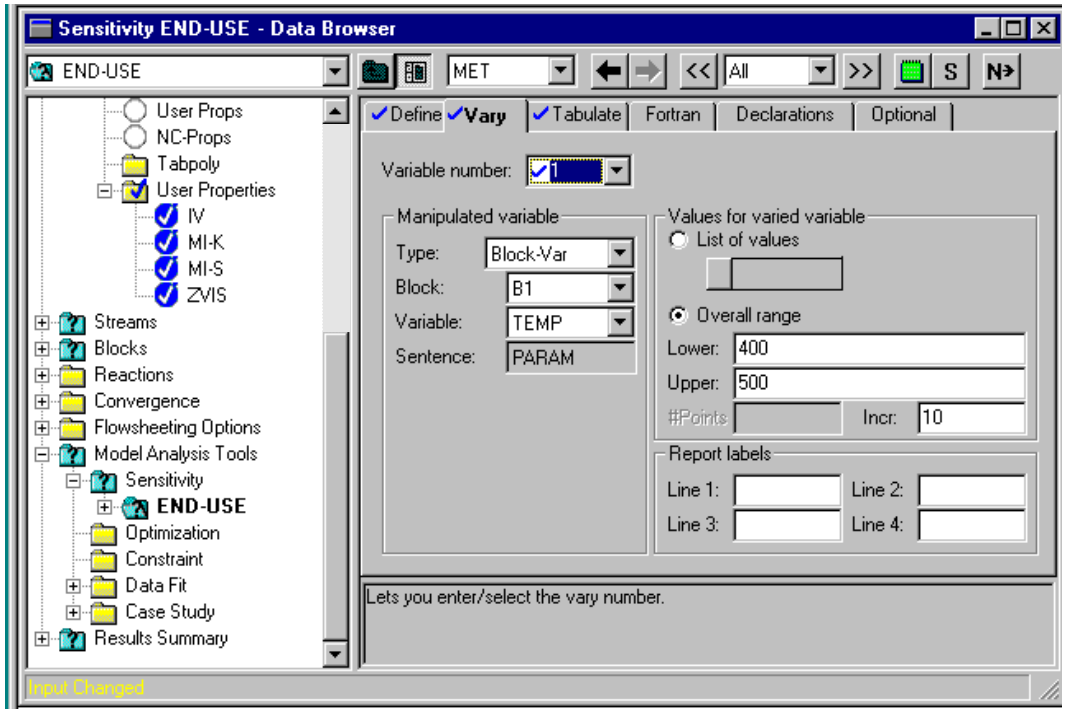
   The **BLOCK B1 Input** form appears.
9. On the **Specifications** tab sheet, enter 420K for **Temperature** of 1 atm for **Pressure**.

Creating a Sensitivity Table

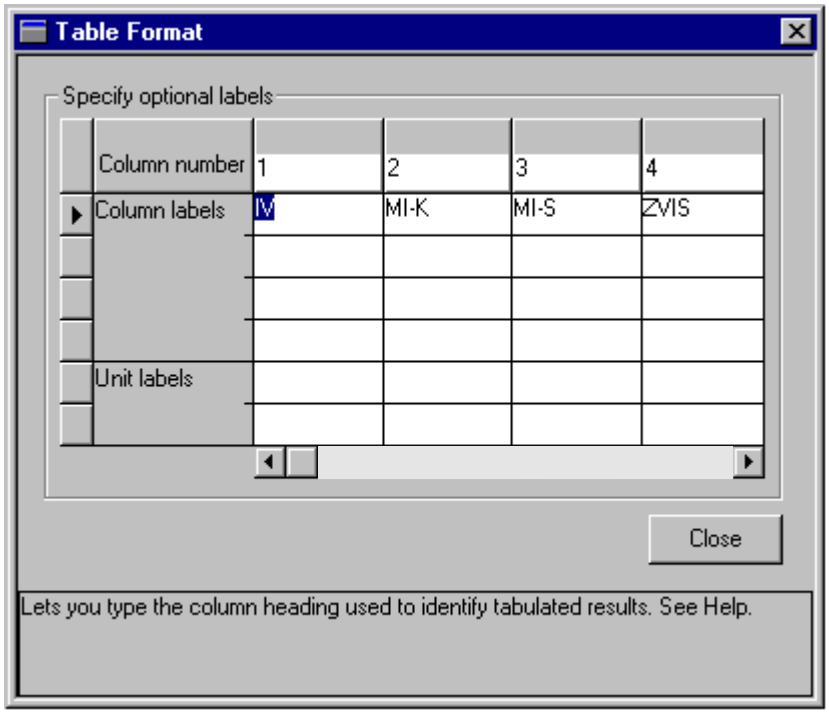
To create a sensitivity table:

1. In the Data Browser, double click on the **Model Analysis Tools** folder.
2. Double click on the **Sensitivity** sub-folder.
3. In the **Object manager**, click **New**.

   Enter END-USE. Click **OK**.
4. On the **Define** tab sheet, click **New**, enter **IV** as the **Variable name** in the **Create a new variable** pop-up form. Click **OK**.
5. In the **Variable Definition** pop-up form, select Streams for the **Category**, Stream-Prop for the Reference **Type**, 2 for the **Stream**, and IV as the **Prop-Set**. Click **Close**.
6. Repeat steps 4 and 5 to define MIK, MIS and ZVIS.
7. From the **Manipulated variable** drop down lists, select the variable as shown. Also be sure to click to select Overall range and enter the temperature to range from 400 to 500 K with increments of 10.



8. Click on the **Tabulate** tab and enter IV, MI-K, MI-S, and ZVIS, in Column numbers 1-4 respectively.
9. Click **Table Format** and label each column with the corresponding parameter name as shown below:



RUNNING THE SIMULATION AND EXAMINING THE RESULTS

To run the simulation:

1. In the Aspen Plus main window toolbar, click on the **Run Control Panel** button to open the **Control Panel**.
2. Click on the Start button to run the simulation.

To examine the results:

The results can be checked by selecting the **Results** option from the drop down list between the << and >> buttons and using the browser forward button >> to navigate to the next form with results.

The input summary is given in Figure 6.1.

Figure 6.1 Input Summary

```
TITLE 'An example illustrating end-use property calculations'

IN-UNITS MET

DEF-STREAMS CONVEN ALL

DESCRIPTION "The objective of this example is to demonstrate how
        to use Polymers Plus to predict important end-use
        properties including melt-index, intrinsic viscosity,
        and zero-shear viscosity for high-density polyethylene
        and other polyolefins using user-defined PROP-SETS.
        This example requires a user Fortran subroutine USRPRP.F.
        Please copy USRPRP.F from the example directory and
        compile it in your local directory."

DATABANKS POLYMER  / SEGMENT  / PURE93  / NOASPENPCD

PROP-SOURCES POLYMER  / SEGMENT  / PURE93

COMPONENTS
    HDPE PE HDPE /
    C2H4-R C2H4-R C2H4-R

FLOWSHEET
    BLOCK B1 IN=1 OUT=2

PROPERTIES POLYFH

POLYMERS
    SEGMENTS C2H4-R REPEAT
    POLYMERS HDPE
    ATTRIBUTES HDPE SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM

USER-PROPERT IV SUBROUTINE=USRPRP

USER-PROPERT MI-K SUBROUTINE=USRPRP

USER-PROPERT MI-S SUBROUTINE=USRPRP

USER-PROPERT ZVIS SUBROUTINE=USRPRP
```

Figure 6.1 Input Summary (cont.)

```
PROP-SET IV IV SUBSTREAM=MIXED

PROP-SET MI-K MI-K SUBSTREAM=MIXED

PROP-SET MI-S MI-S SUBSTREAM=MIXED

PROP-SET ZVIS ZVIS SUBSTREAM=MIXED

STREAM 1
    SUBSTREAM MIXED TEMP=420. <K> PRES=1.
    MASS-FLOW HDPE 1000.
    COMP-ATTR HDPE SFRAC ( 1. )
    COMP-ATTR HDPE DPN ( 1000. )
    COMP-ATTR HDPE PDI ( 3.61 )

BLOCK B1 HEATER
    PARAM TEMP=420. <K> PRES=1.

SENSITIVITY END-USE
    DEFINE IV STREAM-PROP STREAM=2 PROPERTY=IV
    DEFINE MIK STREAM-PROP STREAM=2 PROPERTY=MI-K
    DEFINE MIS STREAM-PROP STREAM=2 PROPERTY=MI-S
    DEFINE ZVIS STREAM-PROP STREAM=2 PROPERTY=ZVIS
    TABULATE 1 "IV" COL-LABEL="IV"
    TABULATE 2 "MI-K" COL-LABEL="MI-K"
    TABULATE 3 "MI-S" COL-LABEL="MI-S"
    TABULATE 4 "ZVIS" COL-LABEL="ZVIS"
    VARY BLOCK-VAR BLOCK=B1 VARIABLE=TEMP SENTENCE=PARAM
    RANGE LOWER="400" UPPER="500" INCR="10"

STREAM-REPOR NOMOLEFLOW MASSFLOW
```

REFERENCES

Karol, F. J., G. L. Brown and J. M. Davison, "Chromocene-Based Catalysts for Ethylene Polymerization: Kinetic Parameters," J. *of Polymer Science: Polymer Chemistry Edition*, **11**, 413-424 (1973).

Sinclair, K. B., "Characteristics of Linear LPPE and Description of UCC Gas Phase Process," Process Economics Report, SRI International, Menlo Park, CA (1983).

1 POLYSTYRENE

BULK POLYMERIZATION BY THERMAL INITIATION

SUMMARY

The polystyrene bulk polymerization by thermal initiation model illustrates the use of Polymers Plus for modeling free-radical bulk polymerization of styrene with thermal and induced initiation. The part of the process modeled is the polymerization stage and subsequent devolatilization. This model is used to study the effect of feed flow rate on styrene conversion, polymer properties, and recycle flowrate.

ABOUT THIS PROCESS

Typically in free-radical polymerization, an initiator decomposes to form free radicals that initiate chain growth. Propagation reactions add successive monomer molecules to a growing polymer chain to increase its chain length. A growing polymer chain terminates by either chain transfer or termination reactions to form dead polymer chains.

Styrene monomer, when heated to polymerization temperatures above 120°C, can generate enough free-radicals to produce high conversion and high molecular weight polymer. Styrene reacts via a Diels-Alder-type mechanism to form dimers which react with an additional styrene molecule to produce free-radicals. The thermal initiation rate has been reported to be third-order in styrene concentration (Hui and Hamielec, 1972).

PROCESS DEFINITION

Styrene is polymerized in a reactor train consisting of two CSTRs followed by a plug flow reactor as shown in Figure 1.1. All of the reactors are considered liquid filled, and are therefore modeled without taking into account vapor-liquid equilibrium. Unreacted monomer is flashed in a devolatilizer to be modeled as an ideal flash unit.

As shown in Figure 1.1, the flowsheet consists of two RCSTR in series, one RPlug, a Heater, and two Flash2 blocks.

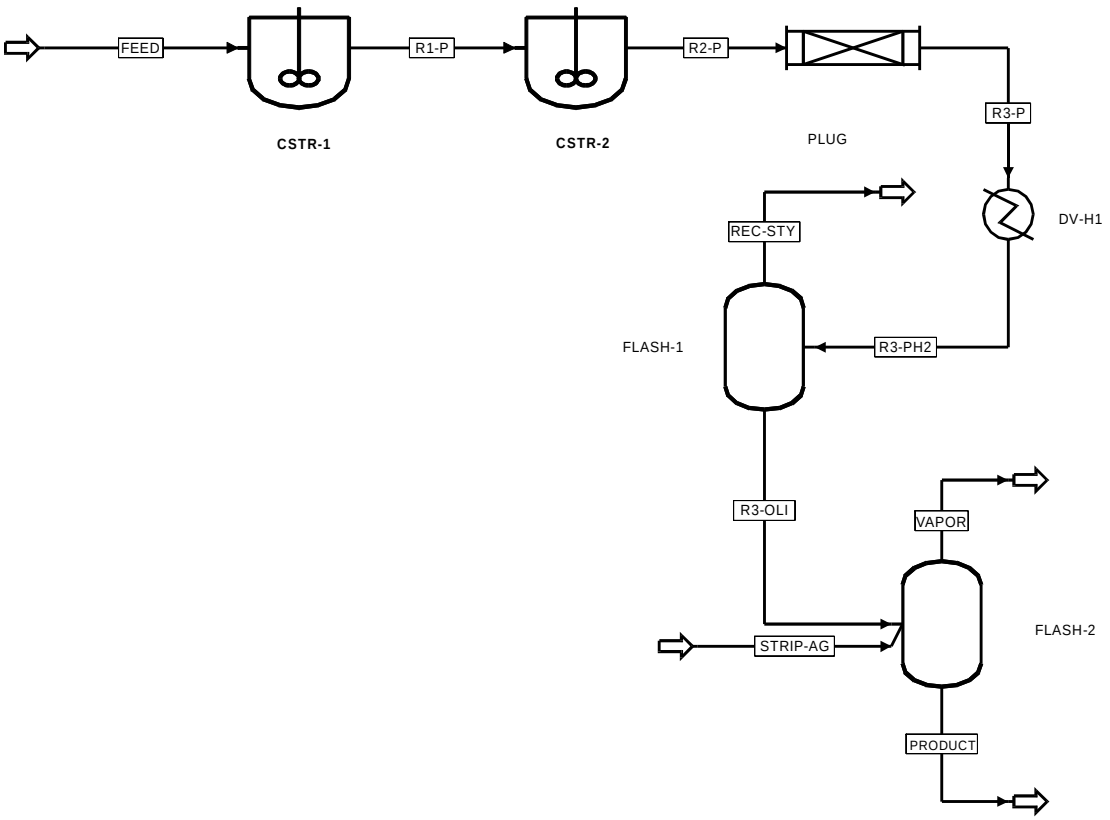


Figure 1.1 *Bulk Polymerization of Styrene Flowsheet*

Process Conditions

The first CSTR operates at 120°C, 1 atm, and the second operates at 160°C, 1 atm. Both have a volume of 20 m^3. The plug flow reactor operates at 1 atm, with a temperature range of 160-200°C from the inlet to the outlet.

The process conditions are listed in Table 1.1.

Table 1.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Styrene	STY	PURECOMP	Monomer
Polystyrene	PS	POLYMER	Polymer component
	STY-SEG	SEGMENT	Styrene segment
Di-tert-butyl peroxide	TBP	---	Initiator (Mw=216.32)
Coinitiator	CINI	---	Coinitiator
Ethylbenzene	EB	PURECOMP	Chain transfer agent
Dodecyl mercaptan	DDM	PURECOMP	Chain transfer agent (Mw=330.0)
Water	H2O	PURECOMP	Stripping agent
Physical Properties	POLYNRTL property method with supplied parameters		
Feeds			
Temperature (°C)	25		
Pressure (atm)	1		
Mass Flow (kg/s)	1.944		
Mass fraction of styrene	.98		
Mass fraction of polystyrene	0.0		
Mass fraction of coinitiator	0.0		
Mass fraction of ethylbenzene	0.01937		
Mass fraction of DDM	0.0006		
Mass fraction of TBP	0.00025		
Kinetics	FREE-RAD model		
Operating Conditions			
Block	**Temp (°C)**	**Pres (atm)**	**Size**
CSTR-1	120	1	20 m^3
CSTR-2	160	1	20 m^3
PLUG	160-200	1	80 m length by 0.40 m diam
DV-H1	220	1	
FLASH-1	220	1	
FLASH-2	220	1	

Physical Property Models and Data

The Polymer Non-Random Two Liquid activity coefficient model physical property method (POLYNRTL) is used. The thermophysical properties (density, heat capacity, etc.) of styrene, ethylbenzene, dodecyl mercaptan, and water are obtained from the Pure Component Databank. Note that di-tert-butyl peroxide and coinitiator are given the properties of styrene with the exception of molecular weight, boiling point, and Antoine parameters. The polymer thermophysical properties are calculated using the van Krevelen group contribution method.

Reactors / Kinetics

The kinetics of bulk and solution polymerization of styrene have been studied extensively. It has been reported (Albright, 1985) that the molecular weight of polystyrene is primarily controlled by chain transfer to the Diels-Alder dimers and monomer. Furthermore, based on chemical evidence and kinetic modeling, it has been reported that termination of the growing chains occurs principally by combination over disproportionation. The reactions included from the free-radical built-in kinetics are shown below.

Description	Reaction
Thermal initiation	$M \rightarrow R^{\bullet}$
Induced initiation	$M + C \rightarrow P_1$
Chain initiation	$R^{\bullet} + M \rightarrow P_1$
Propagation	$P_n + M \rightarrow P_{n+1}$
Chain transfer to monomer	$P_n + M \rightarrow D_n + P_1$
Chain transfer to EB	$P_n + EB \rightarrow D_n + P_1$
Chain transfer to DDM	$P_n + DDM \rightarrow D_n + P_1$
Termination by combination	$P_n + P_m \rightarrow D_{n+m}$

The units for the rate constants for the thermal initiation reaction are $\mathrm{m}^6/\mathrm{kmol}^2/\mathrm{s}$. The units for the rate constants for the other reactions are $\mathrm{m}^3/\mathrm{kmol}^2/\mathrm{s}$.

The induced initiation reaction is configured for thermal initiation by setting third-order thermal initiation with respect to monomer. A coinitiator, which is required for the induced initiation reaction, is included in the list of components, but its feed rate is set to zero so that it will not influence the rate for the thermal initiation reaction.

Process Studies

The model is used to study the effect of feed flow rate on styrene conversion, polymer properties, and recycle flowrate. In order to determine the effect of feed flowrate on styrene conversion, polymer properties, and recycle flowrate, a sensitivity study is carried out with feed mass flow as the varied parameter.

An input summary is given in Figure 1.2

Figure 1.2 Input Summary for Styrene Bulk Polymerization

```
;   Free radical bulk polymerization of styrene by thermal and chemical
;   initiation
;   QSSA case
;

TITLE  &
        'Bulk Polymerization of Styrene by Thermal & Chemical Initiation'

IN-UNITS SI

OUT-UNITS SI PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=2000.0

DESCRIPTION "
        Styrene polymerization in two CSTR's followed by a plug flow reactor
        "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    TBP C8H8 TBP /
    CINI C8H8 CINI /
    STY C8H8 STY /
    PS PS-1 PS /
    STY-SEG C8H8-R STY-SEG /
    EB C8H10-4 EB /
    DDM C12H26S DDM /
    H2O H2O H2O

FLOWSHEET
    BLOCK CSTR-1 IN=FEED OUT=R1-P
    BLOCK CSTR-2 IN=R1-P OUT=R2-P
    BLOCK PLUG IN=R2-P OUT=R3-P
    BLOCK FLASH-1 IN=R3-PH2 OUT=REC-STY R3-OLI
    BLOCK FLASH-2 IN=R3-OLI STRIP-AG OUT=VAPOR PRODUCT
    BLOCK DV-H1 IN=R3-P OUT=R3-PH2
```

Figure 1.2 Input Summary for Styrene Bulk Polymerization (cont.)

```
PROPERTIES POLYNRTL

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST MW / TB
    PVAL TBP 216.320 / 2000.0
    PVAL DDM 330.0 / 2000.0

PROP-DATA PLXANT-1
    IN-UNITS SI
    PROP-LIST PLXANT
    PVAL TBP -30.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL DDM -30.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

POLYMERS
    SEGMENTS STY-SEG REPEAT
    POLYMERS PS
    ATTRIBUTES PS SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM FMOM  &
        SMOM LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW LEFRAC  &
        LPFRAC

STREAM FEED
    SUBSTREAM MIXED TEMP=298.150 PRES=101325.0 MASS-FLOW=1.94440  &
        NPHASE=1 PHASE=L
    MASS-FRAC TBP .000250 / STY .980 / EB .019370 / DDM  &
        .00060

STREAM STRIP-AG
    SUBSTREAM MIXED TEMP=298.150 PRES=202650.0 MASS-FLOW=.040  &
        NPHASE=1 PHASE=L
    MASS-FLOW H2O .040

BLOCK DV-H1 HEATER
    PARAM TEMP=493.150 PRES=101325.0

BLOCK FLASH-1 FLASH2
    PARAM TEMP=493.150 PRES=101325.0 MAXIT=200

BLOCK FLASH-2 FLASH2
    PARAM TEMP=493.150 PRES=101325.0 MAXIT=200

BLOCK CSTR-1 RCSTR
    PARAM VOL=20.0 TEMP=393.150 PRES=101325.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=200 MB-TOL=.000010
    REACTIONS RXN-IDS=R1

BLOCK CSTR-2 RCSTR
    PARAM VOL=20.0 TEMP=433.150 PRES=101325.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=400 MB-TOL=.000010
    REACTIONS RXN-IDS=R1

BLOCK PLUG RPLUG
    PARAM TYPE=T-SPEC LENGTH=80.0 DIAM=.40 PHASE=L  &
        PRES=101325.0 HINIT=1.0000E-07 INT-TOL=.0010  &
        CORR-METHOD=DIRECT
    T-SPEC 0.0 433.150 / 1.0 473.150
    REACTIONS RXN-IDS=R1
```

Figure 1.2 Input Summary for Styrene Bulk Polymerization (cont.)

```
    SENSITIVITY S1
    DEFINE R3MWN COMP-ATTR-VAR STREAM=R3-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWN ELEMENT=1
    DEFINE R3MWW COMP-ATTR-VAR STREAM=R3-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWW ELEMENT=1
    DEFINE R3PDI COMP-ATTR-VAR STREAM=R3-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=PDI ELEMENT=1
    DEFINE R2MWN COMP-ATTR-VAR STREAM=R2-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWN ELEMENT=1
    DEFINE R2MWW COMP-ATTR-VAR STREAM=R2-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWW ELEMENT=1
    DEFINE R2PDI COMP-ATTR-VAR STREAM=R2-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=PDI ELEMENT=1
    DEFINE R1MWN COMP-ATTR-VAR STREAM=R1-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWN ELEMENT=1
    DEFINE R1MWW COMP-ATTR-VAR STREAM=R1-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=MWW ELEMENT=1
    DEFINE R1PDI COMP-ATTR-VAR STREAM=R1-P SUBSTREAM=MIXED  &
        COMPONENT=PS ATTRIBUTE=PDI ELEMENT=1
    DEFINE R3STY MASS-FRAC STREAM=R3-P SUBSTREAM=MIXED  &
        COMPONENT=STY
    DEFINE R3PS MASS-FRAC STREAM=R3-P SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE R2STY MASS-FRAC STREAM=R2-P SUBSTREAM=MIXED  &
        COMPONENT=STY
    DEFINE R2PS MASS-FRAC STREAM=R2-P SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE R1STY MASS-FRAC STREAM=R1-P SUBSTREAM=MIXED  &
        COMPONENT=STY
    DEFINE R1PS MASS-FRAC STREAM=R1-P SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE RECY STREAM-VAR STREAM=REC-STY SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
F        R3CONV = R3PS/(R3STY + R3PS)
F        R2CONV = R2PS/(R2STY + R2PS)
F        R1CONV = R1PS/(R1STY + R1PS)
    TABULATE 1 "R1CONV" COL-LABEL="R1CONV"
    TABULATE 2 "R2CONV" COL-LABEL="R2CONV"
    TABULATE 3 "R3CONV" COL-LABEL="R3CONV"
    TABULATE 4 "R1MWN" COL-LABEL="R1MWN"
    TABULATE 5 "R1MWW" COL-LABEL="R1MWW"
    TABULATE 6 "R2MWN" COL-LABEL="R2MWN"
    TABULATE 7 "R2MWW" COL-LABEL="R2MWW"
    TABULATE 8 "R3MWN" COL-LABEL="R3MWN"
    TABULATE 9 "R3MWW" COL-LABEL="R3MWW"
    TABULATE 10 "R1PDI" COL-LABEL="R1PDI"
    TABULATE 11 "R2PDI" COL-LABEL="R2PDI"
    TABULATE 12 "R3PDI" COL-LABEL="R3PDI"
    TABULATE 13 "RECY" COL-LABEL="RECYCLE"
    VARY STREAM-VAR STREAM=FEED SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    RANGE LOWER="1.0" UPPER="2.5" INCR="0.2"
    REINIT BLOCKS=ALL STREAMS=ALL

CONV-OPTIONS
    PARAM CHECKSEQ=NO
```

Figure 1.2 Input Summary for Styrene Bulk Polymerization (cont.)

```
SEQUENCE S-1 CSTR-1 CSTR-2 PLUG S1 CSTR-1 CSTR-2 PLUG DV-H1  &
        FLASH-1 FLASH-2 (RETURN S1)

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

REACTIONS R1 FREE-RAD
    DESCRIPTION "EXAMPLE: FREE-RADICAL KINETIC SCHEME"
    PARAM QSSA=YES
    SPECIES INITIATOR=TBP COINITIATOR=CINI MONOMER=STY  &
        CHAINTAG=EB DDM POLYMER=PS
    MON-RSEG STY STY-SEG
    INIT-DEC TBP 1.6220E+11 1.1530E+08 0.0 EFFIC=.80 NRADS=2
    INIT-SP STY CINI 438000.0 1.1480E+08 0.0
    CHAIN-INI STY 1.0510E+07 2.9570E+07 0.0
    PROPAGATION STY STY 1.0510E+07 2.9570E+07 0.0
    CHAT-MON STY STY 3310000.0 5.3020E+07 0.0
    CHAT-AGENT STY EB 1051.0 2.9590E+07 0.0
    CHAT-AGENT STY DDM 1051.0 2.9590E+07 0.0
    TERM-COMB STY STY 1.2550E+09 7017000.0 0.0
    INIT-SP-EFF STY COEFFA=0.0 COEFFB=3.0 COEFFC=0.0
;
```

SELECTED SIMULATION RESULTS

A partial stream table for the intermediate process flowstreams is shown in Figure 1.3. Results of the sensitivity studies carried out are shown in Figure 1.4 to Figure 1.8. As shown, since the overall residence time decreases when feed flow increases, conversion and polymer molecular weight decrease as well.

Typically, for free-radical polymerization systems with chain transfer to monomer controlling the MWD, the polydispersity index should be close to 2. However, with termination by combination controlling the molecular weight, the polydispersity index should be close to 1.5.

For this simulation the polydispersity increases to about 1.924, indicating that for the specified kinetics, the molecular weight becomes increasingly controlled by chain transfer to monomer at high conversion. Finally, since the monomer conversion decreases in the plug flow reactor, unreacted monomer recycle increases. Note, however, that the increase in styrene recycle flow is less than the increase in the overall feed flow rate.

Figure 1.3 Simulation Stream Summary

FEED PRODUCT R1-P R2-P R3-OLI

STREAM ID	FEED	PRODUCT	R1-P	R2-P	R3-OLI
FROM :	----	FLASH-2	CSTR-1	CSTR-2	FLASH-1
TO :	CSTR-1	----	CSTR-2	PLUG	FLASH-2
SUBSTREAM: MIXED					
COMPONENTS: KG/SEC					
TBP	4.8599-04	0.0	2.8997-04	1.5135-05	0.0
CINI	0.0	0.0	0.0	0.0	0.0
STY	1.9050	4.0683-02	1.4477	0.7148	0.1343
PS	0.0	1.5639	0.4575	1.1907	1.5639
STY-SEG	0.0	0.0	0.0	0.0	0.0
EB	3.7655-02	3.5346-03	3.7654-02	3.7650-02	1.3249-02
DDM	1.1664-03	1.1661-03	1.1663-03	1.1662-03	1.1661-03
H2O	0.0	3.4675-03	0.0	0.0	0.0
COMPONENTS: MASS FRAC					
TBP	2.4995-04	0.0	1.4913-04	7.7841-06	0.0
CINI	0.0	0.0	0.0	0.0	0.0
STY	0.9797	2.5226-02	0.7445	0.3676	7.8454-02
PS	0.0	0.9697	0.2353	0.6123	0.9131
STY-SEG	0.0	0.0	0.0	0.0	0.0
EB	1.9366-02	2.1917-03	1.9365-02	1.9363-02	7.7360-03
DDM	5.9987-04	7.2308-04	5.9985-04	5.9979-04	6.8089-04
H2O	0.0	2.1500-03	0.0	0.0	0.0
TOTAL FLOW:					
KG/SEC	1.9444	1.6127	1.9444	1.9444	1.7126
STATE VARIABLES:					
TEMP C	25.0000	220.0000	120.0000	160.0000	220.0000
PRES ATM	1.0000	1.0000	1.0000	1.0000	1.0000
VFRAC	0.0	0.0	0.0	0.0	0.0
LFRAC	1.0000	1.0000	1.0000	1.0000	1.0000
SFRAC	0.0	0.0	0.0	0.0	0.0
ENTHALPY:					
J/KG	9.6714+05	8.7185+05	1.0370+06	9.4046+05	9.3009+05
WATT	1.8805+06	1.4061+06	2.0163+06	1.8286+06	1.5930+06
ENTROPY:					
J/KG-K	-3194.0243	-2921.3056	-2839.9228	-2905.7113	-2864.6583
AVG MW	104.2461	103.1465	104.2407	104.2330	104.2153
COMPONENT ATTRIBUTES:					
PS SFRAC					
STY-SEG		1.0000	1.0000	1.0000	1.0000
SFLOW					
STY-SEG		1.5011-02	4.3912-03	1.1428-02	1.5011-02
DPN					
DPN		1222.6621	1881.7423	1342.5898	1222.6621

Figure 1.3 Simulation Stream Summary (cont.)

```
          DPW
            DPW          2348.8151  3298.1909  2529.4260  2348.8151
          PDI
            PDI             1.9210     1.7527     1.8839     1.9210
          MWN
            MWN           1.2734+05  1.9599+05  1.3983+05  1.2734+05
          MWW
            MWW           2.4463+05  3.4351+05  2.6344+05  2.4463+05
          ZMOM
            ZMOM          1.2277-05  2.3336-06  8.5119-06  1.2277-05
          FMOM
            FMOM         1.5011-02  4.3912-03  1.1428-02  1.5011-02
          SMOM
            SMOM            35.2577    14.4829    28.9062    35.2577
          LDPN
            LDPN           566.7391  1220.8031   779.2427   566.7391
          LZMOM
            LZMOM         8.4057-11  6.7597-11  8.8956-11  8.4057-11
          LFMOM
            LFMOM        4.7638-08  8.2522-08  6.9318-08  4.7638-08
          LSFLOW
            STY-SEG        4.7638-08  8.2522-08  6.9318-08  4.7638-08
          LSFRAC
            STY-SEG          1.0000     1.0000     1.0000     1.0000
          LEFLOW
            STY-SEG        8.4057-11  6.7597-11  8.8956-11  8.4057-11
          LEFRAC
            STY-SEG           1.0000     1.0000     1.0000     1.0000
          LPFRAC
            LPFRAC         6.8466-06  2.8967-05  1.0451-05  6.8466-06

R3-P R3-PH2 REC-STY STRIP-AG VAPOR
----------------------------------

STREAM ID               R3-P       R3-PH2     REC-STY    STRIP-AG   VAPOR
FROM :                  PLUG       DV-H1      FLASH-1    ----       FLASH-2
TO   :                  DV-H1      FLASH-1    ----       FLASH-2    ----

SUBSTREAM: MIXED
PHASE:                  LIQUID     MIXED      VAPOR      LIQUID     VAPOR

COMPONENTS: KG/SEC
  TBP                     0.0        0.0        0.0        0.0        0.0
  CINI                    0.0        0.0        0.0        0.0        0.0
  STY                     0.3416     0.3416     0.2073     0.0     9.3683-02
  PS                      1.5639     1.5639     0.0        0.0        0.0
  STY-SEG                 0.0        0.0        0.0        0.0        0.0
  EB                   3.7647-02  3.7647-02  2.4398-02     0.0     9.7148-03
  DDM                  1.1661-03  1.1661-03     0.0        0.0        0.0
  H2O                     0.0        0.0        0.0     4.0000-02  3.6533-02

COMPONENTS: MASS FRAC
  TBP                     0.0        0.0        0.0        0.0        0.0
  CINI                    0.0        0.0        0.0        0.0        0.0
  STY                     0.1757     0.1757     0.8947     0.0        0.6695
  PS                      0.8043     0.8043     0.0        0.0        0.0
  STY-SEG                 0.0        0.0        0.0        0.0        0.0
  EB                   1.9362-02  1.9362-02     0.1052     0.0     6.9426-02
```

Figure 1.3 Simulation Stream Summary (cont.)

```
   DDM                 5.9974-04  5.9974-04     0.0         0.0         0.0
   H2O                    0.0        0.0        0.0         1.0000      0.2610

 TOTAL FLOW:
   KG/SEC                 1.9444     1.9444     0.2317   4.0000-02      0.1399

 STATE VARIABLES:
   TEMP    C            200.0000   220.0000   220.0000    25.0000    220.0000
   PRES    ATM            1.0000     1.0000     1.0000     2.0000      1.0000
   VFRAC                  0.0        0.1190     1.0000     0.0         1.0000
   LFRAC                  1.0000     0.8809     0.0        1.0000      0.0
   SFRAC                  0.0        0.0        0.0        0.0         0.0

ENTHALPY:
   J/KG                9.3042+05  1.0088+06  1.5903+06 -1.5858+07 -2.2232+06

 ENTROPY:
   J/KG-K             -2864.3494 -2699.2445 -1476.6373 -9030.5276 -1364.2486

 AVG MW                 104.2326   104.2326   104.3601    18.0152    46.3521

 COMPONENT ATTRIBUTES:
 PS        SFRAC
             STY-SEG       1.0000     1.0000
           SFLOW
             STY-SEG    1.5011-02  1.5011-02
           DPN
             DPN        1222.6621  1222.6621
           DPW
             DPW        2348.8151  2348.8151
           PDI
             PDI           1.9210     1.9210
           MWN
             MWN        1.2734+05  1.2734+05
           MWW
             MWW        2.4463+05  2.4463+05
           ZMOM
             ZMOM       1.2277-05  1.2277-05
           FMOM
             FMOM       1.5011-02  1.5011-02
           SMOM
             SMOM         35.2577    35.2577
           LDPN
             LDPN        566.7391   566.7391
           LZMOM
             LZMOM      8.4057-11  8.4057-11
           LFMOM
             LFMOM      4.7638-08  4.7638-08
           LSFLOW
             STY-SEG    4.7638-08  4.7638-08
           LSFRAC
             STY-SEG       1.0000     1.0000
           LEFLOW
             STY-SEG    8.4057-11  8.4057-11
           LEFRAC
             STY-SEG       1.0000     1.0000
           LPFRAC
             LPFRAC     6.8466-06  6.8466-06
```

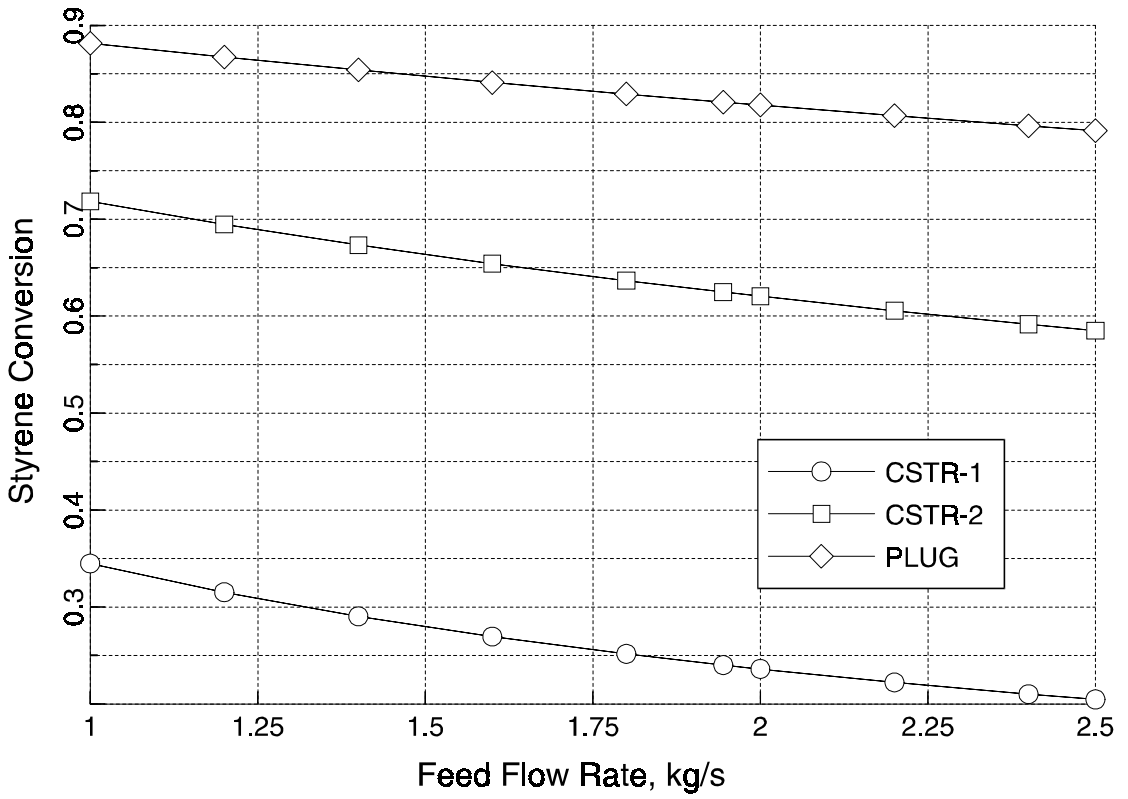


Figure 1.4 *Effect of Feed Flow Rate on Styrene Conversion*

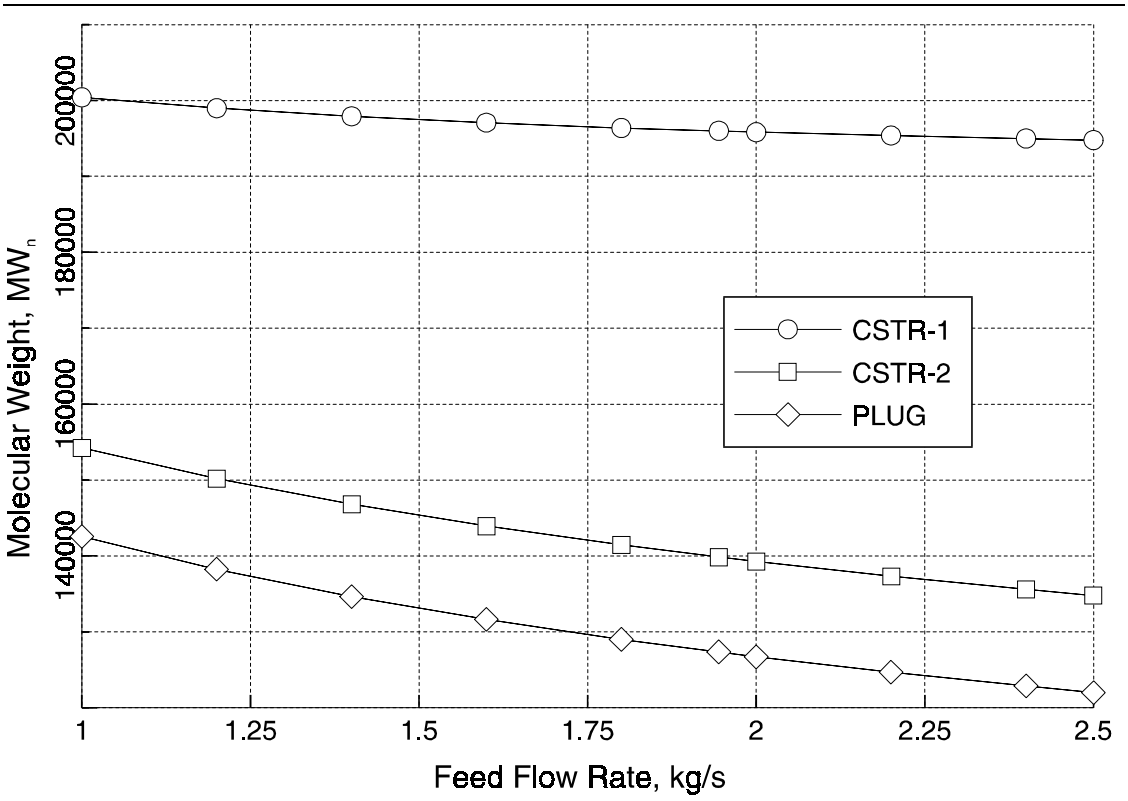


Figure 1.5 *Effect of Feed Flow Rate on the Number Average Molecular Weight*

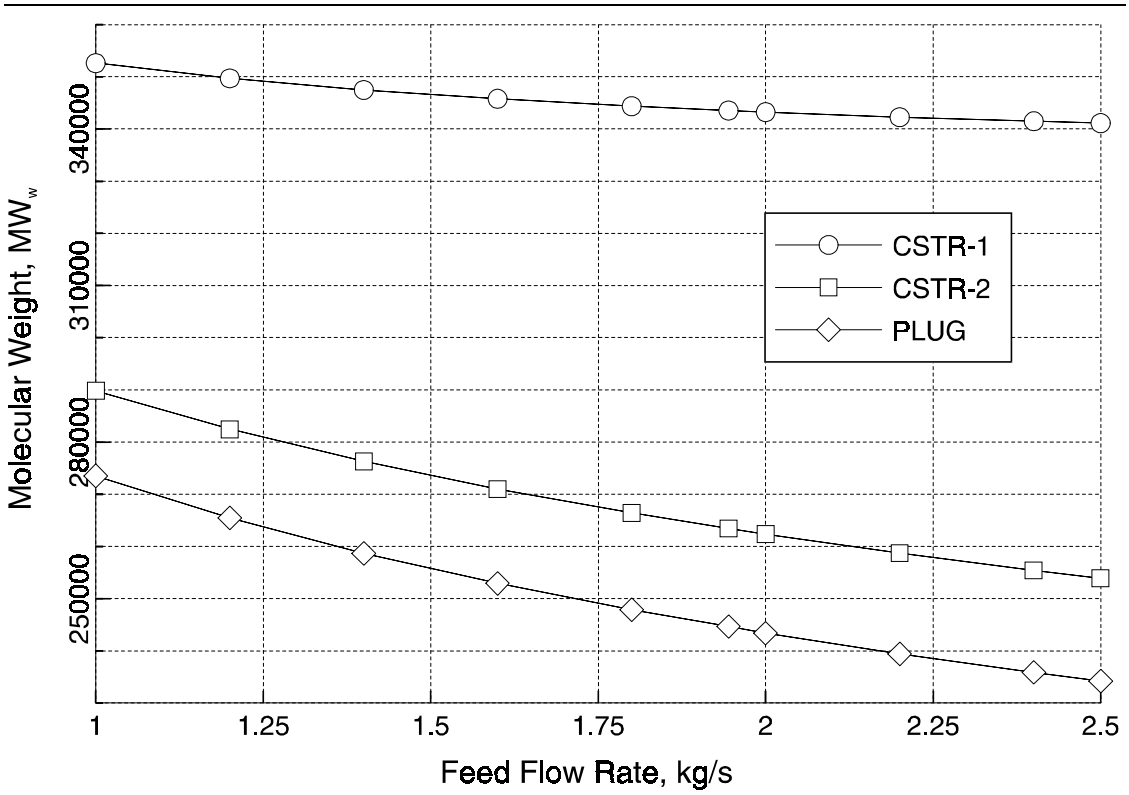


Figure 1.6 *Effect of Flow Rate on the Weight Average Molecular Weight*

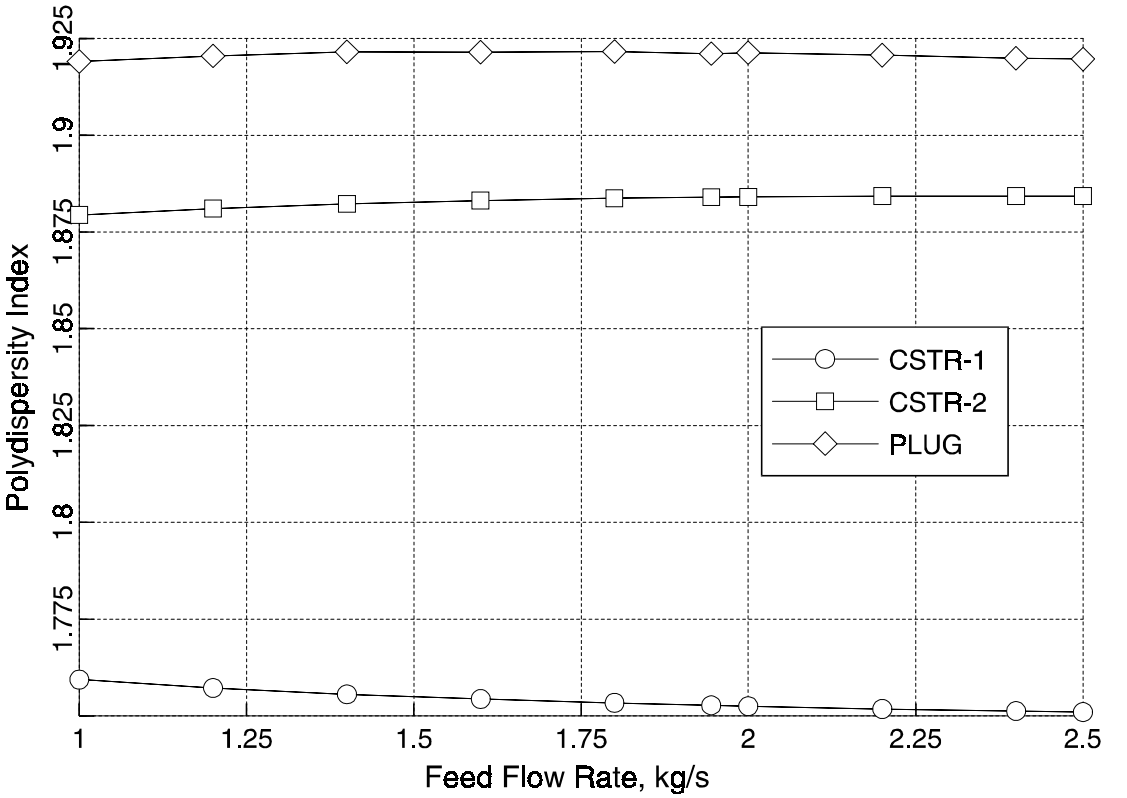


Figure 1.7 *Effect of Feed Flow Rate on the Polydispersity Index*

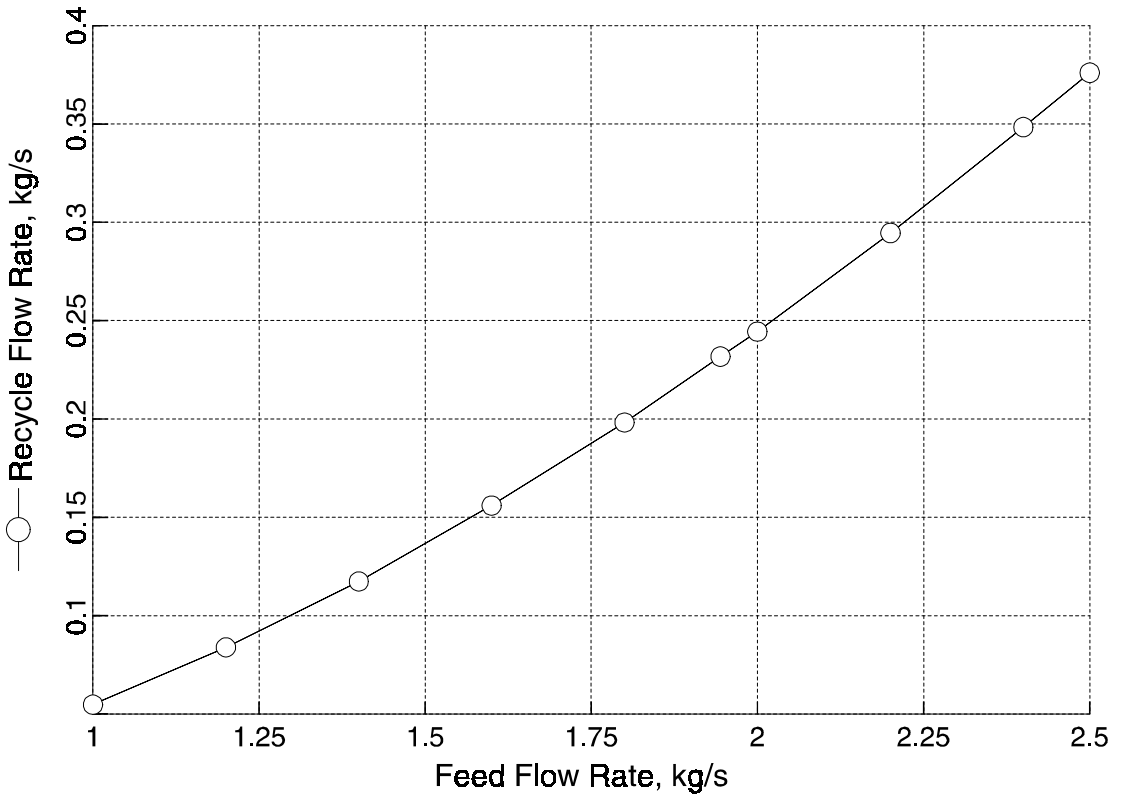


Figure 1.8 *Effect of Feed Flow Rate on the Recycle Flow Rate*

REFERENCES

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2 HIGH-DENSITY POLYETHYLENE

HIGH TEMPERATURE SOLUTION PROCESS

SUMMARY

The HDPE high temperature solution process model illustrates the use of Polymers Plus to model a Ziegler-Natta catalyst solution polymerization of ethylene. The model is used to study the effect of feed flow rate on conversion and polymer properties, and to study the effect of hydrogen concentration on melt index and polydispersity index.

ABOUT THIS PROCESS

Polyethylene is the largest synthetic commodity polymer. It is widely used throughout the world due to its versatile physical and chemical properties. The current worldwide capacity for polyethylene is over 30 million tons and the average annual rate of capacity increase is 5-8%. The commercial production of polyethylene is done in continuous processes, gas-phase processes, slurry processes, or solution processes using highly active Ziegler-Natta catalysts such as titanium supported catalysts.

Polymers Plus has been used to model the high temperature solution process for polyethylene using a Ziegler-Natta catalyst. Ziegler-Natta catalysts are multi-site catalysts containing different site types, with each type having different reactivities. For this reason, each site type produces a polymer with distinct molecular weight. As a result, the composite polymer has a broad molecular weight distribution.

The Ziegler-Natta model in Polymers Plus takes into account the important reactions found in this chemistry, including site activation, chain initiation, chain propagation, chain transfer, site deactivation, site inhibition, branching reactions, etc. The model is quite flexible and can be configured for homopolymerization or copolymerization with any number of monomers. Users can also specify any number of site types for the catalyst. The model predicts the various polymer properties, such as molecular weight, polydispersity index, melt index, and copolymer composition, and returns this information for the polymer produced at each catalyst site.

PROCESS DEFINITION

In this example, the solution polymerization of ethylene is carried out at 160°C using cyclohexane as solvent. Hydrogen is used as a chain transfer agent to control molecular weight. The flowsheet consists of two reactors and a flash unit as shown in Figure 2.1. The first reactor produces a high molecular weight polymer while the second produces a low molecular weight polymer. Solvent, unreacted monomer, and hydrogen are removed from the product in a flash tank.

An intermediate feed stream going to the second reactor is used to set the concentration of hydrogen in that reactor to be several times higher than in the first reactor. A total of four site types are used for the catalyst. Two sites are considered to be active in the first reactor and all four sites are active in the second reactor.

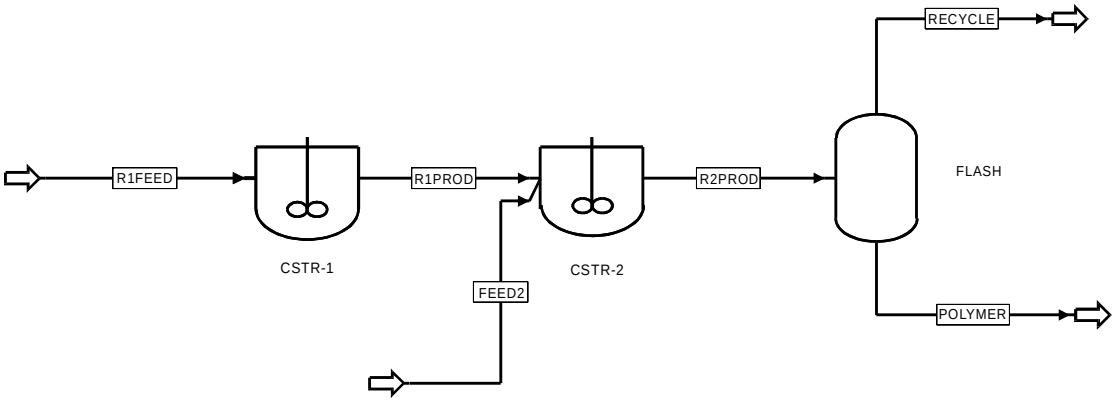

Figure 2.1 *High Temperature Solution Process of Polyethylene Flowsheet*

Process Conditions

The process conditions are as listed in Table 2.1.

Table 2.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Ethylene	E2	PURECOMP	Monomer
Hydrogen	H2	PURECOMP	Chain transfer agent
Hexane	HEXANE	PURECOMP	Solvent
Catalyst	TICl4	PURECOMP	Catalyst (Mw=176.0)
Cocatalyst	TEA	PURECOMP	Cocatalyst (Mw=100.0)
HDPE	HDPE	POLYMER	Polymer
	E-SEG	SEGMENT	Ethylene segment
Physical Properties	POLYNRTL property method with supplied parameters		
Feeds			
	Feed	**R1FEED**	**FEED2**
Composition (% by weight)	Ethylene (E2)	10.0	20.0
	Hydrogen (H2)	5.0E-4	0.02
	Hexane	89.975	79.95
	Catalyst (TICl4)*	0.01	0.01
	Cocatalyst (TEA)	0.015	0.015
Condition	Temperature	70°C	70°C
	Pressure	200atm	200atm
	Phase	Liquid	Liquid
Mass Flow		60,000kg/hr	10,000kg/hr
Kinetics	ZIEGLER-NAT model		
Operating Conditions			
Block	**Temp (°C)**	**Pres(atm)**	**Size**
CSTR-1	160	200	60 m^3
CSTR-2	160	200	60 m^3
FLASH	160	10	---

**** Mole fraction of potential site fraction is one.***

Reactors / Kinetics

The set of reactions included from the built-in kinetics for this model is shown below:

Description	Reaction
Site activation by cocatalyst	$C_{ps} + A_m \rightarrow P_0^k$
Spontaneous site activation	$C_{ps} \rightarrow P_0^k$
Chain initiation	$P_0^k + M_i \rightarrow P_{\delta_i} i$
Propagation	$P_{\underline{n},j}^k + M_i \rightarrow P_{\underline{n}+\delta_i} i$
Chain transfer to hydrogen	$P_{\underline{n},j}^k + H_2 \rightarrow D_{\underline{n}}^k + P_0^k$
Chain transfer to monomer	$P_{\underline{n},j}^k + M_i \rightarrow D_{\underline{n}}^k + P_{\delta_i,i}^k$
Spontaneous chain transfer	$P_{\underline{n},j}^k \rightarrow D_{\underline{n}}^k + P_0^k$
Spontaneous site deactivation	$P_0^k \rightarrow C_{ds}$ $P_{\underline{n},j}^k \rightarrow C_{ds} + D_{\underline{n}}^k$

Process Studies

In order to determine the effect of feed flowrate on conversion and polymer properties, and the effect of hydrogen concentration on melt index and polydispersity index, a sensitivity study is carried out. Melt index is calculated in a user supplied subroutine (Xie, et al, 1994), and is chosen as one of the sampled parameters in a SENSITIVITY block. Other sampled parameters include the polymer properties, the component fractions used to determine conversion, and the flowrates.

An input summary is given in Figure 2.2.

