Reactor Modeling, Convergence Tips and Data-Fit Tool

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Reactor Modeling, Convergence Tips and Data-Fit Tool

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Abstract

This chapter provides a comprehensive exploration of kinetic reactor modeling in Aspen Plus/Polymers for polyolefin manufacturing, introducing three distinct reactor types: continuous stirred-tank reactors (RCSTR), plug-flow reactors (RPLUG), and batch/semi-batch reactors (RBATCH). Detailed configurations and specifications of these reactors are examined, alongside methodologies for representing nonideal reactor behavior. The chapter presents innovative strategies for optimizing computational efficiency, including accelerated solution techniques for conservation equations and phase-equilibrium calculations. It further highlights a robust data-fitting tool, enabling regression of critical simulation parameters such as reaction kinetics, heat-transfer coefficients, and property model inputs. Practical application is emphasized through hands-on workshops demonstrating kinetic parameter estimation using time-evolution concentration profiles and polymer attribute metrics like number-average and weight-average molecular weights. This focused discussion provides actionable insights into advanced reactor modeling and parameter optimization, enhancing predictive accuracy and process efficiency for polyolefin manufacturing systems.

This is a preprint version of a chapter from our book - *Integrated Process Modeling, Advanced Control and Data Analytics for Optimizing Polyolefin Manufacturing.* Please cite the original work if referenced [12,15]

3.1 Kinetic or Rate-Based Reactors

We introduce the three types of kinetic or rate-based reactor models available within Aspen Plus/Polymers for polyolefin manufacturing, including continuous stirred-tank reactor (RCSTR), plug-flow reactor (RPLUG), and batch or semi-batch reactor (RBATCH). We focus on configurations and specifications of the three kinetic reactors in Sections 3.2 to 3.4, and on the representation of nonideal reactors in Section 3.5. We present practical tips to speed up the solution of mass, energy and polymer attribute conservation equations and phase-equilibrium calculations in Sections 3.6 and 3.7. Section 3.8 discusses the data-fit tool for regressing all types of simulation parameters, such as reaction kinetics, heat-transfer coefficients, and any accessible model input parameters (including property model parameters). Sections 3.9 and 3.10 cover hands-on workshops applying the data fit for kinetic parameter estimation using time-evolution concentration profile and polymer attribute values (such as MWN and MWW). Section 3.11 presents the bibliography.

Given the reaction kinetics and operating conditions, kinetic reactor models do mass, energy, and polymer attribute balance calculations. We note that while Aspen Plus also has a FluidBed reactor model, this model can only handle conventional reactions and not polymerization kinetics. In Section 3.5 and in Chapters 4 to 7, we show how to use the continuous stirred-tank reactor model (RCSTR) to represent fluidized-bed reactors in polyolefin manufacturing. We summarize in Table 3.1 the key assumptions of the kinetic or rate-based reactors available in Aspen Pus/Polymers:

Table 3.1 Assumptions of kinetic reactors in Aspen Plus/Polymers

Reactor type	Assumptions
RCSTR	Ideal mixing; homogeneous concentrations inside the reactor; constant temperature and pressure; phase equilibrium
RPLUG	Ideal plug flow of fluids without backmixing; homogeneous in the radial direction; phase equilibrium; allows cocurrent or countercurrent heating
RBATCH	Ideal mixing; homogeneous concentrations; constant temperature; constant pressure at each time step; phase equilibrium; Permit a single charge or time-varying feeds; feed and product stream conditions are time-averaged
FLUIDBED	Ideal solid mixing; plug-flow vapor phase; homogeneous in the radial direction; continuous feeds of vapor and solids

3.2 Continuous Stirred-Tank Reactor (RCSTR)

3.2.1 RCSTR Configurations

We use RCSTR in our slurry HDPE process as showcased by Sharma et. al. [9,17] for modeling polyolefin kinetics.A CSTR model can have a single or multiple feeds. Depending on the valid phases that we set, the model can have a single liquid or vapor product (valid phases = liquid only, or vapor only), a vapor product and a liquid product (valid phases = vapor-liquid), and a vapor product and two liquid products (valid phases = vapor-liquid-liquid). Figure 3.1 illustrates these configurations, in which we can replace the single feed with multiple feeds. Note for RCSTR3, we have added the optional input and output "heat" streams. Figure 3.2 shows where we set the valid phases and key component of the 2nd liquid phase.