Figure 2.2 Input Summary for HDPE High Temperature Polymetization

```
;This application example requires a user FORTRAN subroutine USRPRP.FOR
;Please copy USRPRP.F from the application example directory and compile
;in your local directory. The subroutine provides the correlations for the
;melt viscosity, IV and zero shear viscosity. The parameters are provided in
;the subroutine itself. If you change the component names, you need to change
;the components ID's in the subroutine.
;

TITLE 'Ziegler-Natta Solution Polymerization of Ethylene'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm  &
        TEMPERATURE=C PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=10000.0

DESCRIPTION "
        Solution polymerization of ethylene. This file requires
        user FORTRAN USRPRP to calculate polymer properties.    "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    TICL4 TICL4 TICL4 /
    TEA C2H4 TEA /
    C2H4 C2H4 C2H4 /
    H2 H2 H2 /
    C6H14 C6H14-1 C6H14 /
    HDPE HDPE HDPE /
    C2H4-R C2H4-R C2H4-R

;
;     DEFINE FLOWSHEET INFORMATION
;

FLOWSHEET
    BLOCK CSTR-1 IN=R1FEED OUT=R1PROD
    BLOCK CSTR-2 IN=R1PROD FEED2 OUT=R2PROD
    BLOCK FLASH IN=R2PROD OUT=RECYCLE POLYMER

;
;   THE PROPERTY CALCULATION METHOD (OPTION SET) SPECIFICATION FOLLOWS
;   THE OPTION SET CHOSEN IS POLYSL (SANCHEZ - LACOMBE EQUATION OF STATE.)
;   THIS OPTION SET ACCOUNTS FOR THE BEHAVIOR OF POLYMERS IN THE
;   COMPONENT SYSTEM.
;

PROPERTIES POLYSL
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
PROP-REPLACE POLYSL POLYSL
    PROP MUVMX MUVMX05
    PROP KVMX KVMX02
    PROP KLMX KLMX02
    PROP MUL MULMH
    PROP MUV MUV05
    PROP KV KV01
    PROP KL KL02

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST MW
    PVAL TICL4 176.0
    PVAL TEA 100.0

PROP-DATA MWC
    IN-UNITS MET TEMPERATURE=C THERMAL-COND='Watt/m-K' DELTA-T=C  &
        MASS-HEAT-CA='kJ/kg-K' VOL-HEAT-CAP='kJ/cum-K'
    PROP-LIST CRITMW
    PVAL HDPE 3500.0

PROP-DATA PCES-1
    IN-UNITS ENG DENSITY='kg/cum' PRESSURE=bar TEMPERATURE=K  &
        PDROP=psi
    PROP-LIST SLTSTR / SLPSTR / SLRSTR / TGVK
    PVAL C2H4 333.0 / 2400.0 / 631.0 / 150.0
    PVAL C2H4-R 663.150 / 4000.0 / 896.60 / 237.0
    PVAL H2 45.890 / 1000.0 / 142.660 / 150.0
    PVAL C6H14 483.130 / 2900.0 / 786.0 / 228.0
    PVAL TICL4 6200.0 / 50000.0 / 960.0 / 228.0
    PVAL TEA 6200.0 / 50000.0 / 960.0 / 228.0

PROP-DATA CPIG-1
    IN-UNITS MET MOLE-HEAT-CA='J/kmol-K'
    PROP-LIST CPIG
    PVAL C2H4 23194.0 78.65810
    PVAL C2H4-R 35100.0 68.22370
    PVAL C6H14 16321.0 431.710
    PVAL H2 28332.0 1.960
    PVAL TICL4 16321.0 431.710
    PVAL TEA 16321.0 431.710

PROP-DATA MULMH-1
    IN-UNITS MET
    PROP-LIST MULMH
    PVAL HDPE .0005740 5000.0 7.54220 1.0 1.0

PROP-DATA SLETIJ-1
    IN-UNITS SI PRESSURE=kPa PDROP=kPa
    PROP-LIST SLETIJ
    BPVAL H2 H2 0.0
    BPVAL H2 C2H4 .019860
    BPVAL H2 C6H14 0.0
    BPVAL H2 HDPE 0.0
    BPVAL C2H4 H2 .019860
    BPVAL C2H4 C2H4 0.0
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
    BPVAL C2H4 C6H14 .14760
    BPVAL C2H4 HDPE -.10930
    BPVAL C6H14 H2 0.0
    BPVAL C6H14 C2H4 .14760
    BPVAL C6H14 C6H14 0.0
    BPVAL C6H14 HDPE .05450
    BPVAL HDPE H2 0.0
    BPVAL HDPE C2H4 -.10930
    BPVAL HDPE C6H14 .05450
    BPVAL HDPE HDPE 0.0

PROP-DATA SLKIJ-1
    IN-UNITS SI PRESSURE=kPa PDROP=kPa
    PROP-LIST SLKIJ
    BPVAL H2 H2 0.0

    BPVAL H2 C2H4 0.0
    BPVAL H2 C6H14 0.0
    BPVAL H2 HDPE 0.0
    BPVAL C2H4 H2 0.0
    BPVAL C2H4 C2H4 0.0
    BPVAL C2H4 C6H14 .02480
    BPVAL C2H4 HDPE 0.0
    BPVAL C6H14 H2 0.0
    BPVAL C6H14 C2H4 .02480
    BPVAL C6H14 C6H14 0.0
    BPVAL C6H14 HDPE -.00470
    BPVAL HDPE H2 0.0
    BPVAL HDPE C2H4 0.0
    BPVAL HDPE C6H14 -.00470
    BPVAL HDPE HDPE 0.0

POLYMERS
    PARAM NSITES=4
    SEGMENTS C2H4-R REPEAT
    CATALYST TICL4 .00010
    POLYMERS HDPE
    ATTRIBUTES HDPE SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW  &
        LEFRAC LPFRAC SSFRAC SSFLOW SDPN SDPW SPDI SMWN SMWW  &
        SZMOM SFMOM SSMOM SPFRAC LSDPN LSZMOM LSFMOM LSSFLOW  &
        LSSFRAC LSEFLOW LSEFRAC LSPFRAC
    ATTRIBUTES TICL4 CPSFLOW CPSFRAC CVSFLOW CVSFRAC CDSFLOW  &
        CDSFRAC
    DISTRIBUTION HDPE CHAIN-SIZE CLD NPOINTS=100 10000.0

USER-PROPERT DENS SUBROUTINE=USRPRP UNIT-TYPE=DENSITY

USER-PROPERT IV SUBROUTINE=USRPRP

USER-PROPERT MI-K SUBROUTINE=USRPRP

USER-PROPERT MI-S SUBROUTINE=USRPRP

USER-PROPERT ZVIS SUBROUTINE=USRPRP
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
PROP-SET DENS DENS SUBSTREAM=MIXED

PROP-SET IV IV SUBSTREAM=MIXED

PROP-SET MI-KAR MI-K SUBSTREAM=MIXED

PROP-SET MI-SIN MI-S SUBSTREAM=MIXED

PROP-SET ZVIS ZVIS SUBSTREAM=MIXED

STREAM FEED2
    SUBSTREAM MIXED TEMP=70.0 PRES=200.0 MASS-FLOW=10000.0  &
        NPHASE=1 PHASE=L
    MASS-FRAC TICL4 .00010 / TEA .000150 / C2H4 .20 / H2  &
        .00020 / C6H14 .79950
    COMP-ATTR TICL4 CPSFLOW ( 0.0 )
    COMP-ATTR TICL4 CPSFRAC ( 1.0 )
    COMP-ATTR TICL4 CVSFLOW ( 0.0 )
    COMP-ATTR TICL4 CVSFRAC ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CDSFLOW ( 0.0 )
    COMP-ATTR TICL4 CDSFRAC ( 0.0 )

STREAM R1FEED
    SUBSTREAM MIXED TEMP=70.0 PRES=200.0 MASS-FLOW=60000.0  &
        NPHASE=1 PHASE=L
    MASS-FRAC TICL4 .00010 / TEA .000150 / C2H4 .10 / H2  &
        5.0000E-06 / C6H14 .899750
    COMP-ATTR TICL4 CPSFLOW ( 0.0 )
    COMP-ATTR TICL4 CPSFRAC ( 1.0 )
    COMP-ATTR TICL4 CVSFLOW ( 0.0 )
    COMP-ATTR TICL4 CVSFRAC ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CDSFLOW ( 0.0 )
    COMP-ATTR TICL4 CDSFRAC ( 0.0 )

BLOCK FLASH FLASH2
    PARAM TEMP=160.0 PRES=10.0

BLOCK CSTR-1 RCSTR
    PARAM VOL=60.0 TEMP=160.0 PRES=200.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=500 MB-TOL=.00010 FLASH-MAXIT=50  &
        FLASH-TOL=1.0000E-06
    MOLE-FLOW MIXED TICL4 .0340
    MOLE-FLOW MIXED TEA .090
    MOLE-FLOW MIXED C2H4 200.0
    MOLE-FLOW MIXED H2 .130
    MOLE-FLOW MIXED C6H14 626.40
    MOLE-FLOW MIXED HDPE 8.0
    COMP-ATTR MIXED TICL4 CPSFLOW ( .000010 )
    COMP-ATTR MIXED TICL4 CVSFLOW ( 1.0000E-09 1.2000E-08  &
        2.0000E-09 1.2000E-08 )
    COMP-ATTR MIXED TICL4 CDSFLOW ( 3.9581E-06 )
    COMP-ATTR MIXED HDPE ZMOM ( .4980 )
    COMP-ATTR MIXED HDPE SMOM ( 165000.0 )
    COMP-ATTR MIXED HDPE SFLOW ( 181.90 )
    COMP-ATTR MIXED HDPE LEFLOW ( .010 )
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
    COMP-ATTR MIXED HDPE LSFLOW ( 4.50 )
    COMP-ATTR MIXED HDPE SZMOM ( .40 .10 .40 .10 )
    COMP-ATTR MIXED HDPE SSFLOW ( 181.20 .640 181.20 .640 )
    COMP-ATTR MIXED HDPE SSMOM ( 166000.0 8.50 166000.0 8.50  &
        )
    COMP-ATTR MIXED HDPE LSEFLOW ( .00980 .000670 .00980  &
        .000670 )
    COMP-ATTR MIXED HDPE LSSFLOW ( 4.50 .00420 4.50 .00420 )
    CONVERGENCE SOLVER=NEWTON
    BLOCK-OPTION TERM-LEVEL=7
    REACTIONS RXN-IDS=ZN-R1

BLOCK CSTR-2 RCSTR
    PARAM VOL=60.0 TEMP=160.0 PRES=200.0 NPHASE=1 PHASE=L  &
        MB-MAXIT=500 MB-TOL=.00010 FLASH-MAXIT=50  &
        FLASH-TOL=1.0000E-06 ALGORITHM=INTEGRATOR MAX-NSTEP=200
    MOLE-FLOW MIXED TICL4 .0340
    MOLE-FLOW MIXED TEA .090
    MOLE-FLOW MIXED C2H4 200.0
    MOLE-FLOW MIXED H2 .130
    MOLE-FLOW MIXED C6H14 626.40
    MOLE-FLOW MIXED HDPE 8.0
    COMP-ATTR MIXED TICL4 CPSFLOW ( .000010 )
    COMP-ATTR MIXED TICL4 CVSFLOW ( 1.0000E-09 1.2000E-08  &
        2.0000E-09 1.2000E-08 )
    COMP-ATTR MIXED TICL4 CDSFLOW ( 3.9581E-06 )
    COMP-ATTR MIXED HDPE ZMOM ( .4980 )
    COMP-ATTR MIXED HDPE SMOM ( 165000.0 )
    COMP-ATTR MIXED HDPE SFLOW ( 181.90 )
    COMP-ATTR MIXED HDPE LEFLOW ( .010 )
    COMP-ATTR MIXED HDPE LSFLOW ( 4.50 )
    COMP-ATTR MIXED HDPE SZMOM ( .40 .10 .40 .10 )
    COMP-ATTR MIXED HDPE SSFLOW ( 181.20 .640 181.20 .640 )
    COMP-ATTR MIXED HDPE SSMOM ( 166000.0 8.50 166000.0 8.50  &
        )
    COMP-ATTR MIXED HDPE LSEFLOW ( .00980 .000670 .00980  &
        .000670 )
    COMP-ATTR MIXED HDPE LSSFLOW ( 4.50 .00420 4.50 .00420 )
    CONVERGENCE SOLVER=NEWTON
    BLOCK-OPTION TERM-LEVEL=7
    REACTIONS RXN-IDS=ZN-R2

;

SENSITIVITY RTIME
    PARAM BASE-CASE=LAST
    DEFINE RHDPE2 MASS-FLOW STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE
    DEFINE RMW2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWW ELEMENT=1
    DEFINE RMN2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWN ELEMENT=1
    DEFINE RPDI2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=PDI ELEMENT=1
    DEFINE RE22 MASS-FLOW STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=C2H4
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
    DEFINE RHDPE1 MASS-FLOW STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE
    DEFINE RMW1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWW ELEMENT=1
    DEFINE RMN1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWN ELEMENT=1
    DEFINE RPDI1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=PDI ELEMENT=1
    DEFINE RE21 MASS-FLOW STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=C2H4
    DEFINE RMI2 STREAM-PROP STREAM=R2PROD PROPERTY=MI-KAR
    DEFINE RMI1 STREAM-PROP STREAM=R1PROD PROPERTY=MI-KAR
    DEFINE R2H2 MASS-FRAC STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=H2
    DEFINE R1H2 MASS-FRAC STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=H2
F      CONV2 = RHDPE2/(RHDPE2+RE22) * 100
F      CONV1 = RHDPE1/(RHDPE1+RE21) * 100
    TABULATE 1 "CONV1" COL-LABEL="CONV1"
    TABULATE 2 "CONV2" COL-LABEL="CONV2"
    TABULATE 3 "RMW1" COL-LABEL="MW1"
    TABULATE 4 "RMW2" COL-LABEL="MW2"
    TABULATE 5 "RMN1" COL-LABEL="MN1"
    TABULATE 6 "RMN2" COL-LABEL="MN2"
    TABULATE 7 "RPDI1" COL-LABEL="PDI1"
    TABULATE 8 "RPDI2" COL-LABEL="PDI2"
    TABULATE 9 "R1H2*1.0E6" COL-LABEL="R1H2" "PPM"
    TABULATE 10 "R2H2*1.0E6" COL-LABEL="R2H2" "PPM"
    TABULATE 11 "RMI1" COL-LABEL="MI1"
    TABULATE 12 "RMI2" COL-LABEL="MI2"
    VARY STREAM-VAR STREAM=R1FEED SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    RANGE LOWER="2E4" UPPER="1.5E6" NPOINT="20"

SENSITIVITY RTIME2
    PARAM BASE-CASE=LAST
    DEFINE RHDPE2 MASS-FLOW STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE
    DEFINE RMW2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWW ELEMENT=1
    DEFINE RMN2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWN ELEMENT=1
    DEFINE RPDI2 COMP-ATTR-VAR STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=PDI ELEMENT=1
    DEFINE RE22 MASS-FLOW STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=C2H4
    DEFINE RHDPE1 MASS-FLOW STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE
    DEFINE RMW1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWW ELEMENT=1
    DEFINE RMN1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=MWN ELEMENT=1
    DEFINE RPDI1 COMP-ATTR-VAR STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=HDPE ATTRIBUTE=PDI ELEMENT=1
    DEFINE RE21 MASS-FLOW STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=C2H4
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
    DEFINE RMI2 STREAM-PROP STREAM=R2PROD PROPERTY=MI-KAR
    DEFINE RMI1 STREAM-PROP STREAM=R1PROD PROPERTY=MI-KAR
    DEFINE R2H2 MASS-FRAC STREAM=R2PROD SUBSTREAM=MIXED  &
        COMPONENT=H2
    DEFINE R1H2 MASS-FRAC STREAM=R1PROD SUBSTREAM=MIXED  &
        COMPONENT=H2
F      CONV2 = RHDPE2/(RHDPE2+RE22) * 100
F      CONV1 = RHDPE1/(RHDPE1+RE21) * 100
    TABULATE 1 "CONV1" COL-LABEL="CONV1"
    TABULATE 2 "CONV2" COL-LABEL="CONV2"
    TABULATE 3 "RMW1" COL-LABEL="MW1"
    TABULATE 4 "RMW2" COL-LABEL="MW2"
    TABULATE 5 "RMN1" COL-LABEL="MN1"
    TABULATE 6 "RMN2" COL-LABEL="MN2"
    TABULATE 7 "RPDI1" COL-LABEL="PDI1"
    TABULATE 8 "RPDI2" COL-LABEL="PDI2"
    TABULATE 9 "R1H2*1.0E6" COL-LABEL="R1H2" "PPM"
    TABULATE 10 "R2H2*1.0E6" COL-LABEL="R2H2" "PPM"
    TABULATE 11 "RMI1" COL-LABEL="MI1"
    TABULATE 12 "RMI2" COL-LABEL="MI2"
    VARY MASS-FLOW STREAM=FEED2 SUBSTREAM=MIXED COMPONENT=H2
    RANGE LOWER="0.0" UPPER="20" INCR="2.0"

CONV-OPTIONS
    PARAM CHECKSEQ=NO

SEQUENCE S-1 CSTR-1 CSTR-2 RTIME CSTR-1 CSTR-2 (RETURN RTIME)  &
        RTIME2 CSTR-2 FLASH (RETURN RTIME2)

STREAM-REPOR NARROW MOLEFLOW MASSFLOW MASSFRAC PROPERTIES=DENS  &
        IV MI-KAR MI-SIN ZVIS

REACTIONS ZN-R1 ZIEGLER-NAT
    DESCRIPTION "ZIEGLER-NATTA KINETIC SCHEME"
    PARAM
    SPECIES CATALYST=TICL4 COCATALYST=TEA MONOMER=C2H4  &
        SOLVENT=C6H14 HYDROGEN=H2 POLYMER=HDPE
    MON-RSEG C2H4 C2H4-R
    ACT-SPON 1 TICL4 .080 0.0 1.0
    ACT-SPON 2 TICL4 .080 0.0 1.0
    ACT-SPON 3 TICL4 0.0 0.0 1.0
    ACT-SPON 4 TICL4 0.0 0.0 1.0
    ACT-COCAT 1 TICL4 TEA .150 0.0 1.0
    ACT-COCAT 2 TICL4 TEA .150 0.0 1.0
    ACT-COCAT 3 TICL4 TEA 0.0 0.0 1.0
    ACT-COCAT 4 TICL4 TEA 0.0 0.0 1.0
    CHAIN-INI 1 C2H4 255.0 0.0 1.0
    CHAIN-INI 2 C2H4 90.0 0.0 1.0
    CHAIN-INI 3 C2H4 0.0 0.0 1.0
    CHAIN-INI 4 C2H4 0.0 0.0 1.0
    PROPAGATION 1 C2H4 C2H4 255.0 0.0 1.0
    PROPAGATION 2 C2H4 C2H4 90.0 0.0 1.0
    PROPAGATION 3 C2H4 C2H4 0.0 0.0 1.0
    PROPAGATION 4 C2H4 C2H4 0.0 0.0 1.0
    CHAT-MON 1 C2H4 C2H4 .090 0.0 1.0
    CHAT-MON 2 C2H4 C2H4 .240 0.0 1.0
```

Figure 2.2 Input Summary for HDPE High Temperature Polymerization (cont.)

```
    CHAT-MON 3 C2H4 C2H4 0.0 0.0 1.0
    CHAT-MON 4 C2H4 C2H4 0.0 0.0 1.0
    CHAT-H2 1 C2H4 H2 5.550 0.0 1.0
    CHAT-H2 2 C2H4 H2 18.50 0.0 1.0
    CHAT-H2 3 C2H4 H2 0.0 0.0 1.0
    CHAT-H2 4 C2H4 H2 0.0 0.0 1.0
    CHAT-SPON 1 C2H4 .0040 0.0 1.0
    CHAT-SPON 2 C2H4 .0120 0.0 1.0
    CHAT-SPON 3 C2H4 0.0 0.0 1.0
    CHAT-SPON 4 C2H4 0.0 0.0 1.0
    DEACT-SPON 1 .00010 0.0 1.0
    DEACT-SPON 2 .00060 0.0 1.0
    DEACT-SPON 3 0.0 0.0 1.0
    DEACT-SPON 4 0.0 0.0 1.0

REACTIONS ZN-R2 ZIEGLER-NAT
    DESCRIPTION "ZIEGLER-NATTA KINETIC SCHEME"
    PARAM
    SPECIES CATALYST=TICL4 COCATALYST=TEA MONOMER=C2H4  &
        SOLVENT=C6H14 HYDROGEN=H2 POLYMER=HDPE
    MON-RSEG C2H4 C2H4-R
    ACT-SPON 1 TICL4 .080 0.0 1.0
    ACT-SPON 2 TICL4 .080 0.0 1.0
    ACT-SPON 3 TICL4 .080 0.0 1.0
    ACT-SPON 4 TICL4 .080 0.0 1.0
    ACT-COCAT 1 TICL4 TEA .150 0.0 1.0
    ACT-COCAT 2 TICL4 TEA .150 0.0 1.0
    ACT-COCAT 3 TICL4 TEA .150 0.0 1.0
    ACT-COCAT 4 TICL4 TEA .150 0.0 1.0
    CHAIN-INI 1 C2H4 255.0 0.0 1.0
    CHAIN-INI 2 C2H4 90.0 0.0 1.0
    CHAIN-INI 3 C2H4 255.0 0.0 1.0
    CHAIN-INI 4 C2H4 90.0 0.0 1.0
    PROPAGATION 1 C2H4 C2H4 255.0 0.0 1.0
    PROPAGATION 2 C2H4 C2H4 90.0 0.0 1.0
    PROPAGATION 3 C2H4 C2H4 255.0 0.0 1.0
    PROPAGATION 4 C2H4 C2H4 90.0 0.0 1.0
    CHAT-MON 1 C2H4 C2H4 .090 0.0 1.0
    CHAT-MON 2 C2H4 C2H4 .240 0.0 1.0
    CHAT-MON 3 C2H4 C2H4 .090 0.0 1.0
    CHAT-MON 4 C2H4 C2H4 .240 0.0 1.0
    CHAT-H2 1 C2H4 H2 5.550 0.0 1.0
    CHAT-H2 2 C2H4 H2 18.50 0.0 1.0
    CHAT-H2 3 C2H4 H2 5.550 0.0 1.0
    CHAT-H2 4 C2H4 H2 18.50 0.0 1.0
    CHAT-SPON 1 C2H4 .0040 0.0 1.0
    CHAT-SPON 2 C2H4 .0120 0.0 1.0
    CHAT-SPON 3 C2H4 .0040 0.0 1.0
    CHAT-SPON 4 C2H4 .0120 0.0 1.0
    DEACT-SPON 1 .00010 0.0 1.0
    DEACT-SPON 2 .00060 0.0 1.0
    DEACT-SPON 3 .00010 0.0 1.0
    DEACT-SPON 4 .00060 0.0 1.0
;
```

SELECTED SIMULATION RESULTS

A stream summary for the base case simulation is given in Figure 2.3. The results for the sensitivity study to determine the effect of feed flowrate to CSTR-1 on ethylene conversion, M_n, M_w, PDI, and melt index are shown in Figure 2.4 to Figure 2.9. Properties of the product exiting from CSTR-2 are influenced by the flowrates of both feeds. Increasing the feed to CSTR-1 decreases the residence time in CSTR-1 and CSTR-2, this leads to a decrease in conversion in both reactors as shown in Figure 2.4. Although conversion decreases with increases in CSTR-1 feed, Figure 2.5 and Figure 2.6 show an increase in the CSTR-2 polymer M_n and M_w. This is due to the concentration of hydrogen in CSTR-2. As CSTR-1 feed flow increases, hydrogen concentration in CSTR-2 decreases. As a result, chain transfer rate decreases, allowing longer polymer chain length.

The results for the sensitivity studies to determine the effects of hydrogen flowrate on polymer properties are shown in Figures 2.10-2.12. In this case, hydrogen flowrate in the intermediate feed to CSTR-2 is varied. As hydrogen flowrate increases, average molecular weight of HDPE in CSTR-2 decreases as shown in Figure 2.10. The effect of hydrogen concentration on melt index is shown in Figure 2.11. Finally, Figure 2.12 shows the molecular weight distribution for polymer produced at the different sites. As shown, although the polymer at each site follows the Flory distribution, the composite polymer MWD is quite broad. In conclusion, the studies show the importance of choosing the right operating conditions in order to optimize reactor performance and product properties.

Figure 2.3 Simulation Stream Summary

STREAM ID	FEED2	POLYMER	R1FEED	R1PROD	R2PROD
FROM :	----	FLASH	----	CSTR-1	CSTR-2
TO :	CSTR-2	----	CSTR-1	CSTR-2	FLASH
SUBSTREAM: MIXED					
PHASE:	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
COMPONENTS: KMOL/HR					
TICL4	5.6821-03	3.9773-02	3.4091-02	3.4091-02	3.9773-02
TEA	1.5001-02	0.1050	9.0000-02	8.9999-02	0.1050
C2H4	71.2952	0.3397	213.8740	84.6404	73.7973
H2	0.9921	7.3279-04	0.1488	0.1380	1.0801
C6H14	92.7786	32.2408	626.4389	626.4389	719.2176
HDPE	0.0	211.3763	0.0	129.2343	211.3763
C2H4-R	0.0	0.0	0.0	0.0	0.0
COMPONENTS: KG/HR					
TICL4	1.0000	7.0000	5.9999	5.9999	7.0000
TEA	1.5000	10.4999	8.9999	8.9998	10.4999
C2H4	2000.1000	9.5311	5999.9700	2374.4828	2070.2925
H2	2.0001	1.4772-03	0.3000	0.2783	2.1773
C6H14	7995.3997	2778.4249	5.3985+04	5.3985+04	6.1980+04
HDPE	0.0	5929.9003	0.0	3625.5088	5929.9003
C2H4-R	0.0	0.0	0.0	0.0	0.0
COMPONENTS: MASS FRAC					
TICL4	1.0001-04	8.0134-04	1.0000-04	1.0000-04	1.0000-04
TEA	1.5001-04	1.2020-03	1.5000-04	1.5000-04	1.5000-04
C2H4	0.2000	1.0911-03	0.1000	3.9575-02	2.9576-02
H2	2.0001-04	1.6911-07	5.0000-06	4.6392-06	3.1105-05
C6H14	0.7995	0.3180	0.8997	0.8997	0.8854
HDPE	0.0	0.6788	0.0	6.0425-02	8.4713-02
C2H4-R	0.0	0.0	0.0	0.0	0.0
TOTAL FLOW:					
KG/HR	1.0000+04	8735.3577	6.0000+04	6.0000+04	7.0000+04
STATE VARIABLES:					
TEMP C	70.0000	160.0000	70.0000	160.0000	160.0000
PRES ATM	200.0000	10.0000	200.0000	200.0000	200.0000
VFRAC	0.0	0.0	0.0	0.0	0.0
LFRAC	1.0000	1.0000	1.0000	1.0000	1.0000
SFRAC	0.0	0.0	0.0	0.0	0.0
ENTHALPY:					
J/KG	-1.4000+06	-1.7604+06	-1.7858+06	-1.7716+06	-1.8030+06
ENTROPY:					
J/KG-K	-5515.4330	-5832.6918	-5868.8939	-5669.4671	-5696.5274
DENSITY:					
KG/CUM	622.0457	725.1154	646.1111	582.3813	591.3802
AVG MW	60.5742	35.7856	71.3787	71.3796	69.6090

Figure 2.3 Simulation Stream Summary (cont.)

```
COMPONENT ATTRIBUTES:
TICL4    CPSFLOW
           CPSFLOW    1.0001-04  1.7372-07  6.0000-04  1.7804-06  1.7372-07
         CPSFRAC
           CPSFRAC       1.0000  2.4817-04     1.0000  2.9673-03  2.4817-04
         CVSFLOW
           SITE_1           0.0  7.9316-08        0.0  1.4181-08  7.9316-08
           SITE_2           0.0  2.4230-07        0.0  6.7815-08  2.4230-07
           SITE_3           0.0  7.4688-09        0.0        0.0  7.4688-09
           SITE_4           0.0  3.9196-08        0.0        0.0  3.9196-08
         CVSFRAC
           SITE_1           0.0  1.1331-04        0.0  2.3635-05  1.1331-04
           SITE_2           0.0  3.4615-04        0.0  1.1303-04  3.4615-04
           SITE_3           0.0  1.0670-05        0.0        0.0  1.0670-05
           SITE_4           0.0  5.5994-05        0.0        0.0  5.5994-05
         CDSFLOW
           CDSFLOW          0.0  3.6027-04        0.0  2.1848-04  3.6027-04
         CDSFRAC
           CDSFRAC          0.0     0.5146        0.0     0.3641     0.5146
HDPE     SFRAC
           C2H4-R                   1.0000                1.0000     1.0000
         SFLOW
           C2H4-R                  211.3719               129.2335   211.3719
         DPN
           DPN                     990.4131              1176.9563   990.4131
         DPW
           DPW                    3578.1938              4199.1490  3578.1938
         PDI
           PDI                       3.6128                 3.5678     3.6128
         MWN
           MWN                    2.7785+04              3.3018+04  2.7785+04
         MWW
           MWW                    1.0038+05              1.1780+05  1.0038+05
         ZMOM
           ZMOM                      0.2134                 0.1098     0.2134
         FMOM
           FMOM                    211.3719               129.2335   211.3719
         SMOM
           SMOM                   7.5633+05              5.4267+05  7.5633+05
         LDPN
           LDPN                   1113.6395              1697.9986  1113.6395
         LZMOM
           LZMOM                  3.3919-04              3.7965-04  3.3919-04
         LFMOM
           LFMOM                     0.3777                 0.6446     0.3777
         LSFLOW
           C2H4-R                    0.3777                 0.6446     0.3777
         LSFRAC
           C2H4-R                    1.0000                 1.0000     1.0000
         LEFLOW
           C2H4-R                 3.3919-04              3.7965-04  3.3919-04
         LEFRAC
           C2H4-R                    1.0000                 1.0000     1.0000
         LPFRAC
           LPFRAC                 1.5893-03              3.4576-03  1.5893-03
```

Figure 2.3 Simulation Stream Summary (cont.)

SSFRAC			
C2H4-R_1	1.0000	1.0000	1.0000
C2H4-R_2	1.0000	1.0000	1.0000
C2H4-R_3	1.0000	1.0000	1.0000
C2H4-R_4	1.0000	1.0000	1.0000
SSFLOW			
C2H4-R_1	175.5652	108.6434	175.5652
C2H4-R_2	28.3270	20.5900	28.3270
C2H4-R_3	6.2346	6.5353-22	6.2346
C2H4-R_4	1.2449	6.5353-22	1.2449
SDPN			
SITE_1	1925.6597	2438.2717	1925.6597
SITE_2	256.1980	315.5779	256.1980
SITE_3	1428.0915	1.8680-02	1428.0915
SITE_4	170.2189	1.8680-02	170.2189
SDPW			
SITE_1	4115.2253	4875.5434	4115.2253
SITE_2	551.2514	630.1559	551.2514
SITE_3	2855.1831	5.2568-10	2855.1831
SITE_4	339.4379	5.2568-10	339.4379
SPDI			
SITE_1	2.1370	1.9995	2.1370
SITE_2	2.1516	1.9968	2.1516
SITE_3	1.9993	2.8141-08	1.9993
SITE_4	1.9941	2.8141-08	1.9941
SMWN			
SITE_1	5.4022+04	6.8403+04	5.4022+04
SITE_2	7187.3180	8853.1488	7187.3180
SITE_3	4.0063+04	0.5240	4.0063+04
SITE_4	4775.2825	0.5240	4775.2825
SMWW			
SITE_1	1.1545+05	1.3678+05	1.1545+05
SITE_2	1.5465+04	1.7678+04	1.5465+04
SITE_3	8.0099+04	1.4747-08	8.0099+04
SITE_4	9522.5113	1.4747-08	9522.5113
SZMOM			
SITE_1	9.1171-02	4.4558-02	9.1171-02
SITE_2	0.1105	6.5246-02	0.1105
SITE_3	4.3657-03	3.4986-20	4.3657-03
SITE_4	7.3137-03	3.4986-20	7.3137-03
SFMOM			
SITE_1	175.5652	108.6434	175.5652
SITE_2	28.3270	20.5900	28.3270
SITE_3	6.2346	6.5353-22	6.2346
SITE_4	1.2449	6.5353-22	1.2449
SSMOM			
SITE_1	7.2249+05	5.2970+05	7.2249+05
SITE_2	1.5615+04	1.2975+04	1.5615+04
SITE_3	1.7801+04	3.4355-31	1.7801+04
SITE_4	422.5795	3.4355-31	422.5795
SPFRAC			
SITE_1	0.8306	0.8406	0.8306
SITE_2	0.1340	0.1593	0.1340
SITE_3	2.9496-02	5.0570-24	2.9496-02
SITE_4	5.8898-03	5.0570-24	5.8898-03

Figure 2.3 Simulation Stream Summary (cont.)

```
          LSDPN
            SITE_1              1440.9513            2438.2717  1440.9513
            SITE_2               171.1353             315.5779   171.1353
            SITE_3              1428.0915               0.0     1428.0915
            SITE_4               170.2189               0.0      170.2189
          LSZMOM
            SITE_1             2.3051-04            2.4725-04  2.3051-04
            SITE_2             7.5118-05            1.3240-04  7.5118-05
            SITE_3             2.1475-05               0.0     2.1475-05
            SITE_4             1.2087-05               0.0     1.2087-05
          LSFMOM
            SITE_1                0.3321               0.6028     0.3321
            SITE_2             1.2855-02            4.1783-02  1.2855-02
            SITE_3             3.0669-02               0.0     3.0669-02
            SITE_4             2.0574-03               0.0     2.0574-03
          LSSFLOW
            C2H4-R_1              0.3321               0.6028     0.3321
            C2H4-R_2           1.2855-02            4.1783-02  1.2855-02
            C2H4-R_3           3.0669-02               0.0     3.0669-02
            C2H4-R_4           2.0574-03               0.0     2.0574-03
          LSSFRAC
            C2H4-R_1              1.0000               1.0000     1.0000
            C2H4-R_2              1.0000               1.0000     1.0000
            C2H4-R_3              1.0000               0.0        1.0000
            C2H4-R_4              1.0000               0.0        1.0000
          LSEFLOW
            C2H4-R_1           2.3051-04            2.4725-04  2.3051-04
            C2H4-R_2           7.5118-05            1.3240-04  7.5118-05
            C2H4-R_3           2.1475-05               0.0     2.1475-05
            C2H4-R_4           1.2087-05               0.0     1.2087-05
          LSEFRAC
            C2H4-R_1              1.0000               1.0000     1.0000
            C2H4-R_2              1.0000               1.0000     1.0000
            C2H4-R_3              1.0000               0.0        1.0000
            C2H4-R_4              1.0000               0.0        1.0000
          LSPFRAC
            SITE_1             2.5283-03            5.5491-03  2.5283-03
            SITE_2             6.7939-04            2.0293-03  6.7939-04
            SITE_3             4.9190-03            9.8197-21  4.9190-03
            SITE_4             1.6526-03            9.8197-21  1.6526-03

MIXED     SUBSTREAM PROPERTIES:

***  ALL PHASES   ***
DENS      KG/CUM          0.0      925.7174     0.0      925.7174   925.7174
IV        UNITLESS        0.0        1.0007     0.0        1.0333     1.0007
MI-K      UNITLESS        0.0        0.9059     0.0        0.4730     0.9059
MI-S      UNITLESS        0.0        1.4412     0.0        0.8268     1.4412
ZVIS      UNITLESS        0.0     1.2079+08     0.0     1.4092+08  1.2079+08

STREAM ID              RECYCLE
FROM :                 FLASH
TO   :                 ----
```

Figure 2.3 Simulation Stream Summary (cont.)

```
 SUBSTREAM: MIXED
 PHASE:                    VAPOR
 COMPONENTS: KMOL/HR
   TICL4                    0.0
   TEA                      0.0
   C2H4                    73.4575
   H2                       1.0793
   C6H14                  686.9767
   HDPE                     0.0
   C2H4-R                   0.0
 COMPONENTS: KG/HR
   TICL4                    0.0
   TEA                      0.0
   C2H4                  2060.7614
   H2                       2.1758
   C6H14                5.9202+04
   HDPE                     0.0
   C2H4-R                   0.0
 COMPONENTS: MASS FRAC
   TICL4                    0.0
   TEA                      0.0
   C2H4                 3.3637-02
   H2                   3.5516-05
   C6H14                    0.9663
   HDPE                     0.0
   C2H4-R                   0.0

TOTAL FLOW:
      KG/HR                 6.1265+04

 STATE VARIABLES:
   TEMP   C               160.0000
   PRES   ATM              10.0000
   VFRAC                    1.0000
   LFRAC                    0.0
   SFRAC                    0.0
 ENTHALPY:
   J/KG                -1.5559+06

 ENTROPY:
   J/KG-K              -5802.3786

DENSITY:
   KG/CUM                 26.5809

 AVG MW                   80.4511
```

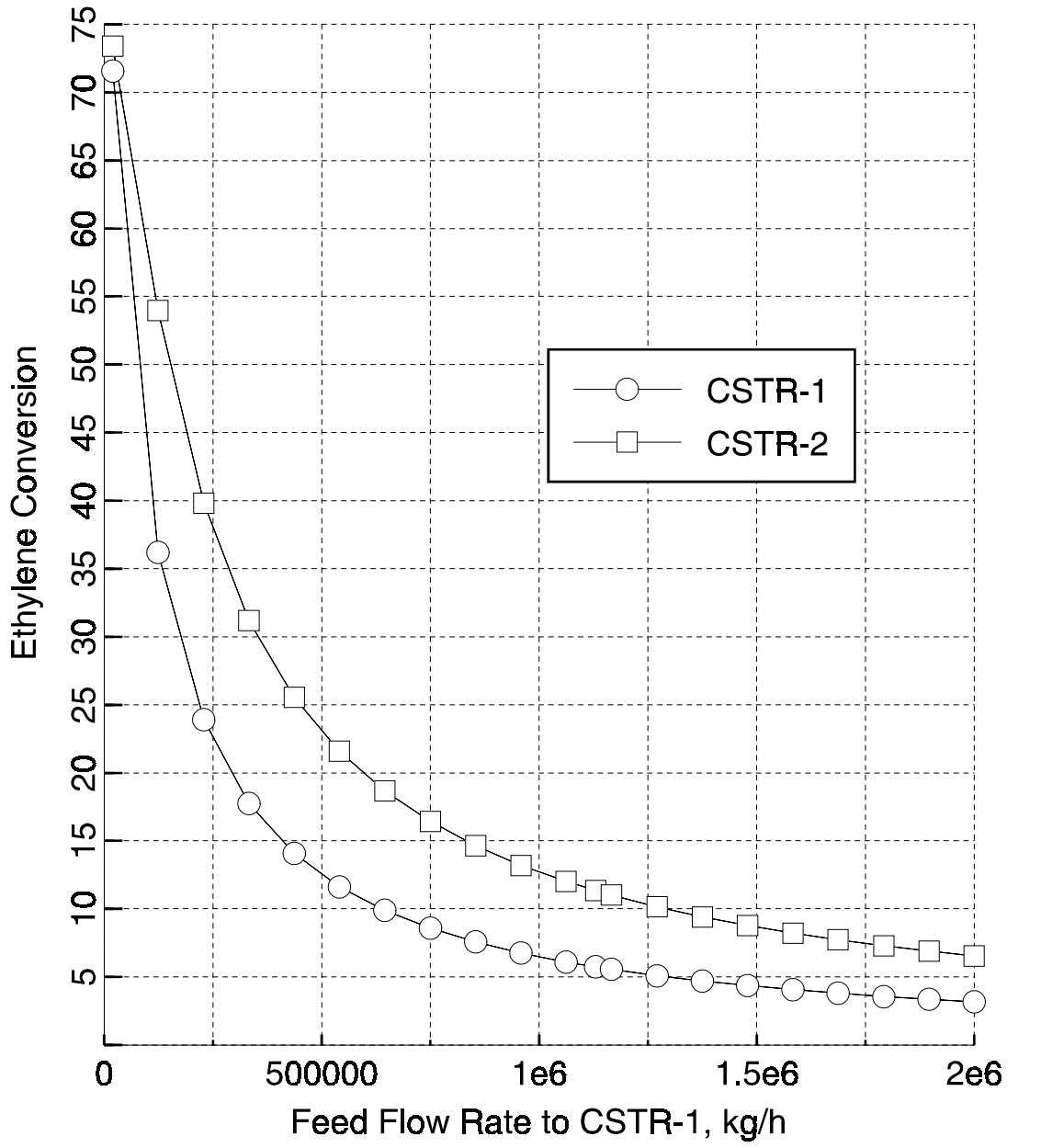

Figure 2.4 *Effect of Feed Flow Rate on Ethylene Conversion*

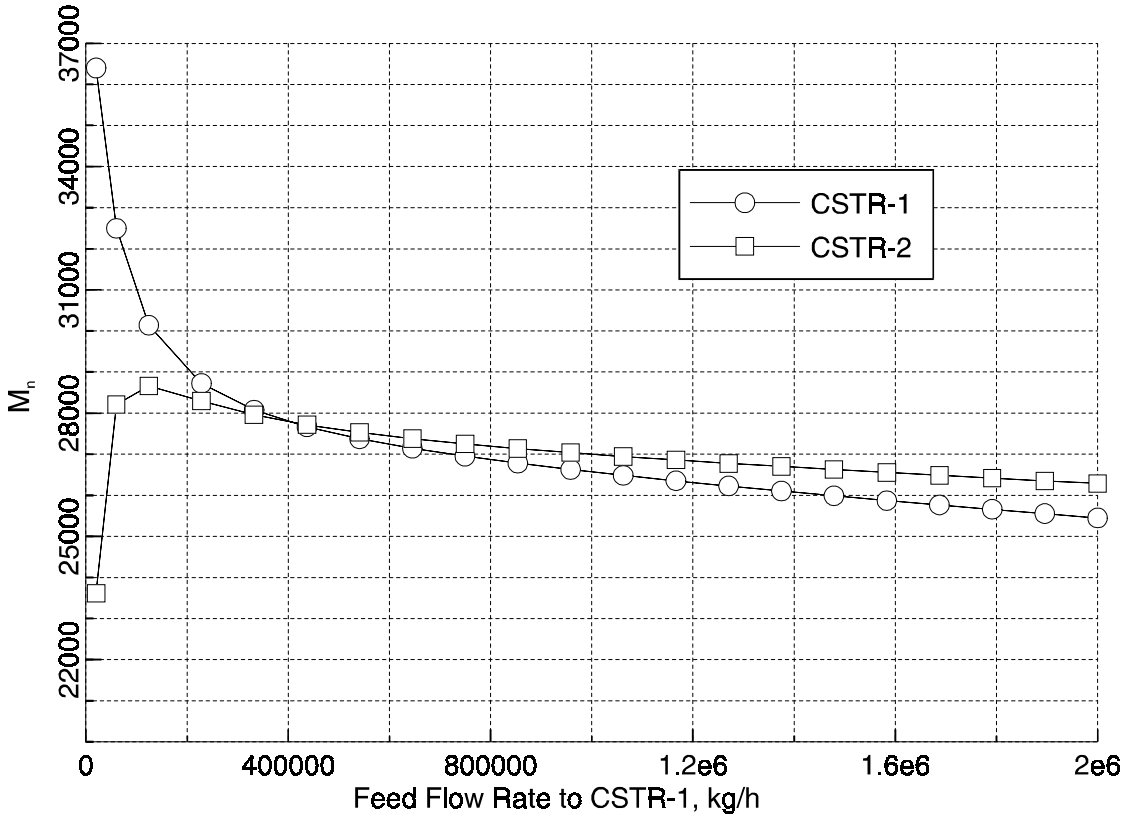

Figure 2.5 *Effect of Feed Flow Rate on* M_n

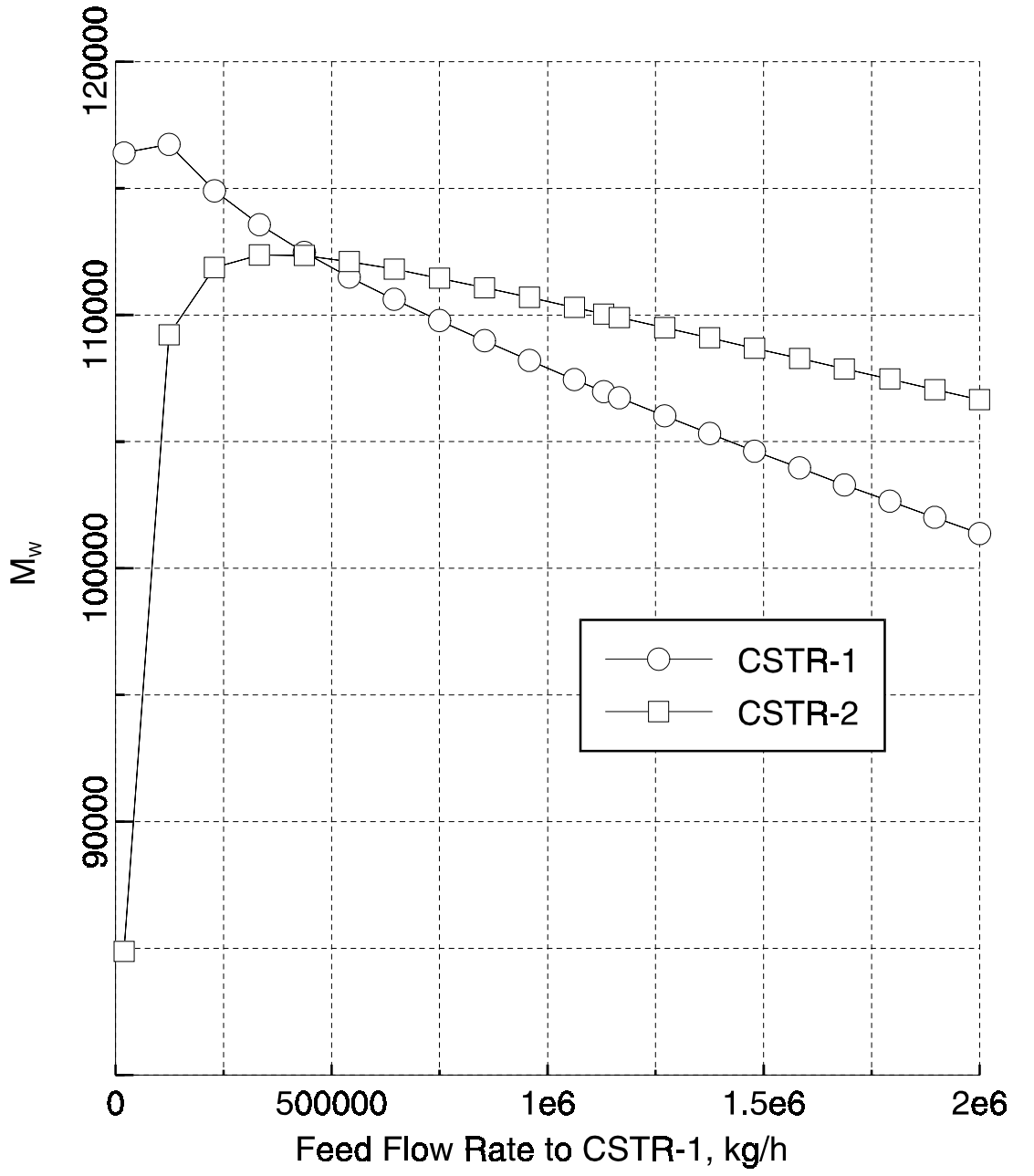

Figure 2.6 *Effect of Feed Flow Rate on* M_w

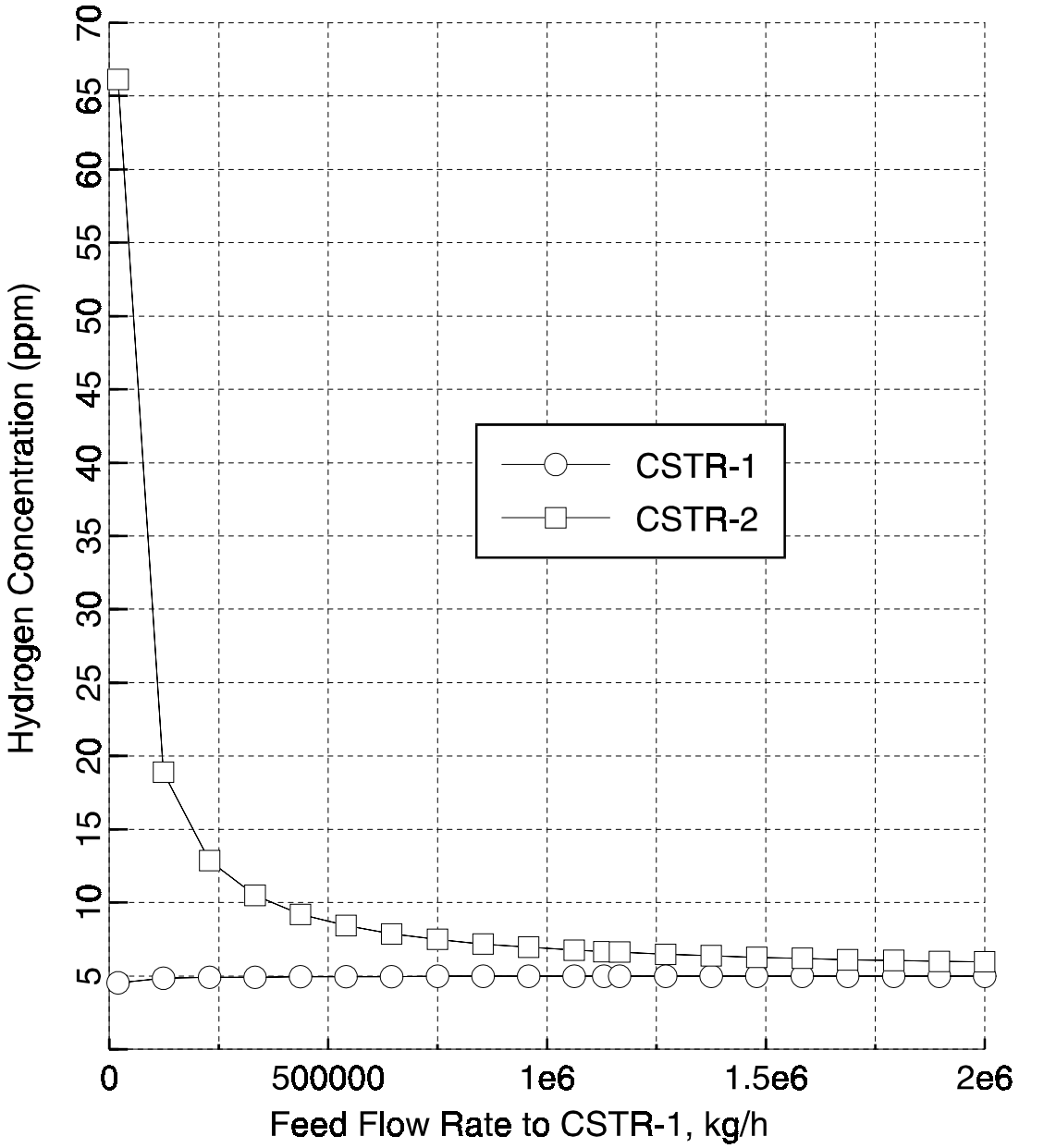

Figure 2.7 *Effect of Feed Flow Rate on the Hydrogen Concentration (PPM)*

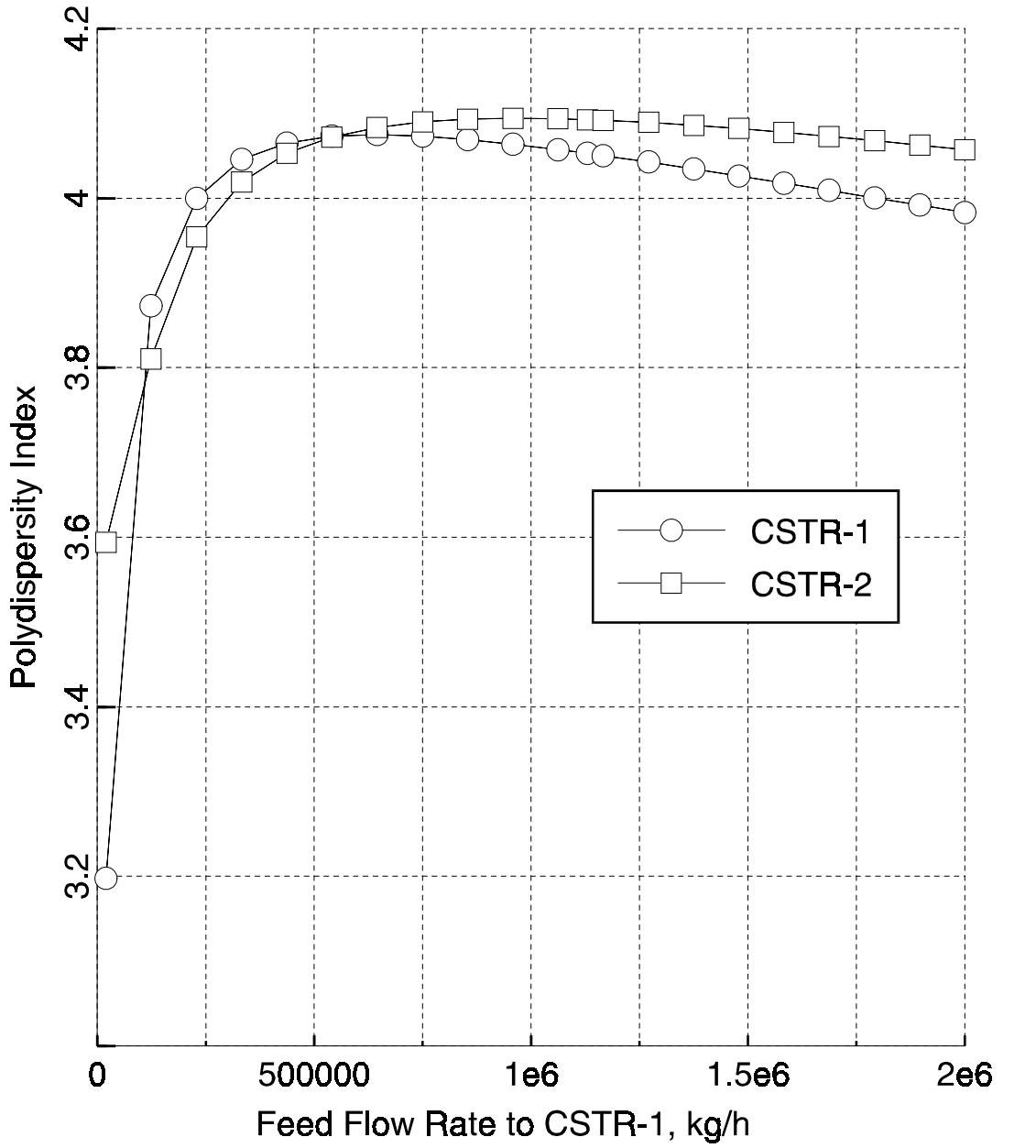

Figure 2.8 *Effect of Feed Flow Rate on the Polydispersity Index*

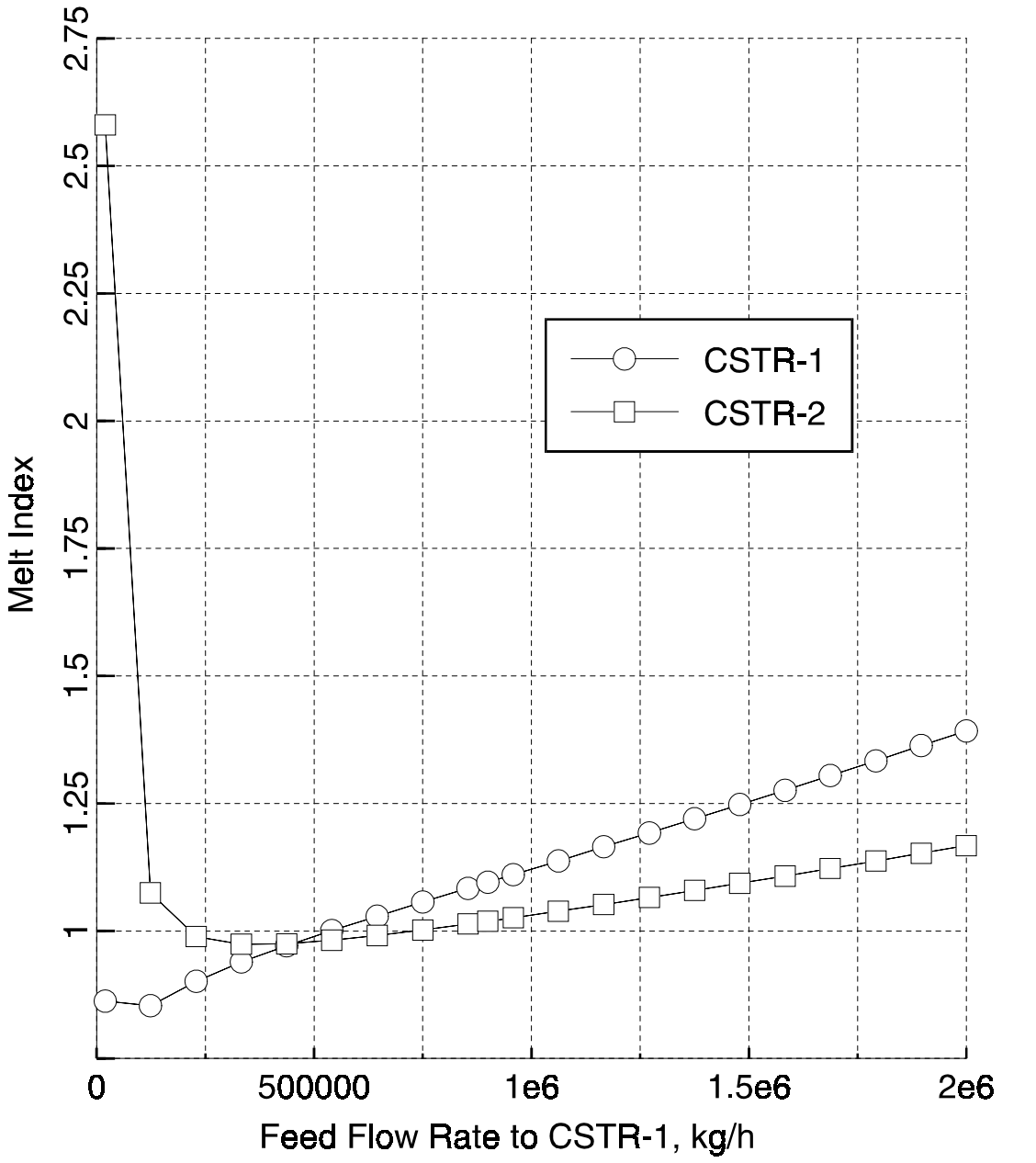

Figure 2.9 *Effect of Feed Flow Rate on the Melt Index*

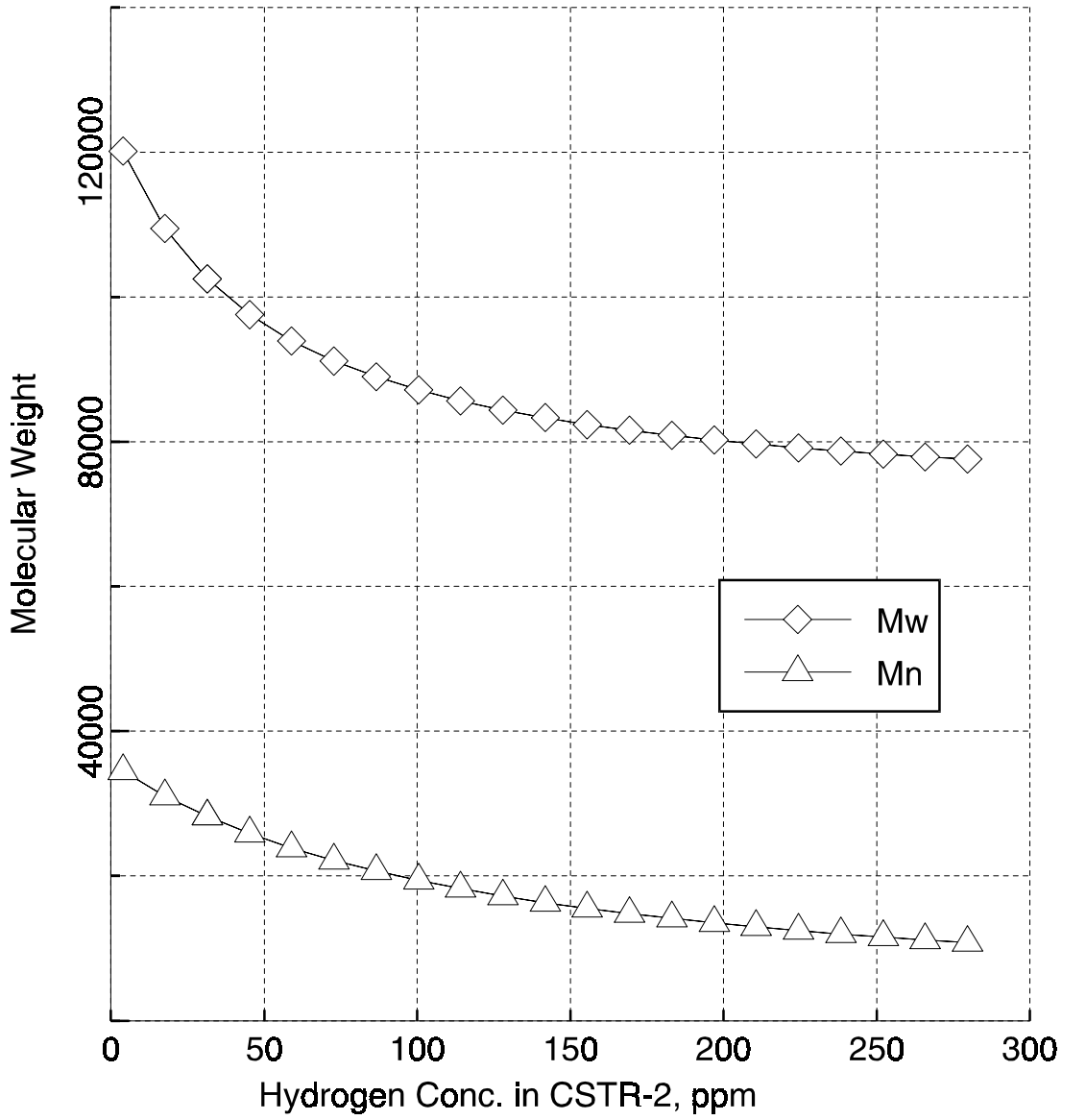

Figure 2.10 *Effect of the Concentration of Hydrogen on* M_n *and* M_w

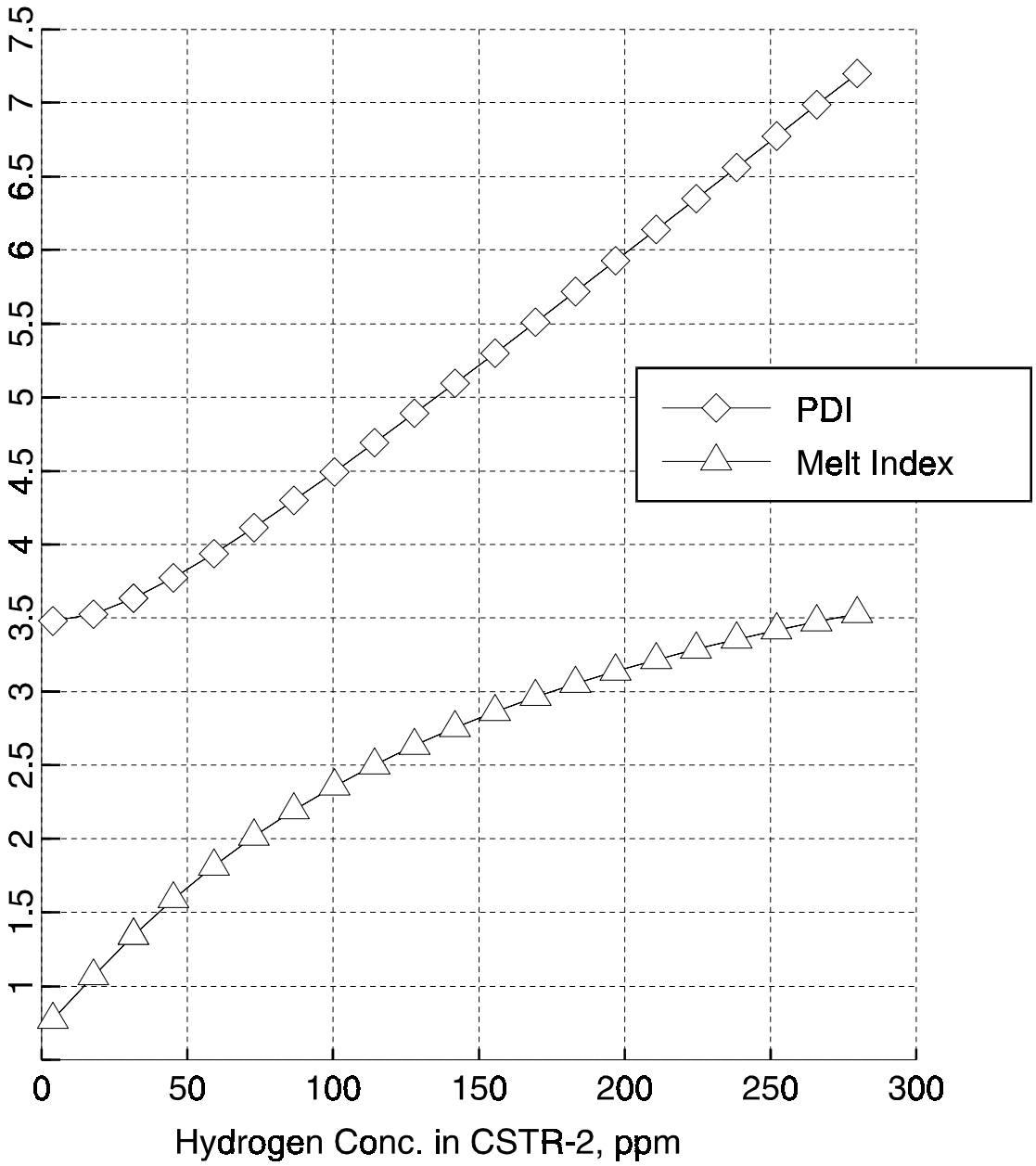

Figure 2.11 *Effect of the Concentration of Hydrogen on the Melt Index and PDI*

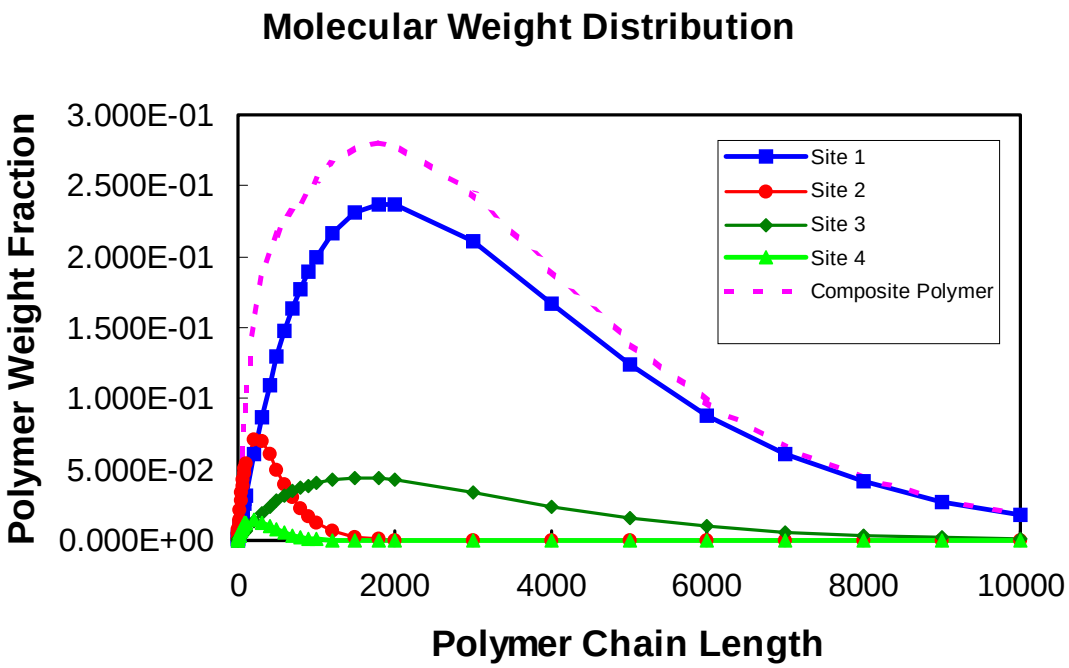

Figure 2.12 *Molecular Weight Distribution of the Polymer Produced at Each Site*

REFERENCES

MacAuley, K. B., J. F. MacGregor, A. E. Hamielec, *AIChE Journal*, **36**, 837 (1990).

Xie, T., K. B. McAuley, J. C.C. Hsu and D. W. Bacon, "Gas phase ethylene polymerization: Production processes, polymer properties and reactor modeling", *Ind. Eng. Chem. Res.*, **33**, 449-479 (1994).

3 LOW-DENSITY POLYETHYLENE

HIGH PRESSURE PROCESS

SUMMARY

The LDPE high pressure process model illustrates the use of Polymers Plus to model a high pressure free-radical process for low-density polyethylene. The model considers the tubular jacketed reactor along with the post-polymerization devolatization. Among the parameters studied in the model are reactor temperature profile, monomer conversion, polymer molecular weight and degree of branching.