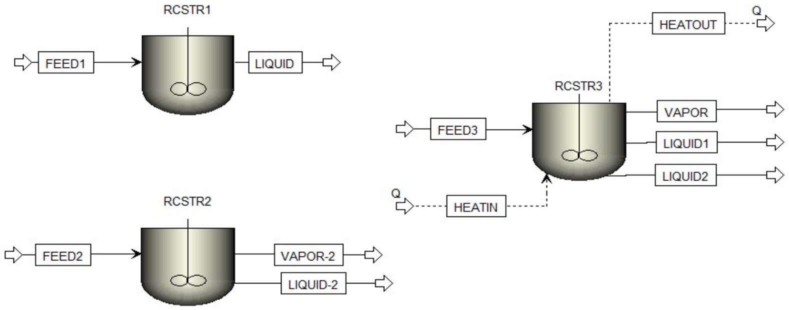
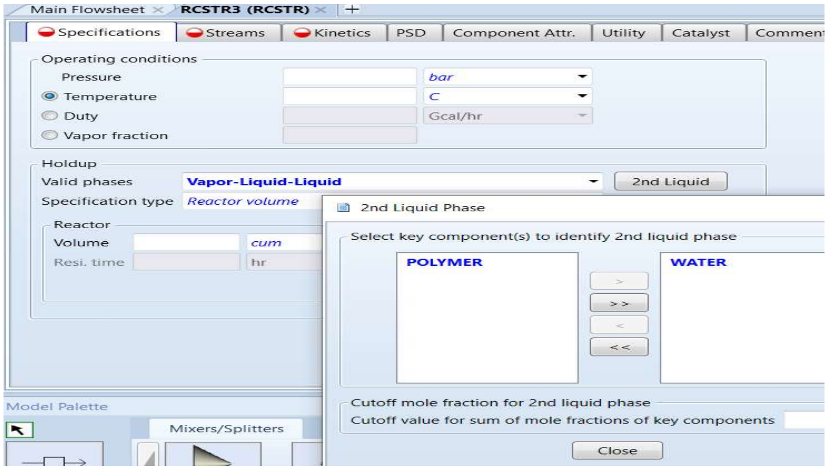


Figure 3.1 RCSTR configurations



Operating conditions

Pressure bar

● Temperature C

○ Duty Gcal/hr

○ Vapor fraction

Holdup

Valid phases Vapor-Liquid-Liquid

Specification type Reactor volume

Reactor

Volume cum

Resi. time hr

2nd Liquid Phase

Select key component(s) to identify 2nd liquid phase

POLYMER

WATER

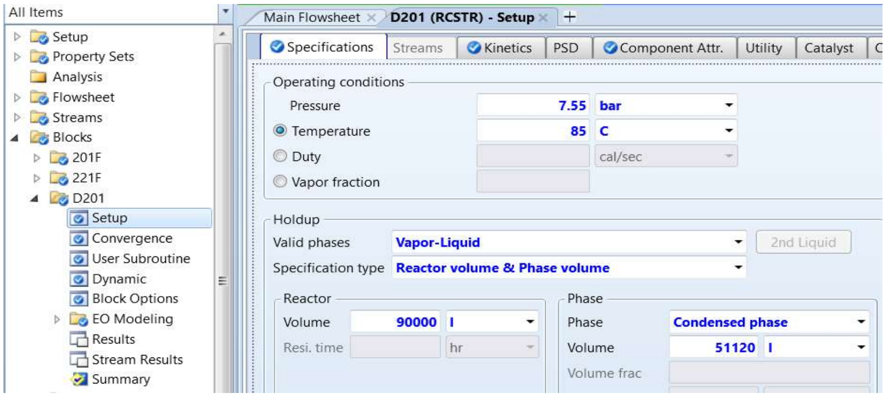
Cutoff mole fraction for 2nd liquid phase

Cutoff value for sum of mole fractions of key components

Figure 3.2 Specification of valid phases and key component of 2nd liquid phase.

3.2.2 RCSTR Specifications

Figure 3.3 illustrates the specifications of a CSTR D201 in Workshop 5.1 for a slurry HDPE process.



Operating conditions

Pressure 7.55 bar

● Temperature 85 C

○ Duty cal/sec

○ Vapor fraction

Holdup

Valid phases Vapor-Liquid

Specification type Reactor volume & Phase volume

Reactor

Volume 90000 l

Resi. time hr

Phase

Phase Condensed phase

Volume 51120 l

Volume frac

Figure 3.3 Specifications of a RCSTR

For operating pressure, we can specify an exit pressure (value positive) or a pressure drop (value zero or negative), and we can enter an exit temperature or a reactor heat duty. For phase, we can specify vapor phase or condensed phase. This chosen phase determines the specification type for the holdup input. Specifically, we may select one of seven types: (1) reactor volume, (2) residence time, (3) reactor volume and phase volume, (4) reactor volume and phase volume fraction, (5) reactor volume and phase residence time, (6) residence time and phase volume fraction, and (7) phase residence time and volume fraction. We will demonstrate the specifications of kinetics and component attributes beginning in Chapter 4, and RCSTR convergence tips in Section 3.5.

3.3 Plug-Flow Reactors (RPLUG)

3.3.1 RPLUG Configurations

We use RPLUG in our high-pressure LDPE process and EVA (ethylene-vinyl acetate copolymer) process in Chapter 4. Figure 3.4 illustrates a RPLUG configuration with valid phases of vapor-liquid-liquid. To specify the valid phases, follow the path: Simulation -> Setup -> Global settings -> Valid phases -> Vapor-liquid-liquid. We follow the same path when specifying the valid phases for RPLUG to be vapor only, liquid only, or vapor-liquid.

A distinct feature of the RPLUG model is the ability to use a heat-transfer fluid (HTFL) or a thermal fluid. We see in Figure 3.4 the inlet and outlet HTFL streams, HTFLIN and HTFLOUT.

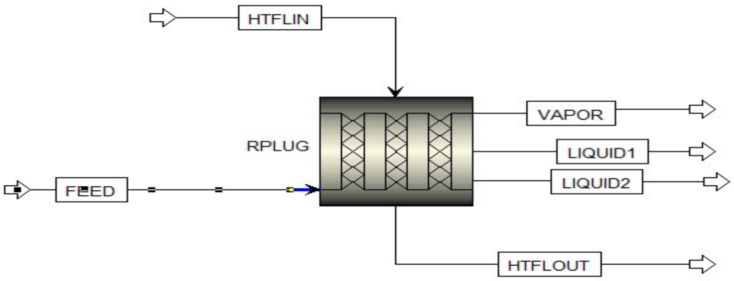
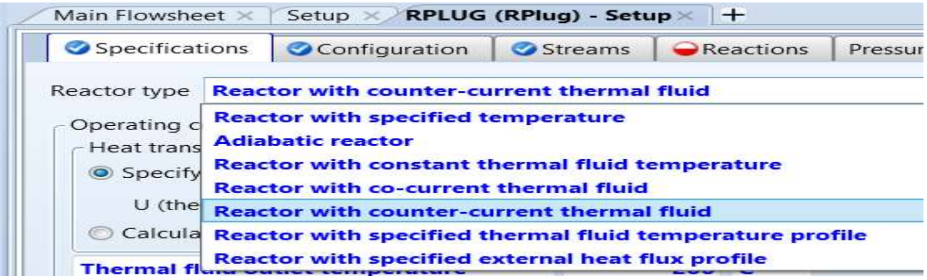


Figure 3.4 RPLUG configuration with heat-transfer fluid (HTFL).

3.3.2 RPLUG Specifications

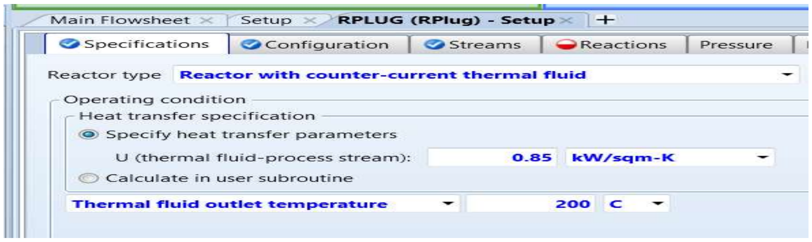
Following the path: Simulation -> Blocks -> RPLUG -> Setup -> Reactor type-> We see the following options available to a thermal fluid in Figure 3.5:



Reactor type: Reactor with counter-current thermal fluid

Figure 3.5 Available reactor types for RPLUG

For RPLUG with a thermal fluid, we see five possible options: (1) constant thermal fluid temperature; (2) co-current thermal fluid; (3) counter-current thermal fluid; (4) specified thermal fluid temperature along the reactor length; and (5) specified external heat flux profile. In the figure, we also see two common reactor types: (1) constant specified temperature; and (2) adiabatic reactor. For a RPLUG with a co-current or a counter-current thermal fluid, Figure 3.6 shows two additional specifications: (1) heat-transfer coefficient of the thermal fluid; and (2) thermal fluid outlet temperature. In Chapter 4, we use the RPLUG model with a thermal fluid in the simulation of a high-pressure LDPE process with tabular reactors.



Reactor type: Reactor with counter-current thermal fluid

Operating condition

Heat transfer specification

● Specify heat transfer parameters

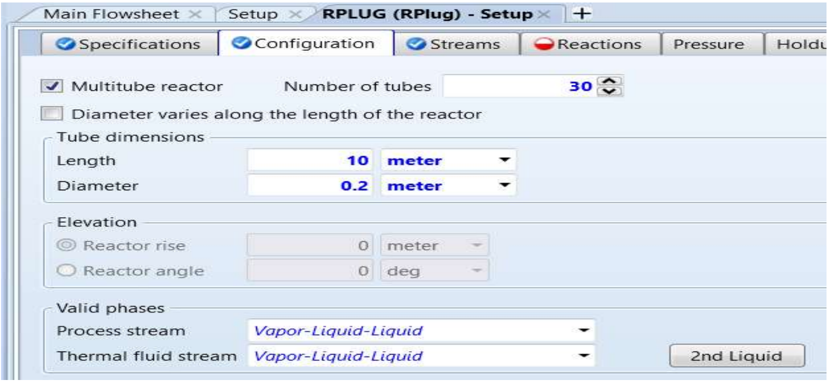
U (thermal fluid-process stream): 0.85 kW/sqm-K

○ Calculate in user subroutine

Thermal fluid outlet temperature: 200 C

Figure 3.6 Specifications of heat-transfer parameter and thermal fluid outlet temperature.

Next, we see the configuration specifications in Figure 3.7.



☑ Multitube reactor Number of tubes 30

☐ Diameter varies along the length of the reactor

Tube dimensions

Length 10 meter

Diameter 0.2 meter

Elevation

○ Reactor rise 0 meter

○ Reactor angle 0 deg

Valid phases

Process stream *Vapor-Liquid-Liquid*

Thermal fluid stream *Vapor-Liquid-Liquid*

Figure 3.7 Configuration specifications of the RPLUG

The Streams folder specifies the products, with VAPOR being vapor phase, LIQUID1 being 1st liquid phase and LIQUID2 being 2nd liquid phase. We will give the details of Reactions specification beginning in Chapter 4. The Pressure folder specifies the pressure at reactor inlet, and the pressure drop. For the Holdup folder, we typically stay with the default condition, assuming no slip between phases.