ABOUT THIS PROCESS

Low density polyethylene (LDPE), is part of the polyolefin family of polymers. This polymer exhibits a number of desirable properties, including strength, flexibility, impact resistance, resistance to solvents, to chemicals, and to oxidating agents. For this reason, it is one of the highest volume polymers in terms of production.

LDPE is produced by free-radical polymerization. It has been produced in batch processes. However, continuous processes are more commonly found, because they allow better control of the polymerization. Polymerization is carried out in tubular and autoclave reactors under high pressure (1300-3400 atm), and high temperatures (150-340°C). At such high compression states, the gaseous ethylene monomer behaves like a liquid. The reactor of choice for the production of LDPE is a tubular reactor. Some processes involve multizone tubular reactors with multiple initiator injection points along the length of the reactor.

PROCESS DEFINITION

In this example, polymerization of ethylene is carried out in a jacketed tubular reactor divided into four sections, with two initiator injection points. High and low pressure separators are also used. The flowsheet for the process is given in Figure 3.1.

The flowsheet is modeled using two RPlug in series, followed by a Mixer block for the second initiator injection point, two more RPlug in series, followed by two Flash2 blocks as the high and low pressure separators.

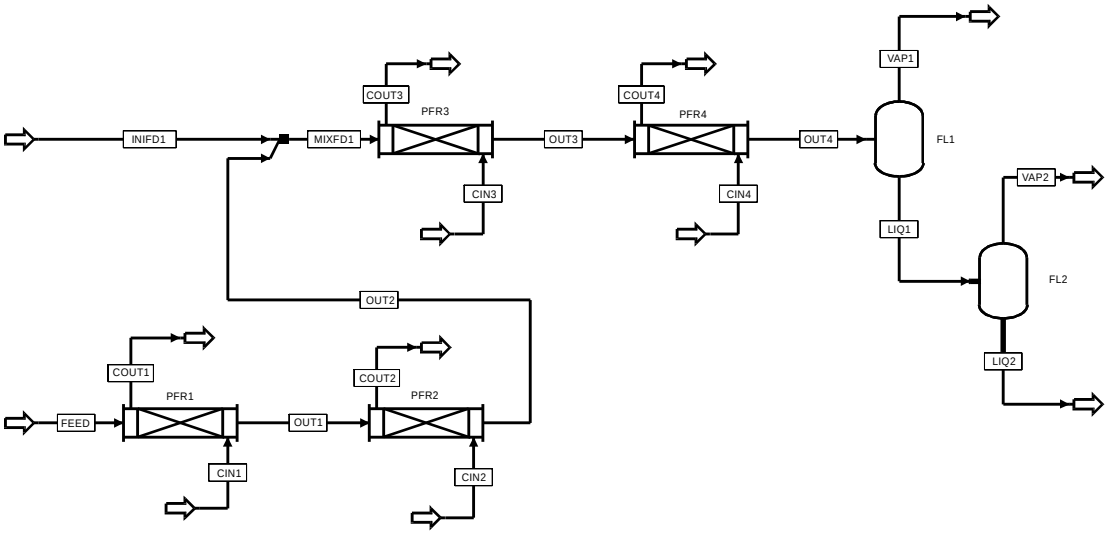

Figure 3.1 *LDPE High Pressure Polymerization Flowsheet*

Process Conditions

The process conditions are as listed in Table 3.1.

Table 3.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Initiator	INI1	PURECOMP	Initiator
2nd initiator	INI2	PURECOMP	Initiator
Ethylene	E2	PURECOMP	Monomer
Polyethylene	PE	POLYMER	Polymer
	E2-SEG	SEGMENT	Ethylene segment
Water	WATER	PURECOMP	Coolant
Physical Properties	POLYSL property method with supplied parameters		
Feeds			
	Feed	**Initiator Injection**	**Coolant**
Temperature (°C)	125	125	160
Pressure (atm)	2000	2000	100
Component flows:		-	-
C2E (kg/sec)	17.4993	--	--
INI1	4.375E-4	1E-4	---
INI2	2.1875E-4	5E-5	---
WATER	---	---	44.4
Kinetics	FREE-RAD model (see Reactor Kinetics for rate constant parameters)		
Operating Conditions			
Block	**Temp (°C)**	**Pres (atm)**	**Size**
PFR1	170 (coolant)	2000	250 m length by 0.059 m diam*
PFR2	170 (coolant)	2000	250 m length by 0.059 m diam*
PFR3	170 (coolant)	2000	250 m length by 0.059 m diam*
PFR4	170 (coolant)	2000	250 m length by 0.059 m diam*
MIX1	---	2000	---
FL1	Duty=0	250	---
FL2	Duty=0	1	---

* ***A user heat transfer subroutine (Carr et al., 1955; Eirmann, 1965) is provided to these plug flow reactors.***

Physical Property Models and Data

The POLYSL equation-of-state property method is used for the physical property calculations and phase equilibria. The unary input parameters for POLYSL are SLTSTR, SLPSTR, and SLRSTR, and correspond to the Sanchez-Lacombe equation of state T*, P*, and ρ* parameters, respectively. The parameters were obtained by Sanchez-Lacombe by fitting experimental data (Sanchez, et al., 1976). An input summary containing these parameter values is given in the Process Studies section.

To improve predictions for phase equilibria in the high- and low-pressure separators, two binary interaction parameters between polyethylene and ethylene were introduced, namely SLKIJ and SLETIJ. These parameters were obtained by fitting VLE experimental data of polyethylene-ethylene binary systems at various temperatures.

Ideal gas heat capacity coefficients (CPIG) are entered for ethylene segment and pure ethylene. The coefficients are obtained from heat capacity data fit. CPIG is used for the calculation of ideal-gas enthalpy and entropy, which are added to the departure values calculated by the Sanchez-Lacombe equation of state. An input summary containing these parameter values is given in the Process Studies section.

Reactors / Kinetics

The built-in free-radical reactions included for this example are listed below along with their rate constant parameters.

Description	k_0 †‡ (m^3 / kmol)	E_a † (J / kmol)	V † (m^3 / kmol)
Initiator 1 decomposition	2.5E14	126E6	0
Initiator 2 decomposition	5.93E18	195E6	0
Chain initiation	2.5E8‡	35.3E6	0
Propagation	2.5E8‡	35.3E6	-21.3E-3
Chain transfer to monomer	1.25E6	45.4E6	0
Chain transfer to polymer	1.24E6	30.4E6	1.6E-3
Termination by combination	2.5E9	4.19E6	1E-3
Termination by disproportionation	2.5E9	4.19E6	1E-3
Beta scission	6.07E7	45.3E6	0
Short chain branching	1.3E9	41.6E6	0

† k_0 is frequency factor, E_a is activation energy and V is activation volume

‡ k_0 is 2 times higher than in Mavridis and Kiparissides (1985).

Process Studies

The model is used to examine the reactor temperature profile, monomer conversion, number and weight average molecular weights, and frequency of short and long chain branches.

An Input Summary is given in Figure 3.2.

Figure 3.2 Input Summary for LDPE High Pressure Polymerization

```
;The LDPE application example requires a FORTRAN subroutine.  Please copy
;the file ( USRHPE.F ) located in the application example directory to
;your working directory and compile. This file uses the component ID's
;of ethylene and LDPE to locate and get the flows and molecular weights.
;Please don't change the component ID's for ethylene and LDPE.
;This subroutine calculates the heat transfer coefficient and returns to
;the RPLUG.
;

TITLE 'High-Pressure LDPE Tubular Reactor with Four Sections'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=bar  &
        TEMPERATURE=C PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=5000.0

DESCRIPTION "This flowsheet models a high-pressure LDPE tubular
        reactor flowsheet with four sections, two initiator
        injection points, and high and low pressure separators.  "

DATABANKS PURE93  / POLYMER  / SEGMENT  / ASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT  / ASPENPCD

COMPONENTS
    INI1 C2H4 INI1 /
    E2 C2H4 E2 /
    LDPE PE LDPE /
    E2-SEG C2H4-R E2-SEG /
    INI2 C2H4 INI2 /
    WATER H2O WATER

FLOWSHEET
    BLOCK PFR1 IN=FEED CIN1 OUT=OUT1 COUT1
    BLOCK PFR2 IN=OUT1 CIN2 OUT=OUT2 COUT2
    BLOCK MIX1 IN=OUT2 INIFD1 OUT=MIXFD1
    BLOCK PFR3 IN=MIXFD1 CIN3 OUT=OUT3 COUT3
    BLOCK PFR4 IN=OUT3 CIN4 OUT=OUT4 COUT4
    BLOCK FL1 IN=OUT4 OUT=VAP1 LIQ1
    BLOCK FL2 IN=LIQ1 OUT=VAP2 LIQ2
```

Figure 3.2 Input Summary for LDPE High Pressure Polymerization (cont.)

```
PROPERTIES POLYSL
    PROPERTIES STEAM-TA

PROP-DATA PCES-2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=bar TEMPERATURE=C PDROP='N/sqm'
    PROP-LIST VLSTD
    PVAL E2-SEG 0.0

PROP-DATA POLYSL
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=bar PDROP='N/sqm'
    PROP-LIST SLTSTR / SLPSTR / SLRSTR
    PVAL E2 333.0 / 2400.0 / 631.0
    PVAL LDPE 667.70 / 3500.0 / 894.0
    PVAL INI1 333.0 / 2400.0 / 631.0
    PVAL INI2 333.0 / 2400.0 / 631.0
    PVAL WATER 623.0 / 2.6871390E+04 / 1105.0

PROP-DATA TGTM
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=bar TEMPERATURE=C PDROP='N/sqm'
    PROP-LIST TGVK / TMVK / CRITMW
    PVAL LDPE -36.0 / 141.60 / 3500.0

PROP-DATA CPIG-1
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=bar TEMPERATURE=C PDROP='N/sqm'
    PROP-LIST CPIG
    PVAL E2-SEG 35342.0 70.20
    PVAL E2 42291.0 47.3550

PROP-DATA MULMH-1
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=bar TEMPERATURE=C PDROP='N/sqm'
    PROP-LIST MULMH
    PVAL LDPE .0005740 5000.0 7.54220 1.0 1.0

PROP-DATA SLETIJ-1
    IN-UNITS SI
    PROP-LIST SLETIJ
    BPVAL LDPE E2 -.148690
    BPVAL E2 LDPE -.148690

PROP-DATA SLKIJ-1
    IN-UNITS SI
    PROP-LIST SLKIJ
    BPVAL LDPE E2 .014170
    BPVAL E2 LDPE .014170

POLYMERS
    SEGMENTS E2-SEG REPEAT
    POLYMERS LDPE
    ATTRIBUTES LDPE DPN DPW PDI MWN MWW ZMOM FMOM SMOM  &
        SFLOW SFRAC FLCB FSCB LCB SCB LSFLOW LSFRAC LEFLOW  &
        LEFRAC
```

Figure 3.2 Input Summary for LDPE High Pressure Polymerization (cont.)

```
STREAM CIN1
    SUBSTREAM MIXED TEMP=160.0 PRES=100.0 NPHASE=1 PHASE=L
    MASS-FLOW WATER 160000.0

STREAM CIN2
    SUBSTREAM MIXED TEMP=160.0 PRES=100.0 NPHASE=1 PHASE=L
    MASS-FLOW WATER 160000.0
STREAM CIN3
    SUBSTREAM MIXED TEMP=160.0 PRES=100.0 NPHASE=1 PHASE=L
    MASS-FLOW WATER 160000.0

STREAM CIN4
    SUBSTREAM MIXED TEMP=160.0 PRES=100.0 NPHASE=1 PHASE=L
    MASS-FLOW WATER 160000.0

STREAM FEED
    SUBSTREAM MIXED TEMP=125.0 PRES=2000.0 MASS-FLOW=63000.0  &
        NPHASE=1 PHASE=L
    MASS-FRAC INI1 .0000250 / E2 .99996250 / INI2 .00001250

STREAM INIFD1
    SUBSTREAM MIXED TEMP=125.0 PRES=2000.0 NPHASE=1 PHASE=L
    MASS-FLOW INI1 .360 / INI2 .180

BLOCK MIX1 MIXER
    PARAM PRES=2000.0 NPHASE=1 PHASE=L

BLOCK FL1 FLASH2
    PARAM PRES=250.0 DUTY=0.0

BLOCK FL2 FLASH2
    PARAM PRES=1.0 DUTY=0.0

BLOCK PFR1 RPLUG
    SUBROUTINE QTRANS=USRHPE
    PARAM TYPE=COUNTER-COOL LENGTH=250.0 DIAM=.0590 NPHASE=1  &
        PHASE=L PRES=2000.0 NPOINT=20 CORR-METHOD=DIRECT  &
        ERR-METHOD=STATIC
    COOLANT PRES=100.0 NPHASE=1 PHASE=L TEMP=170.0
    PROPERTIES POLYSL / STEAM-TA
    REACTIONS RXN-IDS=R1

BLOCK PFR2 RPLUG
    SUBROUTINE QTRANS=USRHPE
    PARAM TYPE=COUNTER-COOL LENGTH=220.0 DIAM=.0590 NPHASE=1  &
        PHASE=L PRES=2000.0 NPOINT=20 CORR-METHOD=NEWTON  &
        ERR-METHOD=STATIC
    COOLANT PRES=100.0 NPHASE=1 PHASE=L TEMP=170.0
    PROPERTIES POLYSL / STEAM-TA
    REACTIONS RXN-IDS=R1

BLOCK PFR3 RPLUG
    SUBROUTINE QTRANS=USRHPE
    PARAM TYPE=COUNTER-COOL LENGTH=250.0 DIAM=.0590 NPHASE=1  &
        PHASE=L PRES=2000.0 NPOINT=20 CORR-METHOD=DIRECT  &
        ERR-METHOD=STATIC
```

Figure 3.2 Input Summary for LDPE High Pressure Polymerization (cont.)

```
    COOLANT PRES=200.0 NPHASE=1 PHASE=L TEMP=170.0
    PROPERTIES POLYSL / STEAM-TA
    REACTIONS RXN-IDS=R1

BLOCK PFR4 RPLUG
    SUBROUTINE QTRANS=USRHPE
    PARAM TYPE=COUNTER-COOL LENGTH=220.0 DIAM=.0590 NPHASE=1  &
        PHASE=L PRES=2000.0 NPOINT=20 CORR-METHOD=NEWTON  &
        ERR-METHOD=STATIC
    COOLANT PRES=200.0 NPHASE=1 PHASE=L TEMP=170.0
    PROPERTIES POLYSL / STEAM-TA
    REACTIONS RXN-IDS=R1

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR NOMOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP NOPCES

;
;     DEFINE POLYMERIZATION KINETICS

REACTIONS R1 FREE-RAD
    DESCRIPTION "EXAMPLE FREE-RADICAL INPUT"
    PARAM QSSA=YES
    SPECIES INITIATOR=INI1 INI2 MONOMER=E2 POLYMER=LDPE
    MON-RSEG E2 E2-SEG
    INIT-DEC INI1 2.5000E+14 1.2600E+08 0.0 EFFIC=.980  &
        NRADS=2
    INIT-DEC INI2 5.9300E+18 1.9500E+08 0.0 EFFIC=.50 NRADS=2
    CHAIN-INI E2 2.5000E+08 3.5300E+07 0.0
    PROPAGATION E2 E2 2.5000E+08 3.5300E+07 -.02130
    CHAT-MON E2 E2 1250000.0 4.5400E+07 0.0
    CHAT-POL E2 E2 1240000.0 3.0400E+07 .00160
    B-SCISSION E2 6.0700E+07 4.5300E+07 0.0
    TERM-DIS E2 E2 2.5000E+09 4190000.0 .0010
    TERM-COMB E2 E2 2.5000E+09 4190000.0 .0010
    SC-BRANCH E2 E2 1.3000E+09 4.1600E+07 0.0
;
```

SELECTED SIMULATION RESULTS

This model was used to study several process parameters for the production of LDPE. The parameters evaluated for the first reactor section (PFR1) included:

- DPn and DPw vs. Reactor Length (Figure 3.4)
- Initiator Decomposition Rate vs. Reactor Length (Figure 3.5)
- Coolant and Reactant Temperature Profiles (Figure 3.6)
- Remaining Ethylene Mole fraction Profile in PFR1 and PFR3 (Figure 3.7)
- Reactor Temperature Profiles (Figure 3.8)

A stream summary is given in Figure 3.3.

Figure 3.3 Simulation Stream Summary

STREAM ID	LIQ1	LIQ2	MIXFD1	OUT1	OUT2
FROM :	FL1	FL2	MIX1	PFR1	PFR2
TO :	FL2	----	PFR3	PFR2	MIX1
SUBSTREAM: MIXED					
PHASE:	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
COMPONENTS: KG/HR					
INI1	0.0	0.0	0.3600	0.0	0.0
E2	1858.1598	5.1679	5.4700+04	5.4700+04	5.4700+04
LDPE	1.2583+04	1.2583+04	8300.4737	8300.4737	8300.4737
E2-SEG	0.0	0.0	0.0	0.0	0.0
INI2	0.0	0.0	0.1800	0.0	5.1647-18
WATER	0.0	0.0	0.0	0.0	0.0
COMPONENTS: MASS FRAC					
INI1	0.0	0.0	5.7142-06	0.0	0.0
E2	0.1286	4.1054-04	0.8682	0.8682	0.8682
LDPE	0.8713	0.9995	0.1317	0.1317	0.1317
E2-SEG	0.0	0.0	0.0	0.0	0.0
INI2	0.0	0.0	2.8571-06	0.0	8.1979-23
WATER	0.0	0.0	0.0	0.0	0.0
TOTAL FLOW:					
KG/HR	1.4441+04	1.2588+04	6.3001+04	6.3000+04	6.3000+04
STATE VARIABLES:					
TEMP C	275.1009	274.1323	210.7043	258.8699	210.7051
PRES BAR	250.0000	1.0000	2000.0000	2000.0000	2000.0000
VFRAC	0.0	0.0	0.0	0.0	0.0
LFRAC	1.0000	1.0000	1.0000	1.0000	1.0000
SFRAC	0.0	0.0	0.0	0.0	0.0
ENTHALPY:					
J/KG	-9.8247+05	-1.4671+06	1.6713+06	1.7759+06	1.6713+06

Figure 3.3 Simulation Stream Summary (cont.)

```
ENTROPY:
   J/KG-K              -5309.4733 -5955.9761 -2682.5826 -2558.6667 -2682.6177

DENSITY:
   KG/CUM               610.2955   701.0621   527.6187   508.5215   527.6185

AVG MW                   28.0537    28.0537    28.0537    28.0537    28.0537

 COMPONENT ATTRIBUTES:
 LDPE     DPN
            DPN         949.7347   949.7347   931.0067   931.0067   931.0067
          DPW
            DPW        3850.3877  3850.3877  3277.7105  3277.7105  3277.7105
          PDI
            PDI           4.0541     4.0541     3.5206     3.5206     3.5206
          MWN
            MWN        2.6644+04  2.6644+04  2.6118+04  2.6118+04  2.6118+04
          MWW
            MWW        1.0802+05  1.0802+05  9.1952+04  9.1952+04  9.1952+04
          ZMOM
            ZMOM          0.4721     0.4721     0.3177     0.3177     0.3177
          FMOM
            FMOM        448.4362   448.4362   295.7931   295.7931   295.7931
          SMOM
            SMOM       1.7267+06  1.7267+06  9.6952+05  9.6952+05  9.6952+05
          SFLOW
            E2-SEG      448.4362   448.4362   295.7931   295.7931   295.7931
          SFRAC
            E2-SEG        1.0000     1.0000     1.0000     1.0000     1.0000
          FLCB
            FLCBN         0.6149     0.6149     0.3846     0.3846     0.3846
          FSCB
            FSCBN        28.7080    28.7080    26.9860    26.9860    26.9860
          LCB
            LCBN          0.2757     0.2757     0.1137     0.1137     0.1137
          SCB
            SCBN         12.8737    12.8737     7.9822     7.9822     7.9822
          LSFLOW
            E2-SEG        0.0        0.0        0.0        0.0        0.0
          LSFRAC
            E2-SEG        0.0        0.0        0.0        0.0        0.0
          LEFLOW
            E2-SEG        0.0        0.0        0.0        0.0        0.0
          LEFRAC
            E2-SEG        0.0        0.0        0.0        0.0        0.0

 STREAM ID                OUT3       OUT4       VAP1       VAP2
 FROM :                   PFR3       PFR4       FL1        FL2
 TO   :                   PFR4       FL1        ----       ----

 SUBSTREAM: MIXED
 PHASE:                   LIQUID     LIQUID     VAPOR      VAPOR
 COMPONENTS: KG/HR
   INI1                     0.0     1.3930-16     0.0        0.0
   E2                   5.0417+04  5.0417+04  4.8559+04  1852.9918
   LDPE                 1.2583+04  1.2583+04     0.0        0.0
   E2-SEG                   0.0        0.0        0.0        0.0
```

Figure 3.3 Simulation Stream Summary (cont.)

```
   INI2                    0.0         0.0         0.0         0.0
   WATER                   0.0         0.0         0.0         0.0
 COMPONENTS: MASS FRAC
   INI1                    0.0      2.2111-21      0.0         0.0
   E2                      0.8002      0.8002      1.0000      1.0000
   LDPE                    0.1997      0.1997      0.0         0.0
   E2-SEG                  0.0         0.0         0.0         0.0
   INI2                    0.0         0.0         0.0         0.0
   WATER                   0.0         0.0         0.0         0.0

TOTAL FLOW:
     KG/HR                6.3001+04   6.3001+04   4.8559+04   1852.9918

 STATE VARIABLES:
   TEMP    C              264.9666    235.5654    275.1009    274.1323
   PRES    BAR           2000.0000   2000.0000    250.0000      1.0000
   VFRAC                    0.0         0.0         1.0000      1.0000
   LFRAC                    1.0000      1.0000      0.0         0.0
   SFRAC                    0.0         0.0         0.0         0.0


ENTHALPY:
   J/KG                 1.5485+06   1.4842+06   2.2177+06   2.3098+06

ENTROPY:
   J/KG-K              -2741.7665  -2818.1600  -2326.0946   -844.1011

DENSITY:
   KG/CUM                519.6656    530.9541    154.8557      0.6167

AVG MW                   28.0537     28.0537     28.0537     28.0537

 COMPONENT ATTRIBUTES:
 LDPE      DPN
             DPN          949.7347    949.7347
           DPW
             DPW         3850.3877   3850.3877
           PDI
             PDI            4.0541      4.0541
           MWN
             MWN         2.6644+04   2.6644+04
           MWW
             MWW         1.0802+05   1.0802+05
           ZMOM
             ZMOM           0.4721      0.4721
           FMOM
             FMOM         448.4362    448.4362
           SMOM
             SMOM        1.7267+06   1.7267+06
           SFLOW
             E2-SEG       448.4362    448.4362
           SFRAC
             E2-SEG         1.0000      1.0000
           FLCB
             FLCBN          0.6149      0.6149     MISSING     MISSING
           FSCB
             FSCBN         28.7080     28.7080     MISSING     MISSING
```

Figure 3.3 Simulation Stream Summary (cont.)

```
          LCB
            LCBN          0.2757     0.2757    MISSING    MISSING
          SCB
            SCBN         12.8737    12.8737    MISSING    MISSING
          LSFLOW
            E2-SEG        0.0        0.0       MISSING    MISSING
          LSFRAC
            E2-SEG        0.0        0.0       MISSING    MISSING
          LEFLOW
            E2-SEG        0.0        0.0       MISSING    MISSING
          LEFRAC
            E2-SEG        0.0        0.0       MISSING    MISSING
```

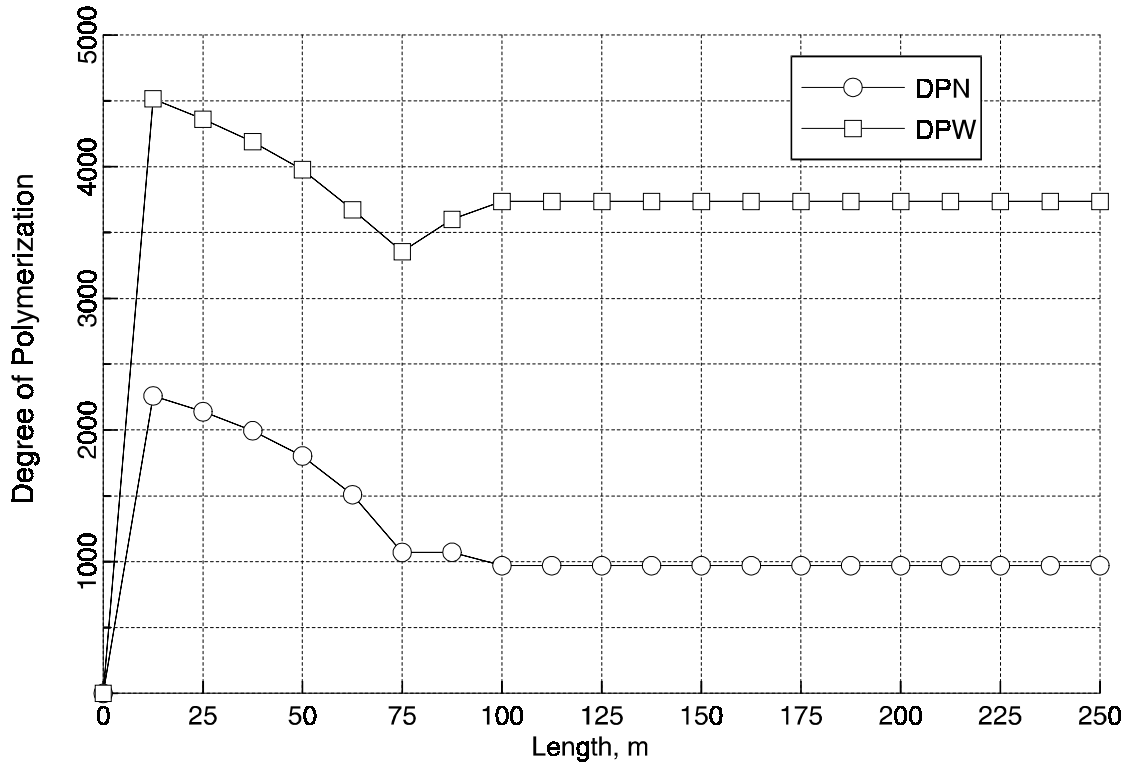

Figure 3.4 *PFR1 DPn and DPw vs. Reactor Length*

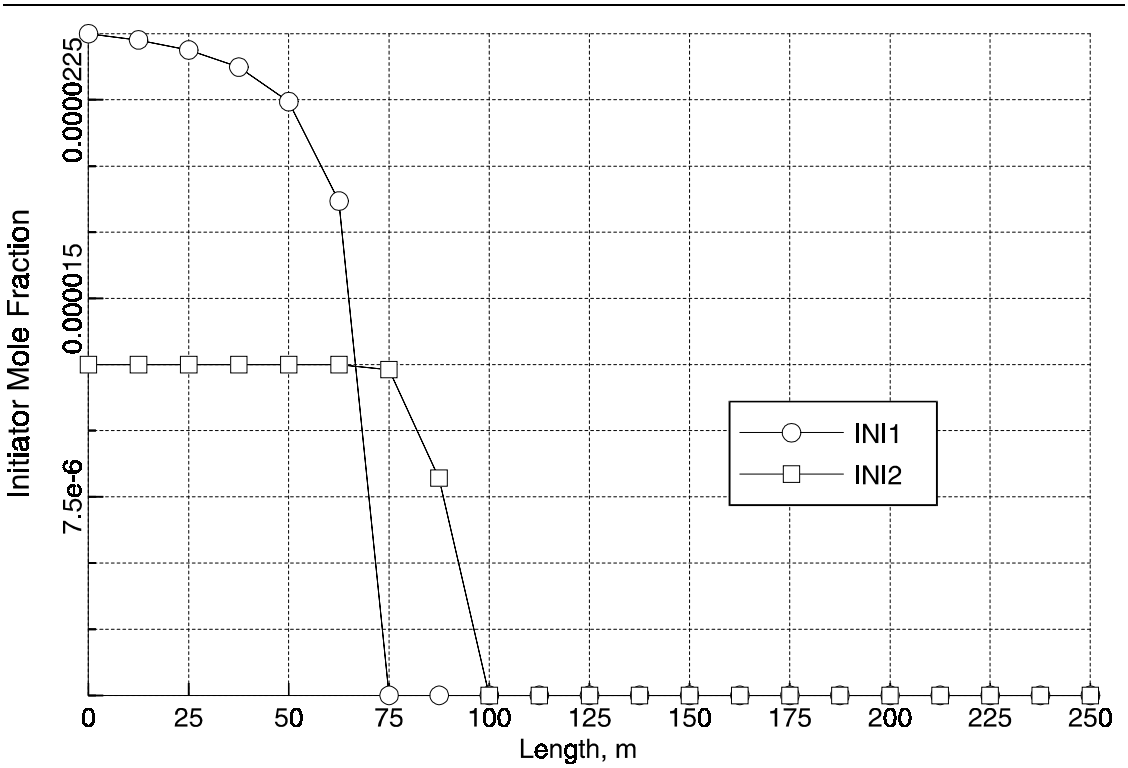

Figure 3.5 *PFR1 Initiator Decomposition Rate vs. Reactor Length*

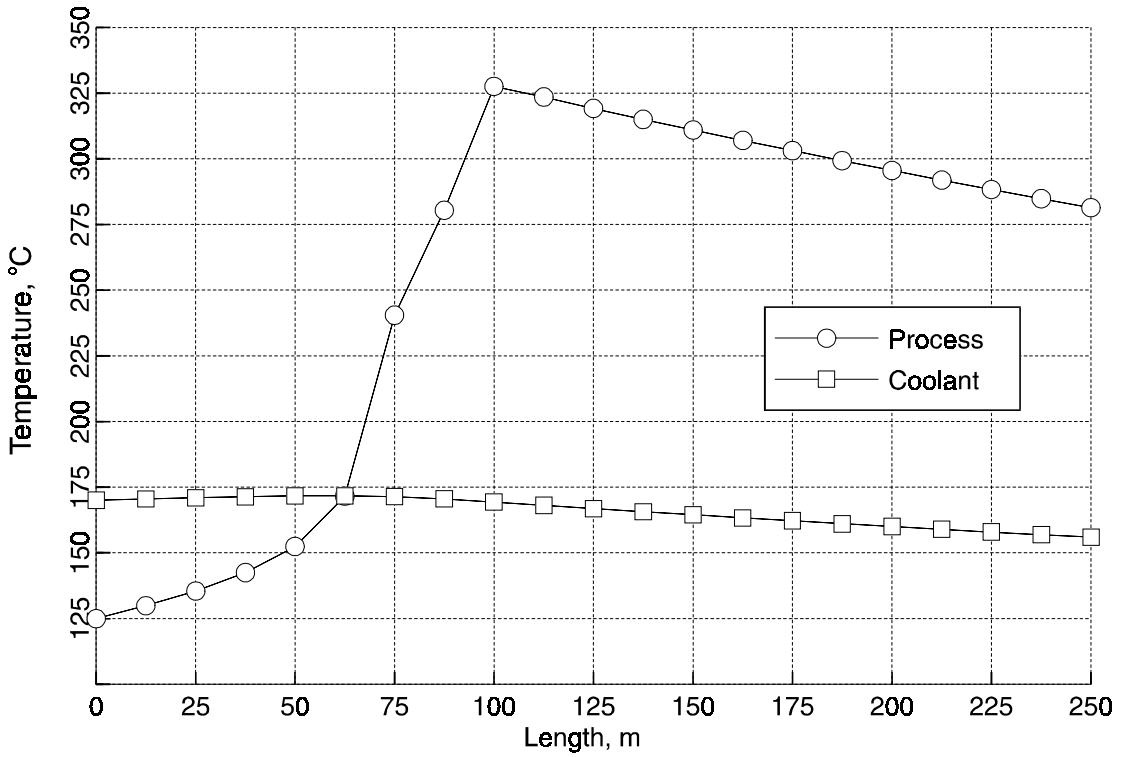

Figure 3.6 *PFR1 Coolant and Reactant Temperature Profiles*

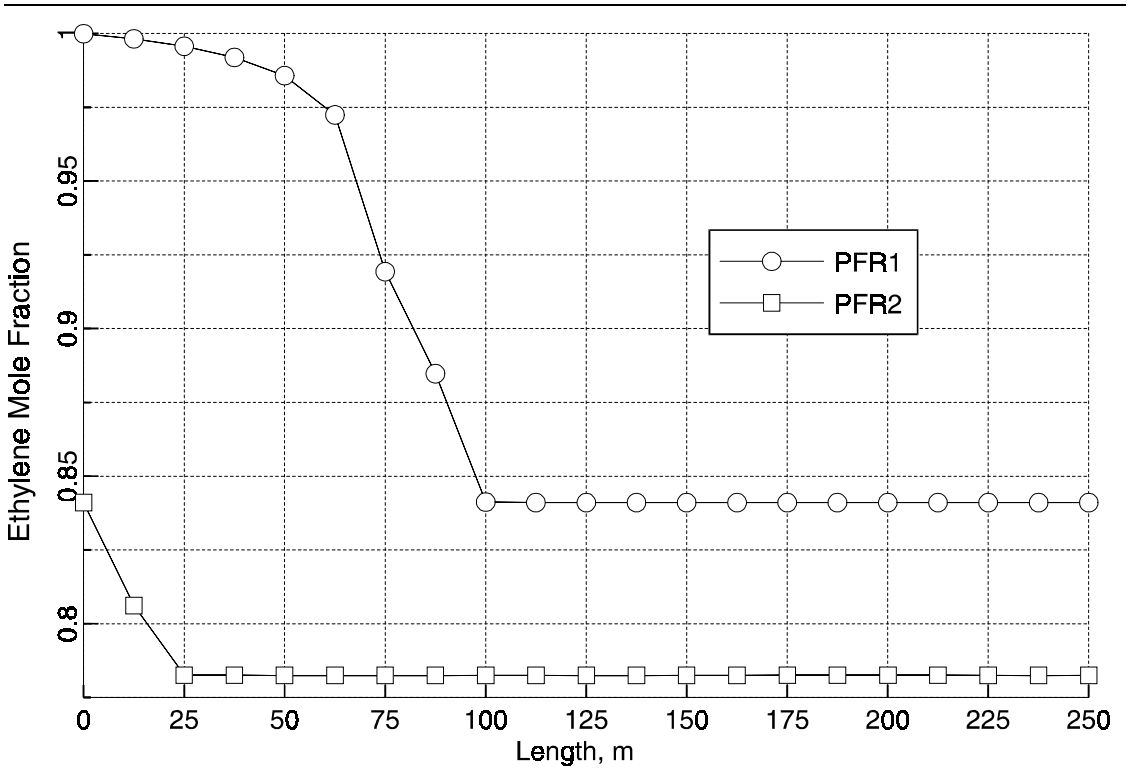

Figure 3.7 *PFR1 and PFR3 Ethylene Mole Fraction Profile*

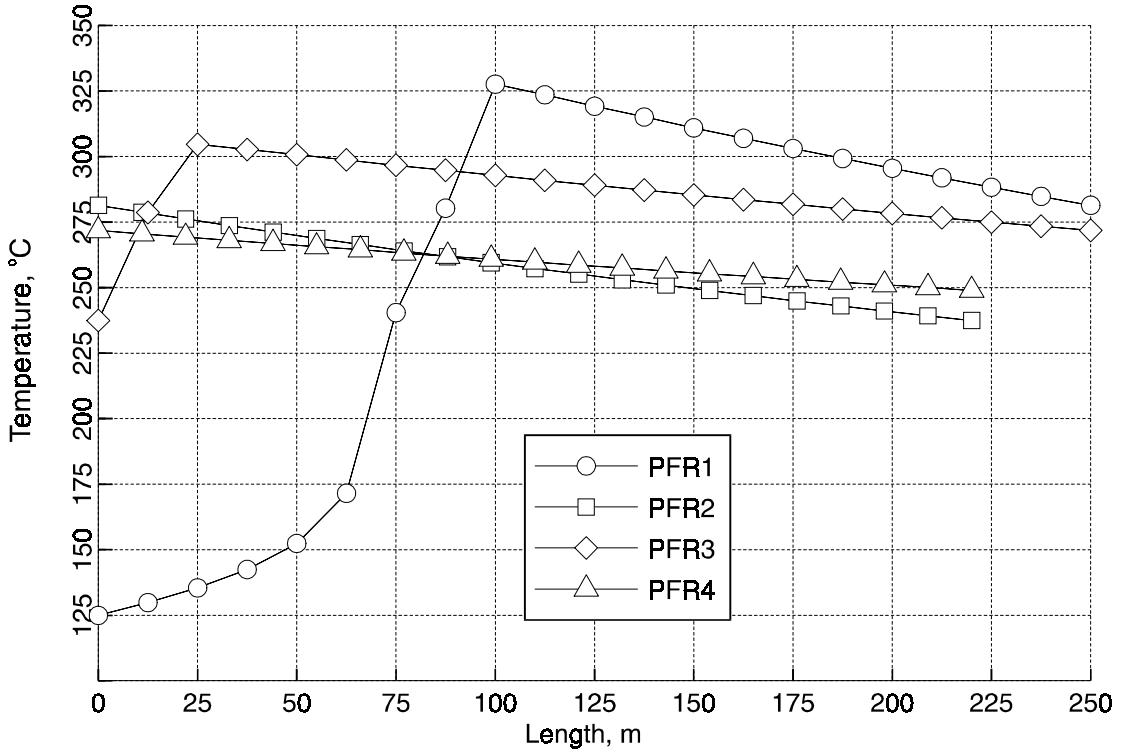

Figure 3.8 *Reactor Temperature Profiles*

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4 NYLON 6

CAPROLACTAM POLYMERIZATION PROCESS

SUMMARY

The nylon 6 caprolactam polymerization process model illustrates the use of Polymers Plus to model the polymerization of caprolactam to Nylon 6. This multistage reactor model accounts for the step-growth polymerization kinetics. This model is used to study the effect of feed flow rate on caprolactam conversion, degree of polymerization, and extraction value.

ABOUT THIS PROCESS

Nylon 6 is produced industrially on a large scale for synthetic fibers, films, plastics, etc. In one process, it is obtained by polymerizing caprolactam in the presence of water in a continuous flowsheet. Process modeling plays an important role in quality control, modification of existing plants, development of new processes, etc.

Nylon is commonly produced in a conventional VK column reactor shown in Figure 4.1. The reactor is essentially a vertical tube operating at atmospheric pressure. A mixture of caprolactam, water and stabilizer is continuously fed to the top of the column. The ring opening reaction initiates polymerization in zone 1 and the excess water is evaporated in this zone. The vapor coming out of zone 1 is sent to a distillation column. Caprolactam from the distillation column is recycled to the reactor and condensate water is removed. In zone 2, polymerization proceeds under near adiabatic conditions. No water is evaporated in this zone.

The feed to the process is a mixture of caprolactam (99% by weight) and water (1% by weight) at 260°C, 1 atm. When this mixture is heated to temperatures above 220-260°C, five main equilibrium reactions occur: (1) ring opening of caprolactam, (2) polycondensation of the end groups, (3) polyaddition of caprolactam, (4) ring opening of cyclic dimer, and (5) polyaddition of cyclic dimer. These reactions must all be taken into account in the model.

PROCESS DEFINITION

In this example, the top portion of the VK column (zone 1) will be modeled as two stirred tank reactors. The bottom portion of the column (zone 2 and below) will be modeled as a plug flow reactor. The distillation column will be included in the simulations as a multistage separator. A flash tank will be inserted after each stirred tank in zone 1 to account for VLE calculations. The plug flow reactor will be considered liquid filled. Figure 4.2 shows the process flow diagram.

As shown in Figure 4.2 the flowsheet consists of two RCSTR in series, with a Flash2 in the middle, a second Flash2 followed by an RPlug, and finally a RadFrac block for the water-caprolactam separation.

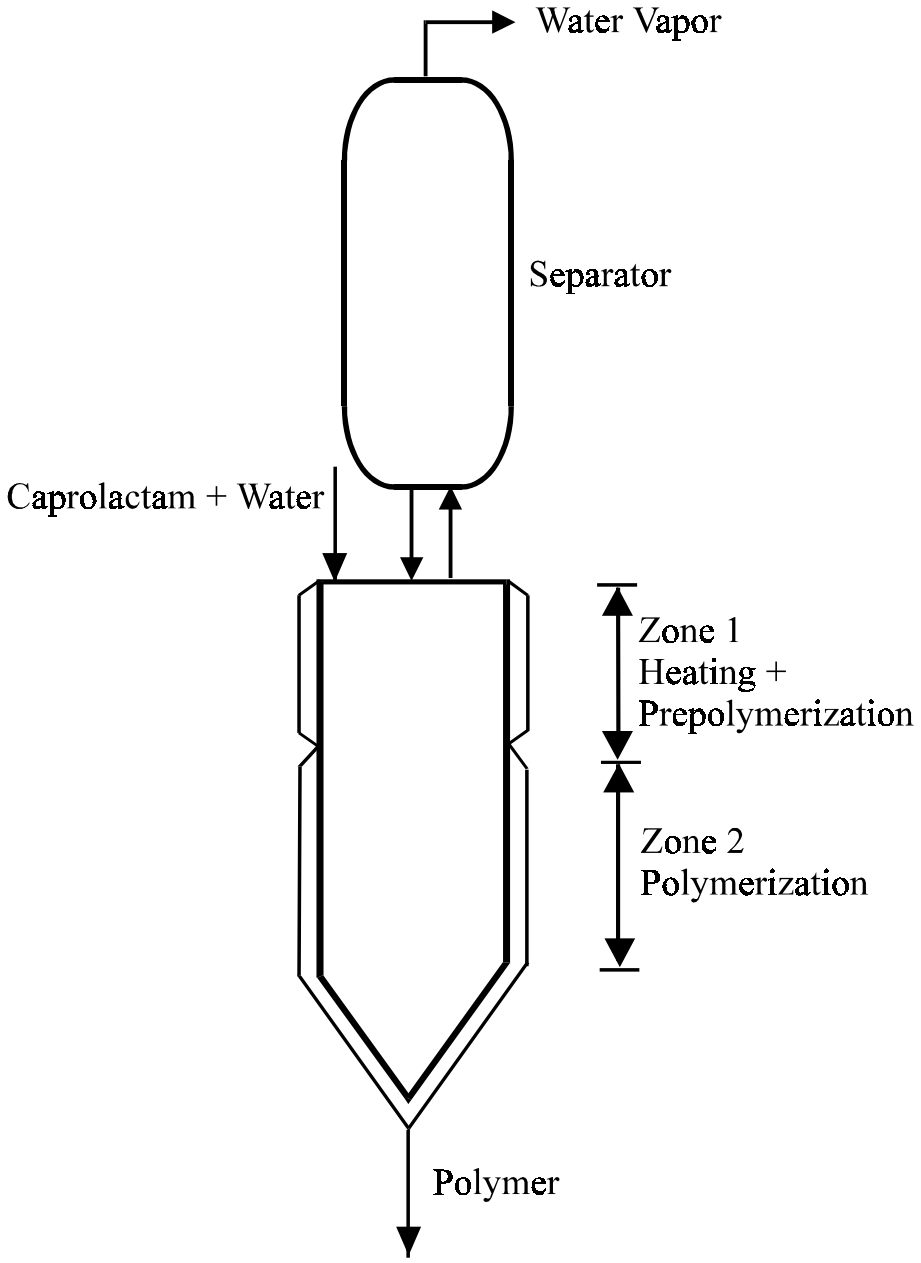

Figure 4.1 *Conventional VK Column for Caprolactam Polymerization*

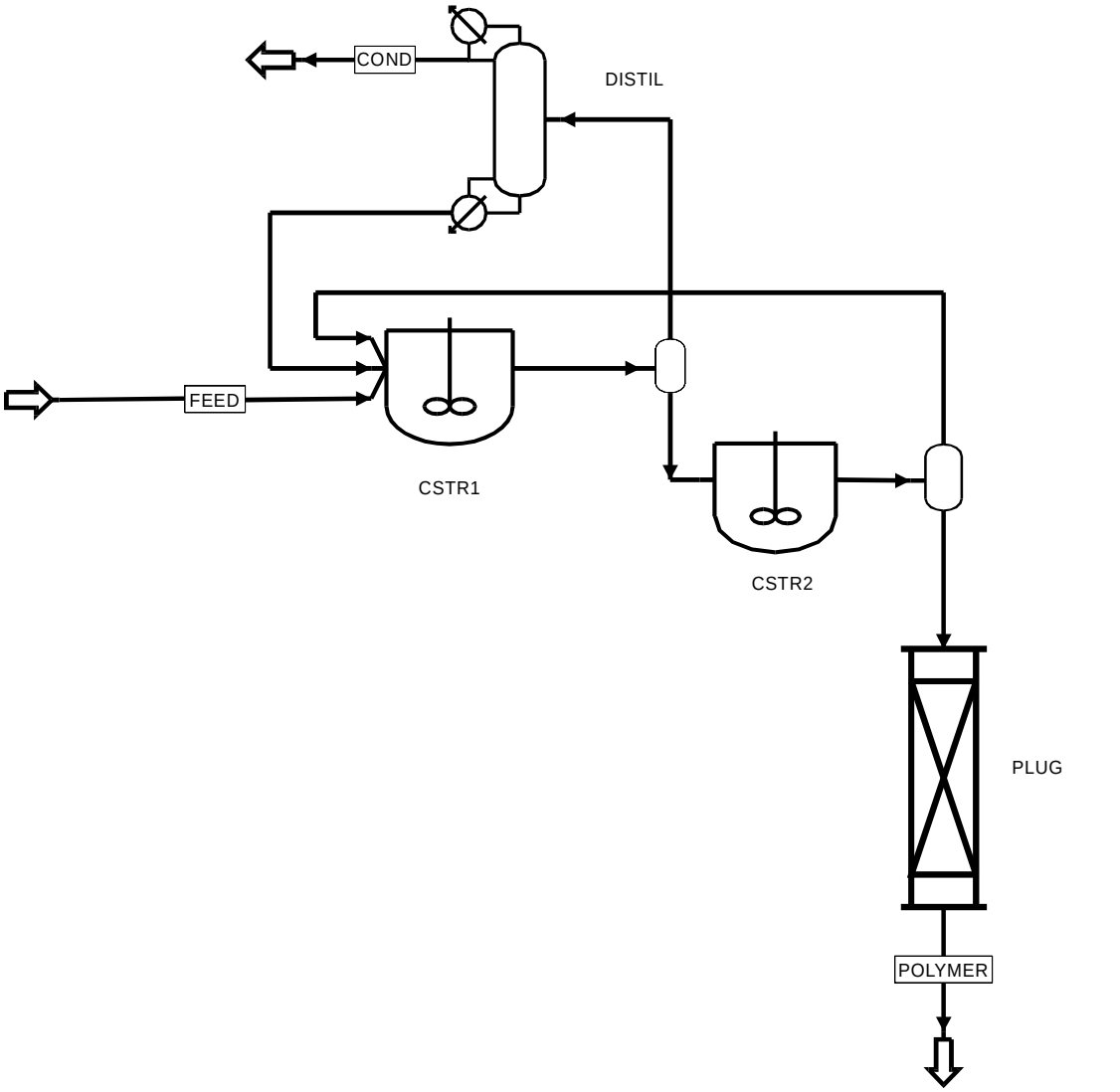

Figure 4.2 *Caprolactam Polymerization Model Flowsheet*

Process Conditions

The process conditions are as listed in Table 4.1.

Table 4.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Caprolactam	CL	PURECOMP	Monomer
Aminocaproic Acid	ACA	PURECOMP	Monomer
Cyclic Dimer	CD	PURECOMP	Monomer
Water	H2O	PURECOMP	Catalyst
Nylon	NYLON T-NH2 T-COOH B-ACA	POLYMER SEGMENT SEGMENT SEGMENT	Polymer NH2 segment COOH segment ACA segment
Physical Properties	POLYNRTL property method with supplied parameters		
Feeds			
Temperature (°C)	260		
Pressure (atm)	1		
Flowrate (kg/hr)	40		
Caprolactam	99.0% by weight		
Water	1.0% by weight		
Kinetics	STEP-GROWTH model		
Operating Conditions			
Block	**Temp (°C)**	**Pres (atm)**	**Size**
CSTR-1	260	1	75 L
CSTR-2	260	1	75 L
PLUG	260	1	500 m length by .0357 m diam
R1FLASH	---	1	Duty=0
R2FLASH	---	1	Duty=0
DISTIL	---	1	19 total condenser, reflux ratio of 3

Physical Property Models and Data

The Polymer Non-Random Two Liquid activity coefficient model property method (POLYNRTL) is used. Antoine constants for vapor pressure are entered for the components. Racket equation parameters for density calculations are also entered.

	ACA	CD	H2O	CL	Nylon
MW	131.17420	226.3180			
Racket	131.17420	226.3180	18.01520	113.1590	113.1590
	1.0	1.0	1.0	1.0	1.0
	0.0	0.0	0.0	0.0	0.0

Reactors / Kinetics

The main reactions used in the step-growth kinetics are as shown below:

	Description	Reaction
1	Ring-opening of caprolactam	$NH(CH_2)_5-CO + H_2O \rightleftharpoons H_2N-(CH_2)_5-COOH$
2	Polycondensation	$\sim NH_2 + HOOC\sim \rightleftharpoons \sim NHCO\sim + H_2O$
3	Polyaddition of caprolactam	$\sim NH_2 + CO-(CH_2)_5 - NH \rightleftharpoons \sim NHCO - (CH_2)_5 - NH_2$
4	Ring-opeining of cyclic dimer	$NH(CH_2)_5CONH(CH_2)_5CO + H_2O \rightleftharpoons H_2N(CH_2)_5CONH(CH_2)_5-COOH$
5	Polyaddition of cyclic dimer	$\sim NH_2 + NH(CH_2)_5CONH(CH_2)_5CO \rightleftharpoons \sim NHCO(CH_2)_5NHCO(CH_2)_5-NH_2$

A set of rate parameters reported in the literature was used in this example and is given in Table 4.2. The polycondensation reaction is modeled using the step growth kinetics. Ring opening and polyaddition of caprolactam and cyclic dimer are modeled using the user kinetics. Both the polycondensation reaction (2) and polyaddition reaction (3) form linear dimer, trimer and so on. The reversible ring opening reaction (4) produces cyclic dimer from linear dimer. The formation of cyclic trimer and higher cyclics considered negligible, is not considered in the present model.

To model the ring opening reaction, one needs to specify both the forward and reverse reactions, for the uncatalyzed reaction, and the reaction catalyzed by the carboxyl ends of polymer and aminocaproic acid. This results in 6 user reactions to include ring-opening of caprolactam in the model, and 6 user reactions to include ring opening of cyclic dimer. Similarly, an additional 30 reactions are needed to include polyaddition of caprolactam and cyclic dimer in the model. In the model, it is assumed that the concentration of linear dimer and trimer is the same as that of aminocaproic acid.

Table 4.2 Rate Parameters for Caprolactam Polymerization Model

	A_o	E_o	A_c	E_c
Ring opening of caprolactam	(f) 5.9874×10^5	19.88	4.3075×10^7	18.806
	(r) 3.1663×10^7	17.962	2.2779×10^9	16.88
Polycondensation	(f) 1.8942×10^{10}	23.271	1.2114×10^{10}	20.670
	(r) 1.17802×10^{10}	29.216	7.5338×10^9	26.616
Polayaddition of caprolactam	(f) 2.8558×10^9	22.845	1.6377×10^{10}	20.107
	(r) 9.4153×10^{10}	26.888	5.3993×10^{11}	24.151
Ring opening of cyclic dimer	(f) 8.5778×10^{11}	42.000	2.3307×10^{12}	37.400
	(r) 1.2793×10^{15}	51.600	3.4761×10^{15}	47.000
Polyaddition of cyclic dimer	(f) 2.5701×10^8	21.300	3.011×10^9	20.400
	(r) 1.9169×10^8	24.469	2.2458×10^9	23.569

o= uncatalyzed c = catalyzed* f = *forward reaction* r = *reverse reaction

A_o in kg/mol/h, A_c in $kg^2/mol^2/h$, E_o and E_c in kcal/mol

Process Studies

In order to determine the effect of feed flow rate on caprolactam conversion, degree of polymerization, and extraction value, a sensitivity study is carried out with the feed mass flow as the varied parameter. The sampled parameters are the polymer properties, the component fractions used to determine conversion, and the flowrates.

An Input Summary is given in Figure 4.3.

Figure 4.3 Input Summary for Caprolactam Polymerization

```
TITLE 'Caprolactam polymerization'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='l/hr' PRESSURE=atm TEMPERATURE=C TIME=hr  &
        VOLUME=l MOLE-ENTHALP='kcal/mol' MOLE-ENTROPY='kcal/mol-K'  &
        INVERSE-TIME='1/hr' LN-INV-TIME='ln(1/hr)' PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

DIAGNOSTICS
    HISTORY SIM-LEVEL=3 PROP-LEVEL=3

RUN-CONTROL MAX-TIME=15000.0

;----------------------------------------------------------------------

DESCRIPTION "This is a model of a NYLON-6 process. "

DATABANKS POLYMER  / PURE93  / SEGMENT  / NOASPENPCD

PROP-SOURCES POLYMER  / PURE93  / SEGMENT

COMPONENTS
    H2O H2O H2O /
    CL C6H11NO CL /
    ACA C6H11NO ACA /
    CD C6H11NO CD /
    NYLON NYLON6 NYLON /
    T-NH2 C6H12NO-E-1 T-NH2 /
    T-COOH C6H12NO2-E-1 T-COOH /
    B-ACA C6H11NO-R-1 B-ACA

FLOWSHEET
    BLOCK CSTR-1 IN=FEED RECYCLE R2-COND OUT=R1OUT
    BLOCK DISTIL IN=R1VAP OUT=COND RECYCLE
    BLOCK CSTR-2 IN=R1-OLIGO OUT=R2OUT
    BLOCK R1FLASH IN=R1OUT OUT=R1VAP R1-OLIGO
    BLOCK R2FLASH IN=R2OUT OUT=R2-COND R2-OLIGO
    BLOCK PLUG IN=R2-OLIGO OUT=POLYMER

PROPERTIES POLYNRTL

; The rate constants in the literature are given in mass units.
; P+ needs the rate constants
; in volume units. In order to use the rate constants in mass units
; fix the density of the components as 1 g/cc. This is done by
; replacing the density models and using the RACKETT parameters.

PROP-REPLACE POLYNRTL POLYNRTL
    PROP PHIVMX PHIVMX00
    PROP VLMX VLMX01
    PROP PHIV PHIV00
    PROP PHIL PHIL00
    MODEL ESIG
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
PROP-DATA MW
    IN-UNITS SI
    PROP-LIST MW
    PVAL ACA 131.17420
    PVAL CD 226.3180

PROP-DATA PLXANT-1
    IN-UNITS SI PRESSURE=atm PDROP='N/sqm'
    PROP-LIST PLXANT
    PVAL ACA -40.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL CD -40.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PROP-DATA RACKET-1
    IN-UNITS SI PRESSURE=atm MOLE-VOLUME='cc/mol' PDROP='N/sqm'
    PROP-LIST RACKET
    PVAL H2O 18.01520 1.0 0.0
    PVAL CL 113.1590 1.0 0.0
    PVAL ACA 131.17420 1.0 0.0
    PVAL CD 226.3180 1.0 0.0
    PVAL NYLON 113.1590 1.0 0.0

POLYMERS
    SEGMENTS T-NH2 END / T-COOH END / B-ACA REPEAT
    POLYMERS NYLON
    ATTRIBUTES NYLON SFLOW ZMOM FMOM DPN MWN EFRAC SFRAC

STREAM FEED
    SUBSTREAM MIXED TEMP=260.0 PRES=1.0 MASS-FLOW=40.0 NPHASE=1  &

        PHASE=L
    MASS-FRAC H2O .010 / CL .990

BLOCK R1FLASH FLASH2
    PARAM PRES=1.0 DUTY=0.0

BLOCK R2FLASH FLASH2
    PARAM PRES=1.0 DUTY=0.0

BLOCK DISTIL RADFRAC
    PARAM NSTAGE=20
    COL-CONFIG REBOILER=NONE CONDENSER=TOTAL
    FEEDS R1VAP 21
    PRODUCTS COND 1 L / RECYCLE 20 L
    P-SPEC 1 1.0
    COL-SPECS MOLE-RR=3.0

BLOCK CSTR-1 RCSTR
    DESCRIPTION "CAPROLACTAM POLYMERIZATION"
    PARAM VOL=75.0 TEMP=260.0 PRES=1.0 PHASE=L MB-MAXIT=350  &
        MB-TOL=.000010 DAMP-FAC=.10
    MOLE-FLOW MIXED CL .068540
    MOLE-FLOW MIXED H2O .017250
    MOLE-FLOW MIXED NYLON .11670
    MOLE-FLOW MIXED ACA .00012620
    REACTIONS RXN-IDS=NYLON
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
BLOCK CSTR-2 RCSTR
    PARAM VOL=75.0 TEMP=260.0 PRES=1.0 PHASE=L MB-MAXIT=350  &
        MB-TOL=.000010 DAMP-FAC=.10
    MOLE-FLOW MIXED H2O .00280
    MOLE-FLOW MIXED CL .03850
    MOLE-FLOW MIXED ACA .00001610
    MOLE-FLOW MIXED NYLON .137780
    REACTIONS RXN-IDS=NYLON

BLOCK PLUG RPLUG
    PARAM TYPE=T-SPEC LENGTH=500.0 DIAM=.03568250 PHASE=L  &
        PRES=1.0 NPOINT=20 INT-TOL=.000010 FLASH=YES
    COOLANT TOL=.000010
    T-SPEC 0.0 260.0 / 1.0 260.0
    REACTIONS RXN-IDS=NYLON

SENSITIVITY FLOW
    PARAM BASE-CASE=LAST
    DEFINE R1CL MASS-FLOW STREAM=R1OUT SUBSTREAM=MIXED  &
        COMPONENT=CL
    DEFINE R1NYL MASS-FLOW STREAM=R1OUT SUBSTREAM=MIXED  &
        COMPONENT=NYLON
    DEFINE R1DP COMP-ATTR-VAR STREAM=R1OUT SUBSTREAM=MIXED  &
        COMPONENT=NYLON ATTRIBUTE=DPN ELEMENT=1
    DEFINE R2CL MASS-FLOW STREAM=R2OUT SUBSTREAM=MIXED  &
        COMPONENT=CL
    DEFINE R2NYL MASS-FLOW STREAM=R2OUT SUBSTREAM=MIXED  &
        COMPONENT=NYLON
    DEFINE R2DP COMP-ATTR-VAR STREAM=R2OUT SUBSTREAM=MIXED  &
        COMPONENT=NYLON ATTRIBUTE=DPN ELEMENT=1
    DEFINE R3DP COMP-ATTR-VAR STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=NYLON ATTRIBUTE=DPN ELEMENT=1
    DEFINE R3CL MASS-FLOW STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=CL
    DEFINE R3NYL MASS-FLOW STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=NYLON
    DEFINE R3ACA MASS-FLOW STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=ACA
    DEFINE R3CD MASS-FLOW STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=CD
    DEFINE R3F STREAM-VAR STREAM=FEED SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE R1COND MASS-FLOW STREAM=COND SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE R3FW MASS-FRAC STREAM=R2-OLIGO SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE R2COND MASS-FLOW STREAM=R2-COND SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE R2FW MASS-FRAC STREAM=R1-OLIGO SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE FWF MASS-FRAC STREAM=FEED SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE R3H2O MASS-FLOW STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=H2O
F      EV = (R3CL+R3H2O+R3ACA+R3CD)/R3F*100
    TABULATE 1 "R1NYL/(R1NYL+R1CL)" COL-LABEL="R1-CONV"
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
    TABULATE 2 "R2NYL/(R2NYL+R2CL)" COL-LABEL="R2-CONV"
    TABULATE 3 "R3NYL/(R3NYL+R3CL)" COL-LABEL="R3-CONV"
    TABULATE 4 "R1DP" COL-LABEL="R1-DP"
    TABULATE 5 "R2DP" COL-LABEL="R2-DP"
    TABULATE 6 "R3DP" COL-LABEL="R3-DP"
    TABULATE 7 "EV" COL-LABEL="EXTRACT"
    TABULATE 8 "FWF*100." COL-LABEL="FEED WF" "WATER" "PERCENT."
    TABULATE 9 "R2FW*100." COL-LABEL="R2OUT" "WATER" "PERCENT."
    TABULATE 10 "R3FW*100." COL-LABEL="R3WF" "WATER" "PERCENT."
    TABULATE 11 "R1COND" COL-LABEL="R1-COND"
    TABULATE 12 "R2COND" COL-LABEL="R2-COND"
    VARY STREAM-VAR STREAM=FEED SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    RANGE LIST=10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0  &
        100.0

CONV-OPTIONS
    PARAM TRACE=.00010 CHECKSEQ=NO
    WEGSTEIN MAXIT=50

STREAM-REPOR NOZEROFLOW MOLEFLOW MASSFLOW MASSFRAC

REACTIONS NYLON STEP-GROWTH
    SPECIES POLYMER=NYLON
    REAC-GROUP TNH2 E-GRP / TCOOH N-GRP / BCAP EN-GRP
    SG-RATE-CON CNT=1 PRE-EXP=1.8940E+10 ACT-ENERGY=23.2710
    SG-RATE-CON CNT=2 CAT-SPEC=ACA PRE-EXP=1.2110E+10  &
        ACT-ENERGY=20.670
    SG-RATE-CON CNT=3 CAT-SPEC=T-COOH PRE-EXP=1.2110E+10  &
        ACT-ENERGY=20.670
    SG-RATE-CON CNT=4 PRE-EXP=1.1780E+10 ACT-ENERGY=29.21680
    SG-RATE-CON CNT=5 CAT-SPEC=ACA PRE-EXP=7.5340E+09  &
        ACT-ENERGY=26.61580
    SG-RATE-CON CNT=6 CAT-SPEC=T-COOH PRE-EXP=7.5340E+09  &
        ACT-ENERGY=26.61580
    RXN-SET CNT3=1 ELECTRO-GRP=TNH2 NUCLEO-GRP=TCOOH RC-SETS=1 2  &
        3
    RXN-SET CNT3=2 NUCLEOPHILE=H2O RC-SETS=4 5 6
    SPECIES-GRP T-NH2 TNH2 1 / T-NH2 BCAP 1 / T-COOH TCOOH  &
        1 / T-COOH BCAP 1 / ACA TNH2 1 / ACA TCOOH 1 /  &
        ACA BCAP 1 / B-ACA BCAP 1 / H2O TNH2 1 / H2O  &
        TCOOH 1
    STOIC 1 CL -1.0 / H2O -1.0 / ACA 1.0
    STOIC 2 CL -1.0 / H2O -1.0 / ACA 1.0
    STOIC 3 CL -1.0 / H2O -1.0 / ACA 1.0
    STOIC 4 ACA -1.0 / CL 1.0 / H2O 1.0
    STOIC 5 ACA -1.0 / CL 1.0 / H2O 1.0
    STOIC 6 ACA -1.0 / CL 1.0 / H2O 1.0
    STOIC 7 CL -1.0 / B-ACA 1.0
    STOIC 8 CL -1.0 / B-ACA 1.0
    STOIC 9 CL -1.0 / B-ACA 1.0
    STOIC 10 B-ACA -1.0 / CL 1.0
    STOIC 11 B-ACA -1.0 / CL 1.0
    STOIC 12 B-ACA -1.0 / CL 1.0
    STOIC 13 CL -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0
    STOIC 14 CL -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
    STOIC 15 CL -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0
    STOIC 16 T-NH2 -1.0 / T-COOH -1.0 / ACA 1.0 / CL 1.0
    STOIC 17 T-NH2 -1.0 / T-COOH -1.0 / ACA 1.0 / CL 1.0
    STOIC 18 T-NH2 -1.0 / T-COOH -1.0 / ACA 1.0 / CL 1.0
    STOIC 19 CL -1.0 / B-ACA 1.0
    STOIC 20 CL -1.0 / B-ACA 1.0
    STOIC 21 CL -1.0 / B-ACA 1.0
    STOIC 22 CD -1.0 / H2O -1.0 / T-NH2 1.0 / T-COOH 1.0
    STOIC 23 CD -1.0 / H2O -1.0 / T-NH2 1.0 / T-COOH 1.0
    STOIC 24 CD -1.0 / H2O -1.0 / T-NH2 1.0 / T-COOH 1.0
    STOIC 25 T-NH2 -1.0 / T-COOH -1.0 / CD 1.0 / H2O 1.0
    STOIC 26 T-NH2 -1.0 / T-COOH -1.0 / CD 1.0 / H2O 1.0
    STOIC 27 T-NH2 -1.0 / T-COOH -1.0 / CD 1.0 / H2O 1.0
    STOIC 28 CD -1.0 / B-ACA 2.0
    STOIC 29 CD -1.0 / B-ACA 2.0
    STOIC 30 CD -1.0 / B-ACA 2.0
    STOIC 31 B-ACA -2.0 / CD 1.0
    STOIC 32 B-ACA -2.0 / CD 1.0
    STOIC 33 B-ACA -2.0 / CD 1.0
    STOIC 34 CD -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0  &
        / B-ACA 1.0
    STOIC 35 CD -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0  &
        / B-ACA 1.0
    STOIC 36 CD -1.0 / ACA -1.0 / T-NH2 1.0 / T-COOH 1.0  &
        / B-ACA 1.0
    STOIC 37 T-NH2 -1.0 / T-COOH -1.0 / B-ACA -1.0 / ACA  &
        1.0 / CD 1.0
    STOIC 38 T-NH2 -1.0 / T-COOH -1.0 / B-ACA -1.0 / ACA  &
        1.0 / CD 1.0
    STOIC 39 T-NH2 -1.0 / T-COOH -1.0 / B-ACA -1.0 / ACA  &
        1.0 / CD 1.0
    STOIC 40 CD -1.0 / B-ACA 2.0
    STOIC 41 CD -1.0 / B-ACA 2.0
    STOIC 42 CD -1.0 / B-ACA 2.0
    RATE-CON 1 598740.0 19.880
    RATE-CON 2 4.3080E+07 18.8060
    RATE-CON 3 4.3080E+07 18.8060
    RATE-CON 4 3.1660E+07 17.9620
    RATE-CON 5 2.2780E+09 16.8880
    RATE-CON 6 2.2780E+09 16.8880
    RATE-CON 7 2.8560E+09 22.8450
    RATE-CON 8 1.6380E+10 20.1070
    RATE-CON 9 1.6380E+10 20.1070
    RATE-CON 10 9.4150E+10 26.8880
    RATE-CON 11 5.3990E+11 24.1510
    RATE-CON 12 5.3990E+11 24.1510
    RATE-CON 13 2.8560E+09 22.8450
    RATE-CON 14 1.6380E+10 20.1070
    RATE-CON 15 1.6380E+10 20.1070
    RATE-CON 16 9.4150E+10 26.8880
    RATE-CON 17 5.3990E+11 24.1510
    RATE-CON 18 5.3990E+11 24.1510
    RATE-CON 19 9.4150E+10 26.8880
    RATE-CON 20 5.3990E+11 24.1510
    RATE-CON 21 5.3990E+11 24.1510
    RATE-CON 22 8.5778E+11 42.0
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
RATE-CON 23 2.3307E+12 37.40
RATE-CON 24 2.3307E+12 37.40
RATE-CON 25 1.2793E+15 51.60
RATE-CON 26 3.4761E+15 47.0
RATE-CON 27 3.4761E+15 47.0
RATE-CON 28 2.5701E+08 21.30
RATE-CON 29 3.0110E+09 20.40
RATE-CON 30 3.0110E+09 20.40
RATE-CON 31 1.9169E+08 24.4690
RATE-CON 32 2.2458E+09 23.5690
RATE-CON 33 2.2458E+09 23.5690
RATE-CON 34 2.5701E+08 21.30
RATE-CON 35 3.0110E+09 20.40
RATE-CON 36 3.0110E+09 20.40
RATE-CON 37 1.9169E+08 24.4690
RATE-CON 38 2.2458E+09 23.5690
RATE-CON 39 2.2458E+09 23.5690
RATE-CON 40 3.8338E+08 24.4690
RATE-CON 41 4.4916E+09 23.5690
RATE-CON 42 4.4916E+09 23.5690
POWLAW-EXP 1 CL 1.0 / H2O 1.0
POWLAW-EXP 2 CL 1.0 / H2O 1.0 / T-COOH 1.0
POWLAW-EXP 3 CL 1.0 / H2O 1.0 / ACA 1.0
POWLAW-EXP 4 ACA 1.0
POWLAW-EXP 5 ACA 1.0 / T-COOH 1.0
POWLAW-EXP 6 ACA 2.0
POWLAW-EXP 7 CL 1.0 / T-NH2 1.0
POWLAW-EXP 8 CL 1.0 / T-NH2 1.0 / T-COOH 1.0
POWLAW-EXP 9 CL 1.0 / T-NH2 1.0 / ACA 1.0
POWLAW-EXP 10 T-NH2 1.0
POWLAW-EXP 11 T-NH2 1.0 / T-COOH 1.0
POWLAW-EXP 12 T-NH2 1.0 / ACA 1.0
POWLAW-EXP 13 CL 1.0 / ACA 1.0
POWLAW-EXP 14 CL 1.0 / ACA 1.0 / T-COOH 1.0
POWLAW-EXP 15 CL 1.0 / ACA 2.0
POWLAW-EXP 16 ACA 1.0
POWLAW-EXP 17 T-COOH 1.0 / ACA 1.0
POWLAW-EXP 18 ACA 2.0
POWLAW-EXP 19 ACA 1.0
POWLAW-EXP 20 ACA 1.0 / T-COOH 1.0
POWLAW-EXP 21 ACA 2.0
POWLAW-EXP 22 CD 1.0 / H2O 1.0
POWLAW-EXP 23 CD 1.0 / H2O 1.0 / T-COOH 1.0
POWLAW-EXP 24 CD 1.0 / H2O 1.0 / ACA 1.0
POWLAW-EXP 25 ACA 1.0
POWLAW-EXP 26 T-COOH 1.0 / ACA 1.0
POWLAW-EXP 27 ACA 2.0
POWLAW-EXP 28 CD 1.0 / T-NH2 1.0
POWLAW-EXP 29 CD 1.0 / T-NH2 1.0 / T-COOH 1.0
POWLAW-EXP 30 CD 1.0 / T-NH2 1.0 / ACA 1.0
POWLAW-EXP 31 T-NH2 1.0
POWLAW-EXP 32 T-NH2 1.0 / T-COOH 1.0
POWLAW-EXP 33 T-NH2 1.0 / ACA 1.0
POWLAW-EXP 34 CD 1.0 / ACA 1.0
POWLAW-EXP 35 CD 1.0 / ACA 1.0 / T-COOH 1.0
```

Figure 4.3 Input Summary for Caprolactam Polymerization (cont.)

```
    POWLAW-EXP 36 CD 1.0 / ACA 2.0
    POWLAW-EXP 37 ACA 1.0
    POWLAW-EXP 38 T-COOH 1.0 / ACA 1.0
    POWLAW-EXP 39 ACA 2.0
    POWLAW-EXP 40 ACA 1.0
    POWLAW-EXP 41 ACA 1.0 / T-COOH 1.0
    POWLAW-EXP 42 ACA 2.0
;
;
```

SELECTED SIMULATION RESULTS

For the base case simulation, Figure 4.4 shows a summary report for the flowsheet streams.

The effect of feed flow rate on caprolactam conversion, degree of polymerization (Dp) and extraction value is shown in Figure 4.5, Figure 4.6, and Figure 4.7 respectively. Increasing the feed to CSTR-1 decreases the total residence time. Therefore, caprolactam conversion decreases in all of the reactors as shown in Figure 4.5. Since the caprolactam conversion decreases, DP of the polymer produced in CSTR-1, CSTR-2 and Plug decreases, and is shown in Figure 4.6.

Extraction value (EV) is the sum of the extractables from the polymer. These include unreacted caprolactam, aminocaproic acid, cyclic dimer and water. Extraction value is an indicator of the cost of recycling unreacted monomers. Since conversion decreases with an increase in feed flow rate, EV increases as shown in Figure 4.7. Therefore, one has to find the optimum feed flow rate which increases the production rate while minimizing the percentage of extractables.

DP in the plug flow reactor is determined by the concentration of water in the feed to the plug flow reactor. An increase of the feed flow rate to CSTR-1 results in an increase of water in the feed to the Plug as shown in Figure 4.8. Figure 4.9 shows the DP profile as a function of reactor length. The plug flow reactor is a closed system and water resulting from polycondensation remains in the polymer melt. At the end of the plug flow reactor, DP reaches an equilibrium value. This results in a flat profile towards the end of the reactor.

Figure 4.4 Simulation Stream Summary

COND FEED POLYMER R1-OLIGO R1OUT

STREAM ID		COND	FEED	POLYMER	R1-OLIGO	R1OUT
FROM :		DISTIL	----	PLUG	R1FLASH	CSTR-1
TO :		----	CSTR-1	----	CSTR-2	R1FLASH
SUBSTREAM: MIXED						
PHASE:		LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
COMPONENTS: KG/HR						
H2O		0.3002	0.4000	6.9704-02	6.3807-02	0.6602
CL		0.0	39.6000	3.3863	11.3952	13.0005
ACA		0.0	0.0	1.1683-03	2.2681-02	2.2681-02
CD		0.0	0.0	0.2300	0.1051	0.1051
NYLON		0.0	0.0	36.0128	28.3241	28.3241
COMPONENTS: MASS FRAC						
H2O		1.0000	1.0000-02	1.7558-03	1.5987-03	1.5677-02
CL		0.0	0.9900	8.5299-02	0.2855	0.3087
ACA		0.0	0.0	2.9429-05	5.6830-04	5.3859-04
CD		0.0	0.0	5.7943-03	2.6351-03	2.4974-03
NYLON		0.0	0.0	0.9071	0.7096	0.6725
TOTAL FLOW:						
KG/HR		0.3002	40.0000	39.7001	39.9110	42.1127
STATE VARIABLES:						
TEMP	C	100.0178	260.0000	260.0000	243.6194	260.0000
PRES	ATM	1.0000	1.0000	1.0000	1.0000	1.0000
ENTHALPY:						
J/KG		-1.5547+07	-2.4544+06	-1.2667+06	-1.5727+06	-1.7461+06
ENTROPY:						
J/KG-K		-8109.9795	-4471.8775	-4625.9284	-4661.0296	-4581.5103
AVG MW		18.0152	107.4829	112.4430	112.3675	104.6345
COMPONENT ATTRIBUTES:						
NYLON	SFLOW					
	T-NH2			1.6580-03	5.0787-03	5.0787-03
	T-COOH			1.6580-03	5.0787-03	5.0787-03
	B-ACA			0.3146	0.2393	0.2393
	ZMOM					
	ZMOM			1.6580-03	5.0787-03	5.0787-03
	FMOM					
	FMOM			0.3179	0.2494	0.2494
	DPN					
	DPN			191.7923	49.1257	49.1274
	MWN					
	MWN			2.1721+04	5577.0586	5577.2502
	EFRAC					
	T-NH2			0.5000	0.5000	0.5000
	T-COOH			0.5000	0.5000	0.5000
	SFRAC					
	T-NH2			5.2140-03	2.0356-02	2.0355-02
	T-COOH			5.2140-03	2.0356-02	2.0355-02
	B-ACA			0.9895	0.9592	0.9592

Figure 4.4 Simulation Stream Summary (cont.)

```
R1VAP R2-COND R2-OLIGO R2OUT RECYCLE
-----------------------------------

STREAM ID                R1VAP      R2-COND    R2-OLIGO   R2OUT      RECYCLE
FROM :                   R1FLASH    R2FLASH    R2FLASH    CSTR-2     DISTIL
TO   :                   DISTIL     CSTR-1     PLUG       R2FLASH    CSTR-1

SUBSTREAM: MIXED
PHASE:                   VAPOR      VAPOR      LIQUID     LIQUID     LIQUID

COMPONENTS: KG/HR
  H2O                     0.5964  5.8683-02  4.4147-02     0.1028     0.2961
  CL                      1.6053     0.1523     6.7594     6.9117     1.6053
  ACA                     0.0        0.0     3.0179-03  3.0179-03     0.0
  CD                      0.0        0.0        0.1451     0.1451     0.0
  NYLON                   0.0        0.0       32.7484    32.7484     0.0
COMPONENTS: MASS FRAC
  H2O                     0.2708     0.2780  1.1120-03  2.5765-03     0.1557
  CL                      0.7291     0.7219     0.1702     0.1731     0.8442
  ACA                     0.0        0.0     7.6016-05  7.5614-05     0.0
  CD                      0.0        0.0     3.6567-03  3.6374-03     0.0
  NYLON                   0.0        0.0        0.8248     0.8205     0.0
TOTAL FLOW:
  KG/HR                   2.2017     0.2110    39.7001    39.9112     1.9014

STATE VARIABLES:
  TEMP   C              243.6194   258.3760   258.3760   260.0000   118.3754
  PRES   ATM              1.0000     1.0000     1.0000     1.0000     1.0000

ENTHALPY:
  J/KG                -4.8894+06 -4.9419+06 -1.3745+06 -1.3934+06 -4.6369+06

ENTROPY:
 J/KG-K               -2922.3338 -2853.6000 -4616.5061 -4607.5387 -5473.6225

AVG MW                   46.5564    45.8409   112.7048   111.8422    62.0918

COMPONENT ATTRIBUTES:
NYLON    SFLOW
           T-NH2                              3.0625-03  3.0625-03
           T-COOH                             3.0625-03  3.0625-03
           B-ACA                                 0.2827     0.2827
         ZMOM
           ZMOM                               3.0625-03  3.0625-03
         FMOM
           FMOM                                  0.2889     0.2889
         DPN
           DPN                                  94.3381    94.3381
         MWN
           MWN                                1.0693+04  1.0693+04
         EFRAC
           T-NH2                                 0.5000     0.5000
           T-COOH                                0.5000     0.5000
         SFRAC
           T-NH2                              1.0600-02  1.0600-02
           T-COOH                             1.0600-02  1.0600-02
           B-ACA                                 0.9788     0.9788
```

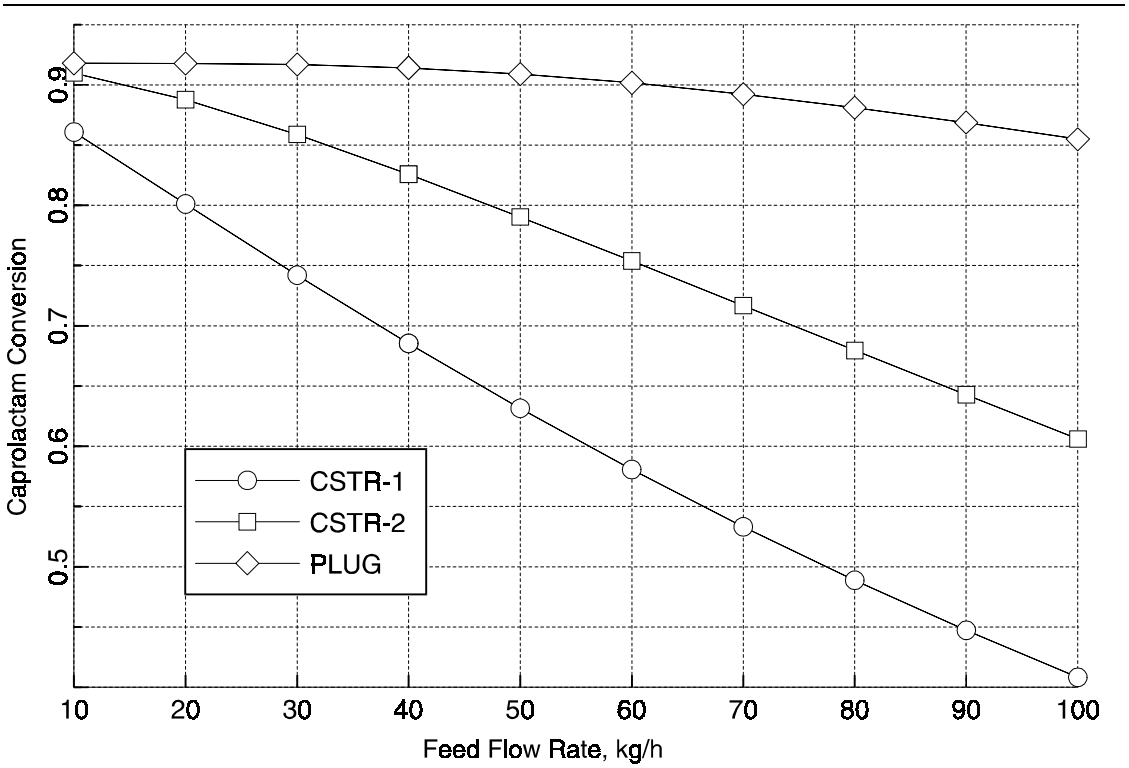

Figure 4.5 *Effect of Feed Flow Rate on the Caprolactam Conversion*

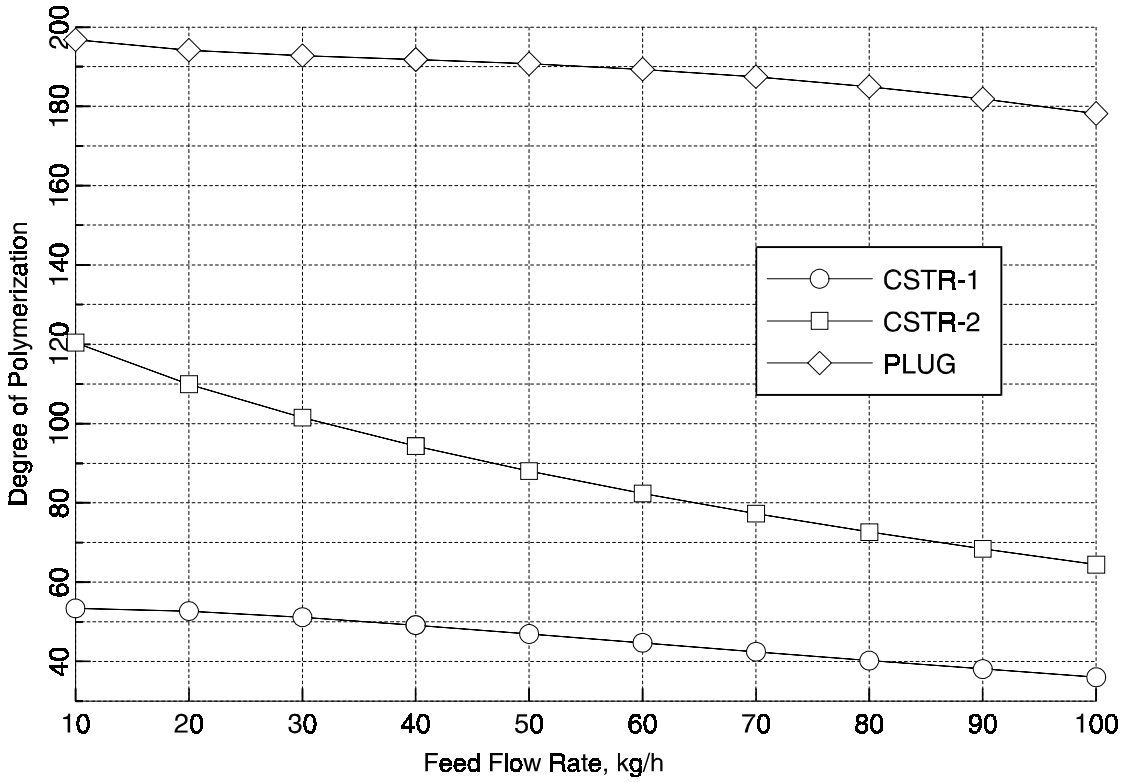

Figure 4.6 *Effect of Feed Flow Rate on the Degree of Polymerization*

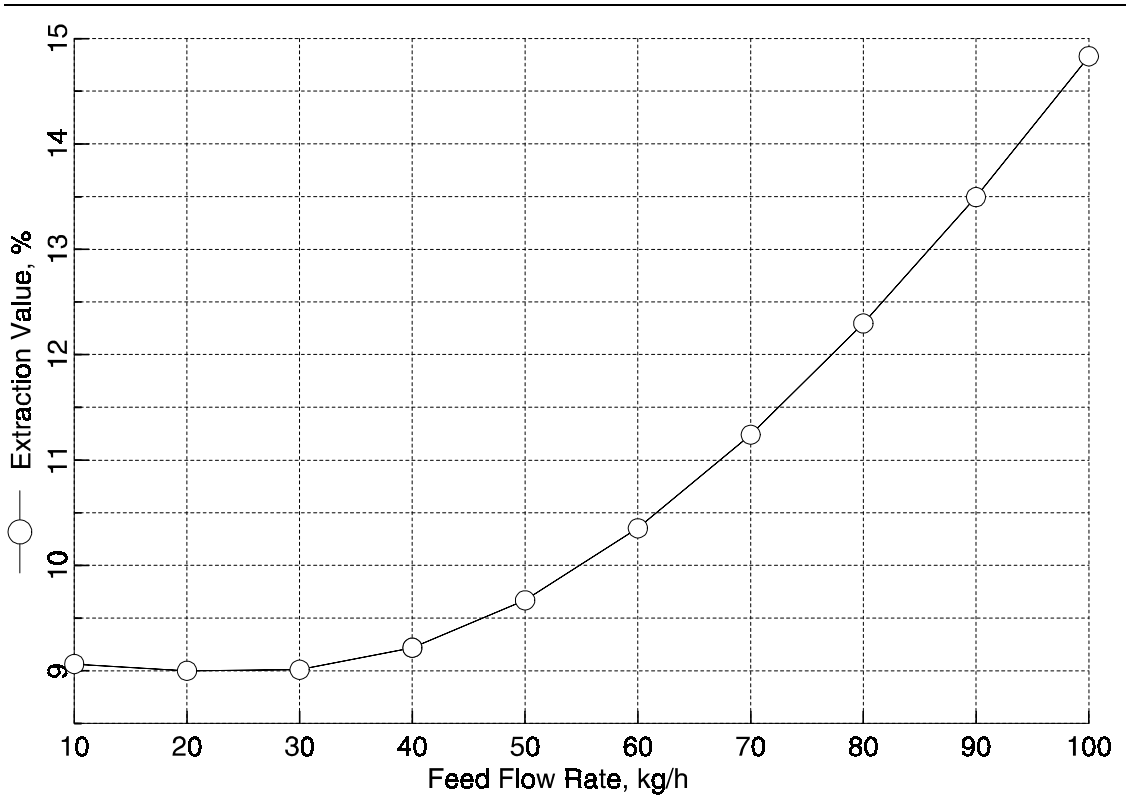

Figure 4.7 *Effect of Feed Flow Rate on the Extraction Value*

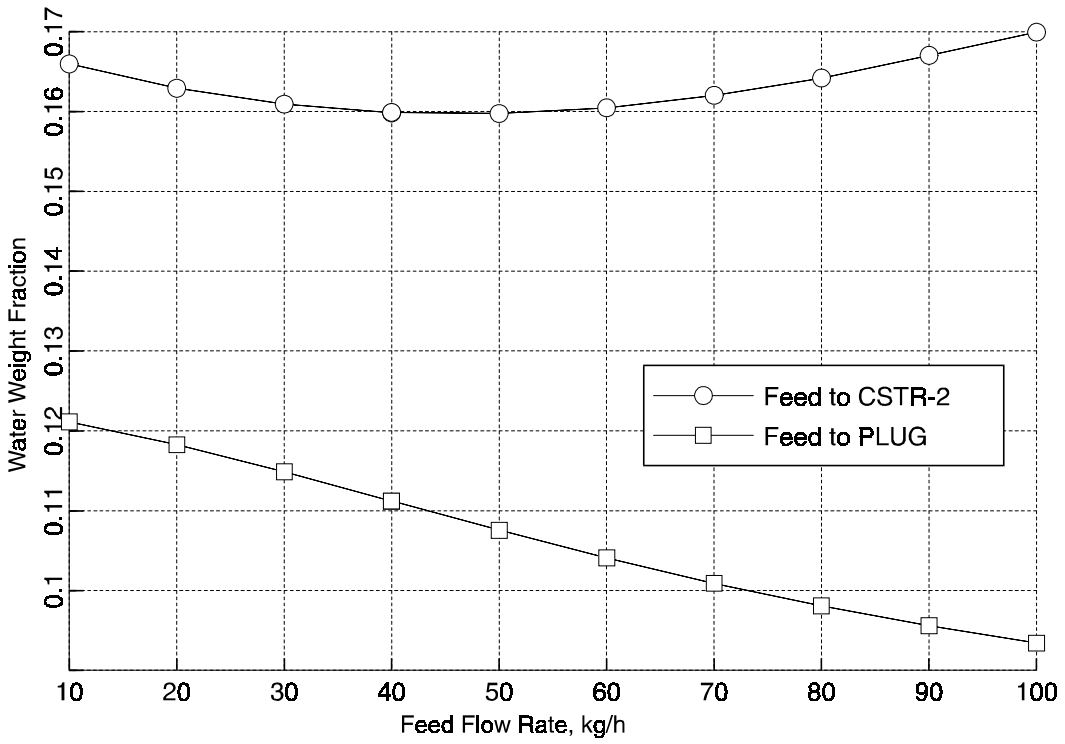

Figure 4.8 *Effect of Feed Flow Rate on the % of Water in the Reactor Feed*

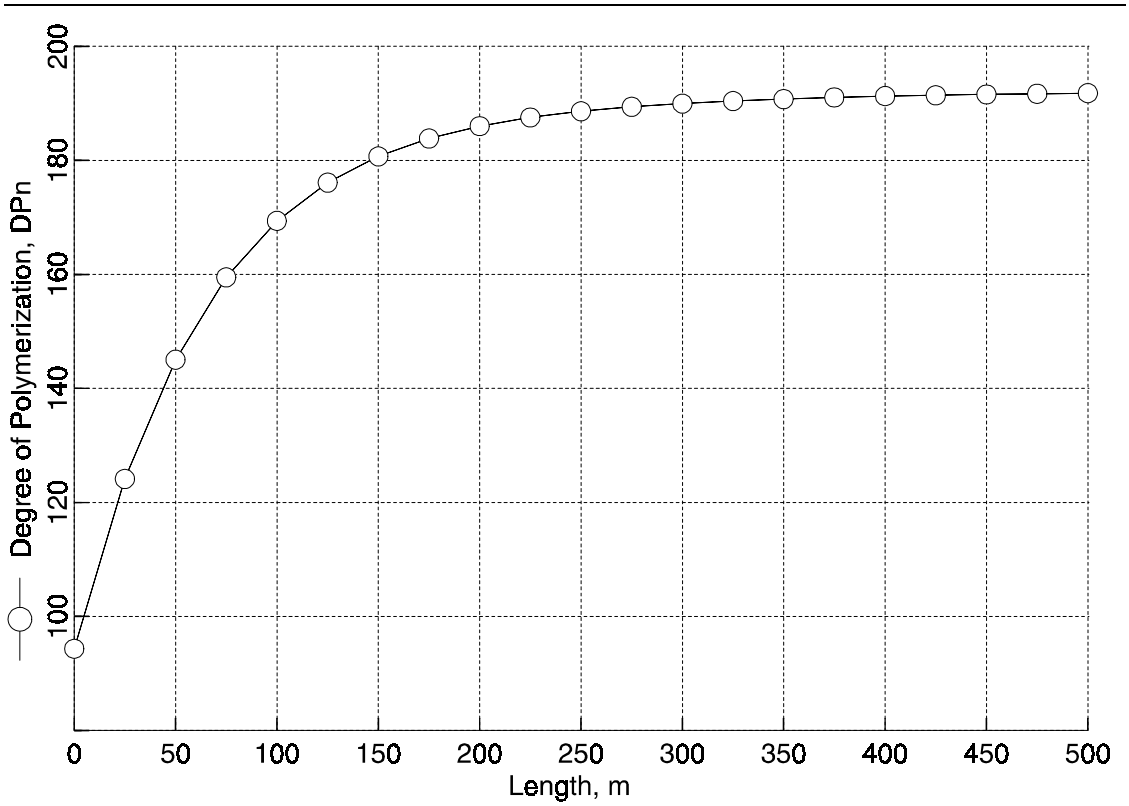

Figure 4.9 *Degree of Polymerization Profile in the Plug Flow Reactor*

REFERENCES

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5 STYRENE BUTADIENE

EMULSION COPOLYMERIZATION PROCESS

SUMMARY

The styrene butadiene emulsion copolymerization process model illustrates the use of Polymers Plus to model the free-radical emulsion polymerization of styrene and butadiene in a semi-batch reactor. The model is used to examine several process parameters as a function of time: average number of radicals per particle, monomer concentration in the various phases, and monomer conversion.

ABOUT THIS PROCESS

In this process, the emulsion copolymerization of styrene and butadiene is carried out in a batch reactor using ammonium persulfate (APS) as the initiator, sodium lauryl sulfate (SLS) as the emulsifier and tertiary dodecyl mercaptane (TDM) as a chain transfer agent. Functionalized styrene-butadiene emulsions are used in a variety of applications such as paper coatings, carpet backings, non-wovens, etc. In addition, emulsion polymerization is the major route for the production of synthetic rubber used in the tire industries. Most styrene-butadiene rubber (SBR) latexes are manufactured in semi-batch reactors. SBR production technology is detailed by Blackley (Blackley, 1983).

In a typical semi-batch process employing *in-situ* seeding, the initial charge is used for the production of seed particles, with the desired particle size and particle size distribution. Usually, anionic emulsifiers and water soluble persulfate initiators are used for particle nucleation by the micellar mechanism.

When the initial mixture is heated, the radicals generated from the initiator become surface active and enter micelles to form particles. Once the particle specifications are met, monomers and other ingredients, such as chain transfer agent, stabilizers, initiators, are continuously added to the reactor, and the particles are grown to the desired final particle size.

The latter stage of the reaction is also known as the growth stage of the reaction, and is responsible for the development of the properties of the emulsion polymer: molecular weight, composition, micro structure, etc. The growth stage is the better understood stage of the process. Therefore, this stage provides more opportunities to control the emulsion process.

The adjustable process parameters include temperature and feeding strategy of monomer and other ingredients. Control of polymer composition is very often achieved by feeding the monomers in a manner such that there is no separate monomer droplet present in the reactor. Very often the productivity of the reactor is limited by its cooling capacity. Chain transfer agents are usually added to control molecular weight, and degree of branching.

PROCESS DEFINITION

As shown in Figure 5.1, the process flowsheet consists of the batch reactor with an initial batch charge and a continuous feed for the addition of monomers and other ingredients.

This model provides the base case which can be used to study various process variables: effect of initiator and emulsifier levels, temperature, Smith-Ewart kinetics, etc.

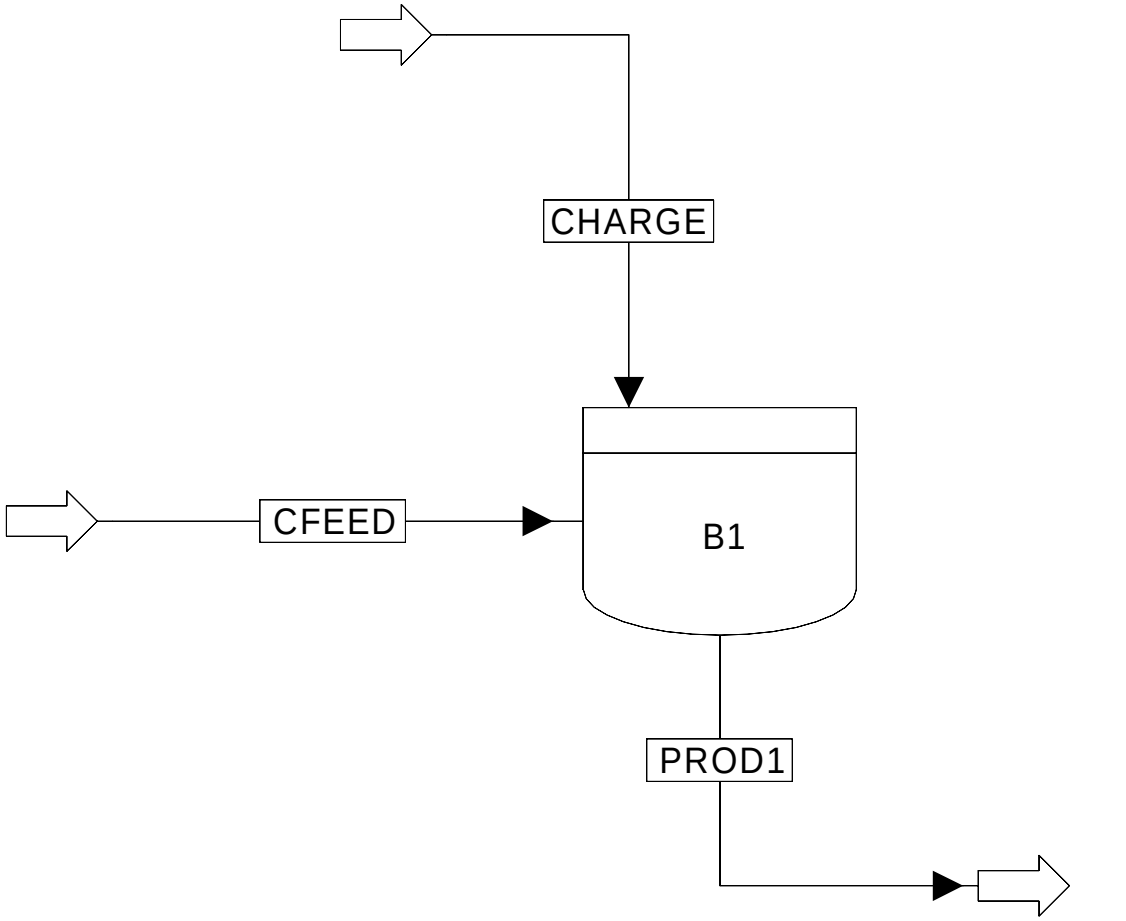


Figure 5.1 *Styrene Butadiene Copolymerization Flowsheet*

Process Conditions

The process conditions are as listed in Table 5.1.

Table 5.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Styrene	STY	PURE10	Monomer
Butadiene	BD	PURE10	Monomer
Water	H2O	PURE10	Dispersant
Ammonia persulfate	APS	PURE103	Initiator (Mw=220.0) Select H2O
Sodium lauryl sulfate	SLS	PURE10	Emulsifier (Mw=288.0) Select H2O
Polymer	POLYMER	POLYMER	Polymer
Styrene-segment	STY-SEG	SEGMENT	Repeat segment
Butadiene-segment	BD-SEG	SEGMENT	Repeat segment
Tert dodecyl mercaptane	TDM	PURE10	Chain transfer agent (MW= 224, select C8H8)
Polymer Characterization	Choose emulsion polymer attributes Distribution = chain-size No. of points = 100 (upper = 100000)		
Physical Properties	POLYNRTL property method with supplied binary interaction parameters		
Feeds			
Charge Stream		**CFEED**	
Temperature (°C)	20	20	
Pressure (atm)	10	10	
Styrene (kg/hr)	300	700	
Butadiene (kg/hr)	300	700	
Sodium laurylsulfate (kg/hr)	30	100	
Ammonium persulfate (kg/hr)	7	3	
TDM (kg/hr)	30	0	
Water (kg/hr)	1000	1000	

continued

Table 5.1 Process Conditions (cont.)

Continuous Feed	
Time (hr)	**Total (kg/hr)**
0.0	0.0
1.0	0.0
1.0	1200.0
2.0	1200.0
2.0	0.0
Kinetics	EMULSION
Operating Conditions	
B1 Pressure (atm)	10
FLASH Option	NO
Temperature profile	
Time (hr)	Temperature (°C)
0.0	65.0
0.5	65.0
0.5	70.0
1.0	70.0
1.0	75.0
2.0	75.0

Physical Property Models and Data

The Polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method. The thermophysical properties (density, heat capacity, etc.) of the monomers are obtained from the Aspen Plus pure component databank. The polymer physical properties are calculated using the van Krevelen method. The NRTL binary interaction parameters supplied are as follows:

NRTL									
H2O	STY-SEG	10.0	0.0	.30	0.0	0.0	0.0	0.0	1000.0
STY-SEG	H2O	10.0	0.0	.30	0.0	0.0	0.0	0.0	1000.0
H2O	STY	3.6260	1513.50	.360	0.0	0.0	0.0	0.0	1000.0
STY	H2O	-4.4360	2869.70	.360	0.0	0.0	0.0	0.0	1000.0
H2O	BD	3.5890	862.820	.30	0.0	0.0	0.0	0.0	1000.0
BD	H2O	-.8520	702.170	.30	0.0	0.0	0.0	0.0	1000.0
STY-SEG	STY	0.0	411.83830	.1670	0.0	0.0	0.0	0.0	1000.0
STY	STY-SEG	0.0	-16.0	.1670	0.0	0.0	0.0	0.0	1000.0

Reactors / Kinetics

There are considerable data available on the kinetics of emulsion copolymerization of styrene and butadiene. It is assumed that the primary chain transfer reaction is similat to that of a monomer. It is also assumed that the molecular weight is controlled solely by the chain transfer events. In other words, the termination reactions do not contribute to the molecular weight development. However, the termination reaction rate constant is used in the calculation of the average number of radicals per particle.

The rate constants for the kinetic scheme are obtained from Broadhead et al. and are summarized in the following table (Broadhead, 1984; Ponnuswamy, et al. 1997):

Reaction	Phase	Comp 1	Comp 2	k_0	E_a (J/kmol)
Initiator decomposition	Dispersant	Ammonium persulfate	---	1.0E16	1.402E8
Propagation	Polymer	Styrene	Styrene	2.2E7	3.2E7
Propagation	Polymer	Styrene	Butadiene	4.4E7	3.2E7
Propagation	Polymer	Butadiene	Butadiene	1.2E8	3.88E7
Propagation	Polymer	Butadiene	Styrene	8.5E7	3.88E7
Chain transfer-monomer	Polymer	Styrene	Styrene	2.2E3	3.2E7
Chain transfer-monomer	Polymer	Styrene	Butadiene	4.4E3	3.2E7
Chain transfer-monomer	Polymer	Butadiene	Butadiene	1.2E4	2.24E6
Chain transfer-monomer	Polymer	Butadiene	Styrene	8.5E3	3.88E7
Chat-agent	Polymer	Styrene	TDM	2.83E5	3.88E7
Chat-agent	Polymer	Butadiene	TDM	8.5E5	2.68E7
Termination by combination	Polymer	Styrene	Styrene	1.3E9	9.9E6
Termination by combination	Polymer	Styrene	Butadiene	1.3E9	9.9E6
Termination by combination	Polymer	Butadiene	Butadiene	1.3E9	9.9E6
Termination by combination	Polymer	Butadiene	Styrene	1.3E9	9.9E6

In addition to the free-radical reaction rate constants, the following rate constants were used for the radical exchange events:

Reaction	k_0	E_a (J/kmol)
Absorption into particle	1.0E-7	0.0
Absorption into micelles	1.0E-7	0.0
Desorption from particle	0.0	0.0

Other parameters affecting the kinetics are the emulsifier parameters and the monomer partitioning are listed below:

	CMC kmol / m^3	Area m^3 / kmole
Emulsifier parameters	0.009	5.0E6
Monomer partitioning (mass)	styrene	.70 homosaturation in polymer
	butadiene	.50 homosaturation in polymer
	TDM	.8 homosaturation in polymer

Process Studies

The model was used to examine the following process parameters as a function of time through user profiles.

Glass transition temperature of the polymer	(K)
Average number of radicals per particle	---
Percent of soap coverage of particles	%
Volume of the monomer phase	(m^3)
Concentration of monomer 1 in monomer phase	(Kmol/ m^3)
Concentration of monomer 2 in monomer phase	(Kmol/ m^3)
Volume of the aqueous phase	(m^3)
Concentration of the monomer 1 in aqueous phase	(Kmol / m^3)
Concentration of the monomer 2 in aqueous phase	(Kmol / m^3)
Volume of the polymer phase	(m^3)
Concentration of the monomer 1 in polymer phase	(Kmol / m^3)
Concentration of the monomer 2 in polymer phase	(Kmol / m^3)
Total mass conversion of monomer to polymer	---

An input summary is given in Figure 5.2.

Figure 5.2 Input Summary for Styrene Butadiene Copolymerization

```
TITLE 'Emulsion Copolymerization of Styrene and Butadiene'

IN-UNITS SI MASS-FLOW='kg/hr' PRESSURE=bar TEMPERATURE=C TIME=hr  &
        PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

DESCRIPTION "This example illustrates the use of Polymers Plus to
        model the copolymerization of styrene and butadiene
        in a batch reactor. "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE10  / POLYMER  / SEGMENT

COMPONENTS
    H2O H2O H2O /
    STY C8H8 STY /
    BD C4H6-4 BD /
    POLYMER POLYMER POLYMER /
    STY-SEG C8H8-R STY-SEG /
    BD-SEG C4H6-R-1 BD-SEG /
    APS H2O APS /
    SLS H2O SLS /
    TDM C8H8 TDM

FLOWSHEET
    BLOCK B1 IN=CHARGE CFEED OUT=PROD1

PROPERTIES POLYNRTL

PROP-DATA MW
    IN-UNITS SI MASS-FLOW='kg/hr' PRESSURE=bar TEMPERATURE=C  &
        TIME=hr PDROP='N/sqm'
    PROP-LIST MW
    PVAL APS 228.0
    PVAL SLS 288.0
    PVAL TDM 202.4

PROP-DATA TGVK
    IN-UNITS SI MASS-FLOW='kg/hr' PRESSURE=bar TEMPERATURE=C  &
        TIME=hr PDROP='N/sqm'
    PROP-LIST TGVK
    PVAL STY-SEG 100.0
    PVAL BD-SEG -54.0
```

Figure 5.2 Input Summary for Styrene Butadiene Copolymerization (cont.)

```
PROP-DATA NRTL-1
    IN-UNITS SI
    PROP-LIST NRTL
    BPVAL H2O STY-SEG 10.0 0.0 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL STY-SEG H2O 10.0 0.0 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL H2O STY 3.6260 1513.50 .360 0.0 0.0 0.0 0.0  &
        1000.0
    BPVAL STY H2O -4.4360 2869.70 .360 0.0 0.0 0.0 0.0  &
        1000.0
    BPVAL H2O BD 3.5890 862.820 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL BD H2O -.8520 702.170 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL STY-SEG STY 0.0 411.83830 .1670 0.0 0.0 0.0 0.0  &
        1000.0
    BPVAL STY STY-SEG 0.0 -16.0 .1670 0.0 0.0 0.0 0.0  &
        1000.0

POLYMERS
    SEGMENTS STY-SEG REPEAT / BD-SEG REPEAT
    POLYMERS POLYMER
    ATTRIBUTES POLYMER SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM PSDZMOM PSDFMOM DIAV LSFLOW LSFRAC LEFLOW  &
        LEFRAC LZMOM LFMOM LSMOM LPFRAC
    DISTRIBUTION POLYMER CHAIN-SIZE CLD NPOINTS=100 100000.

PROP-SET PS-1 MASSFRAC SUBSTREAM=MIXED COMPS=POLYMER PHASE=L

STREAM CFEED
    SUBSTREAM MIXED TEMP=20.0 PRES=10.
    MASS-FLOW H2O 1000.0 / STY 700.0 / BD 700.0 / POLYMER  &
        0.0 / APS 3.0 / SLS 100.

STREAM CHARGE
    SUBSTREAM MIXED TEMP=20.0 PRES=10.
    MASS-FLOW H2O 1000.0 / STY 300.0 / BD 300.0 / POLYMER  &
        0.0 / APS 7.0 / SLS 30.0 / TDM 30.

BLOCK B1 RBATCH
    USER-VECS NUSER-PROF=13
    USERPROF ELEMENT=1 LABEL="TGAVG" UNIT-LABEL="DEG K"
    USERPROF ELEMENT=2 LABEL="NBAR" UNIT-LABEL="#/PARTICLE"
    USERPROF ELEMENT=3 LABEL="S-COVER" UNIT-LABEL="%"
    USERPROF ELEMENT=4 LABEL="M-VOL" UNIT-LABEL="M**3"
    USERPROF ELEMENT=5 LABEL="CM-1" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=6 LABEL="CM-2" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=7 LABEL="AQ-VOL" UNIT-LABEL="M**3"
    USERPROF ELEMENT=8 LABEL="CAQ-1" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=9 LABEL="CAQ-2" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=10 LABEL="POL-VOL" UNIT-LABEL="M**3"
    USERPROF ELEMENT=11 LABEL="CPOL-1" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=12 LABEL="CPOL-2" UNIT-LABEL="KMOL/M**3"
    USERPROF ELEMENT=13 LABEL="CONVER" UNIT-LABEL="MASS FRAC"
    PARAM TYPE=T-PROFILE PRINT-TIME=0.2 CYCLE-TIME=1.0  &
        MAX-TIME=10. MAX-NPOINT=100 PRES=10. NPHASE=1  &
        HINIT=0.00001 FLASH=NO
```

Figure 5.2 Input Summary for Styrene Butadiene Copolymerization (cont.)

```
    INTEG-PARAMS MAXSTEP=30. <sec>
    T-PROF 0.0 65.0 / .50 65.0 / 0.5 70.0 / 1.0 70.0 /  &
        1.0 75.0 / 2.0 75.0
    STOP 1 REACTOR TIME 10.
    PROP-REACTOR PS-1
    BLOCK-OPTION STREAM-LEVEL=4 TERM-LEVEL=7
    REACTIONS RXN-IDS=EMLRXN
    FEED-PROF SID=CFEED TIME=0.0 1.0 1.0 2.0 2.0 FLOW=0.0  &
        0.0 1200.0 1200.0 0.0

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC

REACTIONS EMLRXN EMULSION
    PARAM KBASIS=MASS QSSA=YES
    SPECIES INITIATOR=APS MONOMER=STY BD CHAINTAG=TDM  &
        EMULSIFIER=SLS DISPERSANT=H2O POLYMER=POLYMER
    MON-RSEG STY STY-SEG / BD BD-SEG
    INIT-DEC DISPERSANT APS 1.0000E+16 1.4020E+08 0.0  &
        EFFIC=.80 NRADS=2
    PROPAGATION POLYMER STY STY 2.2E7 3.2E7
    PROPAGATION POLYMER BD BD 1.2E8 38800000.
    PROPAGATION POLYMER STY BD 4.4E7 3.2E7
    PROPAGATION POLYMER BD STY 8.5E7 38800000.
    CHAT-MON POLYMER STY STY 2200. 3.2E7
    CHAT-MON POLYMER STY BD 4400. 3.2E7
    CHAT-MON POLYMER BD STY 8500. 38800000.
    CHAT-MON POLYMER BD BD 12000. 38800000.
    CHAT-AGENT POLYMER STY TDM 283000. 26800000.
    CHAT-AGENT POLYMER BD TDM 850000. 38800000.
    TERM-COMB POLYMER STY STY 1.30E9 9.90E6
    TERM-COMB POLYMER STY BD 1.30E9 9.90E6
    TERM-COMB POLYMER BD BD 1.30E9 9.90E6
    TERM-COMB POLYMER BD STY 1.30E9 9.90E6
    ABS-MIC 1.0000E-07 0.0
    ABS-PART 1.0000E-07 0.0
    DES-PART 0.0 0.0
    EMUL-PARAMS SLS 0.009 5.0E6
    SPLIT-PM STY 0.7
    SPLIT-PM BD 0.5
    SPLIT-PM TDM 0.8
;
```

SELECTED SIMULATION RESULTS

Figures 5.3 through Figure 5.8 give the selected results for emulsion polymerization of styrene and butadiene in a semi-batch reactor.

Figure 5.3 gives the nucleation and growth of emulsion polymer particles in the reactor. It is observed that the number of particles formed early remains constant throughout the reaction. In this figure, first moment which is the total volume of the unswollen polymer particles increases throughout the polymerization as expected. It is also observed that the average diameter of the unswollen particle increases as expected.

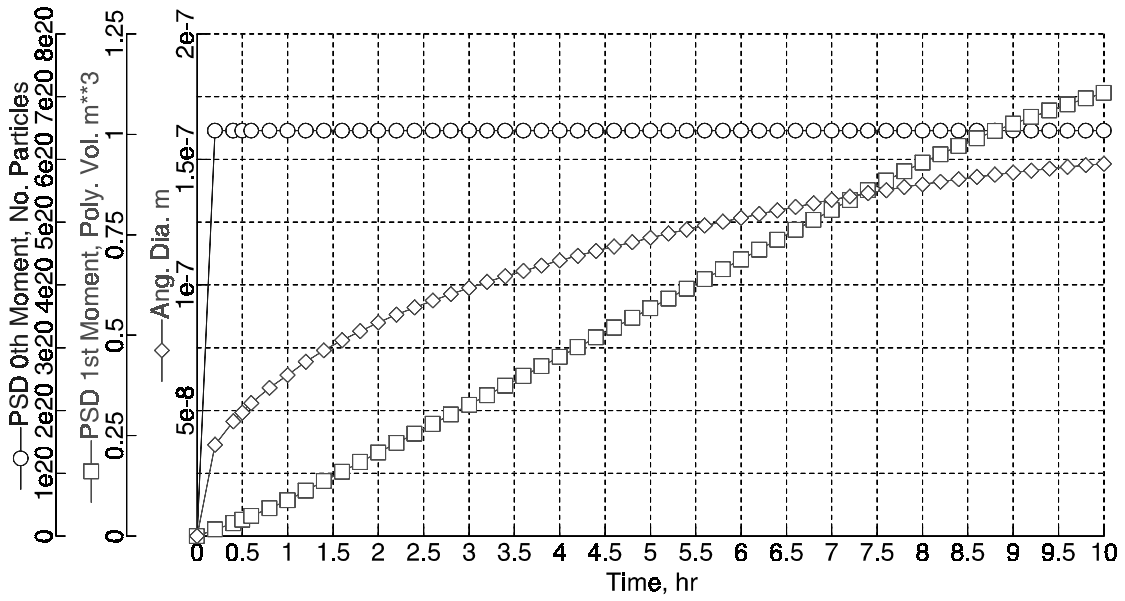


Figure 5.3 *Particle Nucleation and Growth*

Figure 5.4 gives the mass of monomers and polymer in the reactor. Although the flow rates of styrene and butadiene are equal, it is observed that butadiene reacts faster than styrene due to its higher reactivity.

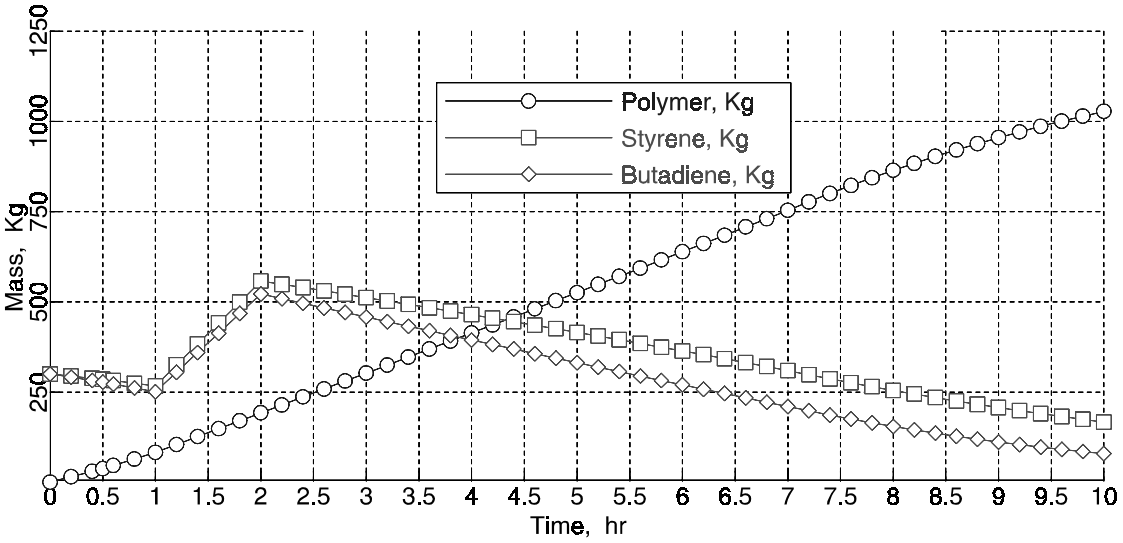


Figure 5.4 *Component Mass Profiles in Reactor*

Figure 5.5 gives the volume of the monomer, polymer, and aqueous phases in the reactor. It is observed that the monomer droplets are completely depleted after 2.5 hours. As expected the volume of the swollen polymer phase decreases after the depletion of the monomer droplets.

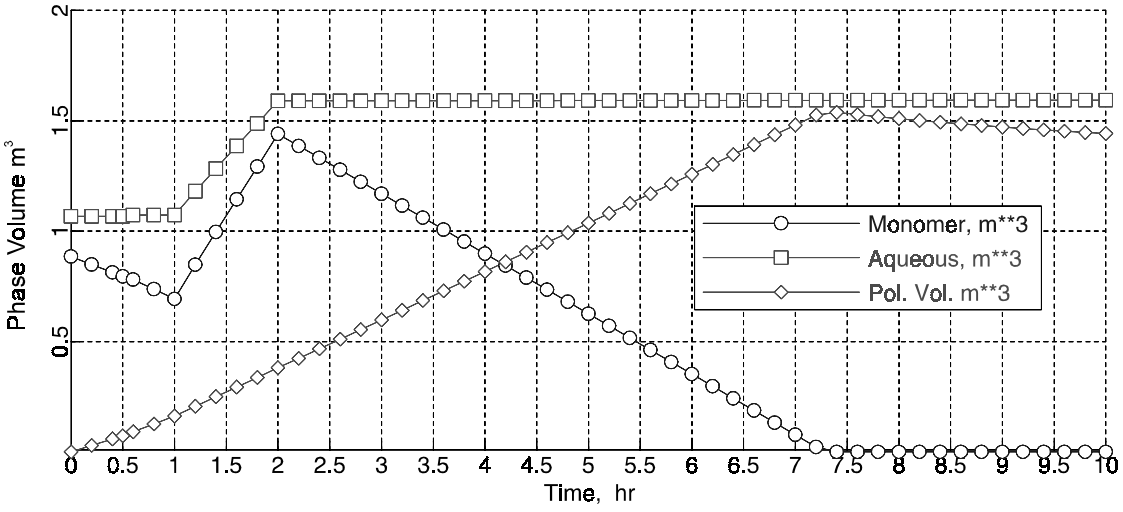


Figure 5.5 *Phase Volume Profiles in Reactor*

Figure 5.6 gives the number average and weight average degree of polymerization.

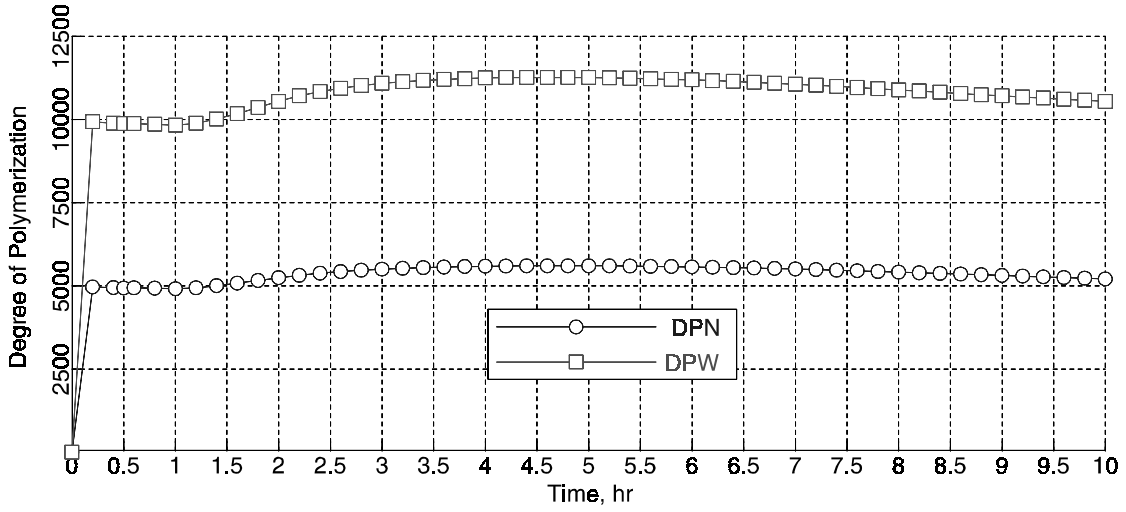


Figure 5.6 *Degree of Polymerization vs. Time*

Figure 5.7 gives the composition of the polymer. As expected the composition of the reactive butadiene monomer in the polymer is higher in comparison to styrene.

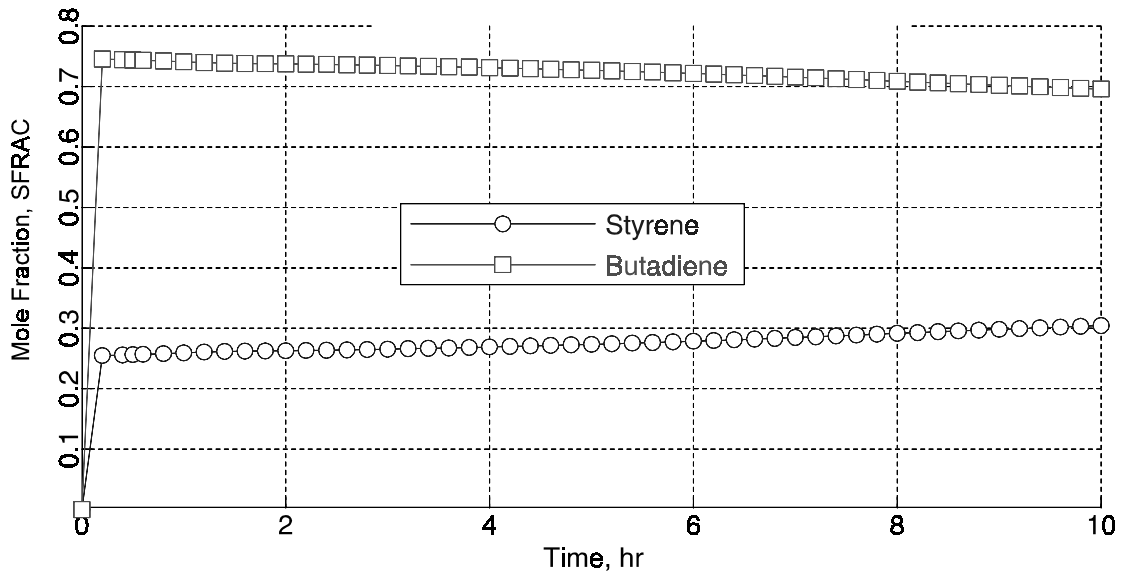


Figure 5.7 *Polymer Composition Profile*

Figure 5.8 plots the chain length distribution

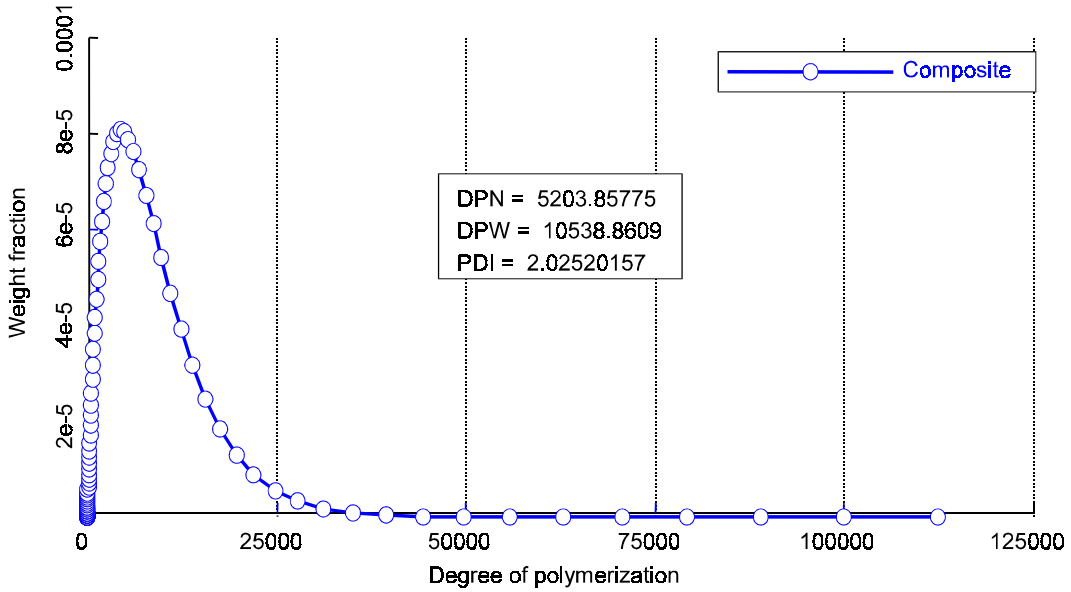


Figure 5.8 *Chain Length Distribution*

REFERENCES

Blackley, D. C., Synthetic Rubbers: Their Chemistry and Technology, Applied Science Publishers, New York (1983).

Broadhead, T. O., "Dynamic Modeling of the Emulsion Copolymerization of Styrene/Butadiene," M. E. Thesis, McMaster Univ. (1984).

Ponnuswamy, S. R. and A. E. Hamielec, "Emulsion Polymerization Theory and Practice," Lecture Notes for Intensive Short Course on Polymer Reaction Engineering, Burlington, Ontario Canada, April (1997).

6 STYRENE ETHYL ACRYLATE

FREE-RADICAL COPOLYMERIZATION PROCESS

SUMMARY

The styrene ethyl acrylate free-radical copolymerization process model illustrates the use of Polymers Plus to model a styrene ethyl acrylate free-radical process. The process modeled is an experimental system developed by McManus and Penlidis at the University of Waterloo. The model is then used along with the experimental data generated at the University of Waterloo to estimate reaction rate constant parameters.