3.4 Batch Reactor (RBATCH)

3.4.1 RBATCH Configuration

The RBTCH model can simulate a batch or a semi-batch operation. We use RBATCH in our SBS (styrene-butadiene-styrene rubber) process in Chapter 7. Figure 3.8 shows a RBATCH configuration. In the figure, BCHARGE represents a single batch charge stream (required). CFEEDs represents one or more continuous feed streams for semi-batch operation (optional). Product represents a single product stream (required). VENT represents a vent stream for semi-batch operation (optional). There is no inlet heat stream, and an optional outlet heat stream is allowed.

RBATCH performs mass, energy, and polymer attribute conservation calculations around an ideal batch reactor, assuming known reaction kinetics and the reactor contents to be well-mixed.

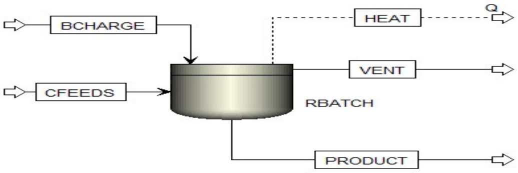
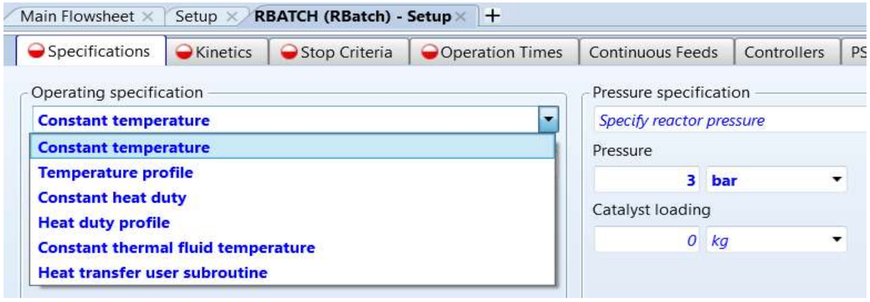


Figure 3.8 RBATCH configuration

3.4.2 RBATCH Specifications

Figure 3.8 illustrates the six options for reactor operating specifications. Choosing each option will lead to additional required specifications: (1) constant temperature – operating temperature; (2) temperature profile – time versus operating temperature; (3) constant heat duty – heat duty; (4) heat duty profile – time versus heat duty; (5) constant thermal fluid temperature – thermal fluid temperature, overall heat-transfer coefficient, and heat-transfer area; and (6) heat-transfer user routine

– see an example for specifying a heat-transfer user routine in Chapter 4 for our high-pressure LDPE reactor (which is a continuous reactor but with essentially similar user subroutine specifications).



Operating specification: Constant temperature

- Constant temperature
- Temperature profile
- Constant heat duty
- Heat duty profile
- Constant thermal fluid temperature
- Heat transfer user subroutine

Pressure specification: Specify reactor pressure

Pressure: 3 bar

Catalyst loading: 0 kg

Figure 3.9 Six options for RBATCH operating specifications

In the figure, we see the pressure specification. Three options are available: (1) specify reactor pressure; (2) specify reactor profile (time versus operating pressure); and (3) calculate reactor pressure. Figure 3.10 illustrates the temperature profile, "calculate reactor pressure" specification, and valid phases. We need to provide the reactor volume to calculate the reactor pressure. When allowing a vent stream during a semi-batch operation, we specify a vent opening pressure together with the reactor volume. In the figure, we also see the specification folders of "Stop Criteria", "Operating Times" and "Continuous Feeds", which we will illustrate in detail in our SBS process in Chapter 6. See Table 6.13 and Figures 6.79a to 6.79c.

Operating specification: Temperature profile

Time	Temperature
hr	C

Pressure specification: Calculate reactor pressure

Volume: cum

Vent opening pressure: bar

Vent closing pressure: bar

Catalyst loading: 0 kg

Valid phases

Reactor: Liquid-Only

Vent accumulator: Liquid-Only

Figure 3.10 Temperature profile, "Calculate reactor pressure" specification and valid phases.

Lastly, we see the specification folder of "Controllers" in Figure 3.10. RBATCH performs controller - calculations if temperature or temperature profile is specified and the reactor is semi-batch with continuous feeds, has vapor and liquid phases, and is venting with constant volume. A search of "RBATCH controllers" in the Aspen Plus online help gives details of the PID (proportional-integral-derivative) controllers for reactor temperature and pressure. We discuss in detail in Chapter 7 about controller specifications and tuning.

3.5 Representation of Nonideal Reactors

This section gives examples where we can use the RCSTR model to represent nonideal reactors in industrial manufacturing of polyolefins.