ABOUT THIS PROCESS

The copolymerization of styrene with ethyl acrylate is of considerable interest to the polymer industry. Recently, McManus and Penlidis at the University of Waterloo conducted a detailed study on the copolymerization of styrene and ethyl acrylate, and generated extensive data by varying the initiator concentration, feed composition, and the reactor temperature (McManus and Penlidis, 1996). Other similar studies have been done for this system (Fehervari, et al, 1981). A number of investigators estimated the kinetic parameters, but there are many discrepancies between kinetic rate constants and the reactivity ratios reported in the literature. McManus and Penlidis reviewed the information available on the kinetic data and estimated the reactivity ratios.

PROCESS DEFINITION

The copolymerization of styrene and ethyl acrylate is carried out in a batch reactor. The batch reactor is charged with a pre-mixed stream of styrene, ethyl acrylate, and the initiator azo-bis-isobutyronitrile. The reactor is operated at a constant temperature and pressure. The flowsheet is shown in Figure 6.1.

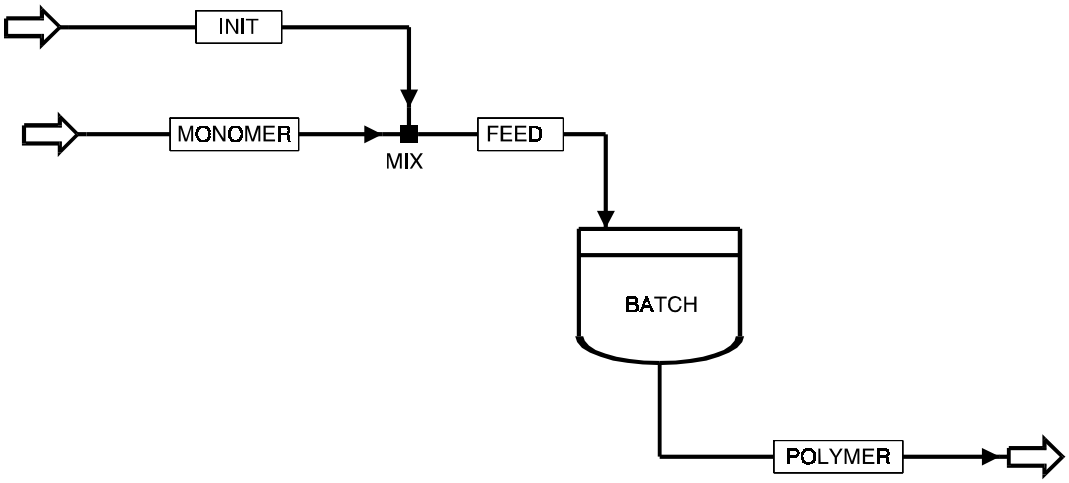


Figure 6.1 *Styrene/Ethyl Acrylate Copolymerization Flowsheet*

Process Conditions

The process conditions are as listed in Table 6.1. More details on the process data and the parameter regressing procedure are given next.

Table 6.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Initiator	AIBN	PURECOMP	Initiator
Styrene	STY	PURECOMP	Monomer
Ethyl Acrylate	EA	PURECOMP	Monomer
Polymer	POLYMER	POLYMER	Polymer
	STY-SEG	SEGMENT	Styrene segment
	EA-SEG	SEGMENT	Ethyl Acrylate segment
Physical Properties	POLYNRTL property method with supplied parameters		
Monomer Stream		**Initiator Stream**	
Temperature (°C)	50 or 60	50 or 60	
Pressure (atm)	1	1	
Mass flow kg/h	1000		
Mole flow of AIBN		0.05 MR/L in reaction mixture	
Mole fraction of styrene	0.762		
Mole fraction of ethyl acrylate	0.238		
Kinetics	EMULSION model		
Operating Conditions			
BATCH			
Temperature (°C)	50 or 60		
Pressure (atm)	1		
Reaction time	22		
Cycle time	1		

Reactors / Kinetics

The reaction set used in this process and the initial rate constant parameters are listed below:

Description	k_0 (m^3 / kmol)	E_a (J / kmol)	V (m^3 / kmol)	EFFIC
INIT-DEC AIBN	1.82E15	1.288E8 E	0.0	0.50808
CHAIN-INI STY	4.5E6	2.6E7	0.0	
CHAIN-INI EA	3.0E6	2.24E7	0.0	
PROPAGATION STY STY	2.3438E6	2.6E7	0.0	
PROPAGATION STY EA	3.26562E6	2.6E7	0.0	
PROPAGATION EA STY	1.49182E7	2.24E7	0.0	
PROPAGATION EA EA	3.000E6	2.24E7	0.0	
CHAT-MON STY STY	117.190	2.6000E+07	0.0	
CHAT-MON STY EA	163.30	2.6000E+07	0.0	
CHAT-MON EA STY	746.0	2.2400E+07	0.0	
CHAT-MON EA EA	95.50	2.2400E+07	0.0	
TERM-COMB STY STY	1.4592E9	7E6	0.0	
TERM-COMB STY EA	6.63E9	14.6E6	0.0	
TERM-COMB EA STY	6.63E9	14.6E6	0.0	
TERM-COMB EA EA	3.00E10	22.2E6	0.0	

Gel effect is applied to the initiation and termination reactors using correlation No. 2.

Reaction	Correlation	Parameters
INIT-DEC	2	-17.40 0.05528 17.8240 -05090 0.0 0.0 0.0 0.0 0.0 2.0
TERMINATION	2	1.0 0.0 2.570 -.005050 9.560 -.01760 -3.030 .007850 0.0 2.0

Parameter Regression

The experimental data reported by the University of Waterloo group includes conversion, polymer composition, number and weight average molecular weights as a function of time. This data was generated by varying: (1) the initial mole ratio of styrene to EA, (2) the initiator concentration, and (3) the reactor temperature. The DATA-FIT capability is used to fit the reaction rate constant parameters.

Monomer conversion and number average molecular weights were used to regress the kinetic parameters. Table 6.2 and Table 6.3 show the experimental data obtained at 50 and 60°C. To indicate the accuracy of the experiments, data obtained with a replicate experiment are also included in Table 6.2 and Table 6.3. An input summary is given in Figure 6.2.

Homo-propagation rate constants are regressed to fit the conversion data. Cross-propagation rate constants are calculated using the reactivity ratios. Homo-termination rate constants are regressed to fit the molecular weights. Cross-termination rate constants are set to the square-root of the product of the homo-termination rate constants.

Table 6.2 Styrene/Ethyl Acrylate Copolymerization Data

T=50°C, Styrene Mole Fraction in the feed=0.762, and AIBN=0.05 mol/L

	Data used in Data-Fit		Replicate Experiment		Simulation Results	
Time (min)	Conversion (mass %)	Molecular Weight (M_n)	Conversion (mass %)	Molecular Weight (M_n)	Conversion (mass %)	Molecular Weight (M_n)
0	0	9.61E+04	0	0.00E+00	0	92990
120	5.68	9.61E+04	5.62	98204	5.36	92990
240	10.79	9.69E+04	11.58	84913	10.6	95576.3
360	16.09	9.85E+04	16.48	89791	15.82	98699.5
480	21.06	1.02E+05	21.86	99669	21.11	1.02E+05
600	26.16	1.02E+05	26.82	99269	26.55	1.07E+05
660			28.63	101179		
720	37.55	1.04E+05	32.3	97121	32.25	1.12E+05
840	36.6	1.05E+05	37.08	105809	38.33	1.18E+05
900			41.8	106172		
930	39.36	1.12E+05				
960		1.12E+05	42.82	101569	44.98	1.26E+05
1020	45.97					
1080					52.44	1.35E+05
1110	54.68	1.12E+05	56.22	99967		
1200	61.44	1.15E+05			61.08	1.46E+05
1290	68.66	1.35E+05	70.71	108848		
1320					71.37	1.60E+05
1410	77.46	1.34E+05	79.37	142398		
1440					83.38	1.78E+05
1560					94.04	1.92E+05
1620	97.44	1.21E+05				
1680					98.37	1.94E+05
1760			99.5	201441		

Table 6.3 Styrene/Ethyl Acrylate Copolymerization Data

T=60°C, Styrene Mole Fraction in the feed=0.762, and AIBN=0.05 mol/L

	Data used in Data-Fit		Replicate Experiment		Simulation Results	
Time (min)	Conversion (mass %)	Molecular Weight (M_n)	Conversion (mass %)	Molecular Weight (M_n)	Conversion (mass %)	Molecular Weight (M_n)
0	0	6.13E+04	0.00E+00	53353	0	60149
60	7.73	6.13E+04			6.9	60149
90			5.62	53353		
120	14.16	6.34E+04			13.44	63142
180	21.14	6.73E+04	11.58	58819	19.788	66606
240	27.25	6.49E+04	16.48	50716	26.088	7.06E+04
300	34.02	7.09E+04	21.86	51287	32.47	7.51E+04
360	40.32	6.17E+04	26.82	59017	39.07	8.04E+04
390			28.63	64038		
420	47.11	6.99E+04			46.04	8.64E+04
465	49.25	7.54E+04				
480			32.3	68012	53.55	9.35E+04
510	57.32	8.09E+04				
540			37.08	73434	61.81	1.02E+05
555	62.15	6.49E+04				
600	71.16	9.14E+04	41.8	74867	71	1.12E+05
645	83.02	9.37E+04				
660			42.82	97000	81	1.23E+05
705	94.8	1.12E+05				
720			56.22	98327	90.39	1.32E+05
780	100	1.26E+05	70.71	120620	96.39	1.38E+05
			79.37	109391		
840					98.67	1.38E+05
900					99.3	1.37E+05

In the styrene-ethyl acrylate kinetic scheme, 11 reactions were chosen and the gel-effect was applied to the termination and initiation reaction. Recall that $k = k_o \exp\left(-\frac{E}{RT} - \frac{\Delta VP}{RT}\right)$.

This results in 34 kinetic parameters and 20 gel-effect parameters available for fitting. The available data is not sufficient to regress all these parameters. The following approach was used to reduce the number of parameters needed for a good fit.

1. Since the batch reactor is operated at 1 atm, the effect of activation volume on the rate constant can be neglected for all the reactions. Therefore, the activation volume was set to zero for all the reactions. Note that at high pressures the effect of activation volume cannot be neglected.
2. The initiator decomposition rate constants were known. Typically these can be obtained from a good polymer handbook or from the supplier. They can also be calculated using the half-life data. (See Appendix G of the *Polymers Plus User Guide*).
3. Chain initiation rate constants are in general faster than the propagation rate constants. Therefore these constants were set to be the same or greater than the propagation rate constants.
4. There are two homo-propagation reactions and two cross-propagation reactions in the kinetic scheme. The number of regressable parameters is then eight excluding the activation volume parameters. The number of regressable propagation parameters can be reduced if the homo-propagation rate constants and/or the reactivity ratios are known. If the homo-propagation rate constants are known then reactivity ratios can be estimated. If the reactivity ratios are known homo-propagation rate constants can be estimated. In this example, reactivity ratios were given (Fehervari, 1981), and the homo-propagation rate constants were regressed. The cross-propagation rate constants were calculated using the following equations.

   $r_1 = k_p^{11} / k_p^{12}$

   $r_2 = k_p^{22} / k_p^{21}$

   Where:

   STY=1

   EA=2

5. Four termination reactions are considered in this scheme. Cross-termination reactions involving STY and EA segments were set to have the same rate constant. This reduces specification of the rate constants to three. If the homo-termination rate constants are known, the cross-termination rate constants can be estimated using the following equations.

   $k_{12} = \sqrt{k_{11} k_{22}}$

   $k_{21} = k_{12}$

   In this example homo-termination rate constants were regressed using the molecular weight data.

6. In the kinetic scheme termination by combination was selected. It is possible that termination by disproportionation can also occur. One needs to know apriori the termination mechanism. As a general rule if polydispersity (PDI) is 1.5 termination by combination is controlling and if PDI is two termination is controlled by the disproportionation reaction.
7. At high conversion termination is diffusion controlled. This is modeled using the gel-effect option. Therefore use of low conversion data is recommended for regression of the kinetic parameters without using gel-effect. High conversion data is then used to regress the gel-effect parameters.
8. Monomer conversion data was used to regress the initiator efficiency, propagation and the termination rate constants. Molecular weight data was used to regress the propagation and the termination rate constants. The gel-effect parameters influence both the conversion and the molecular weight.
9. Chain transfer reactions do not affect the conversion but affect the polymer molecular weight.

Table 6.4 summarizes the approach for fitting the kinetic rate constant parameters.

Table 6.4 Kinetic Parameter Fitting for Free-Radical Polymerization Data

		Required Data					
Reaction	**Parameter**	**Conversion**	**MW_n or DP_n**	**PDI**	**LCB**	**SCB**	**Copolymer Composition**
INIT-DEC	k_d	Initiator					
PROPAGATION	k_p	Monomer	☒	☒			☒
CHAT-MON	k_{trm}		☒	☒			
CHAT-SOL	k_{trs}		☒	☒			
CHAT-AG	k_{tra}		☒	☒			
TERM-DIS	k_{td}	Monomer	☒	☒			
TERM-COM	k_{tc}	Monomer	☒	☒			
INHIBITION	k_x	Monomer	☒	☒			
CHAT-POL	k_{trp}			☒	☒		
SC-BRANCH	k_{scb}					☒	

Figure 6.2 Input Summary for Styrene and Ethyl Acrylate Copolymerization

```
TITLE 'Data-fit Example Using Free Radical Polymerization'


IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm  &
        TEMPERATURE=C TIME=hr VOLUME=l MASS-DENSITY='gm/cc'  &
        PDROP='N/sqm'

OUT-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' PRESSURE=atm  &
        TEMPERATURE=C TIME=min VOLUME=l MASS-DENSITY='gm/cc'  &
        PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1200000.0

DESCRIPTION "Batch reactor data for styrene-ethyl acrylate
        polymerization is used to regress propagation
        and termination rate constants "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    AIBN C8H8 AIBN /
    STY C8H8 STY /
    EA C5H8O2 EA /
    STY-SEG C8H8-R STY-SEG /
    EA-SEG C5H8O2-R-2 EA-SEG /
    POLYMER PS-1 POLYMER

FLOWSHEET
    BLOCK BATCH IN=FEED OUT=POLYMER
    BLOCK MIX IN=MONOMER INIT OUT=FEED

PROPERTIES POLYNRTL

;USER-PROPS GMRENA 1 2 1 / GMRENB 1 2 1 / GMRENC 1 2 1  &
;        / GMREND 1 2 1

PROP-DATA U-1
    IN-UNITS ENG
    PROP-LIST MW
    PVAL AIBN 164.2120

POLYMERS
    SEGMENTS STY-SEG REPEAT / EA-SEG REPEAT
    POLYMERS POLYMER
    ATTRIBUTES POLYMER SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM

;LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW  &
;        LEFRAC LPFRAC
```

Figure 6.2 Input Summary for Styrene and Ethyl Acrylate Copolymerization (cont.)

```
;    DISTRIBUTION POLYMER CHAIN-SIZE NPOINTS=100
;DEF-STREAMS CONVEN POLYMER

PROP-SET INITCONC
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'
    PROPNAME-LIS MOLECONC UNITS='mol/l' SUBSTREAM=MIXED  &
        COMPS=AIBN

PROP-SET PS-2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'
    PROPNAME-LIS MASSFRAC SUBSTREAM=MIXED COMPS=POLYMER PHASE=L

STREAM INIT
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C VOLUME=l MASS-DENSITY='gm/cc'  &
        PDROP='N/sqm'
    SUBSTREAM MIXED TEMP=50.0 PRES=1.0
    MOLE-FLOW AIBN .05710370

STREAM MONOMER
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C VOLUME=l MASS-DENSITY='gm/cc'  &
        PDROP='N/sqm'
    SUBSTREAM MIXED TEMP=60.0 PRES=1.0 MASS-FLOW=1000.0
    MOLE-FRAC STY .7620 / EA .2380

BLOCK MIX MIXER
    IN-UNITS ENG

;    BLOCK-OPTION TERM-LEVEL=7

BLOCK BATCH RBATCH
    PARAM TYPE=T-SPEC PRINT-TIME=1.0 CYCLE-TIME=1.0  &
        MAX-TIME=25.0 MAX-NPOINT=27 TEMP=60.0 ERR-METHOD=DYNAMIC
    STOP 1 REACTOR TIME 25.0
    PROP-REACTOR PS-2
    REACTIONS RXN-IDS=STY-EA

FORTRAN F-1
    DEFINE F PARAMETER 1
F      F = 5
    EXECUTE FIRST

FORTRAN K-PROP
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'
    DEFINE PROP11 REACT-VAR REACTION=STY-EA VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=STY ID2=STY
    DEFINE PROP12 REACT-VAR REACTION=STY-EA VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=STY ID2=EA
    DEFINE PROP21 REACT-VAR REACTION=STY-EA VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=EA ID2=STY
    DEFINE PROP22 REACT-VAR REACTION=STY-EA VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=EA ID2=EA
```

Figure 6.2 Input Summary for Styrene and Ethyl Acrylate Copolymerization (cont.)

```
F       R1     = 0.717
F       R2     = 0.128
F       PROP12 = PROP11/R1
F       PROP21 = PROP22/R2
    READ-VARS PROP11 PROP22
    WRITE-VARS PROP12 PROP21

FORTRAN K-TERM
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'
    DEFINE TC11 REACT-VAR REACTION=STY-EA VARIABLE=TCPRE-EXP  &
        SENTENCE=TERM-COMB ID1=STY ID2=STY
    DEFINE TC12 REACT-VAR REACTION=STY-EA VARIABLE=TCPRE-EXP  &
        SENTENCE=TERM-COMB ID1=STY ID2=EA
    DEFINE TC21 REACT-VAR REACTION=STY-EA VARIABLE=TCPRE-EXP  &
        SENTENCE=TERM-COMB ID1=EA ID2=STY
    DEFINE TC22 REACT-VAR REACTION=STY-EA VARIABLE=TCPRE-EXP  &
        SENTENCE=TERM-COMB ID1=EA ID2=EA
    DEFINE F PARAMETER 1
F       TC12 = F*(TC11*TC22)**0.5
F       TC21 = F*(TC11*TC22)**0.5
    READ-VARS TC11 TC22
    WRITE-VARS TC12 TC21

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC  &
        PROPERTIES=INITCONC

;    PROPAGATION STY STY 23438.0 2.6000E+07
;    Gel effect is added to this file

REACTIONS STY-EA FREE-RAD

    IN-UNITS SI
    PARAM QSSA=YES
    SPECIES INITIATOR=AIBN MONOMER=STY EA POLYMER=POLYMER
    MON-RSEG STY STY-SEG / EA EA-SEG
    INIT-DEC AIBN 1.8200E+15 1.2880E+08 EFFIC=.5080
    CHAIN-INI STY 4500000.0 2.6000E+07
    CHAIN-INI EA 3000000.0 2.2400E+07
    PROPAGATION STY STY 2343800.0 2.6000E+07
    PROPAGATION STY EA 3265620.0 2.6000E+07
    PROPAGATION EA STY 1.4918E+07 2.2400E+07
    PROPAGATION EA EA 3000000.0 2.2400E+07
    CHAT-MON STY STY 117.190 2.6000E+07
    CHAT-MON STY EA 163.30 2.6000E+07
    CHAT-MON EA STY 746.0 2.2400E+07
    CHAT-MON EA EA 95.50 2.2400E+07
    TERM-COMB STY STY 1.4592E+09 7000000.0
    TERM-COMB STY EA 6.6300E+10 1.4600E+07
    TERM-COMB EA STY 6.6300E+10 1.4600E+07
    TERM-COMB EA EA 3.0000E+11 2.2200E+07
    GEL-EFFECT INIT-EFF 2 MAX-PARAMS=10 GE-PARAMS=-17.40  &
        .055280 17.8240 -.05090 0.0 0.0 0.0 0.0 0.0 2.0
```

Figure 6.2 Input Summary for Styrene and Ethyl Acrylate Copolymerization (cont.)

```
    GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1.0 0.0  &
        2.570 -.005050 9.560 -.01760 -3.030 .007850 0.0 2.0

;    DATA MWN
;    VARY PARAMETER 1
;    LIMITS 1 100

REGRESSION K-TERM
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=atm TEMPERATURE=C PDROP='N/sqm'
    DATA WPOLY
    VARY REACT-VAR REACTION=STY-EA VARIABLE=PRPRE-EXP  &
        SENTENCE=PROPAGATION ID1=STY ID2=STY
    LIMITS 5E4 1E7
    ALGORITHM MXPASS=3000

DATA-SET MWN
    IN-UNITS ENG
    DEFINE TIME BLOCK-VAR BLOCK=BATCH VARIABLE=VALUE  &
        SENTENCE=STOP ID1=1
    DEFINE MWN COMP-ATTR-VAR STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=POLYMER ATTRIBUTE=MWN ELEMENT=1
    INPUT TIME
    RESULT MWN
    USE STD-DEV .010 5000.0 / DATA 2.0 96148.0 / DATA 4.0  &
        96939.0 / DATA 6.0 98547.0 / DATA 8.0 102418.0 /  &
        DATA 10.0 101941.0 / DATA 12.0 104354.0 / DATA 14.0  &
        105066.0 / DATA 15.50 112415.0 / DATA 17.0 112159.0  &
        / DATA 18.50 112001.0 / DATA 20.0 114564.0 / DATA  &
        21.50 135065.0 / DATA 23.50 133690.0 / DATA 27.0  &
        120899.0

DATA-SET WPOL-SFR
    IN-UNITS ENG
    DEFINE TIME BLOCK-VAR BLOCK=BATCH VARIABLE=VALUE  &
        SENTENCE=STOP ID1=1
    DEFINE WPOLY MASS-FRAC STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=POLYMER
    DEFINE SFRAC COMP-ATTR-VAR STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=POLYMER ATTRIBUTE=SFRAC ELEMENT=1
    INPUT TIME
    RESULT WPOLY SFRAC
    USE STD-DEV .010 .010 .010 / DATA 2.0 .05680 .7590 /  &
        DATA 4.0 .10790 .7980 / DATA 6.0 .16090 .7660 /  &
        DATA 8.0 .21060 .7360 / DATA 10.0 .26160 .7710 /  &
        DATA 12.0 .37550 .7510 / DATA 14.0 .3660 .7630 /  &
        DATA 20.0 .61440 .780 / DATA 21.50 .68660 .7870 /  &
        DATA 23.50 .77460 .7970 / DATA 27.0 .97440 .7550

;       / DATA 27 .9744
```

Figure 6.2 Input Summary for Styrene and Ethyl Acrylate Copolymerization (cont.)

```
DATA-SET WPOLY
    IN-UNITS ENG
    DEFINE TIME BLOCK-VAR BLOCK=BATCH VARIABLE=VALUE  &
        SENTENCE=STOP ID1=1
    DEFINE WPOLY MASS-FRAC STREAM=POLYMER SUBSTREAM=MIXED  &
        COMPONENT=POLYMER
    INPUT TIME
    RESULT WPOLY
    USE STD-DEV .010 .010 / DATA 2.0 .05680 / DATA 4.0  &
        .10790 / DATA 6.0 .16090 / DATA 8.0 .21060 / DATA  &
        10.0 .26160 / DATA 12.0 .37750 / DATA 14.0 .3660 /  &
        DATA 15.50 .39360 / DATA 17.0 .45970 / DATA 18.50  &
        .54680 / DATA 20.0 .61440 / DATA 21.50 .68660 /  &
        DATA 23.50 .77460
;
```

SELECTED SIMULATION RESULTS

Figure 6.3 and Figure 6.4 show estimated molecular weight and monomer conversion as a function of the experimental data. As shown in these figures a good match is obtained between the predictions and experimental data. The values of the fitted parameters are as follows:

Reaction	Parameter	Estimate	Std. Dev.	Confidence Lower Limit	Internal Upper Limit
Styrene homo-propagation	Pre-exponential factor	2.154×10^7	19169.6	2.1168×10^6	2.1919×10^6
EA homo-propagation	Pre-exponential factor	3.0×10^6	6.65×10^6	5×10^5	1.0×10^7
Styrene homo-termination	Pre-exponential factor	1.26×10^9	---	---	---
EA homo-termination	Pre-exponential factor	2.6×10^9	---	---	---

Figure 6.5 and Figure 6.6 show the conversion and molecular weight data comparison of the simulation results with the experimental data at 50 and 60°C respectively.

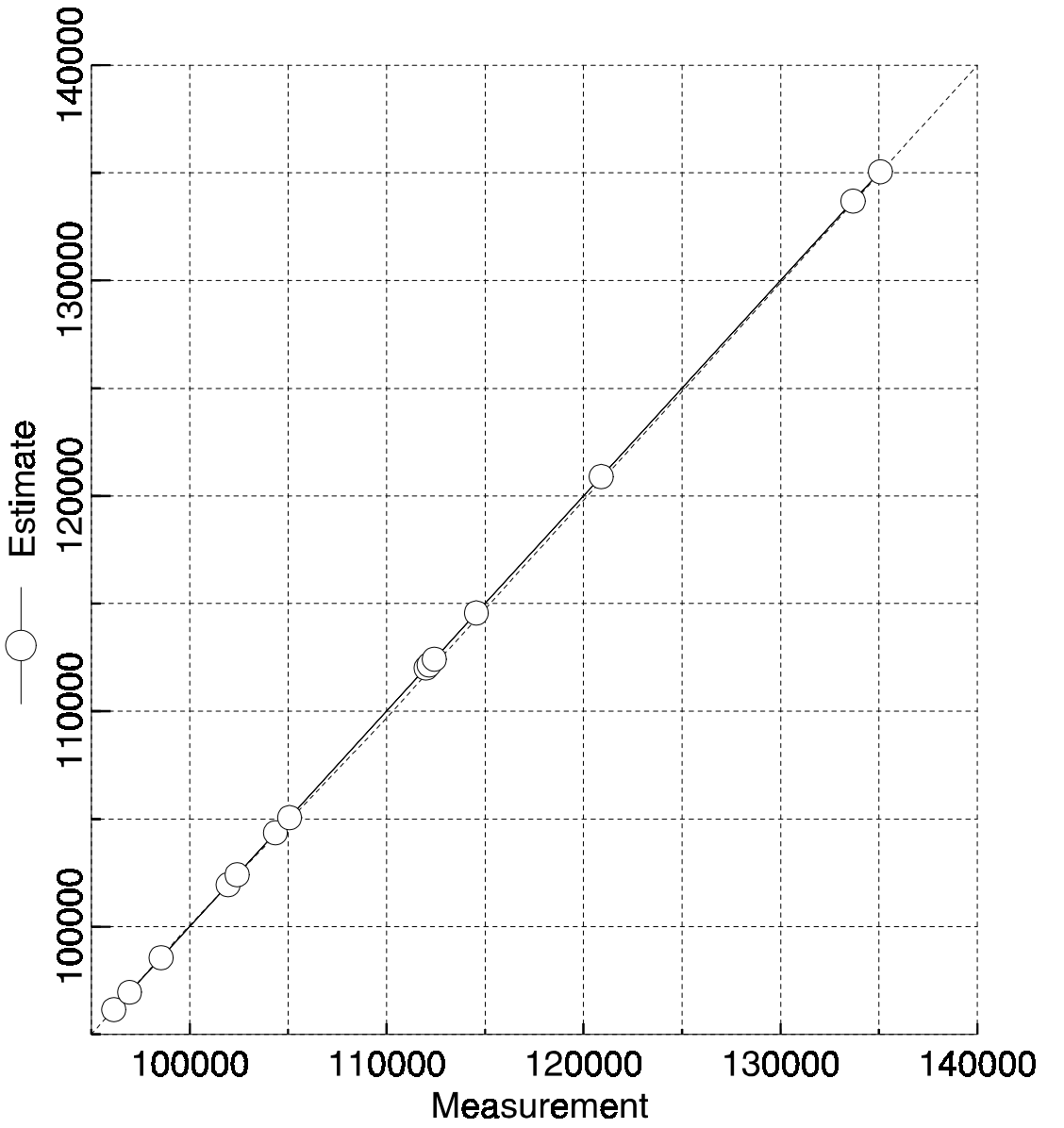


Figure 6.3 *Estimated vs. Measured* MW_n

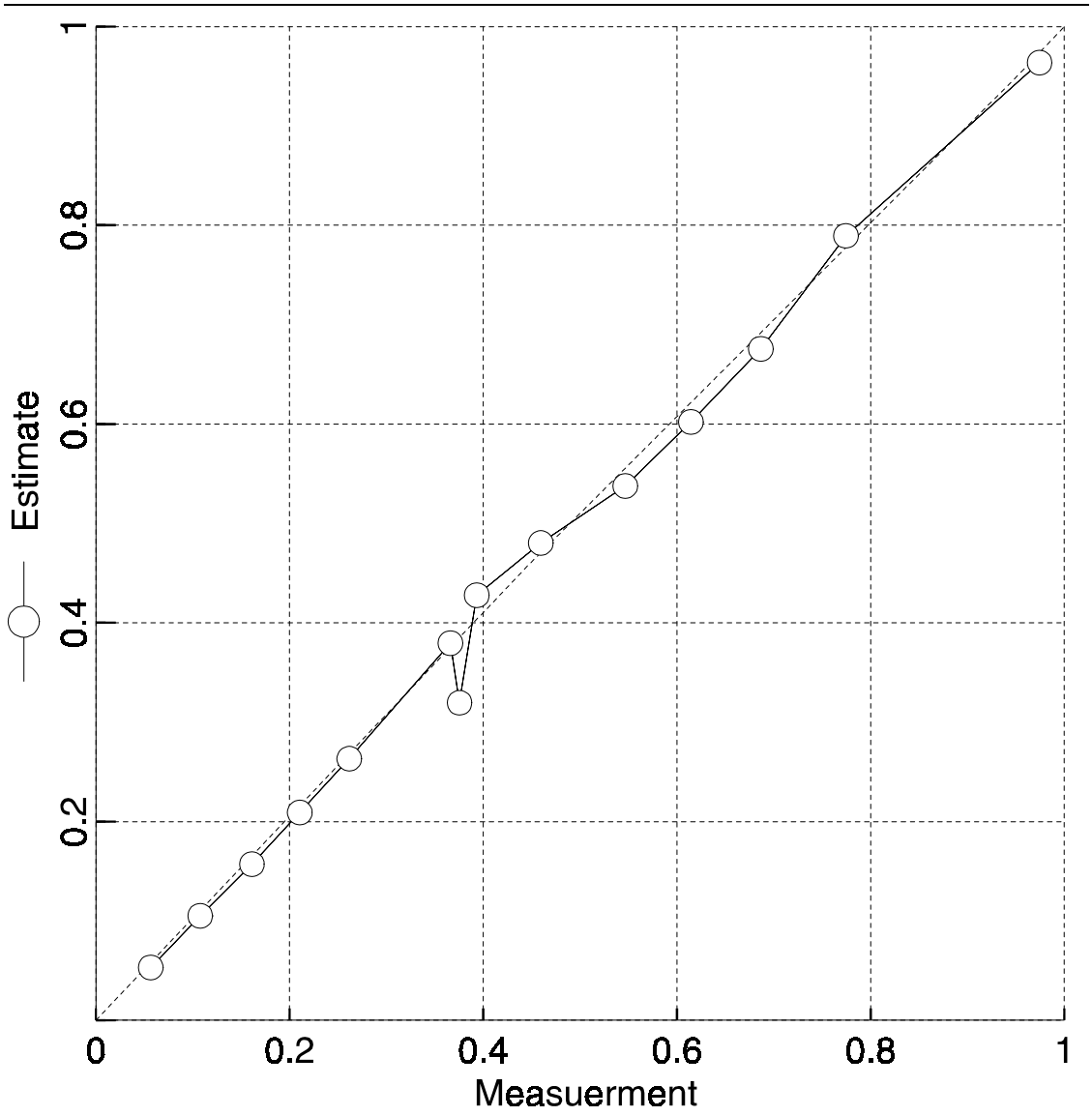
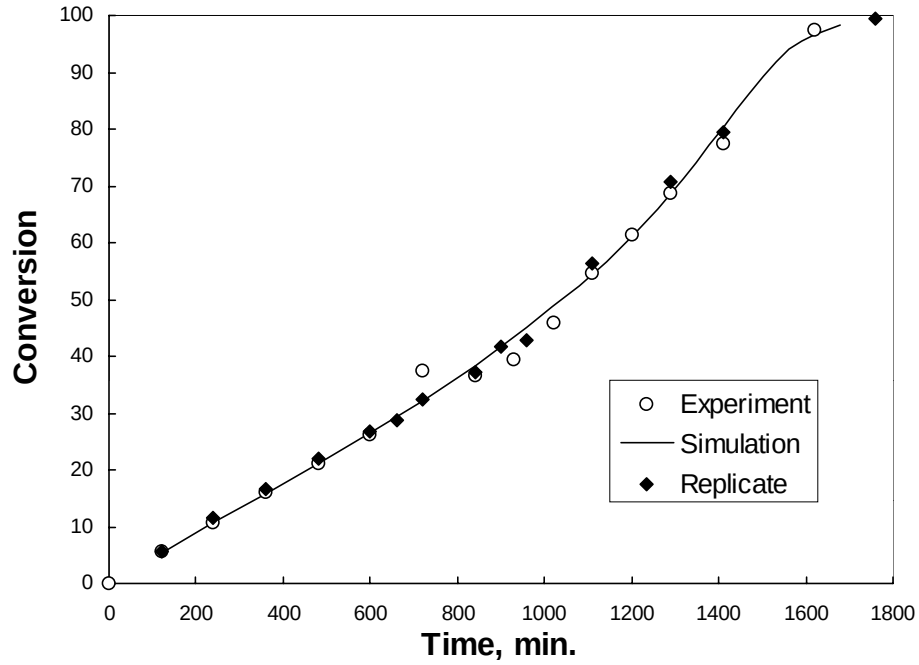


Figure 6.4 *Estimated vs. Measured Monomer Conversion*



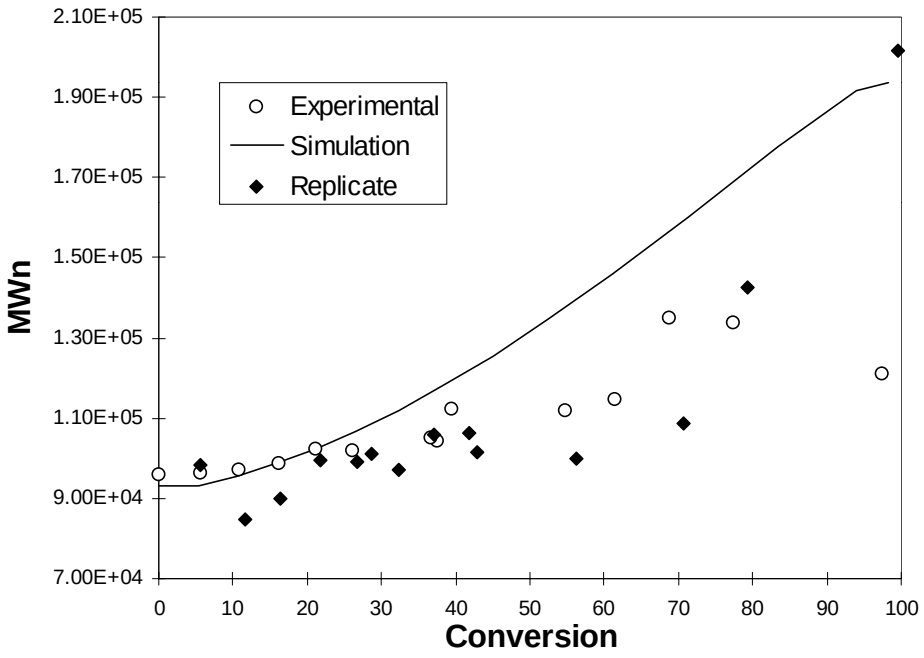


Figure 6.5 *Comparison of Simulation Results and Experimental Data at 50°C*

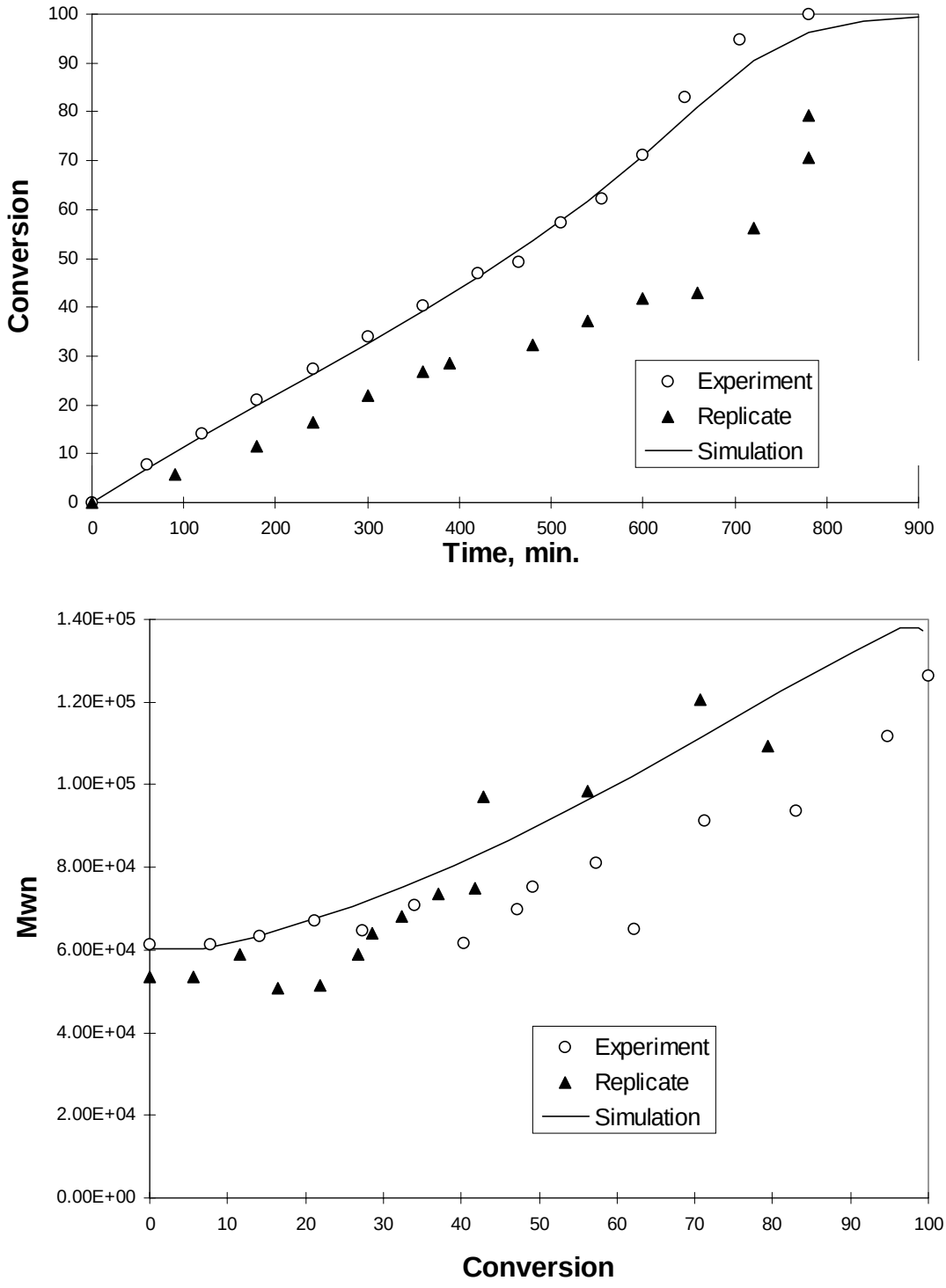


Figure 6.6 *Comparison of Simulation Results and Experimental Data at 60°C*

REFERENCES

Fehervari, A, T. Foldes-Berezsnich, and F. Tudos, *J. Macromol. Sci. Chem.*, **A16**, 993, (1981).

McManus, N. T. and A. Penlidis, "A kinetic investigation of styrene/ethyl acrylate copolymerization", *J. Polym. Sci. Polym. Chem.*, **34** , 237.

7 METHYL METHACRYLATE

POLYMERIZATION IN ETHYL ACETATE

SUMMARY

The methyl methacrylate polymerization in ethyl acetate model illustrates the use of Polymers Plus to model a solution polymerization process for methyl methacrylate in ethyl acetate. Among the studies carried out using this model are the effect of initiator concentration and reactor temperature on molecular weight and conversion.

ABOUT THIS PROCESS

Polymethyl methacrylate is part of the polyacrylic group of polymers. It is used in the manufacture of lenses or other clear coverings and is also known under the trade names plexiglass, lucite, acrylate, etc.

This methyl methacrylate polymerization is carried out in a free-radical solution process. Solution polymerization is used when both the monomer and the initiator are soluble in the solvent. Typically, solution processes result in low viscosity, provide good mixing, and improve heat transfer limitations, while improving temperature control and reducing gel effect. On the other hand, these processes result in lower reaction rate and in lower polymer molecular weight due to chain transfer to solvents. Furthermore, solvent removal can be costly.

The flowsheet for this process consists of a batch reactor followed by a devolatizer for solvent removal. The reactor feed contains methyl methacrylate dissolved in ethyl acetate, with AIBN as the initiator. The reactor operates under constant temperature and pressure.

PROCESS DEFINITION

The batch reactor is modeled using RBatch, and the devolitizer using Flash2 as shown in Figure 7.1.

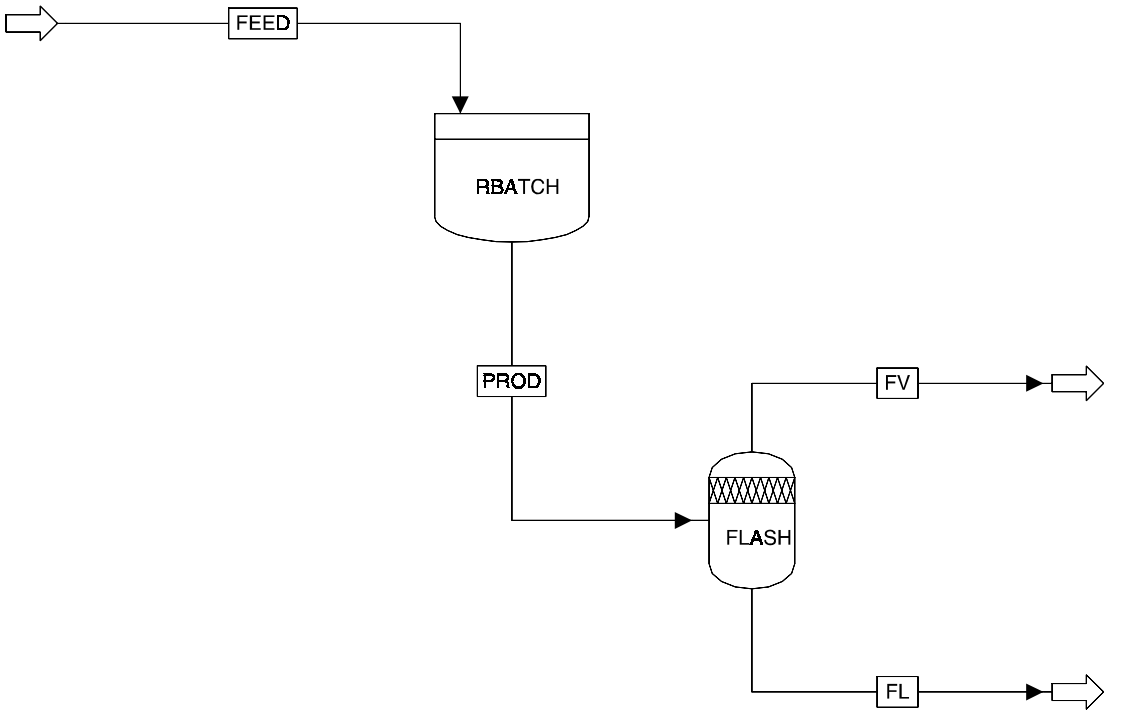


Figure 7.1 *Methyl Methacrylate Polymerization Flowsheet*

Process Conditions

The process conditions are as listed in Table 7.1

Table 7.1 Process Conditions

Components			
	Name	**Databank**	**Description**
Methyl-methacrylate	MMA	PURECOMP	Monomer
Ethyl-acetate	EA	PURECOMP	Solvent
Polymethylmethacrylate	PMMA	POLYMER	Polymer
	MMA-R	SEGMENT	Methyl methacrylate segment
AIBN	AIBN	PURECOMP	Initiator (Mw=164.210)
Physical Properties	POLYNRTL property method with supplied parameters		
Feed Streams			
Temperature (°C)	0		
Pressure (atm)	1		
Methylmethacrylate (kg/h)	100 (25 wt%)		
Ethyl Acetate (kg/hr)	300 (75 wt%)		
Initiator (kg/hr)	3.757 (50 mol/CUM in AIBN		
The feed is sent to RBATCH as a batch feed			
Kinetics	FREE-RAD model		
Operating Conditions			
	RBATCH	**FLASH**	
Temperature (°C)	50	60	
Pressure	1 atm	100 mmHg	

Reactors / Kinetics

The kinetic parameters of solution polymerization of methyl methacrylate are available in literature (Ellis, 1988). The reactions used in this model and their rate constant parameters are listed below:

Description	k_o	(J/Kmol)	Efficiency
Initiator decomposition	1.2525E14	1.228E8	0.5
Chain initiation	4.92E5	1.824E7	---
Propagation	4.92E5	1.82E7	---
Chain transfer to monomer	7.177E9	7.513E7	---
Chain transfer to solvent	4.673E8	6.57E7	---
Termination by disproportionation	9.8E7	2.937E6	---

Because of the presence of large amount of solvents (75% by weight), gel-effect is not significant and is therefore not considered. At high monomer conversion, gel-effect can be used to improve the agreement between the model predictions and experimental data.

In the batch reactor two reactor stop conditions are provided: stop after 5 hours of reaction time, or stop at 99% monomer conversion (corresponds to PMMA mass fraction of 0.2452). The first option is used to obtain conversion and polymer molecular weight information as a function of time. The second option is used to examine the effect of temperature and initiator concentration of PMMA properties at a given conversion.

Process Studies

The PMMA process model is used to examine process variables such as conversion number and weight average molecular weight as a function of time, at three different reactor temperatures. The model predictions are compared against literature data (Ellis, 1990).

The model is also used to study the effects of initiator concentration and polymerization temperature on the following: reaction time to reach 99% monomer conversion, peak heat load, number and weight average molecular weight.

A sensitivity study is also performed to show the percent solids as a function of outlet temperature.

An input summary is given in Figure 7.2.

Figure 7.2 Input Summary for Methyl Methacrylate Polymerization

```
TITLE 'Polymerization of MMA'

IN-UNITS MET

DEF-STREAMS CONVEN ALL

DESCRIPTION "
        Polymerization of methyl methacrylate(MMA) in a batch reactor.
        "

DATABANKS POLYMER  / SEGMENT  / PURE93  / NOASPENPCD

PROP-SOURCES POLYMER  / SEGMENT  / PURE93

COMPONENTS
    MMA C5H8O2-D3 MMA /
    EA C4H8O2-3 EA /
    AIBN C5H8O2-D3 AIBN /
    PMMA PMMA PMMA /
    MMA-R C5H8O2-R-1 MMA-R

FLOWSHEET
    BLOCK FLASH IN=PROD OUT=FV FL
    BLOCK RBATCH IN=FEED OUT=PROD

PROPERTIES POLYNRTL

USER-PROPS GMRENA 1 2 1 / GMRENB 1 2 1 / GMRENC 1 2 1  &
        / GMREND 1 2 1

PROP-DATA U-1
    IN-UNITS MET
    PROP-LIST MW
    PVAL AIBN 164.210
```

Figure 7.2 Input Summary for Methyl Methacrylate Polymerization (cont.)

```
POLYMERS
    SEGMENTS MMA-R REPEAT
    POLYMERS PMMA
    ATTRIBUTES PMMA SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM  &
        FMOM SMOM LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW  &
        LEFRAC LPFRAC
    DISTRIBUTION PMMA CHAIN-SIZE CLD NPOINTS=100 3000.

PROP-SET PS-1 MASSFRAC SUBSTREAM=MIXED COMPS=PMMA MMA EA  &
        PHASE=L
PROP-SET PS-2 MOLECONC UNITS='kmol/cum' SUBSTREAM=MIXED  &
        COMPS=AIBN PHASE=L
PROP-SET PS-3 MOLECONC UNITS='kmol/cum' SUBSTREAM=MIXED  &
        COMPS=AIBN MMA PHASE=L

STREAM FEED
    SUBSTREAM MIXED TEMP=273.0 PRES=1.0
    MASS-FLOW MMA 100.0 / EA 300.0 / AIBN 3.7570

BLOCK FLASH FLASH2
    PARAM TEMP=333.150 PRES=.131578947

BLOCK RBATCH RBATCH
    PARAM TYPE=T-SPEC PRINT-TIME=.50 CYCLE-TIME=1.0  &
        MAX-TIME=100.0 MAX-NPOINT=202 PRES=1.0 TEMP=323.0
    STOP 1 REACTOR MASS-FRAC .24520 FROM-BELOW COMP=PMMA  &
        SSID=MIXED
    PROP-REACTOR PS-1
    REACTIONS RXN-IDS=REAC-1

FORTRAN F-1
    DEFINE FTEMP STREAM-VAR STREAM=FEED SUBSTREAM=MIXED  &
        VARIABLE=TEMP
    DEFINE RTEMP BLOCK-VAR BLOCK=RBATCH VARIABLE=TEMP  &
        SENTENCE=PARAM
F      FTEMP = RTEMP
    EXECUTE BEFORE BLOCK RBATCH

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR NOMOLEFLOW MASSFLOW PROPERTIES=PS-2 PS-3

REACTIONS REAC-1 FREE-RAD
    IN-UNITS SI
    PARAM
    SPECIES INITIATOR=AIBN MONOMER=MMA SOLVENT=EA POLYMER=PMMA
    MON-RSEG MMA MMA-R
    INIT-DEC AIBN 1.2525E+14 1.2280E+08 EFFIC=.50
    CHAIN-INI MMA 492000.0 1.8240E+07
    PROPAGATION MMA MMA 492000.0 1.8240E+07
    CHAT-MON MMA MMA 7.1770E+09 7.5130E+07
    CHAT-SOL MMA EA 4.6730E+08 6.5700E+07
    TERM-DIS MMA MMA 9.8000E+07 2937000.0
```

SELECTED SIMULATION RESULTS

Figure 7.3 shows the mass flow of PMMA versus the time. This is equivalent to monomer conversion versus time since the feed rate is 100 kg/hr. Figure 7.3 indicates that at high temperature, over 90% of monomers are converted within 5 hours, while at low temperature (50°C), only 40% of monomers are converted. These results are within 1% deviation from literature simulation results (Ellis 1988).

Figure 7.4 shows the PMMA number-average molecular weight versus time at different reacting temperatures. As temperature increases, the number-average molecular weight of PMMA decreases. The Polymers Plus predictions agree closely with literature simulation. At high monomer conversion, the addition of gel-effect is needed to improve agreement between the predictions and experimental data.

Figure 7.5 shows the reaction time in hours needed to reach 99% monomer conversion at various temperatures. The five lines correspond to five initiator concentrations. At constant initiator concentration, the reaction time decreases with temperature. At constant temperature, the reaction time decreases as initiator concentration increases. Therefore, higher reaction temperature and initiator concentration allow faster monomer conversion.

Figure 7.6 and Figure 7.7 show the molecular weight dependency of temperature and initiator concentration. In general, both the number and weight-average molecular weight increase as temperature and initiator concentration decrease. The ratio of Mw and Mn gives the polydispersity index (PDI). Figure 7.8 shows that at a given conversion, PDI decreases as temperature increases, and increases as initiator concentration increases.

Figure 7.9 shows the instantaneous reactor heat duty as a function of reactor temperature and initiator concentration. For the case of a reactor with specified temperature, the maximum heat duty occurs immediately after reactions start. In our simulation, the maximum heat duty is reported at 0.5 hr. This is the first data point computed when the time interval is set to 0.5 hr, and is therefore not the true peak heat duty. Smaller time intervals may be used to obtain more accurate peak heat duty.

Figure 7.10 shows the results of the sensitivity study on the flash block. As the flash temperature varies, the polymer content in the liquid output stream changes accordingly. No binary parameters are used in the polymer NRTL model. If liquid-vapor equilibria data is available, the binary parameters may be fitted to allow more accurate predictions.