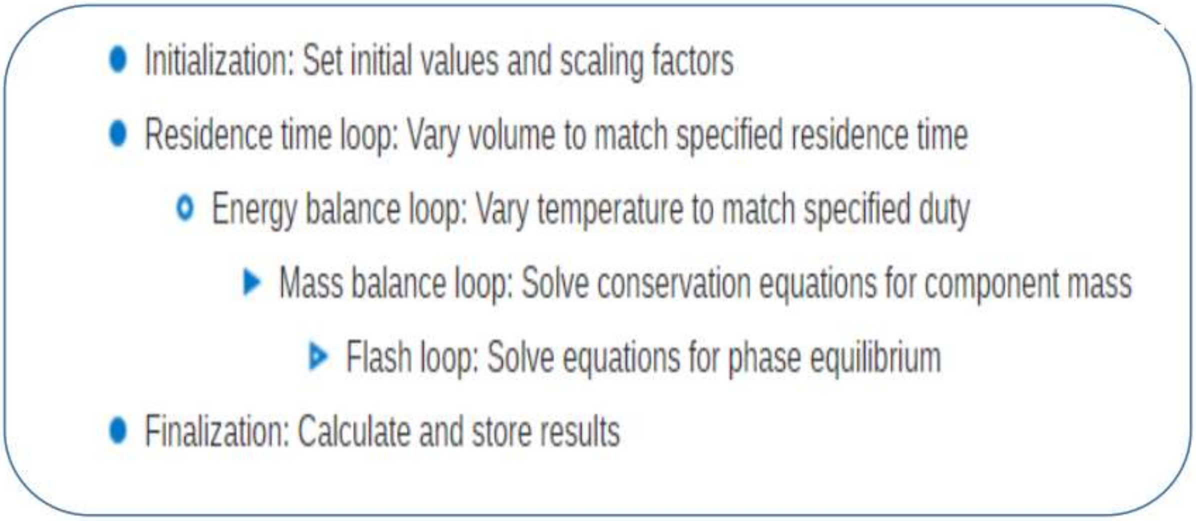
In Section 5.6.4, we discuss the role of solid polymer in phase-equilibrium calculations using a slurry HDPE process as an example. We assume that the polymer is dissolved in the liquid phase with the solvent, as would be the case in solution polymerization of ethylene, where the reactor temperature would be above the melting point of the polymer. Although this modeling simplification does not represent the physical picture of what is happening in the slurry polymerization of ethylene, the effect of it on thermodynamic modeling is relatively small. Figure 5.25 illustrates the difference between the actual conditions and the modeling assumption [3].

In Section 5.7.3, we discuss in detail the modeling of a horizontal stirred-bed reactor for a gas-phase PP process using a series of four RCSTRs [1]. See Figure 5.50. Experimental studies on the residence-time distribution (RTD) of polymers produced in horizontal stirred-bed reactors suggest that the polymer RTD is equivalent to that produced by three to five CSTRs [2].

Figure 5.8 shows a Univation UNIPOL LLDPE process using a fluidized-bed reactor. Current practice is to model UNIPOL and similar fluid-bed reactors as RCSTRs in Aspen Plus. The fluidizing solid polymer phase behaves like a fluid from a phase-equilibrium point of view. Referring to Figure 3.3, we need to specify the volume holdup of the condensed phase based on the known inventory of solids in the bed.

3.6 RCSTR Convergence

Figure 3.11 shows the RCSTR convergence scheme shown in the Aspen Plus online help. We follow this figure and discuss the details of each step below



- Initialization: Set initial values and scaling factors
- Residence time loop: Vary volume to match specified residence time
  - Energy balance loop: Vary temperature to match specified duty
    - Mass balance loop: Solve conservation equations for component mass
      - Flash loop: Solve equations for phase equilibrium
- Finalization: Calculate and store results

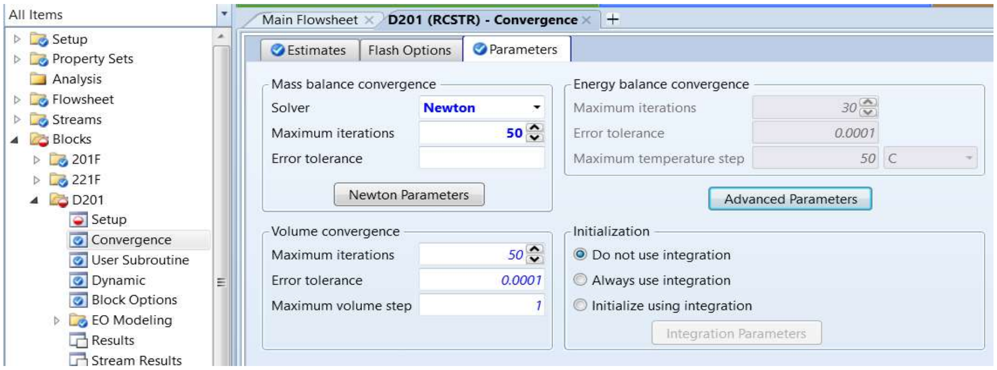
Figure 3.11 Convergence scheme of RCSTR

3.6.1 Initialization

To initialize the mass, energy, and polymer attribute conservation calculations, the default method is called the *solver method.* Specifically, RCSTR sets outlet stream equal to inlet stream, or uses specified estimates of temperature, component flow rates and attribute values, to initialize the RCSTR block, unless previously converged results are available. RCSTR then solves the mass, energy and polymer attribute conservation equations by a trial-and-error technique based on the initial guess.

An alternative initialization scheme is *the integrator method*, in which RCSTR integrates the mass, energy and polymer attribute conservation equations numerically from an initial condition to the steady-state condition. By default, the initial condition refers to setting the outlet stream equal to the inlet stream, temperature to the specified temperature, or heat duty equal to the specified heat duty. When using this method, we do not supply estimates of component flow rates and attribute values.

We follow the path: Simulation -> Blocks -> RCSTR Block -> Convergence -> Parameter -> Initialization -> Choose: (1) Do not use integration; (2) Always use integration; or (3) Initialize using integration. See Figure 3.12.



Mass balance convergence
Solver: Newton
Maximum iterations: 50
Error tolerance:

Energy balance convergence
Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C

Volume convergence
Maximum iterations: 50
Error tolerance: 0.0001
Maximum volume step: 1

Initialization
● Do not use integration
○ Always use integration
○ Initialize using integration

Figure 3.12 An illustration of initialization options.

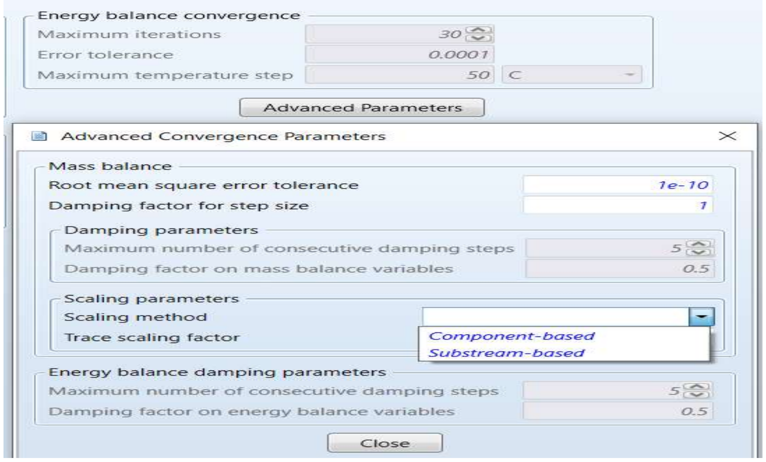
Aspen Plus online help suggests that “numerical integration is more reliable than trial-and-error solvers”. Therefore, when troubleshooting mass-balance convergence problems, *consider deleting initial estimates and initializing using integration.*

3.6.2 Scaling Factors

Scaling factors have a strong influence on the RCSTR convergence behavior. Basically, Aspen Plus uses numerical solvers to solve the mass, energy, and polymer attribute conservation equations and to converge on recycle loop calculations in the kinetic reactors, including RCSTR. The solver algorithms use scaled variables. Ideally, the scale factors for each type of variable should be on the same order of magnitude as the variable itself (e.g., mass fraction from 0 to 1; polymer attribute MWN from 5,000 to 60,000). In other words, the solvers work best when the scaled variables are close to unity. We note that if the scaling factors are large and the variables are small, then the model will be loosely converged; if the scaling factors are small and the variables are large, then the convergence criteria would be unacceptably tight, leading to model convergence failure.

Clicking on “Advanced Parameters” button displayed in Figure 3.13 leads us to two scaling parameter options: component-based and substream-based. Interested readers may search in Aspen Plus online help for “Component Attributes Scale Factors” for additional details. For substream-based scaling, search for “Substream Mixed and Stream Class CONVEN” to understand how Aspen Plus arranges component mole flows, total mole flow rate, temperature, pressure, mass enthalpy, …component attributes for polymer (e.g., SFRAC, MWN, MWW, PDI, …), into a substream vector MIXED for conventional components. Sharma et. al. used this convergence strategy for modeling HDPE and PP processes.

Table 3.2 lists the guidelines on how Aspen Plus determines the scaling factors by the RCSTR component-based and substream-based methods. Note the trace scaling factor displayed in Figure 3.12. When this factor equals 1, both component-based and substream-based scaling methods are identical.



Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C
Root mean square error tolerance: 1e-10
Damping factor for step size: 1
Maximum number of consecutive damping steps: 5
Damping factor on mass balance variables: 0.5
Scaling method:
Trace scaling factor:
Maximum number of consecutive damping steps: 5
Damping factor on energy balance variables: 0.5

Figure 3.13 Scaling parameter options: component-based and substream-based.

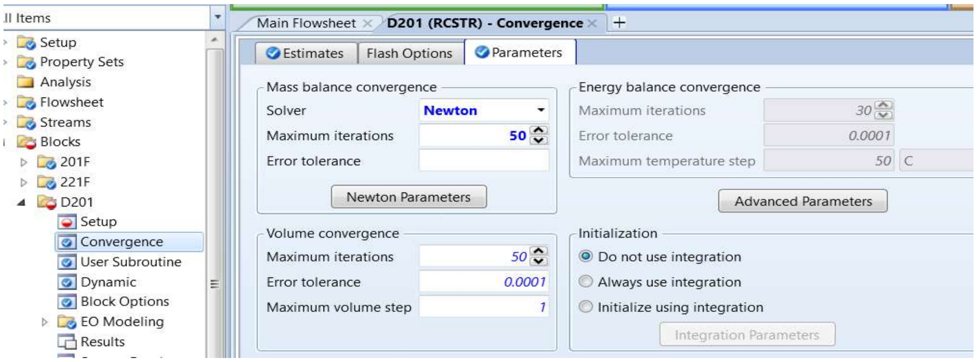
Table 3.2 Guidelines for RCSTR component-based and substream-based scaling factors