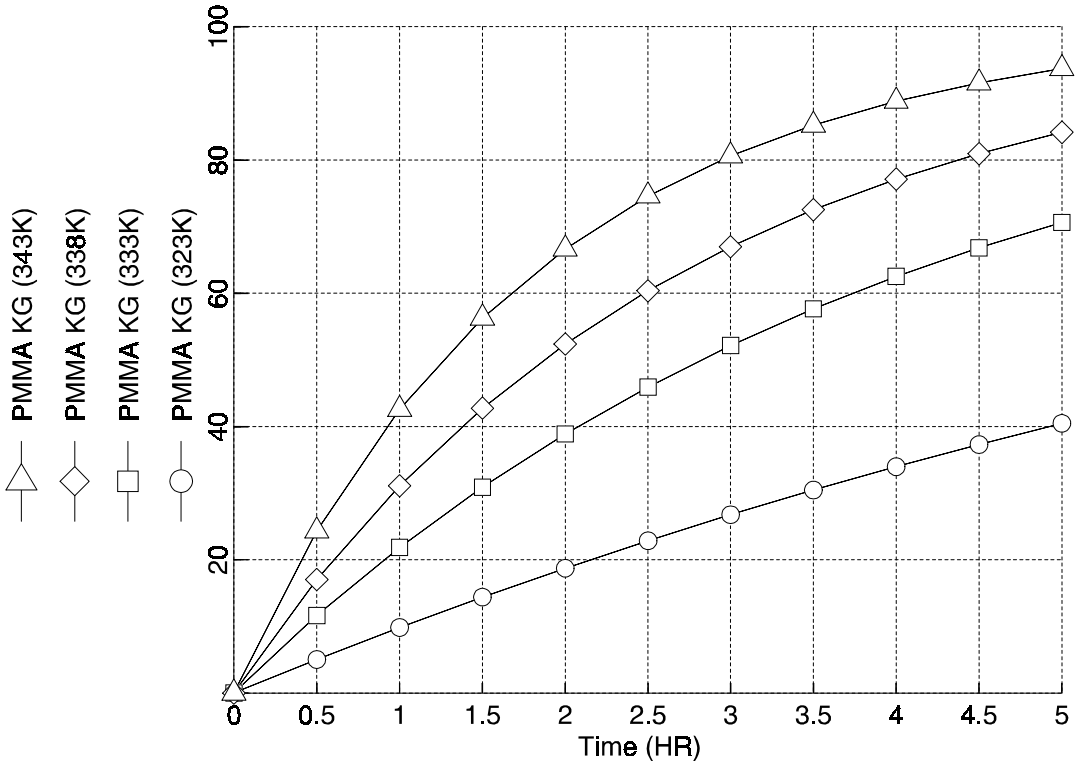


Figure 7.3 *PMMA Mass Flow (Monomer Conversion) vs. Time*

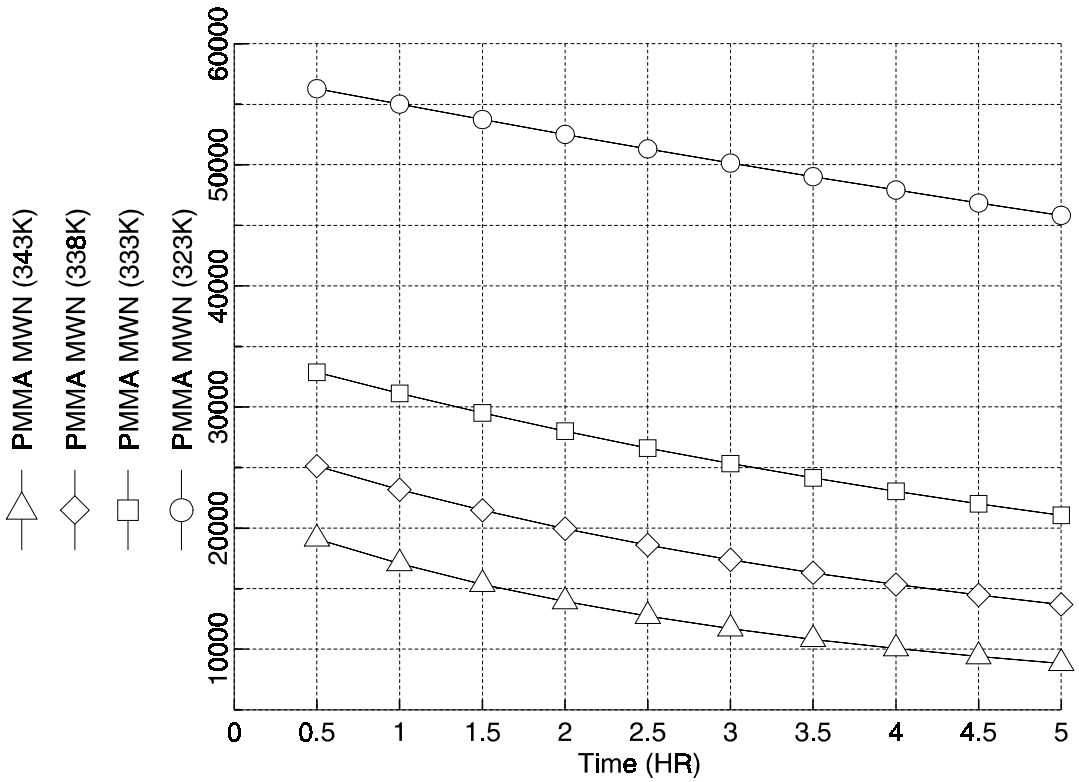


Figure 7.4 *PMMA Number-Averaged Molecular Weight vs. Time*

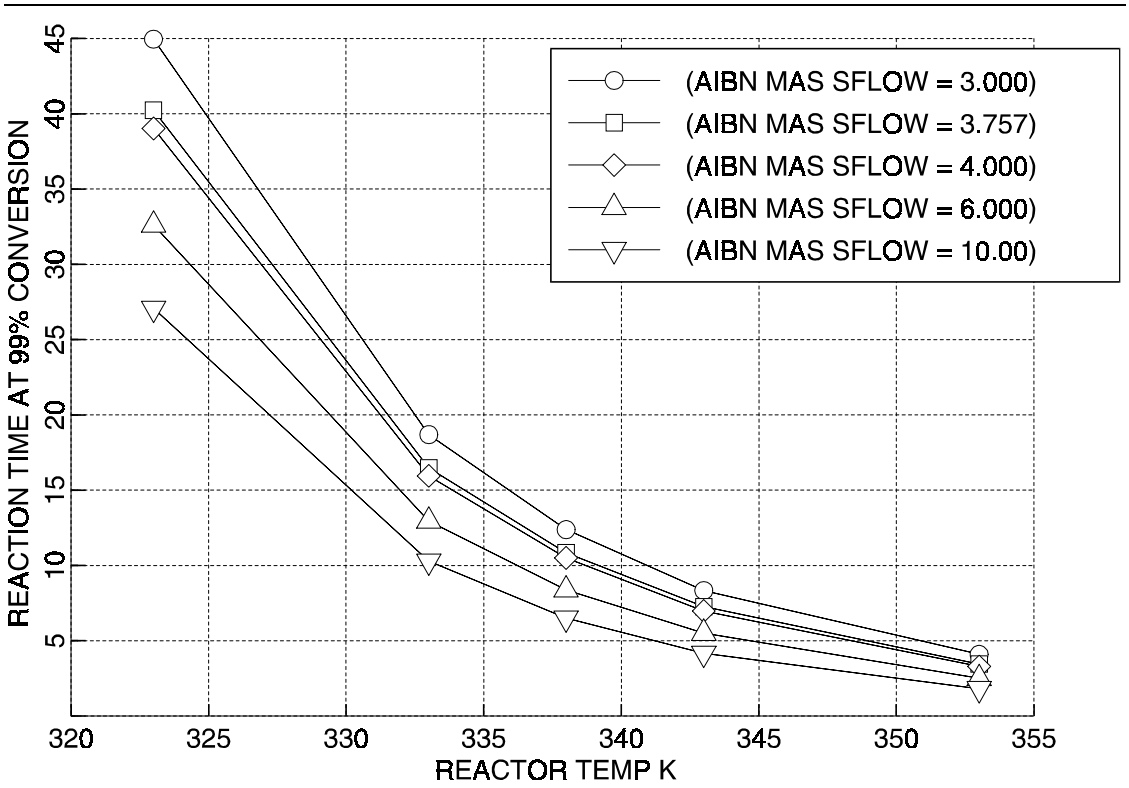


Figure 7.5 *Reaction Time at 99% Conversion vs. Temperature*

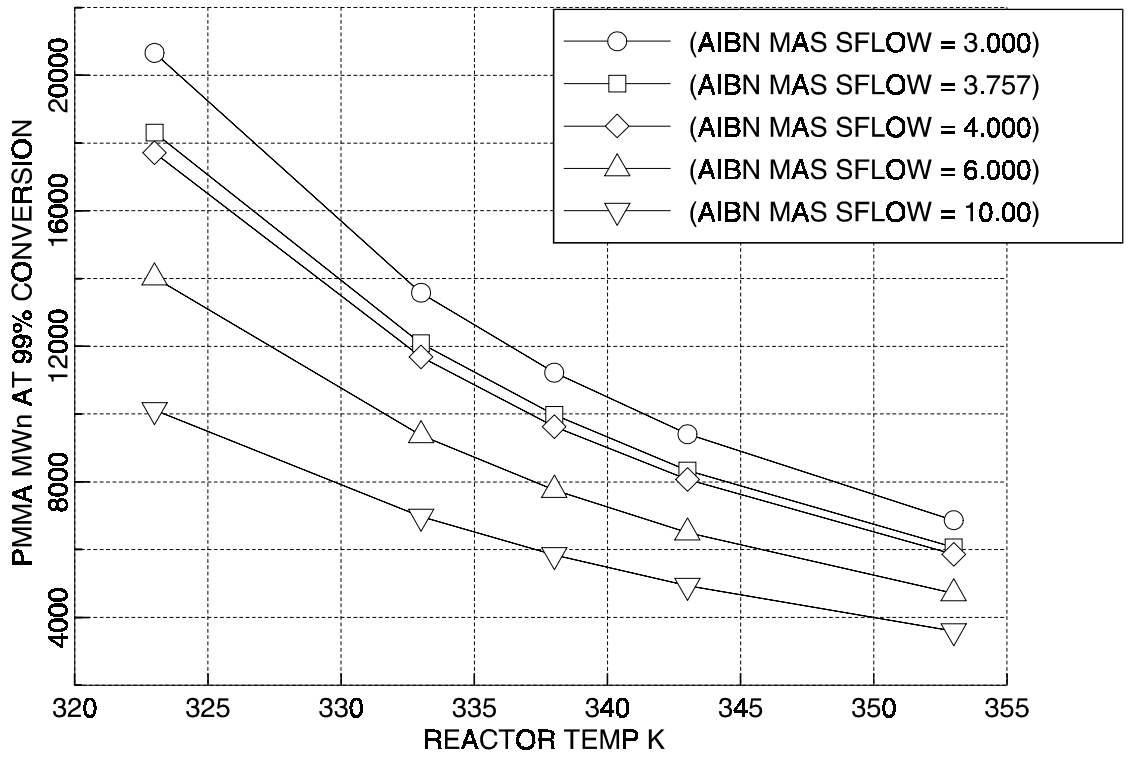


Figure 7.6 *MWn at 99% Conversion vs. Temperature*

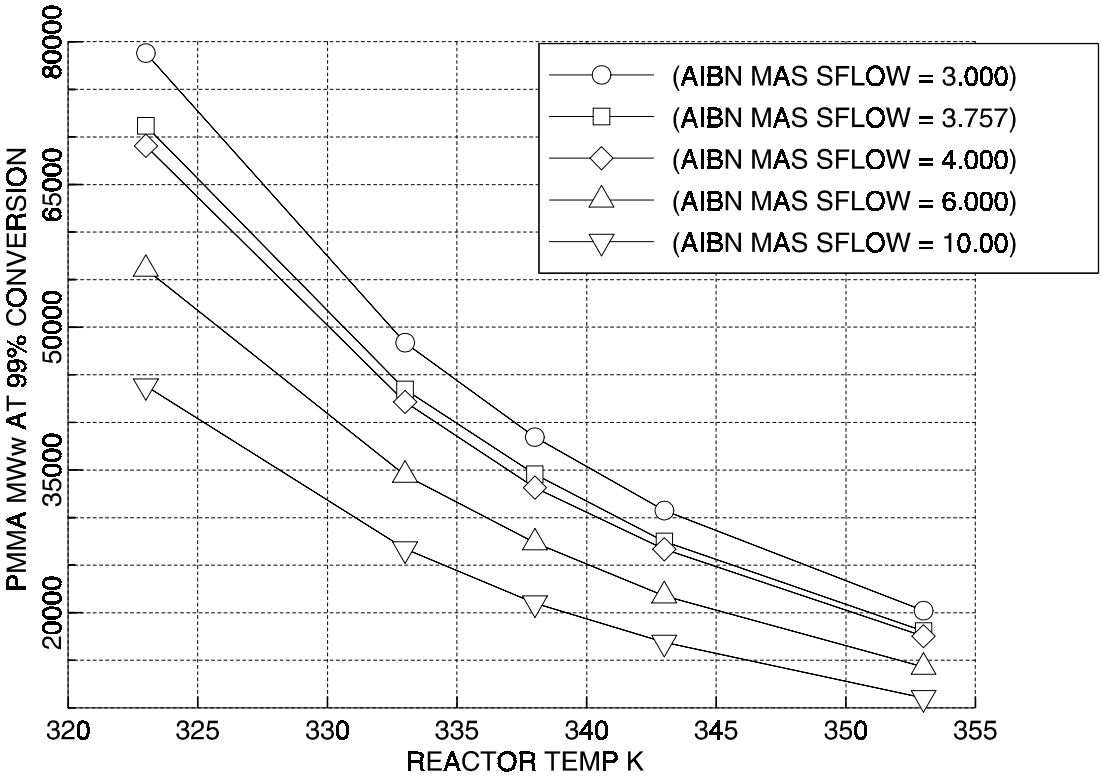


Figure 7.7 *MWw at 99% Conversion vs. Temperature*

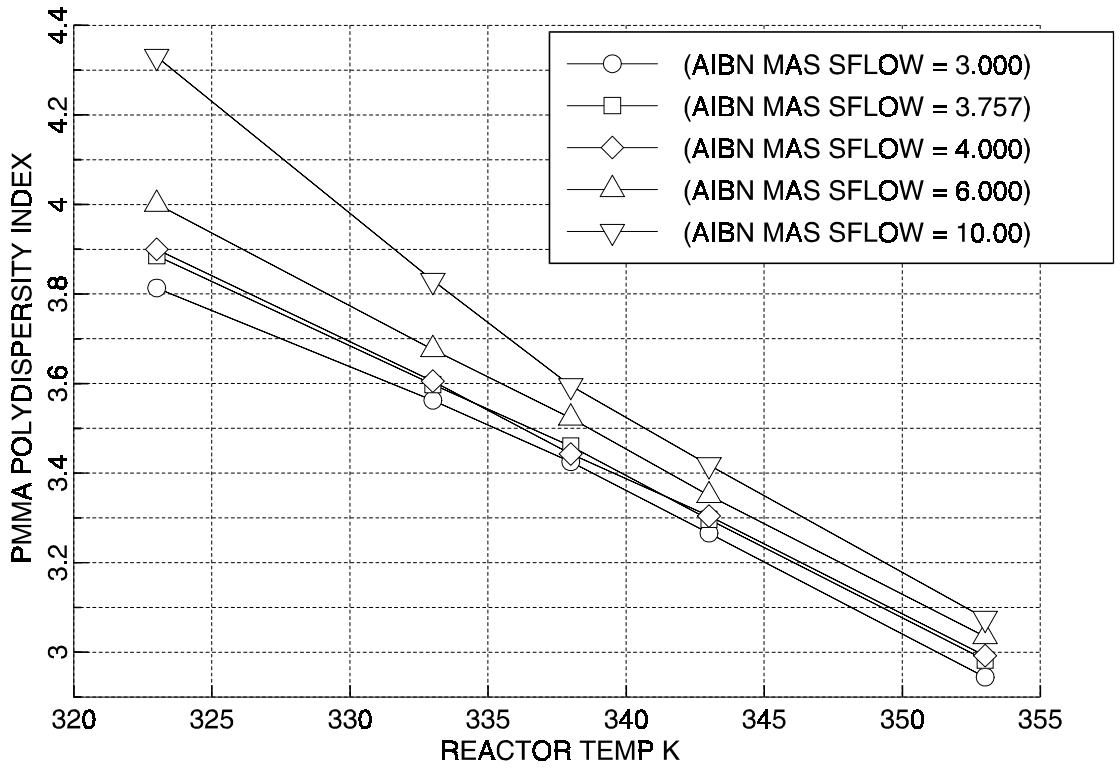


Figure 7.8 *PMMA Polydispersity Index*

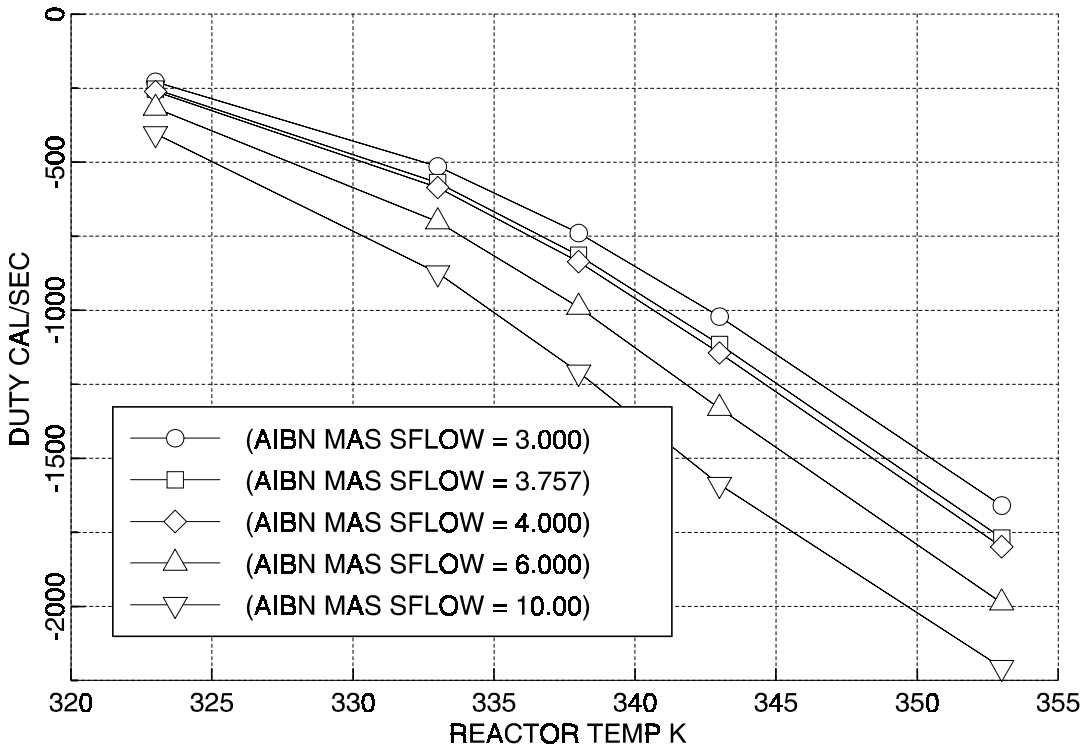


Figure 7.9 *Reactor Heat Duty*

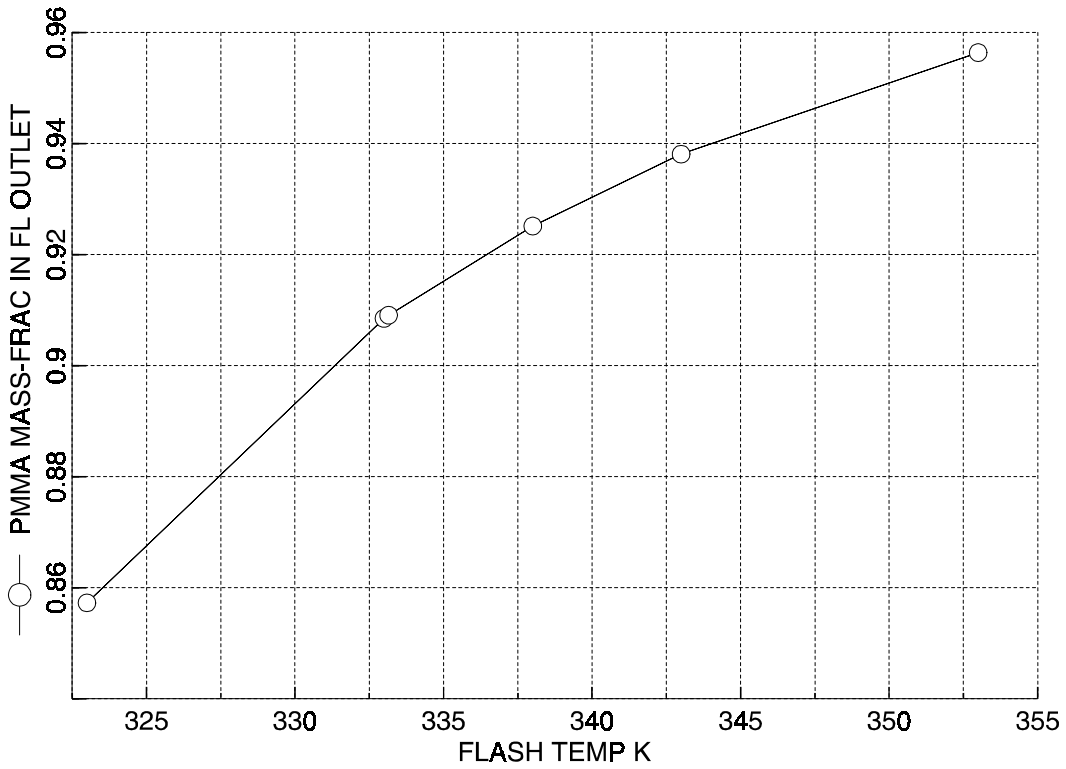


Figure 7.10 *PMMA Percent in Solid Outlet vs. Flash Temperature*

REFERENCES

Ellis, M. F., T. W. X. Taylor, V. Gonzalez, and K. F. Jensen, "Estimation of the Molecular Weight Distribution in Batch Polymerization", *AIChE J*., **34**, 1341 (1988).

Ellis, M. F, "Online Control and Estimation of the Molecular Weight Distribution in a Batch Polymerization Reactor", PhD Thesis, Dept. Of Chem. Engr., Univ. Of Minn. (1990).

Grulke, E. A., Polymer Process Engineering, Prentice Hall, New Jersey (1994).

Tulig, T. J., and M. Tirrell, "Toward a Molecular Theory of the Trommsdorff Effect", *Macromolecules*, **14**, 1501 (1981).

8 POLYSTYRENE

WITH STYRENE MONOMER DISTILLATION

SUMMARY

The polystyrene with styrene monomer distillation model illustrates the use of Polymers Plus to model and predict the extent of polymer formation during styrene distillation. The model examines the optimum level of inhibitor to minimize polymer formation.

ABOUT THIS PROCESS

Product from a styrene plant consists of 60% styrene, 40% ethyl benzene and small amounts of toluene and benzene. Styrene is purified in a series of distillation columns. During distillation styrene polymerization occurs and the extent of polymerization depends on the time and temperature. To reduce polymer formation inhibitor is commonly used in the feed. The amount of inhibitor needs to be optimized since too little will produce more polymer waste and too high concentration of inhibitor will be expensive. The purpose of this example is to find an optimum level of inhibitor needed to minimize polymer formation and to maximize the process profitability.

PROCESS DEFINITION

The key simulation inputs for the problem definition are described below.

As shown in the Figure 8.1, the flowsheet consists of three RadFrac block, each one followed by a CSTR, a Flash and RStoic block.

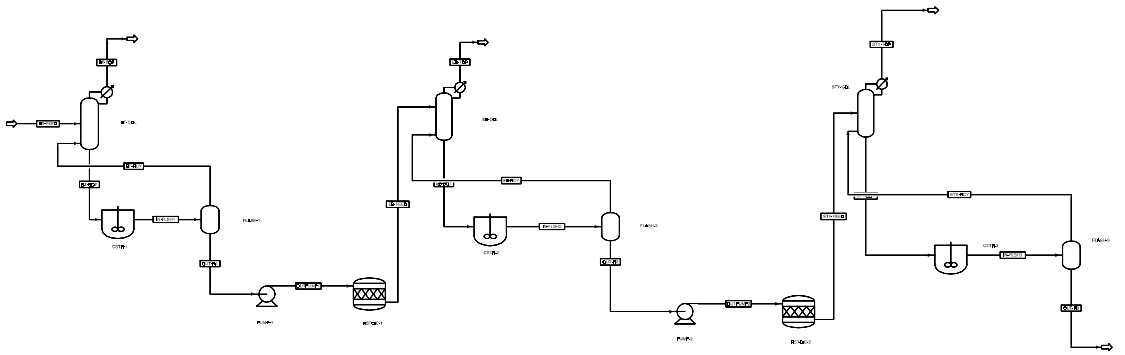


Figure 8.1 *Polystyrene Monomer Distillation Process Flowsheet*

There are three RadFrac blocks in the flowsheet. The purpose of the first column is to separate benzene and toluene from the feed. The purpose of the second column is to recover the ethyl benzene in the overhead product, and the third column is to separate the polymer from the styrene monomer and recover the monomer in the overhead product.

Reboiler of each column is modeled as a single CSTR where the polymerization take place.

The purpose of the RStoic block is to convert the polymer produced in the CSTR into a Dummy polymer since RadFrac block doesn't handle polymer attributes.

Process Conditions

The process conditions are listed in Table 8.1.

Table 8.1 Process Conditions

Component	Name	Databank	Description
Styrene	STY	PURECOMP	Monomer
Etylbenzene	EB	PURECOMP	Chain transfer agent
Benzene	BEN	PURECOMP	Solvent
Toluene	TOL	PURECOMP	Solvent
Inhibitor	INHIBIT	PURECOMP	Inhibitor
Coinitiator	CINI	--	Coinitiator
PS	PS	POLYMER	Polymer
	STY-SEG	SEGMENT	Styrene segment
	PS-DUMMY	PURECOMP	Dummy polymer
Feed Stream			
Temperature	25 °C		
Pressure	4.5 Bar		
Mass Flow	18000 Kg/hr		
Mass fraction of styrene	0.63		
Mass fraction of ethyl benzene	0.34		
Mass fraction of toluene	0.007		
Mass fraction of benzene	0.016		
Mass fraction of inhibitor	0		
Operating Conditions			
Block	**Temp (C)**	**Pres(Bar) Top/Bottom**	**Specifications**
BT-COL		0.27 / 0.4	21 stages + condenser RR = 0.85 Feed - stage 3
CSTR-1	109	0.4	50 m^3 Residence time = 1 hr
EB-COL		0.05 / 0.43	19 stages + condenser RR = 15 Feed - stage 5
CSRT-2	113	0.43	50 m^3 Residence time = 1 hr
STY-COL		0.05 / 0.14	19 stages + condenser RR = 2.7 Feed - stage 2
CSRT-3	100	0.14	50 m^3 Residence time = 1

All the Flash and RStoic blocks are operated at pressure drop zero and duty zero.

Polymers and Segments

Polystyrene is a homopolymer and the styrene segment is the only repeat unit. The set of component attributes required for free-radical polymerization is used for PS.

Physical Property Models and Data

The Polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method. The thermophysical properties (density, heat capacity, etc.) of styrene, ethyl benzene, benzene, toluene and inhibitor are obtained from the Aspen Plus Pure Component Databank. Note that inhibitors are given the properties of styrene with the exception of molecular weight. The polymer thermophysical properties are calculated using the Van Krevelen group contribution method.

The Non-Random Two Liquid activity coefficient model (NRTL) is used as the physical property method inside the RadFrac blocks.

Reactors / Kinetics

The specific reactions included from the built-in kinetics are shown below:

Description	Reaction
Thermal initiation	3M → R*
Chain initiation	R* + M → P1
Propagation	Pn + M → Pn+1
Chain transfer to monomer	Pn + M → Dn + P1
Chain thansfer to EB	Pn + EB → Dn + P1
Termination by combination	Pn + Pm → Dn+m
Termination by inhibition	Pn + X → Dn

The induced initiation reaction is configured for thermal initiation by setting third-order thermal initiation with respect to monomer. A coinitiator, which is required for the induced initiation reaction, is included in the list of components, but its feed rate is set to zero so that it will not influence the rate for the thermal initation reaction.

Inhibitor

Common inhibitors used in this process are nitrobenzene, dinitro-o-bencene, dinitro-m-bencene, dinitro-p-bencene, 4,6 dinitro-o-cresol, etc. In this example 4,6 dinitro-o-cresol is used as inhibitor. (Mw = 198.135)

Process Studies

Input summary is given in Figure 8.2.

Figure 8.2 Input Summary

```
TITLE 'Styrene Distillation '

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=MMkcal MOLE-CONC='mol/l'  &
        PDROP=bar

DEF-STREAMS CONVEN ALL

DESCRIPTION "
        Polystyrene is formed in the reboiler during the distillation
        of styrene. This example shows how to optimize the amount of inhibitor
        required to supress the formation of polystyrene. "

DATABANKS POLYMER  / SEGMENT  / PURE93  / NOASPENPCD

PROP-SOURCES POLYMER  / SEGMENT  / PURE93

COMPONENTS
    STY C8H8 STY /
    PS PS-1 PS /
    STY-SEG C8H8-R STY-SEG /
    EB C8H10-4 EB /
    BEN C6H6 BEN /
    TOL C7H8 TOL /
    PS-DUMMY PS-1 PS-DUMMY /
    PSDUMMY PS-1 PSDUMMY /
    INHIBIT C8H8 INHIBIT /
    CINI C8H8 CINI

FLOWSHEET
    BLOCK FLASH-1 IN=IN-FLSH1 OUT=BT-RCY OUT-R1
    BLOCK BT-COL IN=BT-FEED BT-RCY OUT=BT-TOP BT-BOT
    BLOCK CSTR-1 IN=BT-BOT OUT=IN-FLSH1
    BLOCK EB-COL IN=EB-RCY EB-FEED OUT=EB-TOP EB-BOT
    BLOCK CSTR-2 IN=EB-BOT OUT=IN-FLSH2
    BLOCK FLASH-2 IN=IN-FLSH2 OUT=EB-RCY OUT-R2
```

Figure 8.2 Input Summary (cont.)

```
    BLOCK PUMP-1 IN=OUT-R1 OUT=OUTPUMP1
    BLOCK RSTOIC-1 IN=OUTPUMP1 OUT=EB-FEED
    BLOCK PUMP-2 IN=OUT-R2 OUT=OUTPUMP2
    BLOCK RSTOIC-2 IN=OUTPUMP2 OUT=STY-FEED
    BLOCK STY-COL IN=STY-FEED STY-RCY OUT=STY-TOP STY-BOT
    BLOCK CSTR-3 IN=STY-BOT OUT=IN-FLSH3
    BLOCK FLASH-3 IN=IN-FLSH3 OUT=STY-RCY OUT-R3

PROPERTIES POLYNRTL
    PROPERTIES NRTL

USER-PROPS GMRENA 1 2 1 / GMRENB 1 2 1 / GMRENC 1 2 1  &
        / GMREND 1 2 1

PROP-DATA MW
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=MMkcal MOLE-CONC='mol/l'  &
        PDROP=bar
    PROP-LIST MW
    PVAL INHIBIT 198.1350

PROP-DATA U-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=MMkcal MOLE-CONC='mol/l'  &
        PDROP=bar
    PROP-LIST DHFORM
    PVAL PS-DUMMY 0.0
    PVAL PSDUMMY 0.0

PROP-DATA PLXANT-1
    IN-UNITS SI PRESSURE=bar TEMPERATURE=C PDROP='N/sqm'
    PROP-LIST PLXANT
    PVAL INHIBIT -30.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

POLYMERS
    SEGMENTS STY-SEG REPEAT
    POLYMERS PS
    ATTRIBUTES PS SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM FMOM  &
        SMOM LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW LEFRAC  &
        LPFRAC

STREAM BT-FEED
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=bar TEMPERATURE=C DELTA-T=C  &
        PDROP-PER-HT='mbar/m' PDROP=bar
    SUBSTREAM MIXED TEMP=25.0 PRES=4.50 MASS-FLOW=18000.0
    MASS-FRAC STY .630 / EB .340 / BEN .0160 / TOL .0070  &
        / INHIBIT 0.0
```

Figure 8.2 Input Summary (cont.)

```
STREAM BT-RCY
    IN-UNITS MET MASS-FLOW='kg/sec' MOLE-FLOW='kmol/sec'  &
        VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        TIME=sec VOLUME=cum DELTA-T=C HEAD=meter  &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum'  &
        MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal  &
        MOLE-CONC='mol/l' PDROP=bar
    SUBSTREAM MIXED TEMP=109.0 PRES=.40 MASS-FLOW=.021505555
    MASS-FRAC STY .5650 / EB .3970 / BEN .0190 / TOL  &
        .0180

STREAM EB-RCY
    SUBSTREAM MIXED PRES=.450 VFRAC=1.0 MASS-FLOW=49696.0
    MASS-FRAC STY .8420 / EB .1580

STREAM STY-RCY
    SUBSTREAM MIXED PRES=.40 VFRAC=1.0 MOLE-FLOW=35999.9997
    MASS-FRAC STY .9090 / EB .090

BLOCK FLASH-1 FLASH2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=bar TEMPERATURE=C DELTA-T=C  &
        PDROP-PER-HT='mbar/m' PDROP=bar
    PARAM PRES=0.0 DUTY=0.0

BLOCK FLASH-2 FLASH2
    PARAM PRES=0.0 DUTY=0.0

BLOCK FLASH-3 FLASH2
    PARAM PRES=0.0 DUTY=0.0

BLOCK BT-COL RADFRAC
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=bar TEMPERATURE=C DELTA-T=C  &
        PDROP-PER-HT='mbar/m' PDROP=bar
    PARAM NSTAGE=22 ALGORITHM=STANDARD ABSORBER=NO
    COL-CONFIG REBOILER=NONE CONDENSER=PARTIAL-V
    DIAGNOSTICS TERM=4
    FEEDS BT-FEED 3 / BT-RCY 23
    PRODUCTS BT-TOP 1 V / BT-BOT 22 L
    P-SPEC 1 .270 / 22 .40
    COL-SPECS MOLE-RR=.850
    T-EST 1 43.0 / 2 57.0 / 22 113.0
    PROPERTIES NRTL

BLOCK EB-COL RADFRAC
    PARAM NSTAGE=20
    COL-CONFIG REBOILER=NONE CONDENSER=PARTIAL-V
    FEEDS EB-RCY 21 / EB-FEED 5
    PRODUCTS EB-TOP 1 V / EB-BOT 20 L
    P-SPEC 2 .050 / 20 .430
    COL-SPECS MOLE-RR=15.0
    PROPERTIES NRTL
```

Figure 8.2 Input Summary (cont.)

```
BLOCK STY-COL RADFRAC
    PARAM NSTAGE=20
    COL-CONFIG REBOILER=NONE CONDENSER=PARTIAL-V
    FEEDS STY-FEED 2 / STY-RCY 21
    PRODUCTS STY-TOP 1 V / STY-BOT 20 L
    P-SPEC 1 .050 / 20 .140
    COL-SPECS MOLE-RR=2.70
    PROPERTIES NRTL

BLOCK RSTOIC-1 RSTOIC
    PARAM PRES=0.0 DUTY=0.0
    STOIC 1 MIXED PS -1.0 / PS-DUMMY 1.0
    CONV 1 MIXED PS 1.0

BLOCK RSTOIC-2 RSTOIC
    PARAM PRES=0.0 DUTY=0.0
    STOIC 1 MIXED PS -1.0 / PSDUMMY 1.0
    CONV 1 MIXED PS 1.0

BLOCK CSTR-1 RCSTR
    PARAM VOL=50.0 TEMP=109.0 PRES=.40 NPHASE=2 PHASE=L  &
        PH-RES-TIME=1.0
    REACTIONS RXN-IDS=R-1

BLOCK CSTR-2 RCSTR
    PARAM VOL=50.0 TEMP=113.0 PRES=.430 NPHASE=2 PHASE=L  &
        PH-RES-TIME=1.0
    REACTIONS RXN-IDS=R-1

BLOCK CSTR-3 RCSTR
    PARAM VOL=50.0 TEMP=100.0 PRES=.140 NPHASE=2 PHASE=L  &
        MB-MAXIT=100 ALGORITHM=INTEGRATOR MAX-NSTEP=100  &
        PH-RES-TIME=1.0
    REACTIONS RXN-IDS=R-1

BLOCK PUMP-1 PUMP
    PARAM PRES=4.130

BLOCK PUMP-2 PUMP
    PARAM PRES=6.20

SENSITIVITY S-1
    PARAM BASE-CASE=FIRST
    DEFINE INHI MASS-FRAC STREAM=BT-FEED SUBSTREAM=MIXED  &
        COMPONENT=INHIBIT
    DEFINE R1PS MASS-FLOW STREAM=OUT-R1 SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE R2PS MASS-FLOW STREAM=OUT-R2 SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE R3PS MASS-FLOW STREAM=OUT-R3 SUBSTREAM=MIXED  &
        COMPONENT=PS
    DEFINE STY MASS-FLOW STREAM=BT-FEED SUBSTREAM=MIXED  &
        COMPONENT=STY
    DEFINE FEEDI MASS-FLOW STREAM=BT-FEED SUBSTREAM=MIXED  &
        COMPONENT=INHIBIT
```

Figure 8.2 Input Summary (cont.)

```
F
F               PS1 = R1PS / STY
F               PS2 = R2PS / STY
F               PS3 = R3PS / STY
F               PSTOT =(R1PS+R2PS+R3PS)/STY
F               PS0 = 731 / STY
F
F               PPMIN = INHI * 1.0E6
F
F               P = PS0 - PSTOT
F
F               PROFIT = P - 100 * FEEDI/STY
    TABULATE 1 "PPMIN" COL-LABEL="INHIBIT" "PPM"
    TABULATE 2 "PS1" COL-LABEL="PS1" "POLYMER" "CSTR-1"
    TABULATE 3 "PS2" COL-LABEL="PS2" "POLYMER" "CSTR-2"
    TABULATE 4 "PS3" COL-LABEL="PS3" "POLYMER" "CSTR-3"
    TABULATE 5 "PSTOT" COL-LABEL="PSTOT" "TOTAL" "POLYMER"
    TABULATE 6 "PROFIT" COL-LABEL="PROFIT"
    VARY MASS-FLOW STREAM=BT-FEED SUBSTREAM=MIXED  &
        COMPONENT=INHIBIT
    RANGE LIST=0.0 .60 .90 1.10 1.30 1.540 1.80 2.0 2.20  &
        3.0 3.60

CONV-OPTIONS
    PARAM TEAR-METHOD=BROYDEN CHECKSEQ=NO

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP PARAMS

REACTIONS R-1 FREE-RAD
    IN-UNITS SI
    DESCRIPTION "FREE RADICAL KINETIC SCHEME"
    PARAM QSSA=YES
    SPECIES COINITIATOR=CINI MONOMER=STY CHAINTAG=EB SOLVENT=TOL  &
        BEN INHIBITOR=INHIBIT POLYMER=PS
    MON-RSEG STY STY-SEG
    INIT-SP STY CINI 438000.0 1.1480E+08
    CHAIN-INI STY 1.0510E+07 2.9570E+07
    PROPAGATION STY STY 1.0510E+07 2.9570E+07
    CHAT-MON STY STY 3310000.0 5.3020E+07
    CHAT-AGENT STY EB 1051.0 2.9590E+07
    TERM-COMB STY STY 1.2550E+09 7017000.0
    INHIBITION STY INHIBIT 1.0500E+09 2.9570E+07
    INIT-SP-EFF STY COEFFA=0. COEFFB=3. COEFFC=0.
;
```

SELECTED SIMULATION RESULTS

A sensitivity study is carried out by varying the inhibitor feed mass fraction in the feed stream. The purpose of this sensitivity is to find an optimum level of inhibitor needed to minimize polymer formation and to maximize the process profitability.

Process profitability is calculated as follows with the assumption that inhibitor is 100 times more expensive than styrene monomer:

PROFIT = PS0 - PSTOT - 100 * FEEDI / STY

Where:

PS0 = Mass flow of polymer produced without inhibitor in the feed / Mass flow of styrene in the feed

PSTOT = Mass flow of polymer produced with inhibitor in the feed / Mass flow of styrene in the feed

FEEDI = Mass flow of inhibitor in the feed

STY = Mass flow of styrene in the feed

Result of the sensitivity studies are shown in Table 8.2, Figure 8.3 and Figure 8.4. Figure 8.5 lists the base case results without inhibitor.

Table 8.2 Effect of Inhibitor Feed Mass Fraction on the Polymer Formation and Process Profitability

	VARY 1 BT-FEED MIXED INHIBIT MASSFLOW KG/HR	INHIBIT PPM	PS1 POLYMER CSTR-1	PS2 POLYMER CSTR-2	PS3 POLYMER CSTR-3	PSTOT TOTAL POLYMER	PROFIT
1	0.0	0.0	.0287989	.0346101	5.91407E-4	.0640005	1.03317E-5
2	.6000000	33.33222	3.92755E-3	.0137747	7.81626E-7	.0177030	.0410537
3	.9000000	49.99750	2.37145E-3	6.27258E-3	1.04793E-7	8.64414E-3	.0474857
4	1.100000	61.10738	1.87434E-3	4.46425E-3	5.29183E-8	6.33864E-3	.0480399
5	1.300000	72.21700	1.55031E-3	3.45389E-3	3.40637E-8	5.00424E-3	.0476230
6	1.540000	85.54823	1.28486E-3	2.71437E-3	2.37673E-8	3.99925E-3	.0465264
7	1.800000	99.99000	1.08459E-3	2.20499E-3	1.80608E-8	3.28960E-3	.0449593
8	2.000000	111.0988	9.69132E-4	1.92762E-3	1.53588E-8	2.89676E-3	.0436008
9	2.200000	122.2073	8.76254E-4	1.71301E-3	1.34416E-8	2.58928E-3	.0421570
10	3.000000	166.6389	6.35590E-4	1.18955E-3	9.34595E-9	1.82515E-3	.0359158
11	3.600000	199.9600	5.28641E-4	9.70951E-4	7.88327E-9	1.49960E-3	.0309874

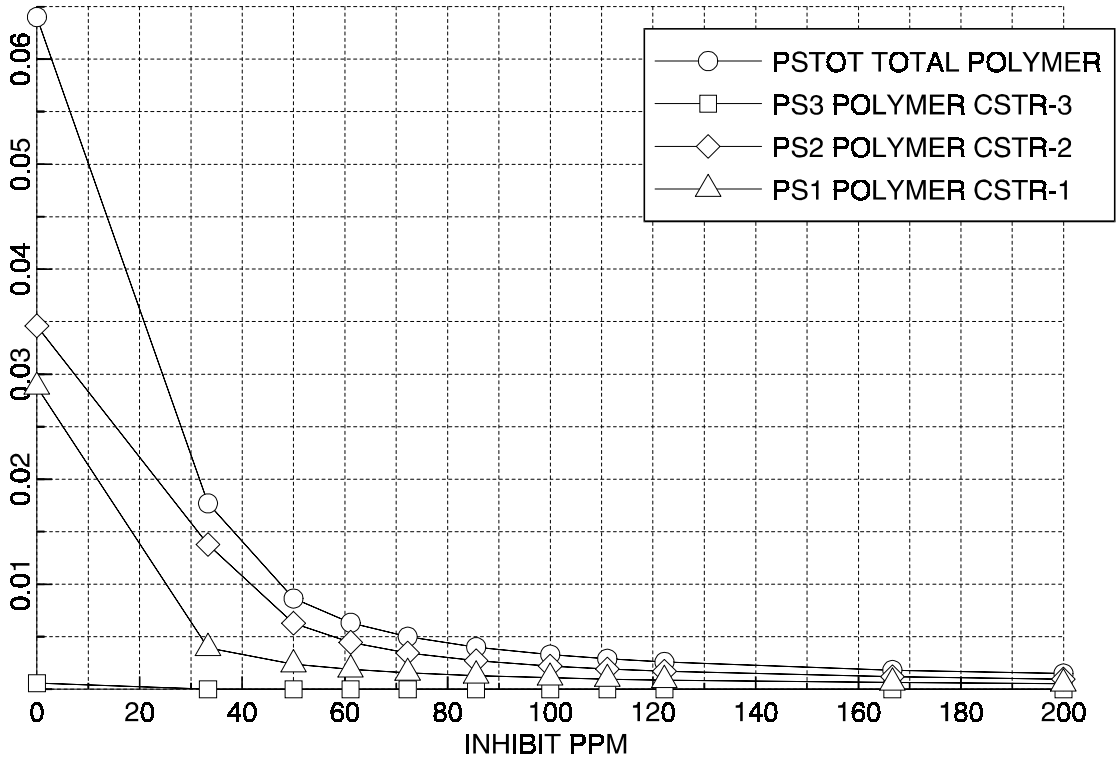


Figure 8.3 *Effect of the Inhibitor Feed Mass Fraction on Polymer Production*

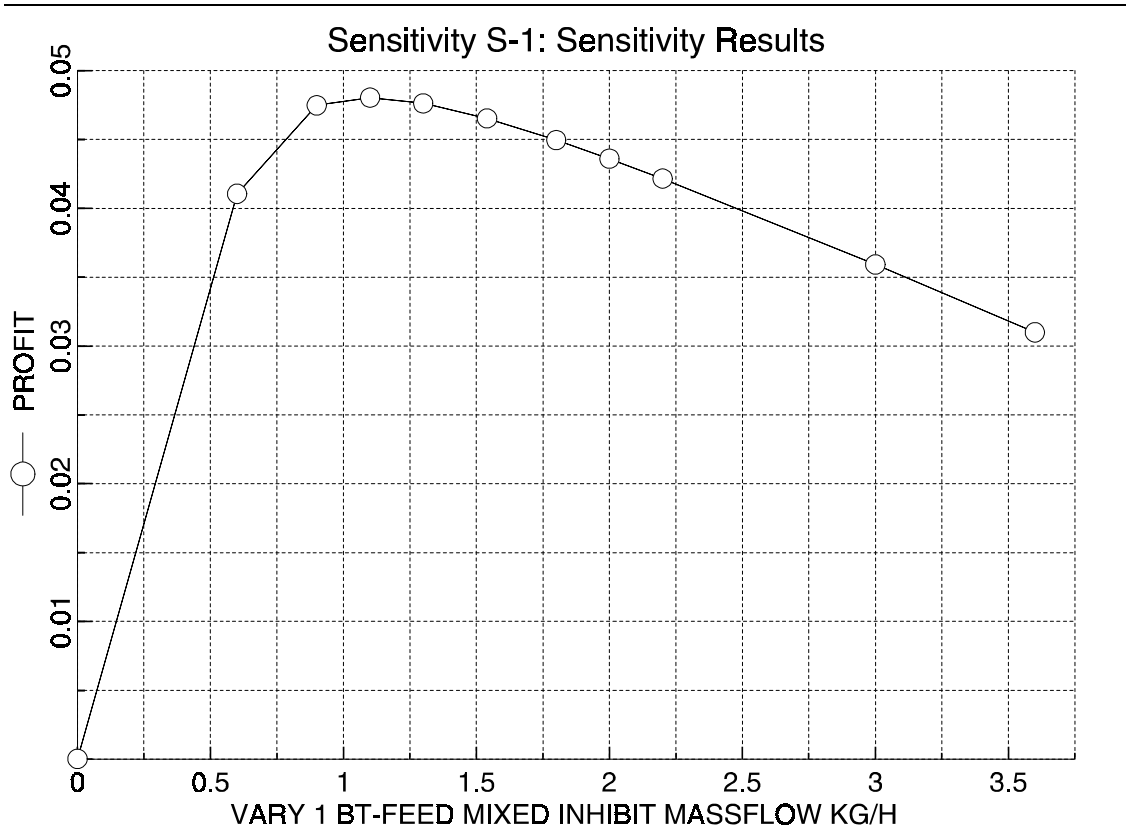


Figure 8.4 *Effect of the Inhibitor Feed Mass Fraction on Process Profitability*

Figure 8.5 Base Case Results (without Inhibitor)

Display STREAMS		BT-FEED	BT-TOP	BT-BOT	EB-TOP	EB-BOT
Units:	From		BT-COL	BT-COL	EB-COL	EB-COL
Format: FULL	To	BT-COL		CSTR-1		CSTR-2
	Phas	LIQUID	VAPOR	LIQUID	VAPOR	LIQUID
Substream: MIXED						
Mass Flow [KG/HR]						
STY		11419.94	23.67650	15991.42	448.0206	40001.33
PS		0.0	0.0	0.0	0.0	0.0
STY-SEG		0.0	0.0	0.0	0.0	0.0
EB		6163.142	29.85802	9384.942	1919.846	18859.06
BEN		290.0302	224.6098	230.1220	65.41839	4.92818E-6
TOL		126.8882	4.381624	257.2611	122.4934	7.75698E-3
PS-DUMMY		0.0	0.0	0.0	1.0000E-35	6.037053
PSDUMMY		0.0	0.0	0.0	0.0	0.0
INHIBIT		3.600000	1.0088E-35	3.600000	1.0079E-35	3.426566
CINI		0.0	0.0	0.0	0.0	0.0
Mass Frac						
STY		.6343142	.0838029	.6182087	.1752972	.6794873
PS		0.0	0.0	0.0	0.0	0.0
STY-SEG		0.0	0.0	0.0	0.0	0.0
EB		.3423283	.1056824	.3628105	.7511786	.3203517
BEN		.0161095	.7950059	8.89624E-3	.0255962	8.3713E-11
TOL		7.04794E-3	.0155087	9.94540E-3	.0479280	1.31765E-7
PS-DUMMY		0.0	0.0	0.0	1.0000E-35	1.02549E-4
PSDUMMY		0.0	0.0	0.0	0.0	0.0
INHIBIT		1.99960E-4	3.5708E-35	1.39172E-4	3.9435E-35	5.82058E-5
CINI		0.0	0.0	0.0	0.0	0.0
Total Flow [KG/HR]		18003.60	282.5259	25867.34	2555.778	58869.86
Temperature [C]		25.00000	62.28629	107.6298	51.66729	112.5972
Pressure [BAR]		4.500000	.2700000	.4000000	.0500000	.4300000

Display STREAMS		STY-TOP	STY-BOT
Units:	From	STY-COL	STY-COL
Format: FULL	To		CSTR-3
	Phas	VAPOR	LIQUID
Substream: MIXED			
Mass Flow [KG/HR]			
STY		10908.77	50280.95
PS		0.0	0.0
STY-SEG		0.0	0.0
EB		4213.336	26.87380
BEN		2.88599E-7	1.8536E-25
TOL		9.54756E-4	1.4825E-13
PS-DUMMY		2.2330E-35	6.037053
PSDUMMY		4.1013E-35	11.08821
INHIBIT		5.0867E-24	3.123351
CINI		0.0	0.0
Mass Frac			
STY		.7213790	.9990637
PS		0.0	0.0
STY-SEG		0.0	0.0
EB		.2786210	5.33973E-4
BEN		1.9085E-11	3.6830E-30
TOL		6.31364E-8	2.9456E-18
PS-DUMMY		1.4766E-35	1.19954E-4
PSDUMMY		2.7121E-35	2.20319E-4
INHIBIT		3.3637E-28	6.20598E-5
CINI		0.0	0.0
Total Flow [KG/HR]		15122.11	50328.07
Temperature [C]		57.32750	83.47446
Pressure [BAR]		.0500000	.1400000

9 POLYPROPYLENE

GAS PHASE POLYMERIZATION PROCESSES

SUMMARY

The polypropylene gas-phase polymerization process model illustrates the use of Polymers Plus to model a gas-phase UNIPOL process for propylene homopolymerization using a four site Ziegler-Natta kinetic model. The atactic content, melt flow ratio and molecular weight averages are some of the polymer product properties and attributes predicted by the simulation.

ABOUT THIS PROCESS

There are three types of processes commonly employed for the manufacture of isotactic polypropylene (PP) homo- and co-polymers. These include liquid slurry processes, bulk or liquid pool processes, and gas-phase processes. Table 9.1 provides basic information on these processes and lists some of the companies that have commercialized the process technology. All of these processes use a Ziegler-Natta catalyst (usually $TiCl_4$) in either a supported or non-supported form together with an alkylaluminum or aluminum chlorides (e.g. triethlyaluminum) cocatalyst.

Liquid slurry processes use an inert hydrocarbon diluent as the slurry medium or polymer suspending agent. This process is still the most widely used process for PP manufacture. Continuous stirred tank reactors are usually used and several reactor may be used in series or parallel arrangements. Typical reactor operating conditions and residence times are listed in Table 9.1.

Table 9.1 Summary of Processes for Propylene Polymerization

Process	Reactor	Diluent / Solvent	Catalyst	Tacticity (%)	Temp. (°C)	Press. (atm)	Residence Time (hr)	Company
Bulk (Liquid Pool)	loop reactor	Liquid monomer	supported Ti Catalyst	up tp 99%	60-80	30-40	1-2	Himont Mitsui
	CSTR	Liquid monomer	unsupported or supported Ti catalyst	up to 98%	60-75	30-40	2.0	Dart El Paso Montedison Sumitomo
Diluent Slurry	CSTR	n-hexane, n-heptane	unsupported or supported Ti catalyst	up to 98%	60-80	15-20	3-4	Amoco Montedison
Gas	fluidized bed	N2	supported Ti catalyst	up to 98%	60-80	20	3-5	Sumitomo Union Carbide
	vertical stirred bed	---	unsupported or supported Ti catalyst	up to 98%	70-90	20	4	BASF ICI USI
	horizontal compartmented stirred bed	---	unsupported or supported Ti catalyst	up to 98%	70-90	20	4	Amoco

Bulk or liquid pool processes are a special case of the slurry processes. They use liquid propylene instead of an inert diluent as the slurry medium to suspend the polymer. The increased monomer concentration leads to higher polymerization rates in liquid pool processes relative to slurry processes. Hence, shorter reactor residence times may be employed. Several reactor types, including stirred autoclaves with evaporative cooling and loop reactors, are used to attain good heat transfer rates.

In gas-phase processes, gaseous propylene is contacted with solid catalyst/polymer powder in fluidized bed or mechanically stirred bed reactors. The reactor temperature is usually controlled by evaporative cooling of liquid propylene. The unreacted monomer is removed from the reactor headspace, condensed or cooled and recirculated to the reactor.

Polymers Plus can be used with Aspen Plus for the simulation of steady-state operation of any of the PP processes described above. Polymers Plus can be used with Aspen Custom Modeler when dynamic simulation or detailed modeling of the flow patterns or heat transfer within the reactor is desired. This example describes a steady-state simulation of a gas-phase UNIPOL flowsheet.

PROCESS DEFINITION

A Polymers Plus model is developed to simulate a PP gas-phase UNIPOL flowsheet. The flowsheet includes the fluidized bed reactor, the gas recycle/cooling loop, discharge and purge units as shown in Figure 9.1.

The fluidized bed reactor is modeled using the CSTR reactor in Aspen Plus with two phases; a gas phase and a polymer phase. The POLYNRTL thermodynamic model is used to relate the gas phase monomer, hydrogen, etc. composition to their concentrations in the polymer phase. The multisite Ziegler-Natta kinetic model is used to describe the polymerization reactions in the polymer phase. The kinetic model calculates the reaction rates for the components and polymer attributes at each site type. User-Property models are used to calculate polymer properties such as melt flow index (MFI), isotactic index (or atactic fraction) from the polymer attributes.

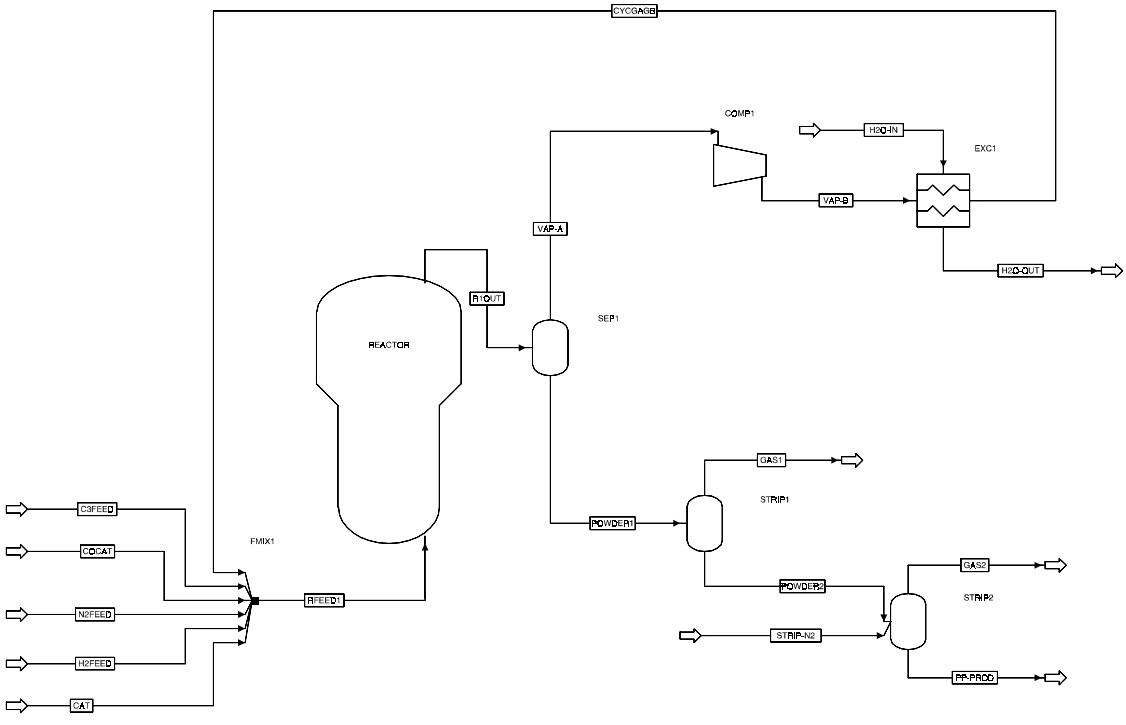


Figure 9.1 *Unipol Process Flowsheet for Propylene Polymerization*

Process Conditions

The process conditions are as listed in Table 9.2.

Table 9.2 Process Conditions

Components	
Titanium Tetrachloride (CAT)	Catalyst
Triethyl-Aluminium (COCAT)	Co-catalyst
Propylene (C3=)	Monomer
Propane (C3)	Inert
Polypropylene (PP)	Polymer
H2	Chain transfer agent
N2	Inert
Water (H2O)	Cooling water
Propylene Segment (C3-SEG)	Polymer segment
Component	**Flow rate (Kg/Hr)**
Catalyst	3.0
Co-catalyst	10.0
Propylene	17462.0
Propane	162.29
H2	1.38
N2	1.45
Operating Conditions	
Temperature	69 °C
Pressure drop	200 KPa
Total volume	90 m^3
Polymer Phase volume	60 m^3

The reactor feed also includes a large recycle stream with partially condensed propylene and other volatile components.

An Aspen Plus CSTR reactor model is used to represent the fluid-bed reactor. The reactor is considered to have two phases; a vapor phase and a polymer phase.

Physical Property Models and Data

The polymer Non-Random Two liquid activity coefficient model (POLYNRTL) is used as physical property method.

Reactors / Kinetics

The Ziegler-Natta kinetic scheme used in the model includes site activation by co-catalyst, chain initiation, propagation, chain transfer to hydrogen, monomer and co-catalyst, and spontaneous site deactivation. Four site types are used in this example to represent the broad molecular weight distributions that are typically observed for Ziegler-Natta polymers. The actual number of site types necessary to model a given catalyst-polymerization system is determined by deconvolution of the polymer molecular weight distribution curve obtained from a GPC analysis. The rate parameters used in the model are:

Reaction	Site ID	Comp. ID 1	Comp. ID 2	Pre-exp	Activation Energy
ACT-COCAT	1	CAT	COCAT	1.62E6	3.2E7
ACT-COCAT	2	CAT	COCAT	1.62E6	3.2E7
ACT-COCAT	3	CAT	COCAT	1.62E6	3.2E7
ACT-COCAT	4	CAT	COCAT	1.62E6	3.2E7
CHAIN-INI	1	"C3="		1.175E7	3.0E7
CHAIN-INI	2	"C3="		0.264E7	3.0E7
CHAIN-INI	3	"C3="		1.844E7	3.0E7
CHAIN-INI	4	"C3="		0.653E7	3.0E7
PROPAGATION	1	"C3="	"C3="	1.175E7	3.0E7
PROPAGATION	2	"C3="	"C3="	0.264E7	3.0E7
PROPAGATION	3	"C3="	"C3="	1.844E7	3.0E7
PROPAGATION	4	"C3="	"C3="	0.653E7	3.0E7
CHAT-MON	1	"C3="	"C3="	1.02E6	5.2E7
CHAT-MON	2	"C3="	"C3="	1.02E6	5.2E7
CHAT-MON	3	"C3="	"C3="	1.02E6	5.2E7
CHAT-MON	4	"C3="	"C3="	1.02E6	5.2E7
CHAT-COCAT	1	"C3="	COCAT	5.0E6	5.0E7
CHAT-COCAT	2	"C3="	COCAT	5.0E6	5.0E7
CHAT-COCAT	3	"C3="	COCAT	5.0E6	5.0E7
CHAT-COCAT	4	"C3="	COCAT	5.0E6	5.0E7
CHAT-H2	1	"C3="	H2	0.529E9	4.5E7
CHAT-H2	2	"C3="	H2	0.979E9	4.5E7
CHAT-H2	3	"C3="	H2	0.29E8	4.5E7
CHAT-H2	4	"C3="	H2	0.729E9	4.5E7
DEACT-SPON	1			4.214E-4	4.1E6
DEACT-SPON	2			4.214E-4	4.1E6
DEACT-SPON	3			4.214E-4	4.1E6
DEACT-SPON	4			4.214E-4	4.1E6

The units for the frequency factor and activation energy are in SI units.

Figure 9.2 gives a listing of the Aspen Plus input file for this example.

Figure 9.2 Input File

```
TITLE 'Ziegler-Natta Gas-Phase Polymerization of Propylene'

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' TEMPERATURE=C  &
        TIME=hr DELTA-T=C

DEF-STREAMS CONVEN ALL

SYS-OPTIONS TRACE=YES

RUN-CONTROL MAX-TIME=10000.0

DESCRIPTION "Ziegler-Natta gas-Phase polymerization of propylene "

DATABANKS PURE93  / POLYMER  / SEGMENT  / NOASPENPCD

PROP-SOURCES PURE93  / POLYMER  / SEGMENT

COMPONENTS
    TICL4 TICL4 TICL4 /
    TEA C6H15AL TEA /
    C3H6 C3H6-2 C3H6 /
    C3H8 C3H8 C3H8 /
    PP PP PP /
    H2 H2 H2 /
    N2 N2 N2 /
    H2O H2O H2O /
    C3H6-R C3H6-R C3H6-R
;
;     DEFINE FLOWSHEET INFORMATION
;
FLOWSHEET
    BLOCK REACTOR IN=RFEED1 OUT=R1OUT
    BLOCK FMIX1 IN=CAT COCAT H2FEED C3FEED N2FEED CYCGAGB  &
        OUT=RFEED1
    BLOCK SEP1 IN=R1OUT OUT=VAP-A POWDER1
    BLOCK EXC1 IN=H2O-IN VAP-B OUT=H2O-OUT CYCGAGB
    BLOCK COMP1 IN=VAP-A OUT=VAP-B
    BLOCK STRIP1 IN=POWDER1 OUT=GAS1 POWDER2
    BLOCK STRIP2 IN=POWDER2 STRIP-N2 OUT=GAS2 PP-PROD
;
;   THE PROPERTY CALCULATION METHOD (OPTION SET) SPECIFICATION FOLLOWS
;   THE OPTION SET CHOSEN IS A MODIFIED VERSION OF THE ASPEN PLUS
;   NRTL OPTION SET.  THIS OPTION SET ACCOUNTS FOR THE BEHAVIOR OF
;   POLYMERS IN THE COMPONENT SYSTEM.
;
```

Figure 9.2 Input File (cont.)

```
PROPERTIES POLYNRTL

PROP-DATA DHFVK
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    PROP-LIST DHFVK
    PVAL C3H6-R -1.070370E+08

PROP-DATA PLXANT-1
    IN-UNITS SI
    PROP-LIST PLXANT
    PVAL TICL4 -50.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0
    PVAL TEA -50.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL C3H6-R C3H6 0.0 1360.0 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL C3H6 C3H6-R 0.0 0.0 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL C3H6-R H2 0.0 -3000.0 .30 0.0 0.0 0.0 0.0 1000.0
    BPVAL H2 C3H6-R 0.0 0.0 .30 0.0 0.0 0.0 0.0 1000.0

POLYMERS
    PARAM NSITES=4
    SEGMENTS C3H6-R REPEAT
    CATALYST TICL4 .00009230
    POLYMERS PP
    ATTRIBUTES PP SFRAC SFLOW DPN DPW PDI MWN MWW ZMOM FMOM  &
        SMOM LDPN LZMOM LFMOM LSFLOW LSFRAC LEFLOW LEFRAC  &
        LPFRAC SSFRAC SSFLOW SDPN SDPW SPDI SMWN SMWW SZMOM  &
        SFMOM SSMOM SPFRAC LSDPN LSZMOM LSFMOM LSSFLOW LSSFRAC  &
        LSEFLOW LSEFRAC LSPFRAC ATFLOW ATFRAC SATFLOW SATFRAC
    ATTRIBUTES TICL4 CPSFLOW CPSFRAC CVSFLOW CVSFRAC CDSFLOW  &
        CDSFRAC

STREAM C3FEED
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=3000.0 MASS-FLOW=45000.0
    MASS-FRAC C3H6 .9980 / C3H8 .0020

STREAM CAT
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=3000.0 MASS-FLOW=300.0  &
        NPHASE=1 PHASE=L
    MASS-FRAC TICL4 .010 / C3H6 .9880 / C3H8 .0020
    COMP-ATTR TICL4 CPSFLOW ( 0.0 )
    COMP-ATTR TICL4 CPSFRAC ( 1.0 )
    COMP-ATTR TICL4 CVSFLOW ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CVSFRAC ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CDSFLOW ( 0.0 )
    COMP-ATTR TICL4 CDSFRAC ( 0.0 )
```

Figure 9.2 Input File (cont.)

```
STREAM COCAT
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=3000.0 MASS-FLOW=10.0  &
        NPHASE=1 PHASE=L
    MASS-FRAC TEA 1.0

STREAM CYCGAGB
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=59.0 PRES=3000.0
    MASS-FLOW C3H6 800300.0 / C3H8 15930.0 / H2 3998.70 /  &
        N2 5098.0

STREAM H2FEED
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=3000.0 MASS-FLOW=4.0
    MASS-FRAC H2 1.0

STREAM H2O-IN
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    SUBSTREAM MIXED TEMP=35.0 PRES=3000.0
    MASS-FLOW H2O 847500.0

STREAM N2FEED
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=3000.0 MASS-FLOW=100.0
    MASS-FRAC N2 1.0

STREAM RFEED1
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    SUBSTREAM MIXED TEMP=65.0 PRES=3000.0
    MASS-FLOW TICL4 3.0 / TEA 10.0 / C3H6 817500.0 / C3H8  &
        16100.0 / H2 4000.0 / N2 5100.0
    COMP-ATTR TICL4 CPSFLOW ( 0.0 )
    COMP-ATTR TICL4 CPSFRAC ( 1.0 )
    COMP-ATTR TICL4 CVSFLOW ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CVSFRAC ( 0.0 0.0 0.0 0.0 )
    COMP-ATTR TICL4 CDSFLOW ( 0.0 )
    COMP-ATTR TICL4 CDSFRAC ( 0.0 )

STREAM STRIP-N2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    SUBSTREAM MIXED TEMP=30.0 PRES=300.0 v
    MASS-FLOW N2 500.0
```

Figure 9.2 Input File (cont.)

```
BLOCK FMIX1 MIXER
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa

BLOCK SEP1 FLASH2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    PARAM PRES=0.0 DUTY=0.0

BLOCK STRIP1 FLASH2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    PARAM TEMP=65.0 PRES=500.0

BLOCK STRIP2 FLASH2
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    PARAM TEMP=60.0 PRES=100.0

BLOCK EXC1 MHEATX
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    COLD-SIDE IN=H2O-IN OUT=H2O-OUT TEMP=50.0 FREE-WATER=NO
    HOT-SIDE IN=VAP-B OUT=CYCGAGB FREE-WATER=NO

BLOCK REACTOR RCSTR
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    USER-VECS NREAL=1
    PARAM VOL=90.0 TEMP=69.0 PRES=-200.0 NPHASE=2 PHASE=L  &
        PHASE-VOL=60.0 MB-MAXIT=70 MB-TOL=.00010  &
        ALGORITHM=INTEGRATOR MAX-NSTEP=50
    MASS-FLOW MIXED PP 16000.0
    MASS-FLOW MIXED C3H6 801200.0
    MASS-FLOW MIXED TICL4 3.0
    COMP-ATTR MIXED TICL4 CPSFLOW ( 1.0000E-08 )
    COMP-ATTR MIXED TICL4 CPSFRAC ( .00010 )
    COMP-ATTR MIXED TICL4 CVSFLOW ( 1.0000E-08 1.0000E-07  &
        1.0000E-09 1.0000E-07 )
    COMP-ATTR MIXED TICL4 CVSFRAC ( .00010 .0010 .000010  &
        .00010 )
    COMP-ATTR MIXED TICL4 CDSFLOW ( .00010 )
    COMP-ATTR MIXED TICL4 CDSFRAC ( .50 )
    CONVERGENCE SOLVER=NEWTON
    BLOCK-OPTION TERM-LEVEL=7
    REACTIONS RXN-IDS=ZN-R1

BLOCK COMP1 COMPR
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
    PARAM TYPE=ISENTROPIC DELP=250.0
```

Figure 9.2 Input File (cont.)

```
FORTRAN SETFEED
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        PRESSURE=kPa TEMPERATURE=C TIME=hr DELTA-T=C PDROP=kPa
    DEFINE RC3E MASS-FLOW STREAM=CYCGAGB SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    DEFINE RC3 MASS-FLOW STREAM=CYCGAGB SUBSTREAM=MIXED  &
        COMPONENT=C3H8
    DEFINE RH2 MASS-FLOW STREAM=CYCGAGB SUBSTREAM=MIXED  &
        COMPONENT=H2
    DEFINE RN2 MASS-FLOW STREAM=CYCGAGB SUBSTREAM=MIXED  &
        COMPONENT=N2
    DEFINE FC3E MASS-FLOW STREAM=C3FEED SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    DEFINE FC3 MASS-FLOW STREAM=C3FEED SUBSTREAM=MIXED  &
        COMPONENT=C3H8
    DEFINE FN2 MASS-FLOW STREAM=N2FEED SUBSTREAM=MIXED  &
        COMPONENT=N2
    DEFINE FH2 MASS-FLOW STREAM=H2FEED SUBSTREAM=MIXED  &
        COMPONENT=H2
    DEFINE FTC3 STREAM-VAR STREAM=C3FEED SUBSTREAM=MIXED  &
        VARIABLE=TEMP
    DEFINE FPC3 STREAM-VAR STREAM=C3FEED SUBSTREAM=MIXED  &
        VARIABLE=PRES
    DEFINE FTH2 STREAM-VAR STREAM=H2FEED SUBSTREAM=MIXED  &
        VARIABLE=TEMP
    DEFINE FPH2 STREAM-VAR STREAM=H2FEED SUBSTREAM=MIXED  &
        VARIABLE=PRES
    DEFINE FTN2 STREAM-VAR STREAM=N2FEED SUBSTREAM=MIXED  &
        VARIABLE=TEMP
    DEFINE FPN2 STREAM-VAR STREAM=N2FEED SUBSTREAM=MIXED  &
        VARIABLE=PRES
F       DC3E = 8.172E5
F       DC3  = 1.61E4
F       DH2  = 4.0E3
F       DN2  = 5.1E3
F       FC3E = DC3E - RC3E
F       FC3  = DC3 - RC3
F       FH2  = DH2 - RH2
F       FN2  = DN2 - RN2
F       FTC3 = 30
F       FPC3 = 3000
F       FTH2 = 30
F       FPH2 = 3000
F       FTN2 = 30
F       FPN2 = 3000
    READ-VARS RC3E RC3 RH2 RN2
    WRITE-VARS FC3E FC3 FN2 FH2 FTC3 FPC3 FTH2 FPH2 FTN2  &
        FPN2

CONV-OPTIONS
    PARAM CHECKSEQ=NO

STREAM-REPOR NOMOLEFLOW MASSFLOW MASSFRAC

REACTIONS ZN-R1 ZIEGLER-NAT
    IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
        VOLUME-FLOW='cum/hr' PRESSURE=kPa TEMPERATURE=C TIME=hr  &
        PDROP=kPa
```

Figure 9.2 Input File (cont.)

```
    DESCRIPTION "ZIEGLER-NATTA KINETIC SCHEME"
    PARAM
    SPECIES CATALYST=TICL4 COCATALYST=TEA MONOMER=C3H6  &
        HYDROGEN=H2 POLYMER=PP
    MON-RSEG C3H6 C3H6-R
    ACT-COCAT 1 TICL4 TEA 1620000.0 3.2000E+07 1.0
    ACT-COCAT 2 TICL4 TEA 1620000.0 3.2000E+07 1.0
    ACT-COCAT 3 TICL4 TEA 1620000.0 3.2000E+07 1.0
    ACT-COCAT 4 TICL4 TEA 1620000.0 3.2000E+07 1.0
    CHAIN-INI 1 C3H6 1.1750E+07 3.0000E+07 1.0
    CHAIN-INI 2 C3H6 2640000.0 3.0000E+07 1.0
    CHAIN-INI 3 C3H6 1.8440E+07 3.0000E+07 1.0
    CHAIN-INI 4 C3H6 6530000.0 3.0000E+07 1.0
    PROPAGATION 1 C3H6 C3H6 1.1750E+07 3.0000E+07 1.0
    PROPAGATION 2 C3H6 C3H6 2640000.0 3.0000E+07 1.0
    PROPAGATION 3 C3H6 C3H6 1.8440E+07 3.0000E+07 1.0
    PROPAGATION 4 C3H6 C3H6 6530000.0 3.0000E+07 1.0
    CHAT-MON 1 C3H6 C3H6 1020000.0 5.2000E+07 1.0
    CHAT-MON 2 C3H6 C3H6 1020000.0 5.2000E+07 1.0
    CHAT-MON 3 C3H6 C3H6 1020000.0 5.2000E+07 1.0
    CHAT-MON 4 C3H6 C3H6 1020000.0 5.2000E+07 1.0
    CHAT-COCAT 1 C3H6 TEA 5000000.0 5.0000E+07 1.0
    CHAT-COCAT 2 C3H6 TEA 5000000.0 5.0000E+07 1.0
    CHAT-COCAT 3 C3H6 TEA 5000000.0 5.0000E+07 1.0
    CHAT-COCAT 4 C3H6 TEA 5000000.0 5.0000E+07 1.0
    CHAT-H2 1 C3H6 H2 5.2900E+08 4.5000E+07 .50
    CHAT-H2 2 C3H6 H2 9.7900E+08 4.5000E+07 .50
    CHAT-H2 3 C3H6 H2 2.9000E+08 4.5000E+07 .50
    CHAT-H2 4 C3H6 H2 7.2900E+08 4.5000E+07 .50
    DEACT-SPON 1 .00042140 4100000.0 1.0
    DEACT-SPON 2 .00042140 4100000.0 1.0
    DEACT-SPON 3 .00042140 4100000.0 1.0
    DEACT-SPON 4 .00042140 4100000.0 1.0
    ATACT-PROP 1 C3H6 C3H6 500000. 30000000.
    ATACT-PROP 2 C3H6 C3H6 1200000. 30000000.
    ATACT-PROP 3 C3H6 C3H6 300000. 30000000.
    ATACT-PROP 4 C3H6 C3H6 700000. 30000000.
;
```

SELECTED SIMULATION RESULTS

Figure 9.3 shows the stream summary results for selected streams. The results include component mass flowrates, thermophysical information (temperature, pressure, enthalpy, etc.) and catalyst and polymer attributes. The polymer attributes are reported for the composite polymer and the polymer made at each site type. The polymer atactic fraction and melt flow ratio are reported at the end of the stream report.

Figure 9.3 Stream Summary Results

STREAM ID	C3FEED	CAT	COCAT	CYCGAGB	GAS1
FROM :	----	----	----	EXC1	STRIP1
TO :	FMIX1	FMIX1	FMIX1	FMIX1	----
SUBSTREAM: MIXED					
PHASE:	LIQUID	LIQUID	LIQUID	MIXED	VAPOR
COMPONENTS: KG/HR					
TICL4	0.0	3.0000	0.0	0.0	0.0
TEA	0.0	0.0	10.0000	0.0	0.0
C3H6	1.7166+04	296.4000	0.0	8.0003+05	887.5729
C3H8	161.6863	0.6000	0.0	1.5938+04	54.5188
PP	0.0	0.0	0.0	0.0	0.0
H2	0.0	0.0	0.0	3998.6199	1.6257-03
N2	0.0	0.0	0.0	5098.5474	1.4005
H2O	0.0	0.0	0.0	0.0	0.0
C3H6-R	0.0	0.0	0.0	0.0	0.0
COMPONENTS: MASS FRAC					
TICL4	0.0	1.0000-02	0.0	0.0	0.0
TEA	0.0	0.0	1.0000	0.0	0.0
C3H6	0.9906	0.9880	0.0	0.9696	0.9407
C3H8	9.3313-03	2.0000-03	0.0	1.9318-02	5.7784-02
PP	0.0	0.0	0.0	0.0	0.0
H2	0.0	0.0	0.0	4.8464-03	1.7231-06
N2	0.0	0.0	0.0	6.1795-03	1.4845-03
H2O	0.0	0.0	0.0	0.0	0.0
C3H6-R	0.0	0.0	0.0	0.0	0.0
TOTAL FLOW:					
KMOL/HR	411.5884	7.0730	8.7591-02	2.1539+04	22.3793
KG/HR	1.7327+04	300.0000	10.0000	8.2507+05	943.4940
CUM/SEC	9.7573-03	1.6771-04	3.3486-06	3.4582	3.3300-02
STATE VARIABLES:					
TEMP C	30.0000	30.0000	30.0000	59.0579	65.0000
PRES N/SQM	3.0000+06	3.0000+06	3.0000+06	3.0500+06	5.0000+05
VFRAC	0.0	0.0	0.0	0.8696	1.0000
LFRAC	1.0000	1.0000	1.0000	0.1303	0.0
SFRAC	0.0	0.0	0.0	0.0	0.0
ENTHALPY:					
J/KMOL	5.2134+06	4.2837+06	-2.3700+08	1.4361+07	1.5151+07
J/KG	1.2384+05	1.0100+05	-2.0759+06	3.7489+05	3.5937+05
WATT	5.9605+05	8416.3929	-5766.3165	8.5920+07	9.4184+04

Figure 9.3 Stream Summary Results (cont.)

```
ENTROPY:
  J/KMOL-K          -2.0850+05 -2.0672+05 -2.7926+05 -1.5641+05 -1.5253+05
  J/KG-K            -4952.7060 -4873.8889 -2446.0425 -4083.1369 -3617.8583
DENSITY:
  KMOL/CUM             11.7173    11.7152     7.2660     1.7300     0.1866
  KG/CUM              493.2853   496.8980   829.5434    66.2720     7.8703
AVG MW                 42.0986    42.4145   114.1666    38.3059    42.1591
COMPONENT ATTRIBUTES:
TICL4    CPSFLOW
           CPSFLOW               2.7690-04
         CPSFRAC
           CPSFRAC                  1.0000
         CVSFLOW
           SITE_1                   0.0
           SITE_2                   0.0
           SITE_3                   0.0
           SITE_4                   0.0
         CVSFRAC
           SITE_1                   0.0
           SITE_2                   0.0
           SITE_3                   0.0
           SITE_4                   0.0
         CDSFLOW
           CDSFLOW                  0.0
         CDSFRAC
           CDSFRAC                  0.0

STREAM ID              POWDER1    POWDER2    PP-PROD    R1OUT      RFEED1
FROM :                 SEP1       STRIP1     STRIP2     REACTOR    FMIX1
TO   :                 STRIP1     STRIP2     ----       SEP1       REACTOR

SUBSTREAM: MIXED
PHASE:                 LIQUID     LIQUID     LIQUID     MIXED      MIXED
COMPONENTS: KG/HR
  TICL4                  3.0000     3.0000     3.0000     3.0000     3.0000
  TEA                    9.8999     9.9000     9.9000     9.8999    10.0000
  C3H6                1062.5824   175.0041     6.0973  8.0110+05  8.1750+05
  C3H8                 162.2863   107.7672    30.8911  1.6101+04  1.6101+04
  PP                  1.6401+04  1.6401+04  1.6401+04  1.6401+04     0.0
  H2                  1.6258-03  7.1999-08     0.0     3998.6216  4000.0000
  N2                     1.4525  5.1987-02     3.4925  5100.0000  5100.0000
  H2O                    0.0        0.0        0.0        0.0        0.0
  C3H6-R                 0.0        0.0        0.0        0.0        0.0
COMPONENTS: MASS FRAC
  TICL4               1.7007-04  1.7968-04  1.8232-04  3.5599-06  3.5599-06
  TEA                 5.6122-04  5.9293-04  6.0167-04  1.1748-05  1.1866-05
  C3H6                6.0237-02  1.0481-02  3.7056-04     0.9506     0.9700
  C3H8                9.1998-03  6.4544-03  1.8774-03  1.9106-02  1.9106-02
  PP                     0.9297     0.9822     0.9967  1.9462-02     0.0
  H2                  9.2166-08  4.3122-12     0.0     4.7450-03  4.7466-03
  N2                  8.2346-05  3.1136-06  2.1226-04  6.0519-03  6.0519-03
  H2O                    0.0        0.0        0.0        0.0        0.0
  C3H6-R                 0.0        0.0        0.0        0.0        0.0
TOTAL FLOW:
  KMOL/HR              418.8360   396.4566   390.8222  2.1958+04  2.1958+04
  KG/HR               1.7640+04  1.6697+04  1.6454+04  8.4271+05  8.4271+05
  CUM/SEC             6.3006-03  5.6342-03  5.4556-03     4.6544     3.5110
```

Figure 9.3 Stream Summary Results (cont.)

```
STATE VARIABLES:
  TEMP    C              69.0000    65.0000    60.0000    69.0000    58.2471
  PRES    N/SQM       2.8000+06  5.0000+05  1.0000+05  2.8000+06  3.0000+06
  VFRAC                  0.0        0.0        0.0        0.9809     0.8453
  LFRAC                  1.0000     1.0000     1.0000  1.9075-02     0.1547
  SFRAC                  0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  J/KMOL             -1.0236+08 -1.0914+08 -1.1087+08  1.4184+07  1.4184+07
  J/KG               -2.4303+06 -2.5915+06 -2.6333+06  3.6958+05  3.6960+05
  WATT               -1.1909+07 -1.2019+07 -1.2036+07  8.6515+07  8.6519+07
ENTROPY:
  J/KMOL-K           -4.2324+05 -4.3836+05 -4.4323+05 -1.5461+05 -1.5734+05
  J/KG-K             -1.0049+04 -1.0409+04 -1.0528+04 -4028.4587 -4099.7923
DENSITY:
  KMOL/CUM             18.4655    19.5461    19.8989     1.3104     1.7372
  KG/CUM              777.7128   823.1797   837.7815    50.2934    66.6715
AVG MW                 42.1170    42.1146    42.1017    38.3786    38.3775
COMPONENT ATTRIBUTES:
TICL4     CPSFLOW
            CPSFLOW    9.0094-08  9.0094-08  9.0094-08  9.0094-08  2.7690-04
          CPSFRAC
            CPSFRAC    3.2537-04  3.2537-04  3.2537-04  3.2537-04     1.0000
          CVSFLOW
            SITE_1     4.3911-08  4.3911-08  4.3911-08  4.3911-08     0.0
            SITE_2     3.5823-07  3.5823-07  3.5823-07  3.5823-07     0.0
            SITE_3     1.5370-08  1.5370-08  1.5370-08  1.5370-08     0.0
            SITE_4     1.0864-07  1.0864-07  1.0864-07  1.0864-07     0.0
          CVSFRAC
            SITE_1     1.5858-04  1.5858-04  1.5858-04  1.5858-04     0.0
            SITE_2     1.2937-03  1.2937-03  1.2937-03  1.2937-03     0.0
            SITE_3     5.5509-05  5.5509-05  5.5509-05  5.5509-05     0.0
            SITE_4     3.9235-04  3.9235-04  3.9235-04  3.9235-04     0.0
          CDSFLOW
            CDSFLOW    1.3483-04  1.3483-04  1.3483-04  1.3483-04     0.0
          CDSFRAC
            CDSFRAC       0.4869     0.4869     0.4869     0.4869     0.0
PP        SFRAC
            C3H6-R        1.0000     1.0000     1.0000     1.0000     0.0
          SFLOW
            C3H6-R      389.7143   389.7144   389.7144   389.7143
          DPN
            DPN         554.9418   554.9418   554.9418   554.9418     0.0
          DPW
            DPW        2635.7010  2635.7010  2635.7010  2635.7010     0.0
          PDI
            PDI           4.7495     4.7495     4.7495     4.7495     0.0
          MWN
            MWN        2.3352+04  2.3352+04  2.3352+04  2.3352+04     0.0
          MWW
            MWW        1.1091+05  1.1091+05  1.1091+05  1.1091+05
          ZMOM
            ZMOM          0.7022     0.7022     0.7022     0.7022
          FMOM
            FMOM        389.7143   389.7144   389.7144   389.7143
          SMOM
            SMOM       1.0272+06  1.0272+06  1.0272+06  1.0272+06
          LDPN
            LDPN        849.3209   849.3209   849.3209   849.3209     0.0
```

Figure 9.3 Stream Summary Results (cont.)

```
LZMOM
  LZMOM      1.4146-04  1.4146-04  1.4146-04  1.4146-04
LFMOM
  LFMOM         0.1201     0.1201     0.1201     0.1201
LSFLOW
  C3H6-R        0.1201     0.1201     0.1201     0.1201     0.0
LSFRAC
  C3H6-R        1.0000     1.0000     1.0000     1.0000
LEFLOW
  C3H6-R     1.4146-04  1.4146-04  1.4146-04  1.4146-04
LEFRAC
  C3H6-R        1.0000     1.0000     1.0000     1.0000
LPFRAC
  LPFRAC     2.0143-04  2.0143-04  2.0143-04  2.0143-04
SSFRAC
  C3H6-R_1      1.0000     1.0000     1.0000     1.0000
  C3H6-R_2      1.0000     1.0000     1.0000     1.0000     0.0
  C3H6-R_3      1.0000     1.0000     1.0000     1.0000
  C3H6-R_4      1.0000     1.0000     1.0000     1.0000     0.0
SSFLOW
  C3H6-R_1    116.3391   116.3392   116.3392   116.3391
  C3H6-R_2     26.1425    26.1425    26.1425    26.1425
  C3H6-R_3    182.5757   182.5758   182.5758   182.5757
  C3H6-R_4     64.6568    64.6568    64.6568    64.6568     0.0
SDPN
  SITE_1      784.3242   784.3242   784.3242   784.3242
  SITE_2       97.4862    97.4862    97.4862    97.4862     0.0
  SITE_3     2187.1345  2187.1345  2187.1345  2187.1345
  SITE_4      319.6289   319.6289   319.6289   319.6289
SDPW
  SITE_1     1567.6485  1567.6485  1567.6485  1567.6485
  SITE_2      193.9724   193.9724   193.9724   193.9724
  SITE_3     4373.2690  4373.2690  4373.2690  4373.2690
  SITE_4      638.2578   638.2578   638.2578   638.2578
SPDI
  SITE_1        1.9987     1.9987     1.9987     1.9987     0.0
  SITE_2        1.9897     1.9897     1.9897     1.9897     0.0
  SITE_3        1.9995     1.9995     1.9995     1.9995     0.0
  SITE_4        1.9968     1.9968     1.9968     1.9968     0.0
SMWN
  SITE_1     3.3005+04  3.3005+04  3.3005+04  3.3005+04
  SITE_2     4102.2830  4102.2830  4102.2830  4102.2830
  SITE_3     9.2036+04  9.2036+04  9.2036+04  9.2036+04
  SITE_4     1.3450+04  1.3450+04  1.3450+04  1.3450+04
SMWW
  SITE_1     6.5968+04  6.5968+04  6.5968+04  6.5968+04
  SITE_2     8162.4853  8162.4853  8162.4853  8162.4853
  SITE_3     1.8403+05  1.8403+05  1.8403+05  1.8403+05
  SITE_4     2.6858+04  2.6858+04  2.6858+04  2.6858+04
SZMOM
  SITE_1        0.1483     0.1483     0.1483     0.1483
  SITE_2        0.2681     0.2681     0.2681     0.2681
  SITE_3     8.3477-02  8.3477-02  8.3477-02  8.3477-02
  SITE_4        0.2022     0.2022     0.2022     0.2022
SFMOM
  SITE_1      116.3391   116.3392   116.3392   116.3391
  SITE_2       26.1425    26.1425    26.1425    26.1425
```

Figure 9.3 Stream Summary Results (cont.)

SITE_3	182.5757	182.5758	182.5758	182.5757	
SITE_4	64.6568	64.6568	64.6568	64.6568	
SSMOM					
SITE_1	1.8238+05	1.8238+05	1.8238+05	1.8238+05	
SITE_2	5070.9390	5070.9407	5070.9407	5070.9390	
SITE_3	7.9845+05	7.9845+05	7.9845+05	7.9845+05	
SITE_4	4.1268+04	4.1268+04	4.1268+04	4.1268+04	
SPFRAC					
SITE_1	0.2985	0.2985	0.2985	0.2985	0.0
SITE_2	6.7081-02	6.7081-02	6.7081-02	6.7081-02	0.0
SITE_3	0.4684	0.4684	0.4684	0.4684	0.0
SITE_4	0.1659	0.1659	0.1659	0.1659	0.0
LSDPN					
SITE_1	784.3242	784.3242	784.3242	784.3242	
SITE_2	97.4862	97.4862	97.4862	97.4862	
SITE_3	2187.1345	2187.1345	2187.1345	2187.1345	
SITE_4	319.6289	319.6289	319.6289	319.6289	
LSZMOM					
SITE_1	3.5452-05	3.5452-05	3.5452-05	3.5452-05	0.0
SITE_2	3.5138-05	3.5138-05	3.5138-05	3.5138-05	0.0
SITE_3	3.5481-05	3.5481-05	3.5481-05	3.5481-05	0.0
SITE_4	3.5387-05	3.5387-05	3.5387-05	3.5387-05	0.0
LSFMOM					
SITE_1	2.7806-02	2.7806-02	2.7806-02	2.7806-02	
SITE_2	3.4254-03	3.4255-03	3.4255-03	3.4254-03	
SITE_3	7.7601-02	7.7601-02	7.7601-02	7.7601-02	
SITE_4	1.1311-02	1.1311-02	1.1311-02	1.1311-02	
LSSFLOW					
C3H6-R_1	2.7806-02	2.7806-02	2.7806-02	2.7806-02	
C3H6-R_2	3.4254-03	3.4255-03	3.4255-03	3.4254-03	
C3H6-R_3	7.7601-02	7.7601-02	7.7601-02	7.7601-02	
C3H6-R_4	1.1311-02	1.1311-02	1.1311-02	1.1311-02	
LSSFRAC					
C3H6-R_1	1.0000	1.0000	1.0000	1.0000	
C3H6-R_2	1.0000	1.0000	1.0000	1.0000	
C3H6-R_3	1.0000	1.0000	1.0000	1.0000	
C3H6-R_4	1.0000	1.0000	1.0000	1.0000	
LSEFLOW					
C3H6-R_1	3.5452-05	3.5452-05	3.5452-05	3.5452-05	
C3H6-R_2	3.5138-05	3.5138-05	3.5138-05	3.5138-05	
C3H6-R_3	3.5481-05	3.5481-05	3.5481-05	3.5481-05	
C3H6-R_4	3.5387-05	3.5387-05	3.5387-05	3.5387-05	
LSEFRAC					
C3H6-R_1	1.0000	1.0000	1.0000	1.0000	0.0
C3H6-R_2	1.0000	1.0000	1.0000	1.0000	0.0
C3H6-R_3	1.0000	1.0000	1.0000	1.0000	0.0
C3H6-R_4	1.0000	1.0000	1.0000	1.0000	0.0
LSPFRAC					
SITE_1	2.3901-04	2.3901-04	2.3901-04	2.3901-04	
SITE_2	1.3103-04	1.3103-04	1.3103-04	1.3103-04	
SITE_3	4.2503-04	4.2503-04	4.2503-04	4.2503-04	
SITE_4	1.7494-04	1.7494-04	1.7494-04	1.7494-04	
ATFLOW					
ATFLOW	26.5837	26.5837	26.5837	26.5837	0.0
ATFRAC					
ATFRAC	6.8213-02	6.8213-02	6.8213-02	6.8213-02	0.0
SATFLOW					
SITE_1	4.9442	4.9442	4.9442	4.9442	0.0

Figure 9.3 Stream Summary Results (cont.)

```
            SITE_2       11.7610    11.7611    11.7611    11.7610     0.0
            SITE_3        2.9689     2.9689     2.9689     2.9689
            SITE_4        6.9093     6.9093     6.9093     6.9093
          SATFRAC
            SITE_1     4.2499-02  4.2499-02  4.2499-02  4.2499-02
            SITE_2        0.4498     0.4498     0.4498     0.4498
            SITE_3     1.6262-02  1.6262-02  1.6262-02  1.6262-02
            SITE_4        0.1068     0.1068     0.1068     0.1068

 STREAM ID                STRIP-N2   VAP-A      VAP-B
 FROM :                   ----       SEP1       COMP1
 TO   :                   STRIP2     COMP1      EXC1

 SUBSTREAM: MIXED
 PHASE:                   VAPOR      VAPOR      VAPOR
 COMPONENTS: KG/HR
   TICL4                    0.0        0.0        0.0
   TEA                      0.0        0.0        0.0
   C3H6                     0.0     8.0003+05  8.0003+05
   C3H8                     0.0     1.5938+04  1.5938+04
   PP                       0.0        0.0        0.0
   H2                       0.0     3998.6199  3998.6199
   N2                     500.0000  5098.5474  5098.5474
   H2O                      0.0        0.0        0.0
   C3H6-R                   0.0        0.0        0.0
 COMPONENTS: MASS FRAC
   TICL4                    0.0        0.0        0.0
   TEA                      0.0        0.0        0.0
   C3H6                     0.0        0.9696     0.9696
   C3H8                     0.0     1.9318-02  1.9318-02
   PP                       0.0        0.0        0.0
   H2                       0.0     4.8464-03  4.8464-03
   N2                       1.0000  6.1795-03  6.1795-03
   H2O                      0.0        0.0        0.0
   C3H6-R                   0.0        0.0        0.0
 TOTAL FLOW:
   KMOL/HR                17.8485  2.1539+04  2.1539+04
   KG/HR                 500.0000  8.2507+05  8.2507+05
   CUM/SEC              4.1613-02     4.6481     4.2866
 STATE VARIABLES:
   TEMP   C               30.0000    69.0000    74.7964
   PRES   N/SQM        3.0000+05  2.8000+06  3.0500+06
   VFRAC                   1.0000     1.0000     1.0000
   LFRAC                   0.0        0.0        0.0
   SFRAC                   0.0        0.0        0.0
 ENTHALPY:
   J/KMOL              1.2715+05  1.6450+07  1.6709+07
   J/KG                4538.8119  4.2945+05  4.3619+05
   WATT                 630.3905  9.8423+07  9.9968+07
 ENTROPY:
   J/KMOL-K           -8592.8427 -1.4938+05 -1.4918+05
   J/KG-K              -306.7395 -3899.7360 -3894.3041
 DENSITY:
   KMOL/CUM               0.1191     1.2872     1.3957
   KG/CUM                 3.3376    49.3073    53.4653
 AVG MW                  28.0134    38.3059    38.3059
```

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1 POLYETHYLENE TEREPHTHALATE

SEMI-BATCH / BATCH PROCESS

SUMMARY

Minimizing batch cycle time and producing consistent product are the major concerns for batch mode processes. It is often difficult to achieve both objectives because of the uncertainties in a complex polymerization process. This application illustrates the use of Polymers Plus and Aspen Custom Modeler (ACM) to simulate a semi-batch/batch polymerization of ethylene terephthalate (PET). The model is capable of predicting several PET properties of interest, thus you can adjust the process accordingly to produce consistent product with the minimum batch cycle time.

ABOUT THIS PROCESS

PET is typically polymerized from an esterification reaction between terephthalatic acid (TPA) and ethylene glycol (EG). Water produced during the reaction has to be removed in order to achieve high conversion. A batch process consists of a reactor connected by a column for separating unreacted EG from water. The EG recovered in the bottom of the column is recycled to the reactor and the water is discharged from the system from the top tray of the column. A batch starts with the reactor partially filled with the preceding batch product. The TPA and EG paste is continuously fed into the reactor. The feed stops at a given time and the process continues until a predetermined conversion is reached.

Because of its flexible operation, the batch polymerization of PET is used extensively by manufacturers. This flexibility, however, provides a challenge for producing a consistent quality of PET from batch to batch. Dynamic simulation offers an alternative to predict critical properties of PET, which are often difficult, costly, and time-consuming to obtain from measurements. This application demonstrates the use of a dynamic model to predict the state of process and the product properties thereby ensuring consistent product qualities. Based on the prediction, the batch process can be terminated when the desired product properties are achieved to avoid unnecessary processing time shortening the batch cycle time. This application also studies the effects of the recycle ratio on the throughput.

PROCESS DEFINITION

The esterification reactor is attached with a component splitter simulating the EG recovery column and associated temperature and level controllers. The reactor temperature is controlled by manipulating the flow rate of heating fluid (Dowtherm). The operating temperature in the component splitter is controlled by adjusting the reflux ratio.

Process Conditions

The flowsheet of a batch PET process is depicted in Figure 1.1. The batch process starts with the reactor partially filled with the PET from the preceding batch. A TPA/EG paste is fed into the reactor for a certain period, then the process is switched to batch mode and continues until the desired conversion 93.4% is achieved. The reactor temperature is operated at 260°C. There are two feeds to the reactor, the TPA/EG paste slurry and the reflux from the recovery column. The temperature of the slurry feed is 40°C.

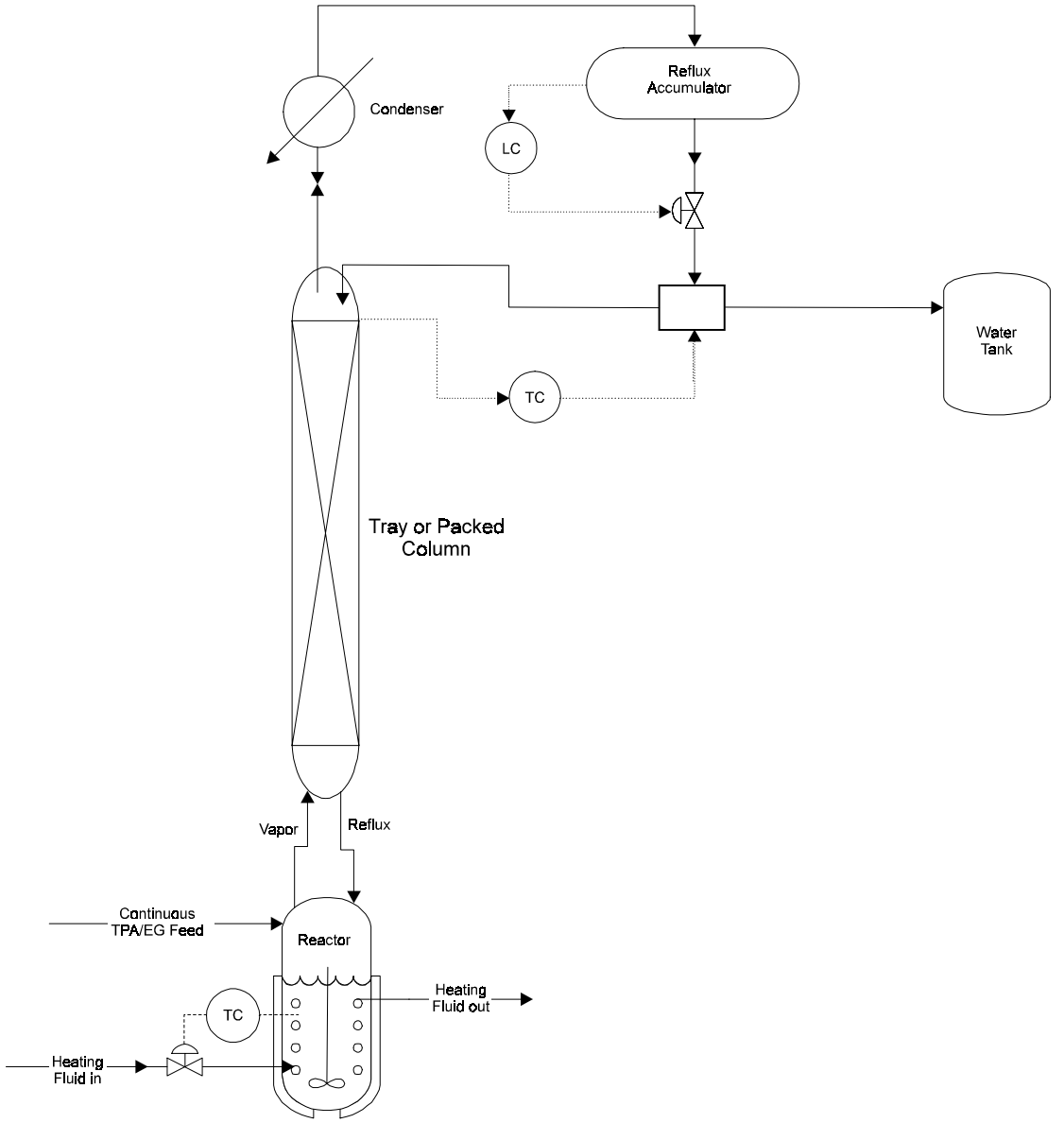

Figure 1.1 *Batch PET Process Flowsheet*

Physical Property Model and Data

Polymers Plus provides all the polymer properties and polymer phase equilibrium. All non-polymer properties are provided by Properties Plus.

Reactors / Kinetics

The esterification reactor is modeled with a CSTR2P in the Aspen Custom Modeler Polymer library. The model is modified to include a solid TPA phase. The TPA diffuses into the liquid phase. The vapor and liquid phases are assumed in equilibrium in the reactor. The model assumes that the reactions only occur in the liquid phase. It contains a thermal inertia term to take into account the energy required for changing the temperature of reactor.

The reaction kinetics are step-growth condensation reactions described in the Aspen Plus input file (*.inp). The basic reaction is an acid reacting with an alcohol producing an ester and water.

Process Studies

The batch PET process is simulated with the developed model. The effects of the recycle ratio is studied as an operating variable in the light of increase in production rate. The recycle ratio is defined as the ratio of initial mass PET to the total mass PET in the end of batch. The production rate is roughly evaluated as the ratio of the net PET produced, i.e., the difference between the total mass PET in the end of batch and the initial mass PET in the reactor, to the batch time required to produce the consistent PET. The batch is terminated as soon as these properties become consistent. The batch cycle time is determined through the comparison of the PET properties in the end of the current batch with those of the preceding batch.

SELECTED SIMULATION RESULTS

Table 1.1 and Table 1.2 list the simulation results of the two selected recycle ratios. You may extend this application to find the optimal recycle ratio.

Table 1.1 Simulation Results with the Recycle Ratio of 0.3511

Recycle ratio = 0.3511	Acid value (MMOL/KG)	OH value (MMOL/KG)	Conversion (%)	PET mass (KG)
Initial PET properties	626.5	2856.7	93.4	2595
Final PET properties	622.2	3217.9	93.4	7393
Net production per batch (KG/Batch)	---	---	---	4798
Batch cycle time (HR)	---	---	---	8.47
Equivalent production rate (KG/HR)	---	---	---	566

Table 1.2 Simulation Results with the Recycle Ratio of 0.4891

Recycle ratio = 0.4891	Acid value (MMOL/KG)	OH value (MMOL/KG)	Conversion (%)	PET mass (KG)
Initial PET properties	626.5	2856.7	93.4	3461
Final PET properties	622.7	3147.3	93.4	7077
Net production per batch (KG/Batch)	---	---	---	3616
Batch cycle time (HR)	---	---	---	7.11
Equivalent production rate (KG/HR)	---	---	---	508

These tables' results show that in the end of each batch, the qualities of PET in terms of acid and alcohol values and conversion are consistent with those in the beginning of the batch. As expected, the batch cycle time is prolonged as the recycle ratio is decreased. They also show that although the absolute batch cycle time with the recycle ratio of 0.3511 is longer than that of 0.4891, the production rate is increased by using the cycle ratio of 0.3511.

Figure 1.2 displays the reactor's operating conditions. The slurry feed containing TPA/EG paste stops at 2.67 hours. The pressure of the reactor constantly increases from the beginning of batch and starts to drop at 2.67 hours because of the consumption of EG. The temperature of the reactor is maintained at 260°C.

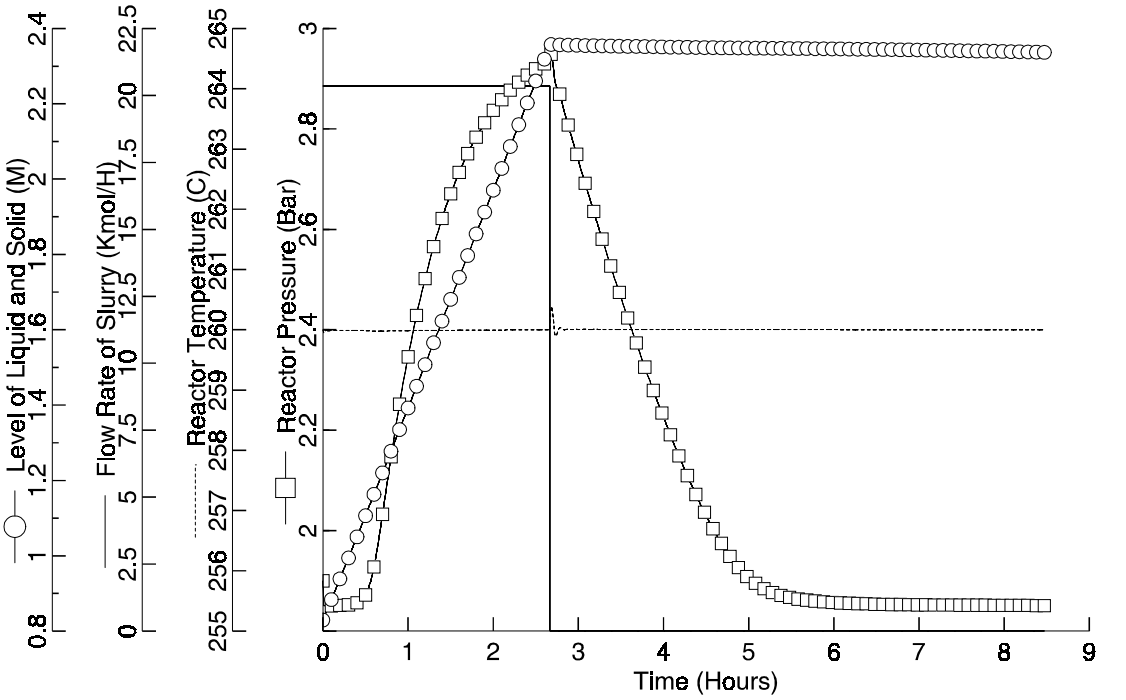

Figure 1.2 *Reactor Operating Conditions*

The predicted properties of PET are plotted in Figure 1.3. The acid value and alcohol value increase as the TPA and EG are fed into the reactor, then they decrease after the feed stops and as the batch continues. The plot shows that the process should stop at 8.47 hours because the conversion is identical to the initial value and the acid and alcohol values are close to their initial values as well. Consequently, the consistent batches are reproduced.

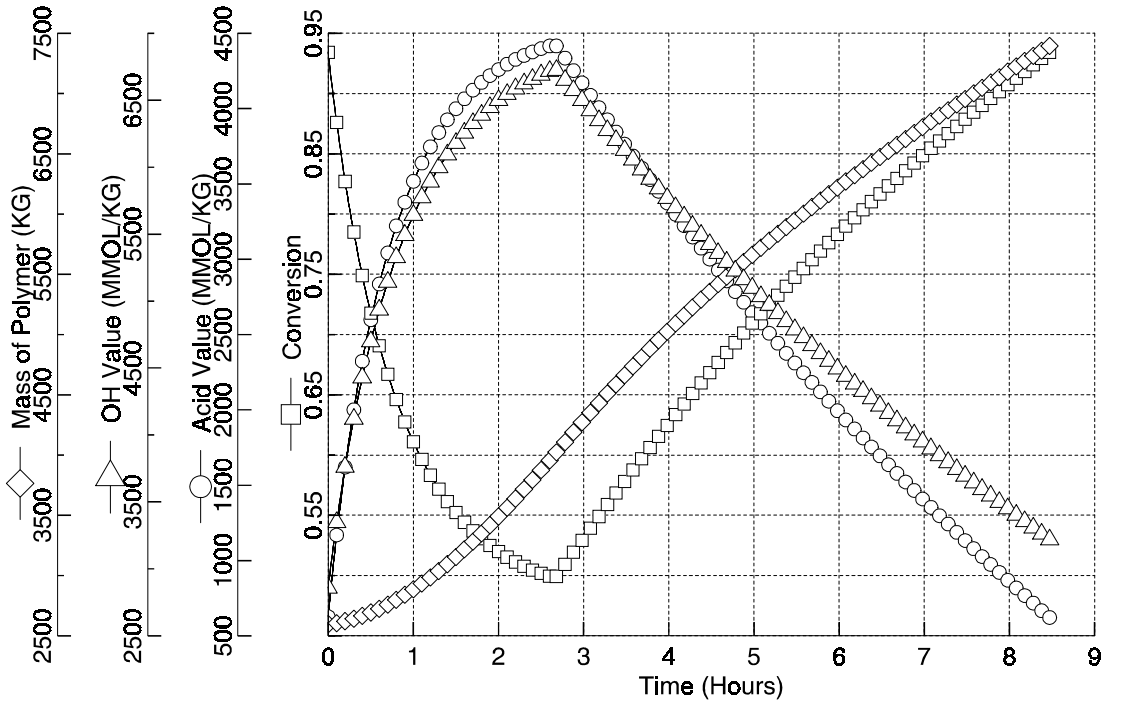

Figure 1.3 *PET Properties*

The water generated during the polymerization is flashed and accumulated in the water tank as seen in Figure 1.4.

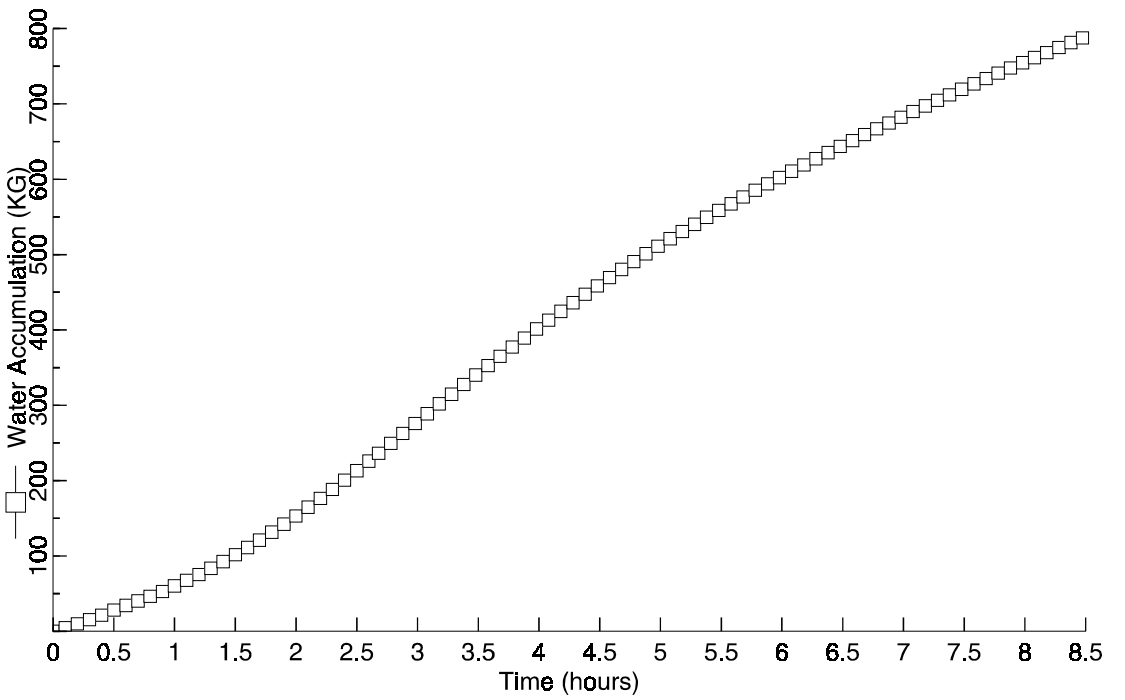

Figure 1.4 *Water Flashed to the Accumulator*

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2 POLYETHYLENE TEREPHTHALATE

CONTINUOUS PROCESS

SUMMARY

Fast and stable response of a polymerization process to disturbances is essential, otherwise a significant amount of off-spec product may be produced. A better control scheme may improve and stabilize the process response, which, in turn, reduces off-spec product caused by unstable processes. The PET continuous process application demonstrates the use of dynamic modeling to improve operation stability of a continuous polyethylene terephthalate (PET) reactor system with Aspen Custom Modeler and Polymers Plus. The developed PET model is generic and can be readily implemented into a user's application.

ABOUT THIS PROCESS

Typically, PET is produced from esterification of acid and glycol, e.g., condensation of terephthalic acid (TPA) and ethylene glycol (EG). The polymerization occurs in a series of three or four agitated reactors followed by future polymerization in extrusion reactors. The degree of polymerization is very sensitive to the water content and the glycol-acid ratio in the reactor. During reaction, EG in vapor phase needs to be recovered to minimize loss. Meanwhile, the water generated from the polymerization must be removed from the reactor to allow the forward reaction to proceed. A column attached with the reactor is used to recover EG and remove water.

Typically, the esterification reactor residence time is large (approximately two hours) in order to achieve a high conversion. The column residence time, however, is comparatively small. These two systems are highly coupled because the reaction rate defines the water production rate which affects the reactor duty and the boilup rate. The boilup rate, in turn, has influences on the reflux duty and reflux inventory control of the column.

PROCESS DEFINITION

The model of PET process includes an esterification reactor (CSTR), mixer, and ethylene glycol (EG) recovery column. It also includes a flow ratio controller to maintain the EG to TPA ratio. The model flowsheet is plotted in Figure 2.1. The feeds of the MIXER include TPA, EG, and a catalyst stream. The ratio controller is placed to maintain the EG to TPA ratio. The fourth feed of the MIXER is the bottom stream from the recovery column DYNCOL. The reactor simulated as a CSTR is operated under the constant level, temperature, and pressure with the controllers. The vapor output of the reactor is fed to DYNCOL which separates EG from water. The recovered EG is recycled to the MIXER. A reflux drum level control is associated with DYNCOL. A temperature controller is used to maintain the temperature of DYNCOL through manipulating the reflux ratio.

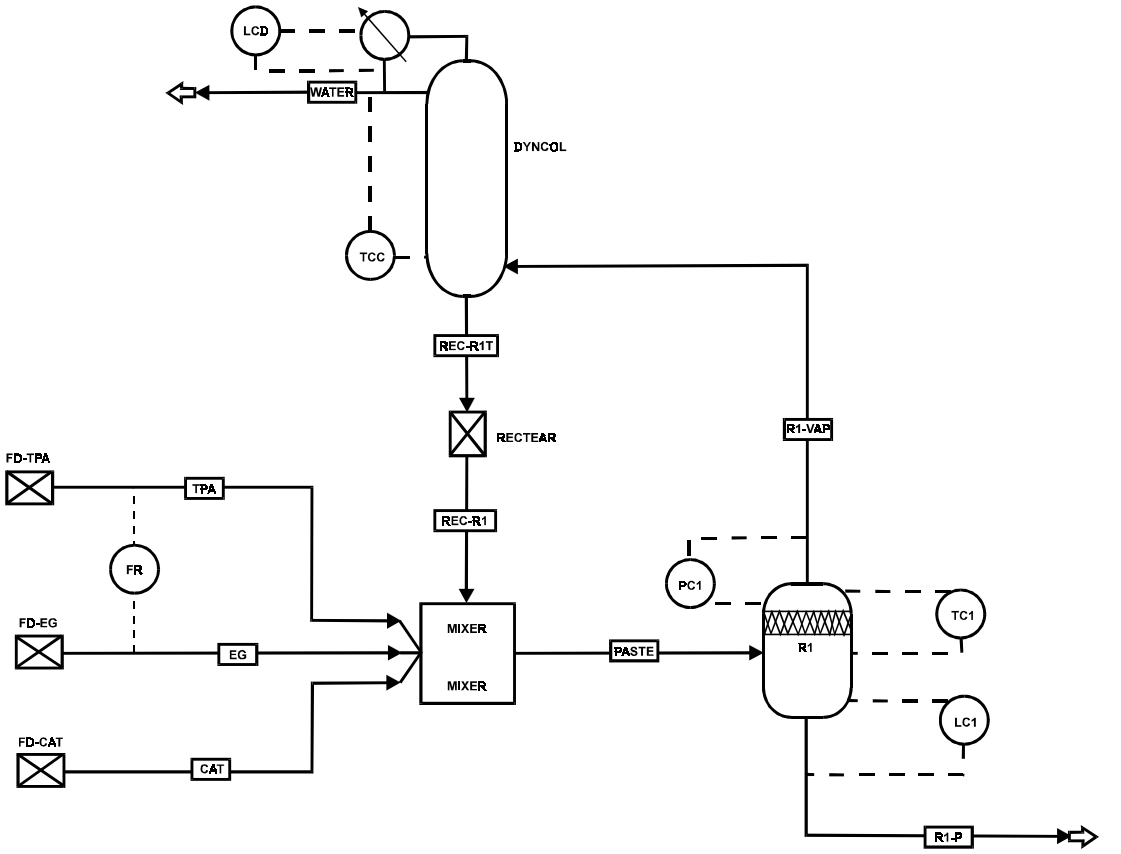

Figure 2.1 *PET Primary Esterification System Flowsheet*

Process Conditions

Table 2.1 lists the components considered in the model.

Table 2.1 Process Conditions

Components	Name	Databank	Description
Terephthalate acid	TPA	PURE10	Monomer
Ethylene glycol	EG	PURE10	Monomer
PET	PET	POLYPCD	Polymer
TPA segment	R-TPA	SEGPCD	Repeat segment
	E-TPA	SEGPCD	End segment
EG segment	R-EG	SEGPCD	Repeat segment
	E-EG	SEGPCD	End segment
SBAC3	SBAC3	PURE10	Catalyst
Water	H2O	PURE10	Product of polymerization
Feed	**Flow Rate, Kg/Hr †**	**Temperature, °C**	**Pressure, Bar**
TPA*	t < 0.25 7128.0	25	1
	t < .5 7128+4000*(t - 0.25)		
	t > 0.5 8128.0		
EG	Molar EG/TPA = 1.15	25	1
SBAC3	4.0	25	1

† ***t = time in hour***

* ***A ramp increase in TPA flow rate is imposed as a disturbance to the process***

Physical Property Models and Data

The polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method to calculate properties.

Reactor / Kinetics

The reactor is simulated with a CSTR2P model from the Aspen Custom Modeler Polymer model library. The model accommodates two phases, gas and liquid, with variable liquid holdup. It contains mass and energy balances and moment balances for calculating PET polymer attributes. The equilibrium is assumed between the gas phase and liquid phase. Polymers Plus provides the thermal properties including partition coefficients and the reaction rates based on the condensation polymerization kinetics. The molar ratio of EG to TPA is set at 1.15 with the ratio controller.

Process Studies

This application examines the temperature control strategy to improve the process stability. Two cases are studied. First, a controller is used to control the temperature at the top tray of the recovery column. Second, the temperature at the bottom tray of the EG recovery column is controlled.

SELECTED SIMULATION RESULTS

In the case of temperature control on the top tray, the top tray temperature of the recovery column is quickly settled around its setpoint of 139.56°C after the TPA flow rate increase as shown in Figure 2.2. The bottom tray temperature, however, slowly approaches its new steady state value. This results in the slow PET reactor responses as displayed in Figure 2.3. As shown initially there is a quick transition in the acid value and the number average MW. These values then move slowly to their new steady states. In fact, the steady-states are not achieved in 10 hours. The problem with this control is that it gives tight control on the EG concentration in the water distillation stream, but loses control on the composition of the EG return stream from the bottom tray to the reactor.

In the case of temperature control on the bottom tray, the bottom tray temperature is controlled at the value prior to the TPA flow rate change and the top tray temperature gradually approaches to its new steady state as plotted in Figure 2.4. As the result, the responses of the esterification reactor displayed in Figure 2.5 show that the system moves to the steady state in less than 5 hours for the same feed disturbance. Since the bottom tray temperature is controlled at the desired value, it ensures that the temperature and composition of reflux to the reactor is relatively constant, although the distillate composition is not constant. This reduces the disturbances to the reactor. In addition, the simulation demonstrates that the amount of deviation in the distillate composition does not vary substantially. The cost of this deviation is far less than that of slow transient behavior of the reactor. This application demonstrates the advantages by using a dynamic model which provides a viable tool to optimize the operation of a polymerization process.

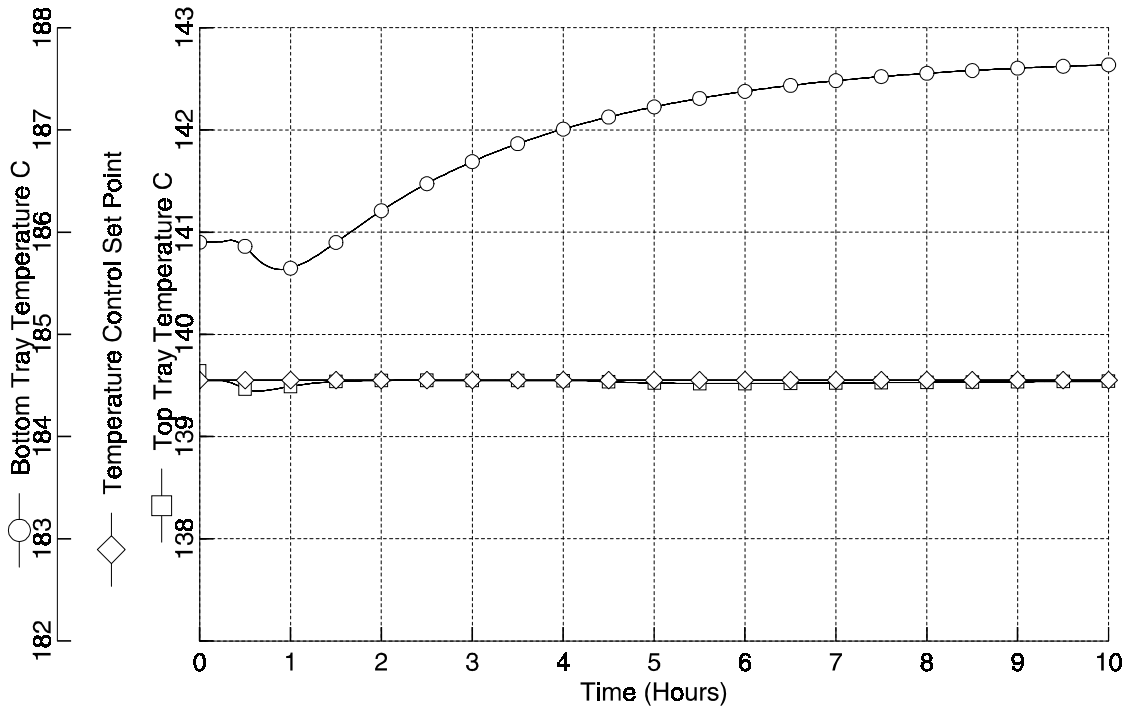

Figure 2.2 *Temperatures in the Recovery Column in the Top Tray Temperature Control Case*

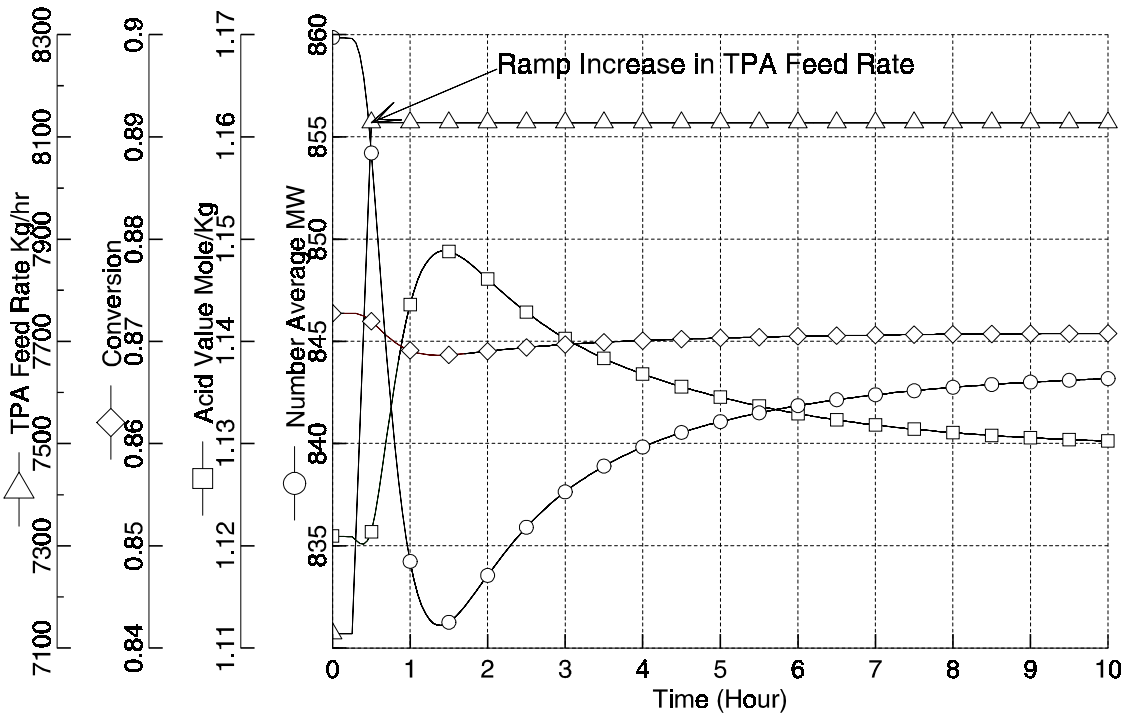

Figure 2.3 *Responses of Esterification Reactor in the Top Tray Temperature Control Case*

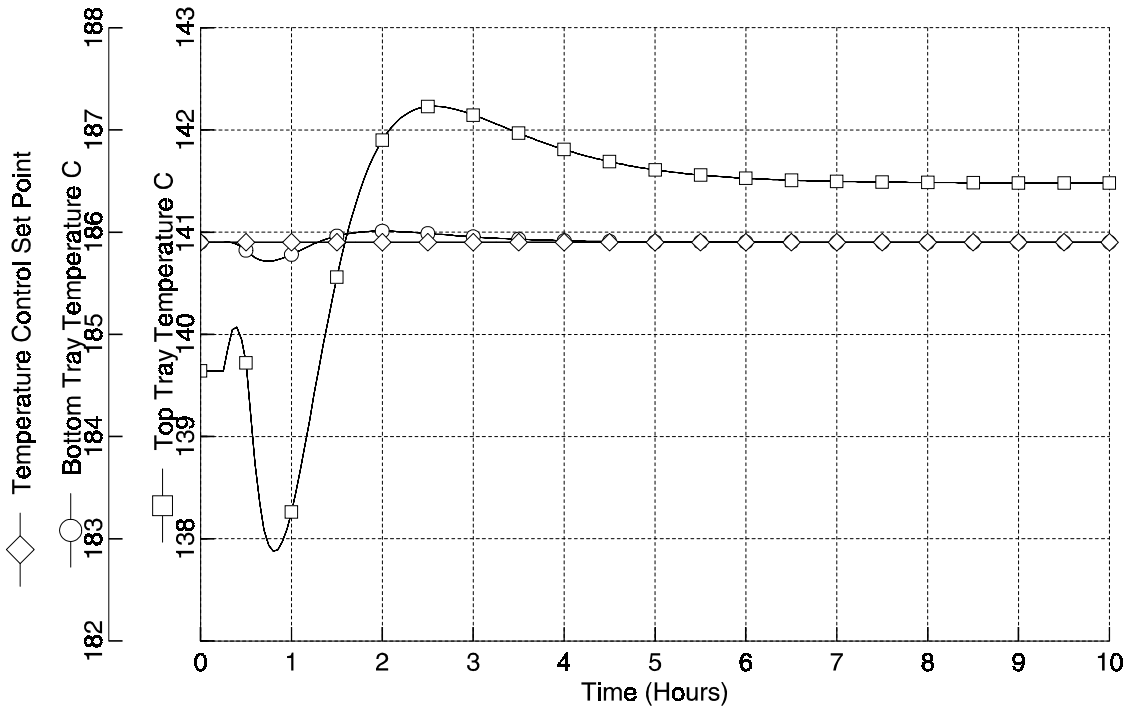

Figure 2.4 *Temperatures of the Recovery Column in the Bottom Tray Temperature Control Case*

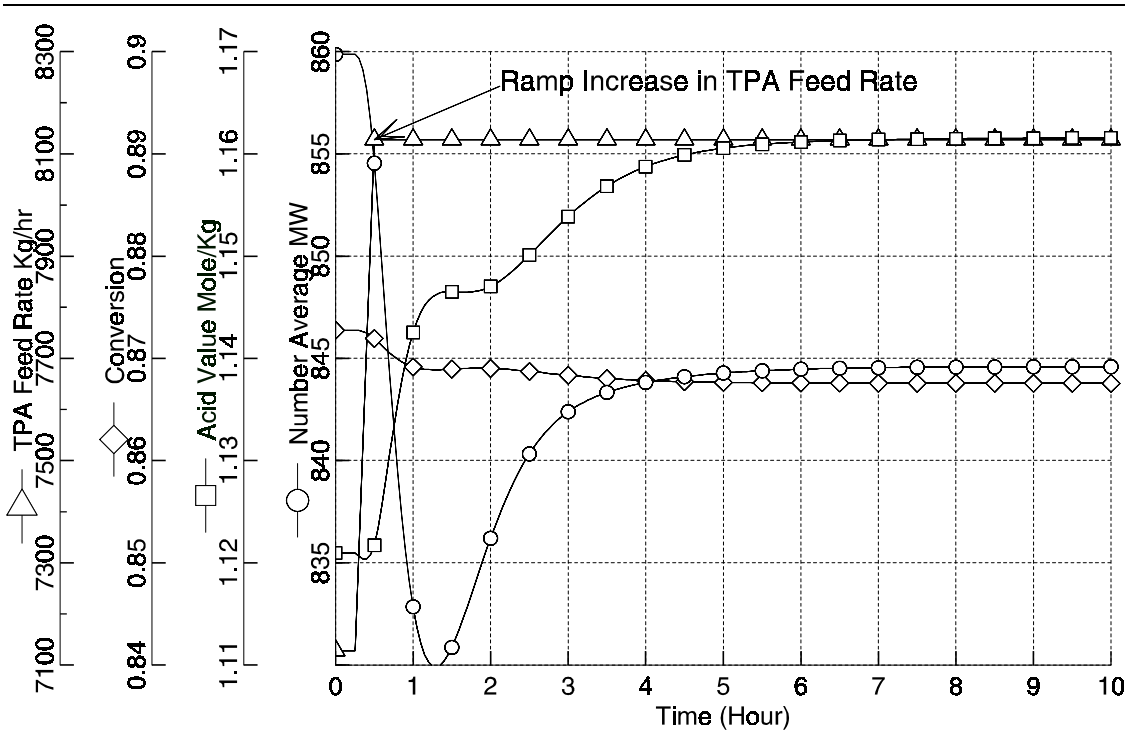

Figure 2.5 *Responses of Esterification Reactor in the Bottom Tray Temperature Control Case*

REFERENCES

Gupta, S. K, and A. Kumar, Reaction Engineering of Step-Growth Polymerization, Plenum, New York (1987).

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3 POLYSTYRENE

DYNAMIC BULK POLYMERIZATION PROCESS

SUMMARY

Constantly changing demands require flexible operation of polymerization processes. The bulk polystyrene dynamic process application demonstrates the dynamic simulation with Polymers Plus and Aspen Custom Modeler for rating the cooling/heating system to respond to the changes in the throughput of bulk polymerization of styrene. The developed model is generic and can be readily customized for other applications.

ABOUT THIS PROCESS

Styrene is polymerized through stepwise addition of monomer units. The polymerization is usually initiated by thermal means and/or peroxide initiators to form free-radicals which initiate chain growth. The reaction is highly exothermic approximating 160.2 kcal/Kg of styrene polymerized (Boundy, 1952). Typically, the continuous polymerization of styrene consists of one or more CSTRs followed by a reactor designed for handling viscous solutions. These reactors are usually equipped with coils for heat addition or removal or through direct vapor cooling. The highly exothermic polymerization reactions render the heating/cooling systems of reactors vulnerable to changes in states of the polystyrene process. Rating the existing heating/cooling systems or other utilities is essential to ensure a feasible change in process, e.g., increase in throughput.

PROCESS DEFINITION

The polymerization of styrene in this application consists of three reactors in series, two liquid CSTR's followed by one liquid PFR, one HEATER for devolatilization, and two FLASH units for purifying the products. The flowsheet of this process is plotted in Figure 3.1.