Variable type	**Component-based scaling**	**Substream-based scaling**
Enthalpy	Estimated outlet stream enthalpy	10E5
Component mole flows	The larger of: (1) Estimated mole flow in the outlet stream; (2) (Trace scaling factor between 0 and 1)*(Total estimated flow rate of the outlet stream)	Total estimated mole flow rate of the outlet stream
Conserved polymer attributes	The larger of : (1) Estimates value in the outlet stream; (2) (Default attribute scaling factor)*(Estimated component mole flow); and (3) (Trace scaling factor)*(total estimated mole flow)*(default attribute scaling factor)	Default attribute scaling factors

3.6.3 Residence Time Loop

In Figure 3.3, we have provided the reactor volume and phase volume. If we choose to specify the residence time, instead of volume, RCSTR adjusts the volume to satisfy the residence time specification. We can alleviate the convergence problem in the residence time loop by providing initial volume estimates. We follow the path: RCSTR -> Convergence -> Estimates -> Volume: fill in estimates of reactor volume. If convergence problems persist, we change the maximum volume step by following the path:

RCSTR -> Convergence -> Parameters -> Volume Convergence -> Maximum Volume Step -> Reduce from 1 to a smaller value. See Figure 3.14.



Mass balance convergence
Solver: Newton
Maximum iterations: 50
Error tolerance:

Energy balance convergence
Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C

Volume convergence
Maximum iterations: 50
Error tolerance: 0.0001
Maximum volume step: 1

Initialization
● Do not use integration
○ Always use integration
○ Initialize using integration

Figure 3.14 Reducing the maximum volume step parameter to speed up residence to loop convergence

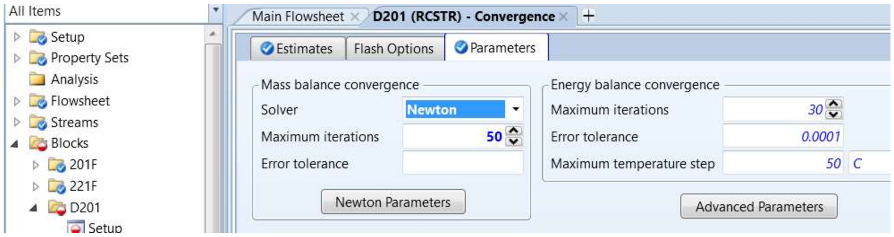
When troubleshooting convergence problems, Aspen online help recommends that we simplify the problem by specifying temperature and volume, instead of heat duty and residence time.

3.6.4 Energy Balance Loop

In the energy balance loop, RCSTR adjusts the reactor temperature to match the specified reactor heat duty. If we specify the reactor temperature, instead of the reactor heat duty, RCSTR bypasses this loop, and move on to the mass balance loop, thus greatly simplifying the mass and energy balance calculations. This also suggests that *when it is feasible, simply the RCSTR (and RPLUG and RBATCH) calculations by specifying the reactor temperature, instead of het duty or heat-transfer parameters (thermal fluid temperature, overall heat transfer coefficient, or thermal fluid stream).*

We note that the reaction rates are sensitive to temperature, and any large changes in the reactor temperature may cause the energy balance loop to diverge.

If we follow the path to specify both pressure and heat duty as the reactor operating conditions: Simulation -> Blocks -> RCSTR -> Setup -> Operating conditions -> specify pressure and heat duty, we may avoid reactor convergence problem by providing a good temperature estimate. We do this by following the path: Simulation -> Blocks -> RCSTR -> Convergence -> Estimates -> Temperature: fill in the estimate. If the convergence problem persists, we could reduce the maximum temperature step size from the default of 50°C to a smaller value. See Figure 3.15.



Mass balance convergence
Solver: Newton
Maximum iterations: 50
Error tolerance:

Energy balance convergence
Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C

Figure 3.15 Energy balance convergence: reducing the maximum temperature step size.

3.6.5 Mass Balance Loop

RCSTR has two solvers to converge the mass, energy and polymer attribute conservation equations for component mole flow and conserved component attributes (e.g., SFRAC, MWN, MWW, etc.): (1) *Broyden algorithm*: tends to be relatively fast, but may be unstable if the number of components and attributes is large, and the reaction rates are high; and (2) *Newton algorithm*: tends to be slower, but more stable for many classes of problems.

Before we talk about the number of mass-balance iterations to achieve convergence for each algorithm, let us see Figure 3.16 and understand the concept of damping [4]. Process simulation software tools typically include provisions to apply a *damping factor* to reduce the ratio of the root-mean-squared (RMS) error of process variables to the error tolerance to less than 1 within a finite number of iterations and thus achieve convergence. This figure illustrates how this ratio reduces to less than 1 (i.e., 10^0) within a finite number of iterations in a well-damped system after applying a damping factor, and how this ratio grows in an under-damped system.