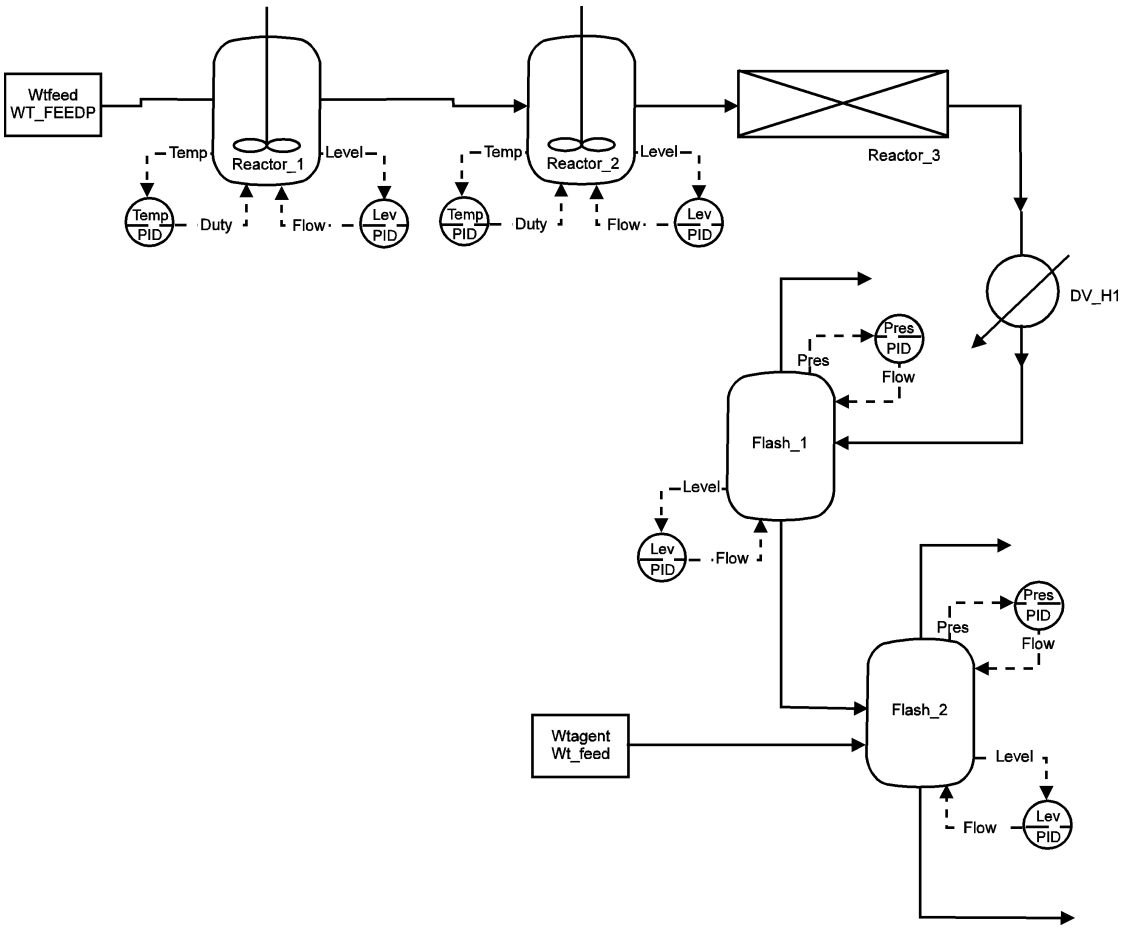

Figure 3.1 *Bulk Polystyrene Aspen Custom Modeler Dynamic Model Flowsheet*

Process Conditions

Eight components including one segment component are considered and listed in Table 3.1.

Table 3.1 Process Conditions

Components	Name	Databank	Description
Styrene	STY	PURECOMP	Monomer
Polystrene	PS	POLYCD	Comonomer
Styrene segment	STY-SEG	SEGPCD	Repeat segment
Di-tert-butyl peroxide	TBP	PURECOMP	Initiator
Coinitiator	CINI	PURECOMP	Coinitiator
Ethylbenzene	EB	PURECOMP	Chain transfer agent
Dodecyl mercaptan	DDM	PURECOMP	Chain transfer agent
Water	H2O	PURECOMP	Stripping agent
Feed	**FEED_1**		
Temperature (°C)	25		
Pressure (atm)	1		
Mass flow rate (Kg/Hr)	If t<0.5 then 7000 else 7500 endif		
Mass fraction of styrene	0.9797		
Mass fraction of polystyrene	0.0		
Mass fraction of coinitiator	0.0		
Mass fraction of ethylbenzene	1.94e-2		
Mass fraction of DDM	6.5e-4		
Mass fraction of TBP	2.5e-4		

Operating Conditions

Block	Temperature (°C)	Pressure (atm)	Size	Level Setpoint (m)
CSTR-1	120	1	20 m^3	2
CSTR-2	160	1	20 m^3	2
PLUG-1	160-200	1	80 m length by 0.40 m diameter	---
DV-H1	220	1	---	---
FLASH-1	220	1	---	---
FLASH-2	220	1	---	---

Physical Property Models and Data

The polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method to calculate properties. Note that the heat of polymerization is used with available data and is therefore considered more accurate than property model predictions.

Process Studies

The developed polystyrene model is employed to evaluate the required heating/cooling rates of the first two reactors, CSTR-1 and CSTR-2. The required heating/cooling rates are based on the values for maintaining the reactor temperature constant.

SELECTED SIMULATION RESULTS

The monomer feed to the CSTR 1 reactor is increased from 7000 to 7500 Kg/Hour as displayed in Figure 3.2. The conversions in CSTRs 1 and 2 are slightly decreased due to the decrease in the resident times. However, the decrease is less than 1% in both reactors.

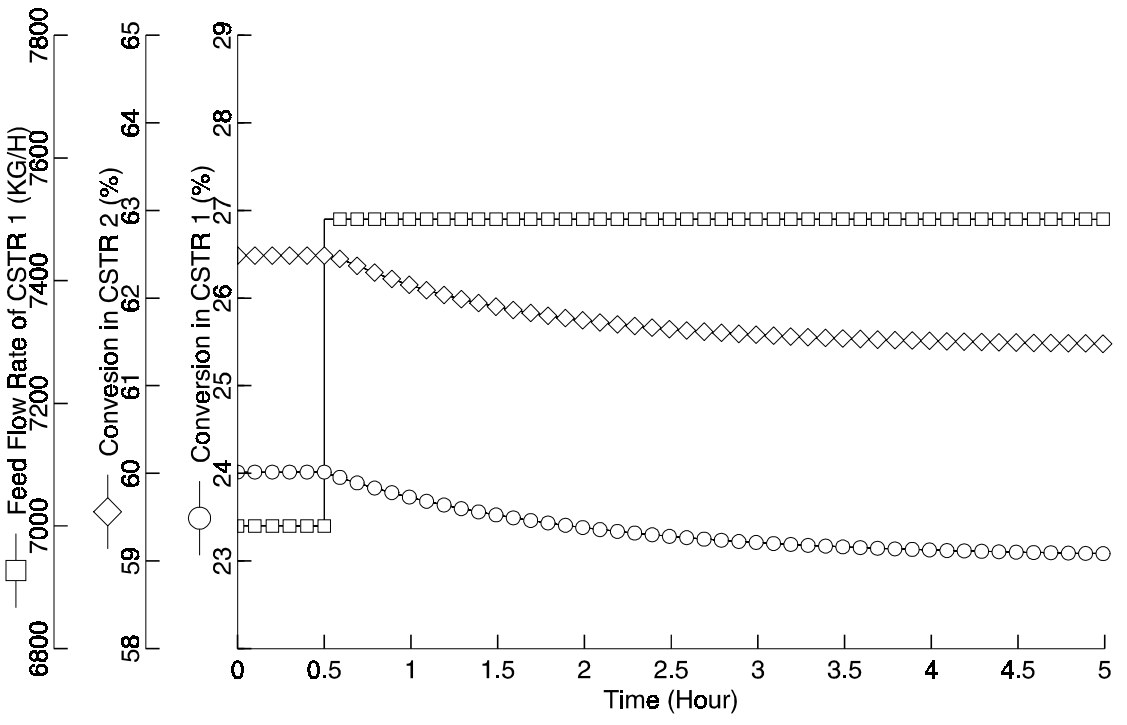

Figure 3.2 *Dynamics of Reactor*

The heating and cooling rate required for these two CSTRs, however, is significantly changed in order to maintain the constant operating conditions. For instance, when the inlet flow rate is 7000 kg/hr, CSTR 1 requires the heating rate to be 0.48 GJ/hr. The 7500 kg/hr flow rate needs about 0.56 GJ/hr to maintain the temperature of CSTR 1 at the desired value. This change is about 16.7% increase from the previous heating rate requirement. It is worth mentioning that the maximum instant heating rate required by the temperature controller of this reactor is up to 0.60 GJ/hr, which requires a 25.0% higher rate than its original steady-state heating rate.

The second CSTR needs a cooling system. Figure 3.3 demonstrates that increase in the throughput from 7000 to 7500 Kg/hr. Here the cooling rate required by this reactor is changed from 0.67 to 0.72 GJ/s, which is about a 7.5% increase in the cooling rate.

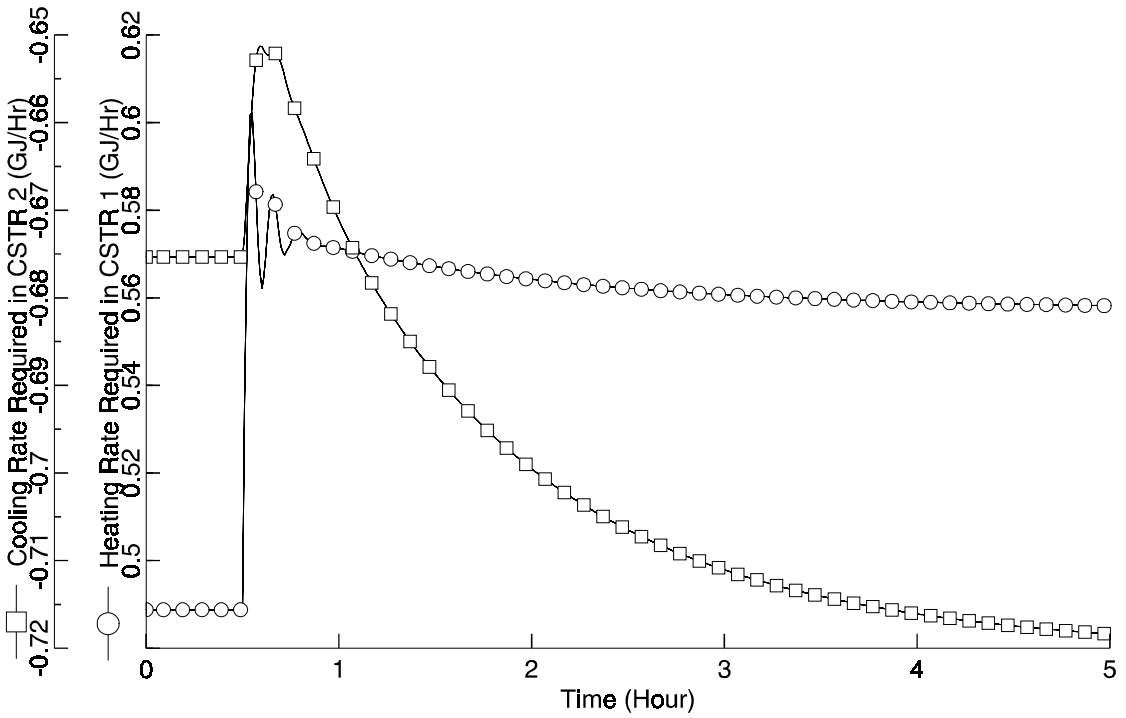

Figure 3.3 *Utility Requirement*

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4 LLDPE / HDPE

DYNAMIC PROCESS

SUMMARY

A generic dynamic model is developed from Polymers Plus and Aspen Custom Modeler to simulate both linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) processes. The model can be applied to study these processes in various ways. To illustrate its applications, an example for optimizing grade transition is used. Certainly, the model can be readily extended to other applications. Changing grade is often required in polymer manufacturing processes to meet customer's demands. The transition disturbs the states of a polymerization process and may produce a large amount of off-spec product during transition period. This application illustrates the use of the developed dynamic model to evaluate alternative operating policies to minimize the transition period.

ABOUT THIS PROCESS

Polyethylene is the largest volume thermal plastic produced and used in the world. The polymerization is carried in a reactor containing gas ethylene monomer and comonomer with Ziegler-Natta solid catalyst particles under high temperature and pressure conditions. Ziegler-Natta catalysts are highly reactive and contain multiple sites and site types. Each site type has different reactivity and produces a polymer with distinct molecular weight. Polyethylene's end-use properties can be predictably varied by changing the density, average molecular weight correlated by melt index, and molecular weight distribution through manipulation of operating variables. For instance, different end-use properties of polyethylene can usually be achieved in terms of melt index and correlated density by adjusting the concentrations of monomer, comonomer, and chain transfer agent in the reactor.

PROCESS DEFINITION

The process flowsheet shown in Figure 4.1 consists of a two-phase CSTR, mixer, purge, heat exchanger, range splitter, and PID controllers for the temperature, level, and pressure. In the reactor, the polymerization reaction in the gas phase is assumed to be negligible, thus the reaction occurs only in the polymer phase. The Ziegler-Natta model in Polymers Plus is used to simulate important features of this type of reactions including site activation, chain initiation, chain propagation, chain transfer, site deactivation, site inhibition, branching reactions, etc. The dynamic behavior and control systems are developed with Aspen Custom Modeler models and the control loops are of a typical UNIPOL process.

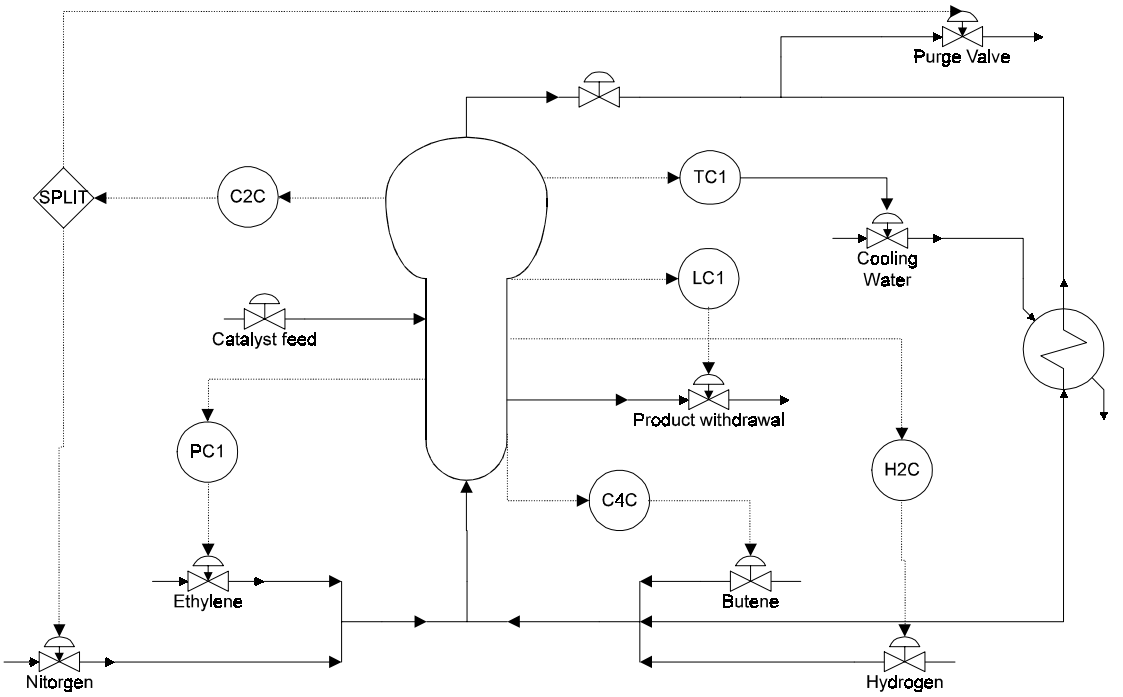

Figure 4.1 *Polyethylene Process Flowsheet*

Process Conditions

The reactor is fed by catalysts, a mixture of monomer and comonomer, ethylene and butene. N2 is used as inert diluent and H2 as chain transfer agent. The recycle gas containing 61.6% volume of nitrogen has a constant volumetric flow. In the reactor, the phase equilibrium and ideal mixing are assumed. The polymer product is removed and the gas product is cooled with cooling water and recycled. The process conditions are summarized in Table 4.1.

Table 4.1 Process Conditions

Components	Name	Databank	Description
Ethylene	E2	PURE10	Monomer
Butene	Butene	PURE10	Comonomer
HDPE	HDPE	POLYPCD	Polymer
Ethylene segement	E-SEG	SEGPCD	Repeat segment
Butene segment	B-SEG	SEGPCD	Repeat segment
TiCl4	CAT	PURE10	Catalyst
C6H15Al	CCAT	PURE10	Co-catalyst
H2	H2	PURE10	Chain transfer
N2	N2	PURE10	Inert diluent
WATER	WATER	PURE10	Cooling agent
Feed	**Flow Rate (kg/hr)**	**Temperature (°C)**	**Pressure (Bar)**
GFEED: E2	1407.740	40	30
BUTENE	140.0		
H2	0.00650		
N2	2251.2		
CFEED: CAT	0.50	40	30
CCAT	0.50		
Unit Operations	**Temperature (°C)**	**Pressure (Bar)**	
REACTOR	90	30	
MIXER	40	30	

Physical Property Models and Data

The polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method to calculate the properties required in the simulation.

Reactor / Kinetics

The reactor is modeled with a CSTR2P in the Aspen Custom Modeler Polymer model library. The model accommodates two phase, gas and liquid, with variable liquid holdup. It contains mass, energy, and moment balances and other equations for calculating the properties of polyethylene polymer such as melt index, density, number degree of polymerization, etc. The equilibrium is assumed between gas phase and liquid phase. Polymers Plus provides the thermal properties including partition coefficients. The reaction rates are also provided by the Polymers Plus reaction section. The reactions are based on one site of Ziegler-Natta polymerization kinetics which are listed as follows:

Reaction	k_0	E_a (J/kmol)	Order
ACT-COCAT 1 CAT CCAT	9.03E5	8000.0	1.0
CHAIN-INI 1 E2	4.49E7	7000.0	1.0
CHAIN-INI 1 BUTENE	5.96E5	7000.0	1.0
PROPAGATION 1 E2 E2	4.49E7	7000.0	1.0
PROPAGATION 1 E2 BUTENE	1.50E6	7000.0	1.0
PROPAGATION 1 BUTENE E2	4.49E6	7000.0	1.0
PROPAGATION 1 BUTENE BUTENE	5.96E5	7000.0	1.0
CHAT-MON 1 E2 E2	1.5E3	7200.0	1.0
CHAT-MON 1 E2 BUTENE	1.5E3	7200.0	1.0
CHAT-MON 1 BUTENE E2	1.5E3	7200.0	1.0
CHAT-MON 1 BUTENE BUTENE	1.5E3	7200.0	1.0
CHAT-H2 1 E2 H2	5.6E7	8000.0	1.0
CHAT-H2 1 BUTENE H2	5.6E7	8000.0	1.0
DEACT-SPON 1	1.6E-6	1000.0	1.0

Process Studies

The developed model is highly versatile allowing examination of many aspects of the polyethylene process. Devising an operating policy for grade transition to minimize off-spec product during grade transition is provided as an example to illustrate the applications of the model. The following two tables specify the desired polymer properties and the required operating variables identified with the Polymers Plus steady state simulation.

Definition of grades in terms of melt index and density:

Property	Grade 1	Grade 2
Melt Index	0.281	1.594
Density (kg / m^3)	932.8	901.1
MWN	80,154	48,665

Required concentrations in the reactor:

Concentration	Grade 1	Grade 2
Butene	18.8E-3	52.3E-3
H_2	2.133E-3	2.253E-3
Ethylene	0.3634	0.2874

In the beginning of the process, the Grade 1 polymer is produced. At a given time, the process is switched from the state for producing the Grade1 product to the state for producing the Grade 2 polymer. The first policy is implemented as an intuitive approach. The setpoints of three concentration controllers, Y3C1 for ethylene monomer, Y4C1 for butene comonomer, and Y5C1 for H2, are directly switched from the values for producing the Grade 1 to those for producing the Grade 2. The second is an overshooting policy. It assigns the setpoint of Y3C1 slightly lower than the value for producing Grade 2 and assigns the setpoints of Y4C1 and Y5C1 slightly larger than their values for producing Grade 2 for the predetermined periods. These three setpoints of the controllers, then, are switched to their states for producing Grade 2.

SELECTED SIMULATION RESULTS

Figure 4.2 shows the profiles of the three manipulated concentrations and Figure 4.3 displays the transient responses of the polymer properties under operating policy 1. The system takes more than 21 hours to achieve the steady state of Grade 2 from that of Grade 1 for both melt index and density.

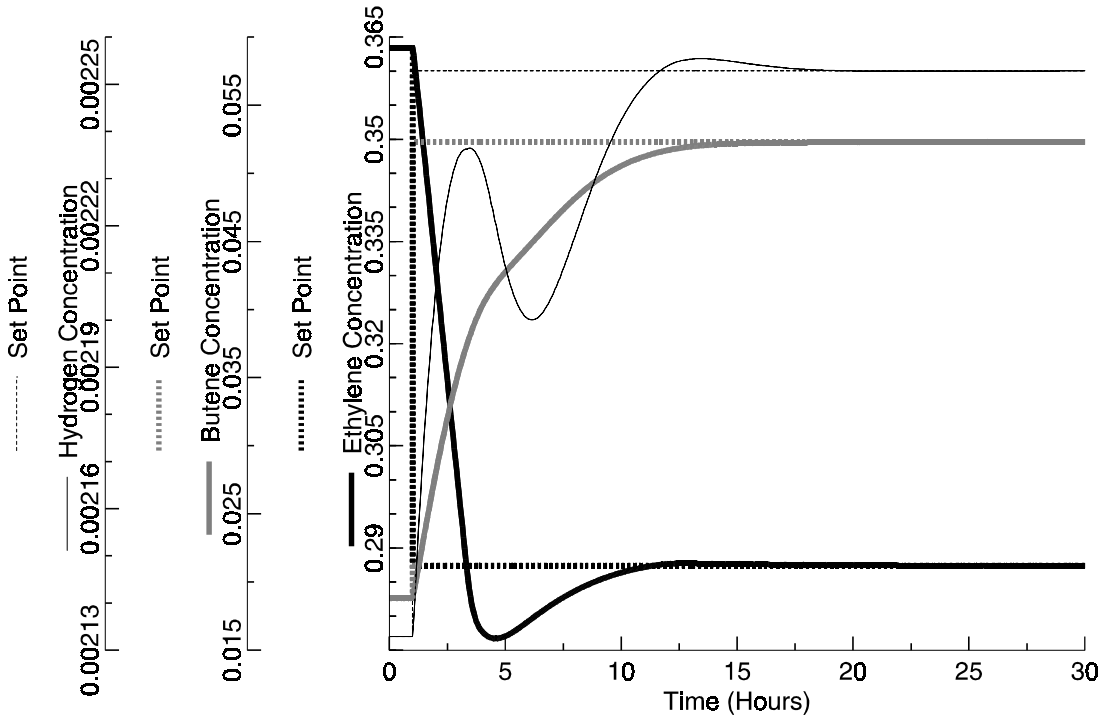

Figure 4.2 *Concentration Profiles with Operating Policy 1*

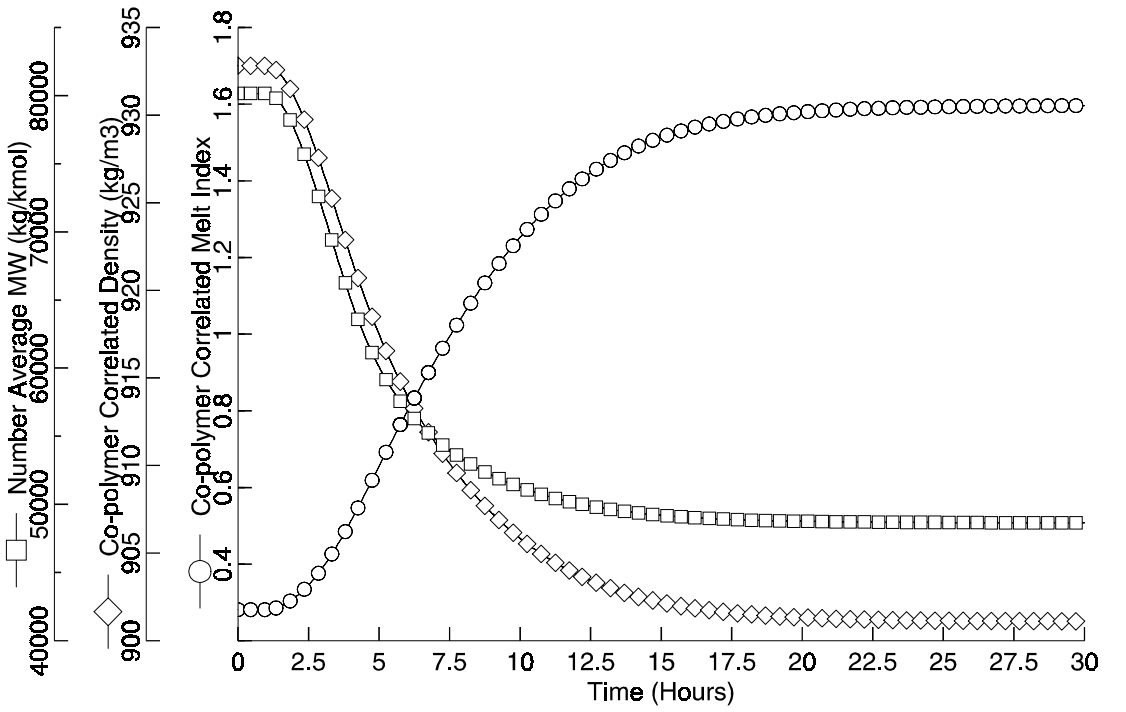

Figure 4.3 *Responses of Reactor with Operating Policy 1*

Figure 4.4 shows the concentration profiles of ethylene, butene, and H2. The dynamics of polymer properties are plotted in Figure 4.5. Policy 2 achieves the steady state of grade 2 in 16 hours which is 5 hours less than that with policy 1.

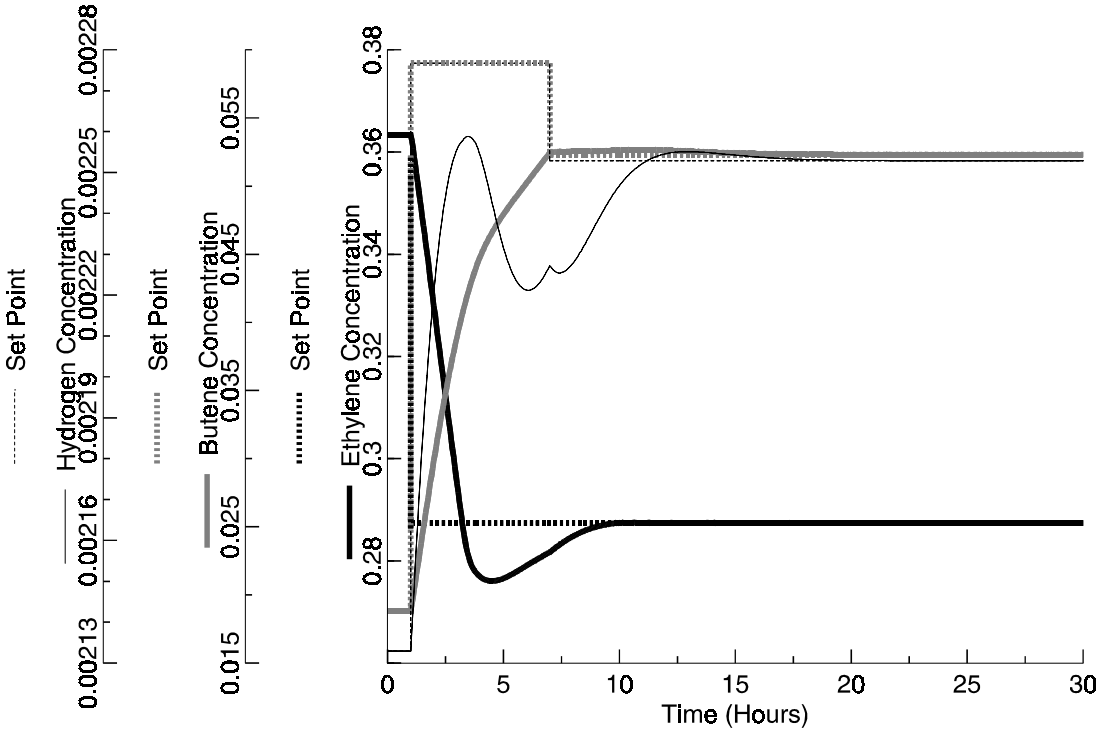

Figure 4.4 *Concentration Profiles with Operating Policy 2*

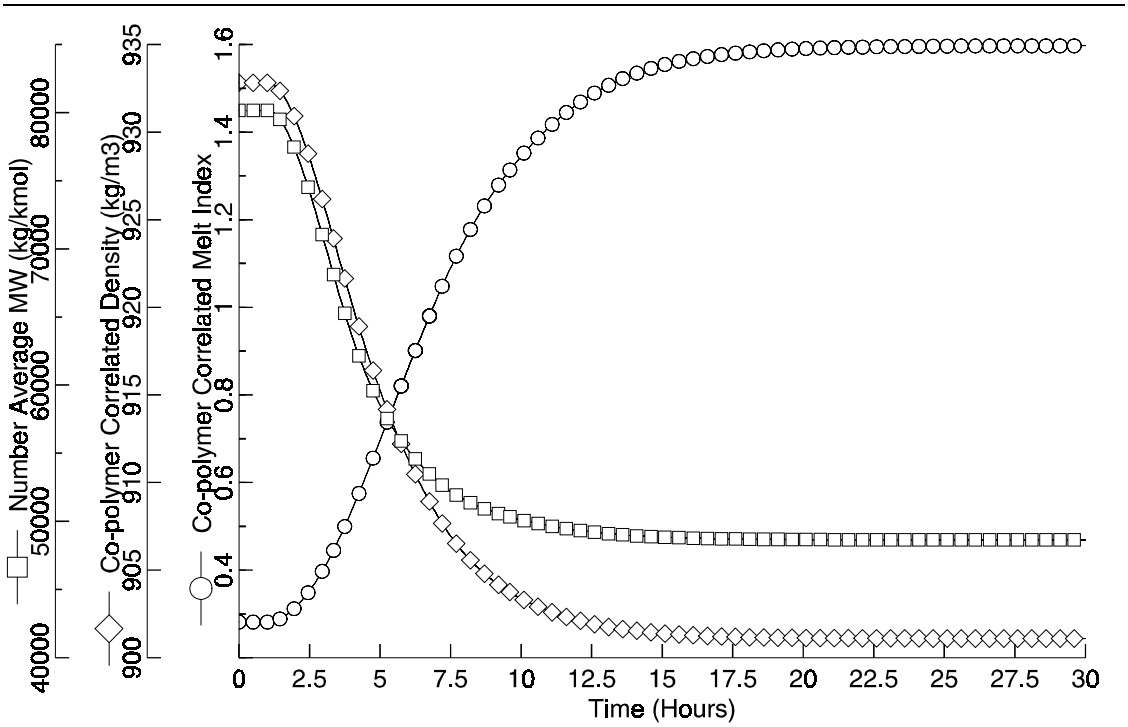

Figure 4.5 *Responses of Reactor with Operating Policy 2*

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5 POLYVINYL CHLORIDE

DYNAMIC POLYMERIZATION PROCESS

SUMMARY

The polyvinyl chloride application simulates a typical batch suspension polymerization of vinyl chloride with Aspen Custom Modeler and Polymers Plus. The model simulates a four-phase batch reactor of polyvinyl chloride (PVC). The simulation shows the dynamic behavior of the polymerization process such as phase change and monomer distribution among the phases which will help you to gain a better understanding of this process. The simulation estimates several attributes of polymer including number and weight average molecular weight, number and weight of degree of polymerization, and polydispersity in both monomer and polymer phases. The PVC model may be used to train operators or it can serve as a state estimator of a PVC process. The model may also be applied for debottlenecking and optimizing the batch time for an existing PVC process to increase the throughput. The model can also be used to minimize the extent of initiator required and what cocktail of initiators to use to improve the overall productivity and profitability.

ABOUT THIS PROCESS

Polyvinyl chloride (PVC) is one of the oldest polymers and the second largest in volume thermoplastic manufactured in the world. Approximately 75% of the world's PVC is produced by the suspension polymerization process (Kiparissides, et al., 1997). In suspension polymerization liquid vinyl chloride monomer (VCM) containing oil soluble initiators are dispersed in the continuous aqueous phase by a combination of stirring and suspending agents. Reactor is heated to the desired temperature and reaction occurs in the monomer droplets. As soon as a small amount of polymer is formed, a separate polymer

phase is present because of very low solubility of PVC in VCM. As long as a monomer phase is present, the polymer phase is saturated with the monomer. Reaction takes place in both the monomer and polymer phases. The heat of polymerization is transformed from monomer droplets to aqueous phase and then to the reactor walls which are cooled by the cooling water. Reactor pressure is determined by the vapor pressure of monomer and it remains constant as long as a monomer phase is present. As soon as the monomer phase disappears, reactor pressure drops and batch operation is stopped after a certain predetermined pressure drop is reached.

Reactor model RBatch in Aspen Plus can be used to simulate a batch reactor. The RBatch model considers only one liquid and one vapor phase. Whereas the suspension PVC process has three liquid phases (monomer, polymer and water phases) and one vapor phase. Any model for a suspension PVC process should consider all four phases, and polymerization reactions in the monomer and polymer phases. Therefore the present model is developed in Aspen Customer Modeler considering all the important features of the PVC suspension polymerization process.

PROCESS DEFINITION

An Aspen Custom Modeler model is developed to simulate the suspension PVC process and considers four phases in the reactor: monomer, polymer, aqueous and vapor phases. Polymerization reactions are considered in the monomer phase and polymer phase. Polymerization reactions in the aqueous phase and vapor phase are assumed to be negligible.

Process Conditions

Table 5.1 shows the components considered in the simulation. Additional components can be readily added into the model.

Table 5.1 Process Conditions

Components	Name	Databank	Description
Vinyl chloride	VCM	PURE10	Monomer
Poly(vinyl chloride)	PVC	POLYPCD	Polymer component
Vinyl chloride segment	VCM-SEG	SEGPCD	Vinyl chloride segment
Dilauroyl peroxide	DLP	PURE10	Initiator 1
Diethylperoxydicarbonate	DEPC	PURE10	Initiator 2
Water	H2O	PURE10	Aqueous phase

The initial conditions of reactor are 60°C and 10 bar. The volume of reactor is $15\,m^3$ with the initial $3.5\,m^3$ of VCM and $7.0\,m^3$ of water.

Physical Property Models and Data

The polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is used as the physical property method to calculate properties.

Reactor

The reactor model is developed from a DynPLUS three phase flash vessel, with the consideration of separate polymerization reactions in the monomer and polymer phases. At the start of the batch when there is no polymer phase, reaction occurs only in the monomer phase. The polymer produced forms a separate polymer phase. VCM, H2O, initiators and other species dissolve in the polymer phase according to the supplied partition coefficients. The phase equilibrium assumes no PVC is dissolved in the monomer and aqueous phases, and PVC generated in the monomer phase adds to the polymer phase. At the critical conversion where the monomer phase disappears, the polymer is produced only in the polymer phase. The total mass of polymer produced in each phase and the moments of molecular weight distribution in each phase are recorded for estimating the polymer properties. Reactor pressure determined by the vapor pressure of monomer remains constant until the monomer phase disappears.

Rigorous three phase flash calculations are performed for the vapor, monomer, and aqueous phases, and a partition coefficient is used to calculate the concentrations in the polymer phase. Thus the flash is performed excluding the polymer phase. NRTL parameters between polymer segments and other species are not required in this model. The model may have one feed and one vapor product stream used to attach a condenser system for accommodating a recycle. In addition, the temperature controller of the reactor may be replaced by an alternative heat removal system, e.g., heat exchanger.

Kinetics

The free radical kinetic scheme used in the model includes initiator decomposition, chain initiation, chain propagation, chain transfer to monomer, and chain termination. Gel effect, known as Trommsdorff effect, is applied to the termination reaction in the polymer phase. Except the termination rate constant and the gel effect, same rate parameters are used for the polymerization reactions in the monomer and polymer phases.

The units for the frequency factor are in SI units. The following gel-effect correlation was used in the model for the termination reaction:

$$GF = \left(\frac{A}{1 - a_9 X_p} \exp\left[-\left(BX_p + CX_p^2 + DX_p^3 \right) \right] \right)^{a_{10}}$$

The effective rate coefficient for the termination reaction will be $k_{eff} = k_t * GF$.

The rate parameters and gel-effect parameters are from the article by Xie, Hamielec, Wood and Woods (Xie et al 1991).

	Frequency Factor	Activation Energy (J/KMol)	Activation Volume (m^3)
INIT-DEC DLP	1.44E15	1.274E8	0.0
INIT-DEC DEHPC	7.45E15	1.245E8	0.0
CHAIN-INI VCM	5.0E7	2.76E7	0.0
PROPAGATION VCM VCM	5.0E7	2.76E7	0.0
CHAT-MON VCM VCM	2.89E8	5.0618E7	0.0
TERM-COMB VCM VCM	1.19E13	2.422E7	0.0 (Monomer Phase)
TERM-COMB VCM VCM	5.0E13	2.422E7	0.0 (Polymer Phase)
GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1 0 2.57 & 0.00505 9.56 -0.0176 -3.03 .00785 0 2			

SELECTED SIMULATION RESULTS

As shown in Figure 5.1, PVC is only generated in the monomer phase at the beginning of the batch. After 1 hour, PVC generated in the polymer phase exceeds that generated in the monomer phase. Before the monomer phase completely disappears at two hours, the volume of monomer phase continuously decreases due to the consumption of monomers. At 65% conversion (2 hours), the monomer phase disappears. The pressure drops from 10 to 1 bar in an additional three hours when the conversion finally reaches 98%. A total off 3,600 Kg of polymer is generated by the end of the batch.

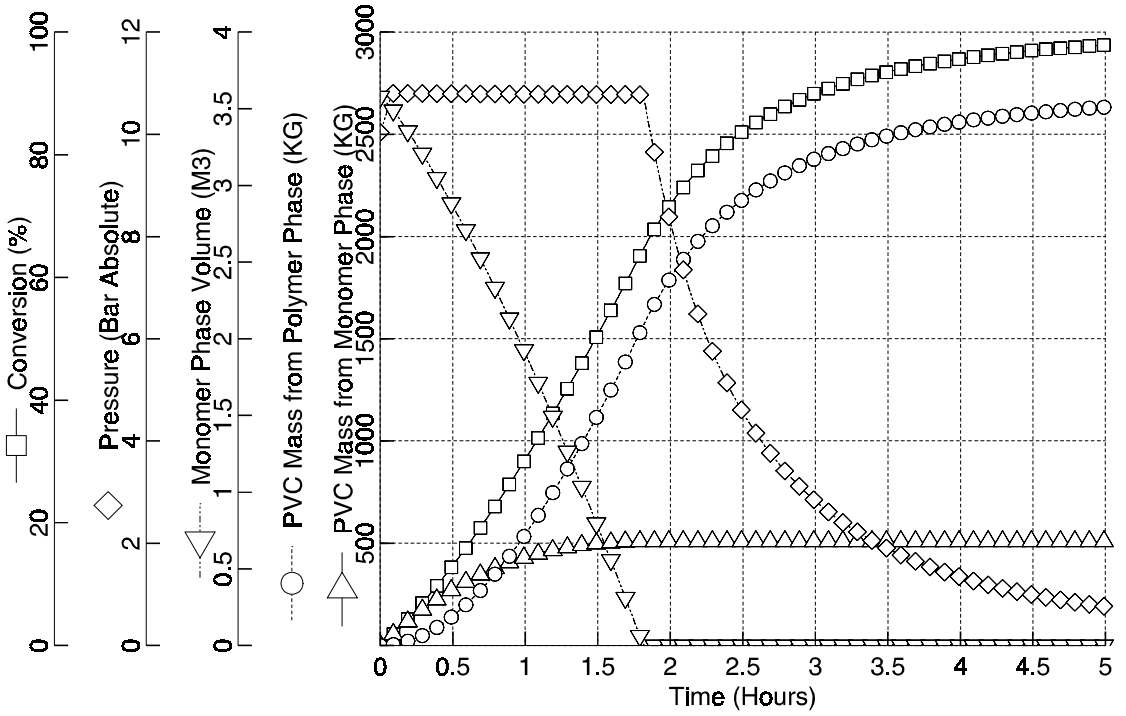

Figure 5.1 *PVC Summary Results*

Figure 5.2 displays VCM distribution in four phases. Initially, 3125 Kg (50 kmol) of VCM in the monomer phase is gradually reduced to zero while the VCM in the polymer phase increases as the volume of polymer phase increases and the polymerization proceeds to a 2 hour processing time. After the critical conversion where the monomer phase completely disappears, the VCM in the polymer phase is consumed causing the volume of polymer phase to shrink and reducing the pressure (less VCM in the vapor phase).

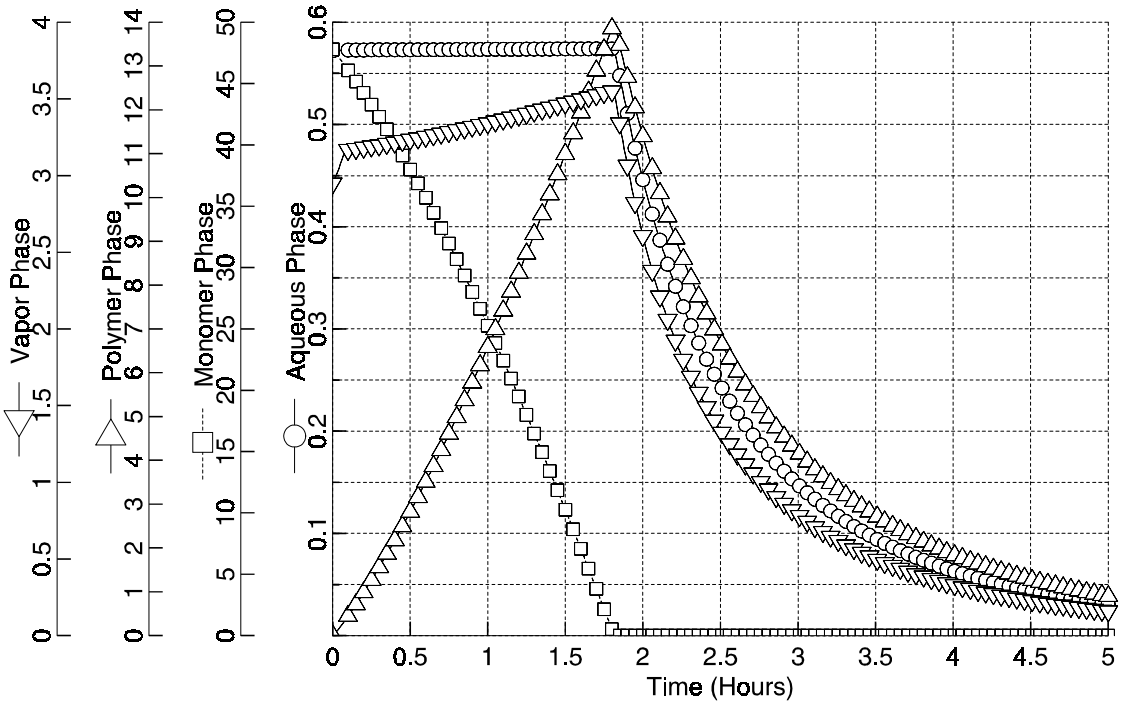

Figure 5.2 *VCM Distribution in Four Phases (Kmol)*

Figure 5.3 and Figure 5.4 show the attributes of polymer including number average molecular weight, number and weight of degree of polymerization, and polydispersity for monomer and polymer phases, respectively. Note that the properties of PVC produced in the monomer phase are unchanged after two hours because no PVC is produced in this phase.

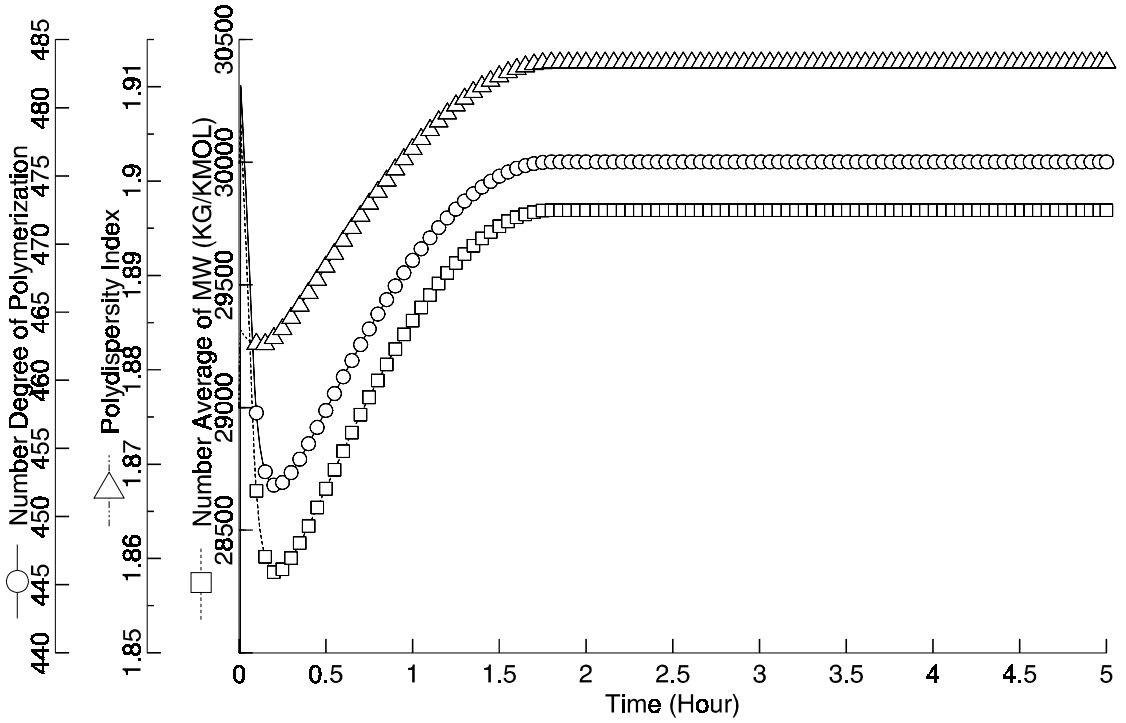

Figure 5.3 *PVC Properties in Monomer Phase*

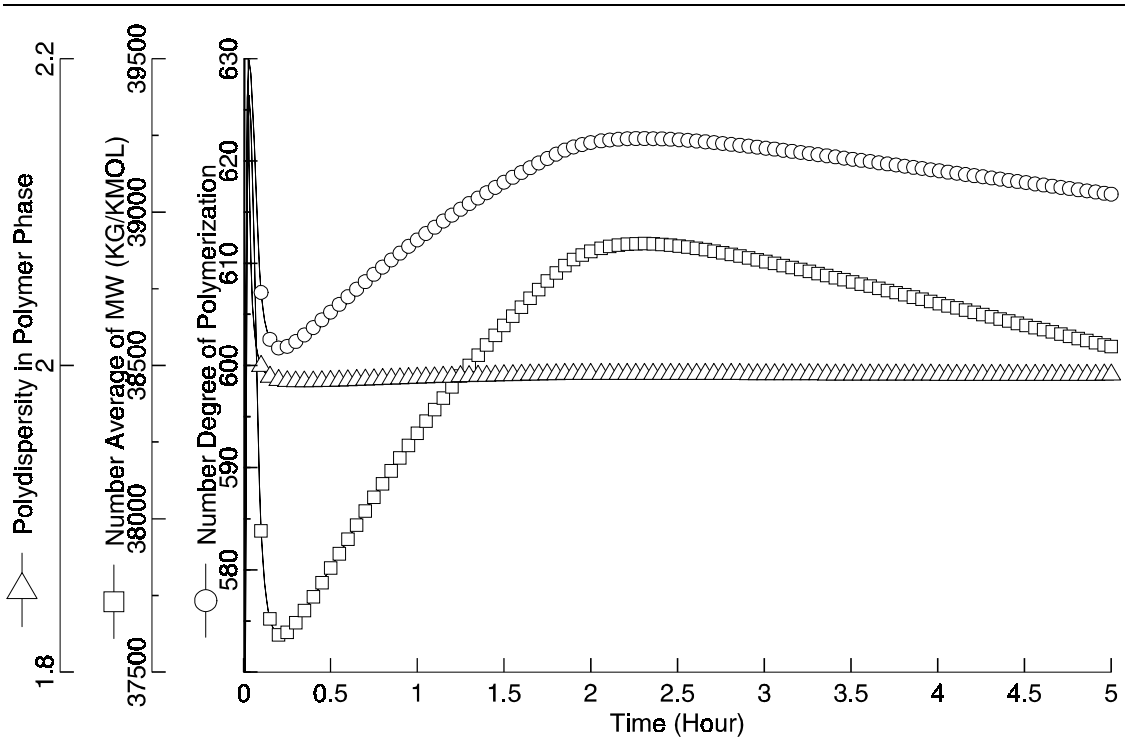

Figure 5.4 *PVC Properties in Polymer Phase*

Figure 5.5 demonstrates an application for debottlenecking a batch PVC process. It shows that the required cooling rate is constantly increased and reaches the maximum just before the VCM phase completely disappears at the critical conversion, therefore, the bottleneck of this process in terms of cooling rate is located. In order to increase production capacity, one must rate the existing cooling system that can accommodate the increase.

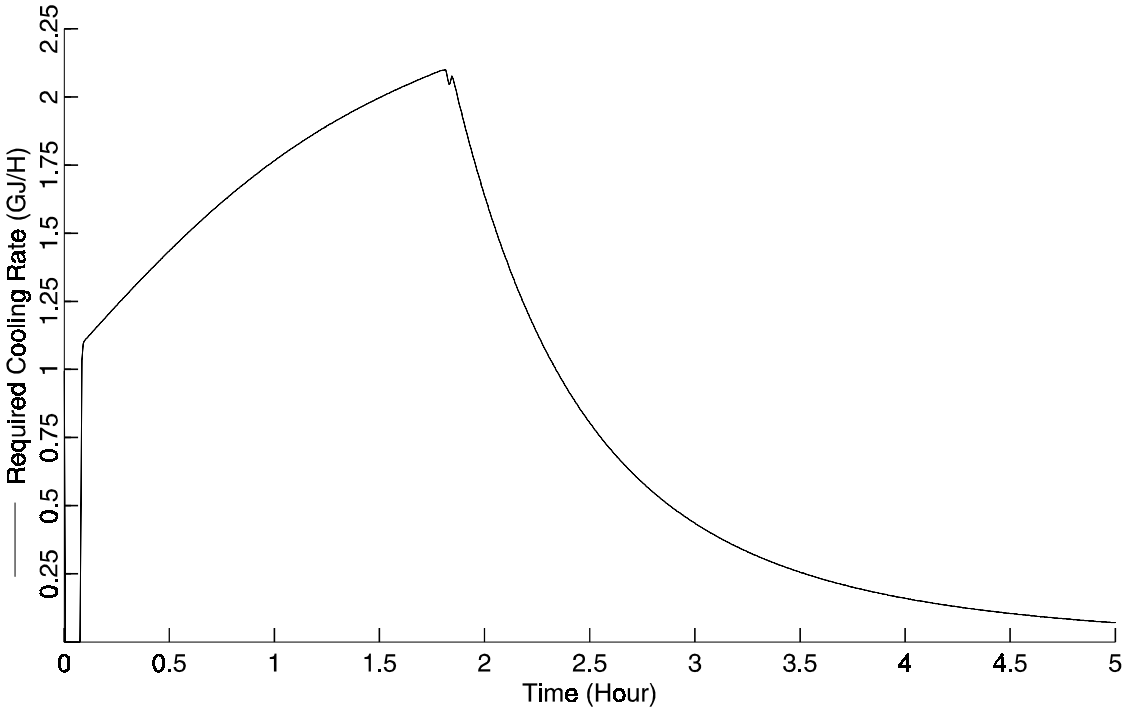

Figure 5.5 *Utility Requirement*

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6 EXPANDABLE POLYSTYRENE

BATCH POLYMERIZATION PROCESS

SUMMARY

The batch polymerization process illustrates the use of Polymers Plus and Aspen Custom Modeler to model the expandable polystyrene process. The batch reactor model considers two liquid phases and one vapor phase.

ABOUT THIS PROCESS

Manufacture of expandable polystyrene (EPS) involves two stages. During the first stage, polymerization of styrene is carried out in a stirred batch reactor at temperatures between 80 and 90°C using water as the dispersed phase. The volume ratio of water to monomer is in the range of 0.4 to 0.6. Monomer styrene is suspended in the form of droplets in the water phase and polymerization occurs in these droplets until the mixture reaches its glass transition temperature. The mean particle size is determined by the droplet coalescence and the droplet breakage caused by the agitation system. The particle growth is controlled by the aid of suspending agents which are usually inorganic powders such as tricalcium phosphate.

In the second stage, also known as the impregnation stage, a blowing agent, such as n-pentane, is loaded into the reactor and the agent diffuses into the beads. The residual monomer is polymerized using an initiator of half-life higher than the one used in the polymerization process. The batch reactor is operated at elevated pressures during the impregnation stage.

A main manufacturing objective is to minimize the long batch times necessary to carry the polymerization to completion. Polymerization at higher temperatures as a means to increase productivity is not successful due to lower molecular weight of the polymer and the enhanced particle coalescence due to higher temperature. Addition of blowing agent influences the polymerization rate. The objective of plant engineers is to optimize the time of addition of the blowing agent and the extent of initiator needed to improve the overall productivity.

The reactor model RBatch in Aspen Plus can be used to simulate a batch reactor. But the RBatch model assumes only one liquid and one vapor phase. Whereas the EPS process involves two liquid phases (monomer and water) and one vapor phase. RBatch can be used if the following is assumed:

- Each drop in the reactor acts like a mini batch reactor
- There is no interaction between the two liquid phases
- The reactor is operated isothermally

The RBatch model can provide information about monomer conversion and the polymer molecular weight. To consider interactions between the two liquid phases and to address reactor controllability issues a dynamic model is necessary. This example uses Aspen Custom Modeler.

PROCESS DEFINITION

A dynamic model is developed to simulate the EPS process. The model considers two liquid phases and one vapor phase, and polymerization reactions are assumed to occur in the monomer phase. However the model can be extended to consider reactions in both the liquid phases. Phase equilibrium determines the concentration of all the components in all the three phases.

Process Conditions

The process conditions for the expandable polystyrene model are as listed in Table 6.1.

Table 6.1 Process Conditions

Components	
Benzoyl peroxide (BPO)	Initiator
Co-initiator (CINI)	Dummy component for thermal initiation
Ethyl benzene (EB)	Chain transfer agent
Dodecylmercaptan (DDM)	Inhibitor
Water	Aqueous Phase
Pentane	Blowing agent
Tricalcium phosphate (TCP)	Suspending agent
Polystyrene (PS)	Polymer
Styrene Segment (E-STY)	Polymer segment

Physical Property Models and Data

The polymer Non-Random Two liquid activity coefficient model (POLYNRTL) is used as the physical property method.

Reactors / Kinetics

The free radical kinetic scheme used in the model includes chemical and thermal initiation (third order with respect to monomer), propagation, chain transfer, termination and gel effect applied to the termination reaction. The rate parameters used in the model are:

	Frequency factor	Activation Energy (J/KMol)	Activation Volume (m^3)
INIT-DEC BPO	3.816E12	1.1396E8	0.0 EFFIC=.60 NRADS=2
INIT-SP	2.19E5STY CINI	1.1480E+08	0.0
CHAIN-INI STY	1.02133E7	2.9570E+07	0.0
PROPAGATION STY STY	1.02133E7	2.9570E+07	0.0
CHAT-MON STY STY	1.021E+07	5.6280E+07	0.0
TERM-COMB STY STY	1.2583E9	7017000.0	0.0
INIT-SP-EFF STY COEFFA=0.0 COEFFB=3.0 COEFFC=0.0			
GEL-EFFECT TERMINATION 2 MAX-PARAMS=10 GE-PARAMS=1 0 2.57 & 0.00505 9.56 -0.0176 -3.03 .00785 0 2			

The units for the frequency factor are in SI units. A co-initiator which is required for thermal initiation is included in the list of components. The feed rate of co-initiator is set to zero so that it will not influence the thermal initiation rate. The following gel-effect correlation was used in the model for the termination reaction.

$$GF = \left(\frac{A}{1 - a_9 X_p} \exp\left[-\left(BX_p + CX_p^2 + DX_p^3 \right) \right] \right)^{a_{10}}$$

The effective rate coefficient for the termination reaction is $k_{eff} = k_t * GF$

The rate parameters and gel-effect parameters are from the reference Hui and Hamielec (Hui and Hamielec, 1972).

Dynamic Model

The dynamic model is based on the library model CSTR2P and is modified to consider two liquid phases and one vapor phase. Input and output flow rate in the reactor model were set to zero to simulate a batch reactor. The reactor conditions are:

Initial charge:

Styrene	100 Kg
Initiator	0.3 Kg
Water	150 Kg

Reactor temperature is maintained isothermally at 900°C by the controller and the jacket temperature is fixed at 200°C. The phase equilibrium constants obtained from the Aspen Plus model are specified in the model. We assume K values for BPO, CINI, EB, DDM, pentane are the same as those for styrene. K values for TCP are same as those for water. Polystyrene is assumed to negligible in the aqueous phase.

	Organic phase (K1)	Aqueous phase (K2)
Benzoyl peroxide (BPO)	0.177	1086.0
Co-initiator (CINI)	0.177	1086.0
Styrene (STY)	0.177	1086.0
Polystyrene (PS)	0.177	10860.0
Ethyl benzene (EB)	0.177	1086.0
Dodecylmercaptan (DDM)	0.177	1086.0
Water	53.6	0.7
Pentane	0.177	1086.0
Tricalcium phosphate (TCP)	53.6	0.7

Reactor heat transfer coefficient and heat transfer area are assumed to be 2.0×10^{-3} $kW/m^2/h$ and 0.2 m^2/m^3. These variables can vary depending on the heat transfer medium and the reactor geometry.

SELECTED SIMULATION RESULTS

Figure 6.1 shows a plot of conversion as a function of time and Figure 6.2 shows the number and weight average molecular weight for the batch polymerization process.

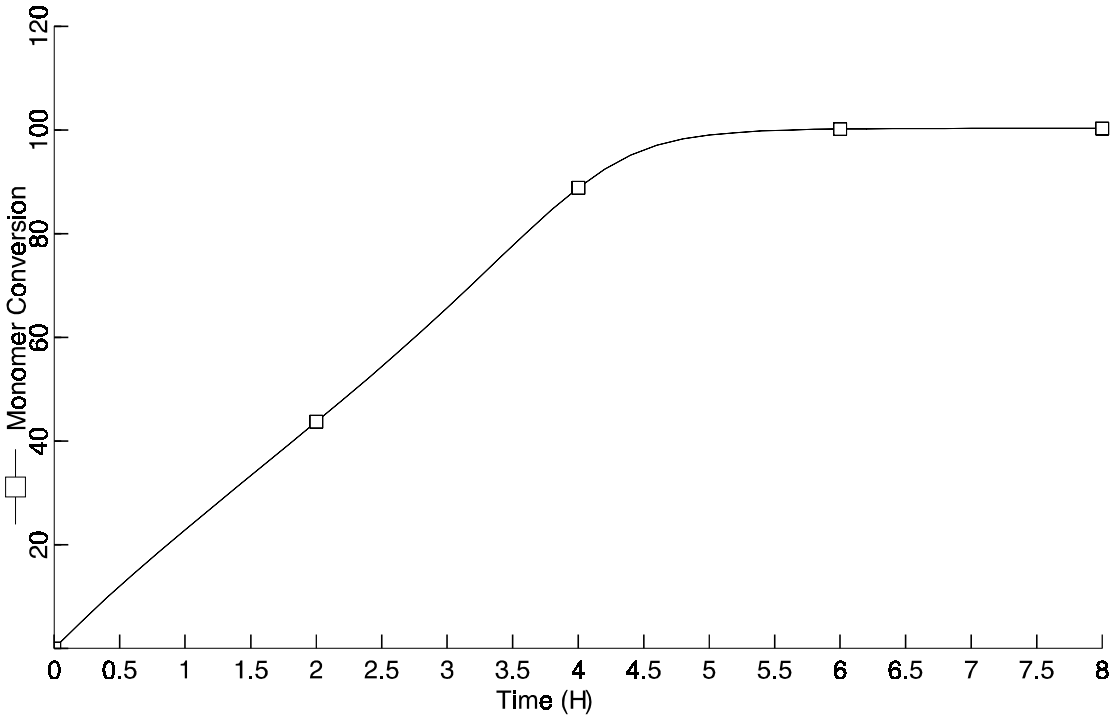

Figure 6.1 *Monomer Conversion*

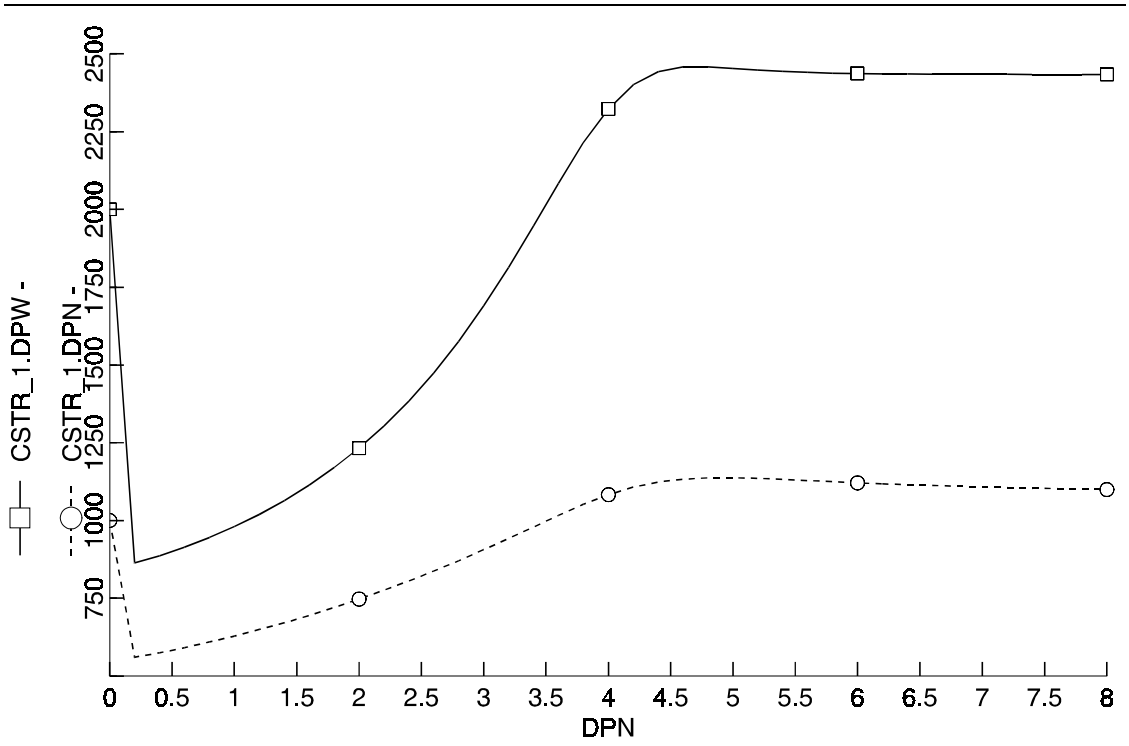

Figure 6.2 *Number and Weight Average Molecular Weights vs. Time*

REFERENCES

Hui, A. W and A. E. Hamielec, "Thermal polymerizations of styrene at high conversion and temperatures. An experimental study," *J. Appl. Polym. Sci*., **16**, 749-769 (1972).

Marco A. V., A. E. Hamielec and P. E. Wood, "Bulk and suspension polymerization of styrene in the presence of n-pentane. An evaluation of monofunctional and bifunctional initiation," *J. Appl. Polym. Sci*., **50**, 327-343 (1993).

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