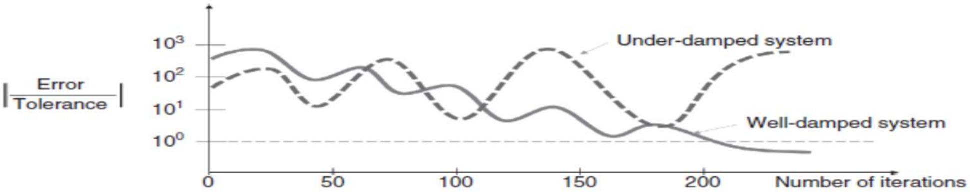
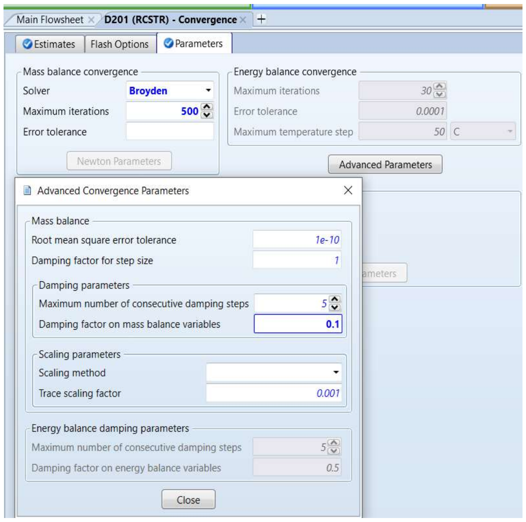


Figure 3.16 An illustration of the concept of damping

Figure 3.17 shows that the default number of iterations for the mass-balance convergence solver, the Broyden algorithm, is 50. *This default is sufficient for the Newton algorithm, but is usually too small for the Broyden algorithm.* This is illustrated in Figure 3.17, where Aspen Plus online help recommends increasing the number of iterations for the Broyden algorithm for polymer process simulation to at least 500, and to apply a small damping factor between 0.1 and 0.001 (accessed by clicking on the "Advanced Parameters" button displayed in the figure).



Mass balance convergence
Solver: Broyden
Maximum iterations: 500
Error tolerance:

Energy balance convergence
Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C

Advanced Convergence Parameters

Mass balance
Root mean square error tolerance: 1e-10
Damping factor for step size: 1

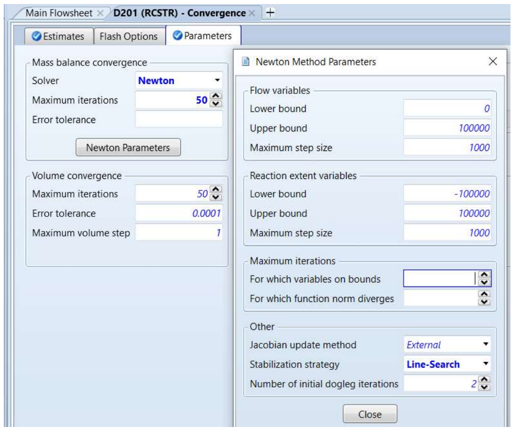
Damping parameters
Maximum number of consecutive damping steps: 5
Damping factor on mass balance variables: 0.1

Scaling parameters
Scaling method:
Trace scaling factor: 0.001

Energy balance damping parameters
Maximum number of consecutive damping steps: 5
Damping factor on energy balance variables: 0.5

Figure 3.17 Setting the maximum number of iterations for the Broyden algorithm to 500 and adding a small damping factor on mass balance variables between 0.1 and 0.001.

When using the Newton algorithm for mass-balance iterations, applying a stabilization strategy to specify the method used to stabilize the Newton algorithm. There are two options: (1) *dogleg strategy* (default) that uses Powell's dogleg strategy in optimization theory to combine Newton and steepest descent directions; and (2) *line search strategy* that uses one-dimensional search along Newton direction. Line search is recommended for polymerization kinetics and systems where reaction rates are sensitive to the concentrations of trace species which are also reacting (such as reacting catalysts or inhibitors). Changing the stabilization strategy within "Newton Parameters" from "dogleg" to "line search" could improve the convergence behavior, especially for ionic and Ziegler-Natta polymerization kinetics. See Figure 3.18.



Mass balance convergence
Solver: Newton
Maximum iterations: 50
Error tolerance:

Volume convergence
Maximum iterations: 50
Error tolerance: 0.0001
Maximum volume step: 1

Flow variables
Lower bound: 0
Upper bound: 100000
Maximum step size: 1000

Reaction extent variables
Lower bound: -100000
Upper bound: 100000
Maximum step size: 1000

Maximum iterations
For which variables on bounds:
For which function norm diverges:

Other
Jacobian update method: External
Stabilization strategy: Line-Search
Number of initial dogleg iterations: 2

Figure 3.18 Changing the stabilization strategy to "line search" to improve mass-balance convergence.

3.6.6 Flash Loop

As illustrated in Figure 3.11, we see from the bottom up that the flash loop is the inner-most loop, while the energy balance loop and the residence time loop represent the outer loops. The flash loop does the phase-equilibrium calculations. It is essential to have accurate physical properties over the entire range of temperatures and pressures found in the process. When we see the message of "initial flash failure" in the control panel, this is likely the result of a physical property problem. Check the heat of formation (DHFORM) and the ideal gas heat capacity (CPIG) of the polymer and oligomer components. If these property values are missing, apply the property estimation methods of Chapter 2 (see Section 2.7). If a supercritical component (light gases and low molecular weight hydrocarbons) is present, consider treating them as Henry components when using the POLYNRTL property method (see Section 2.2.5). When flash failures appear during the mass-balance loop, change the parameters of flash options by following the path: Simulation -> Blocks -> RCSTR -> Convergence -> Flash options > Increase "maximum iterations" to 200, and decrease flash tolerance to less than 0.0001.

3.6.7 Recommendation for RCSTR Mass-Balance Algorithm for Polyolefin Process Simulation

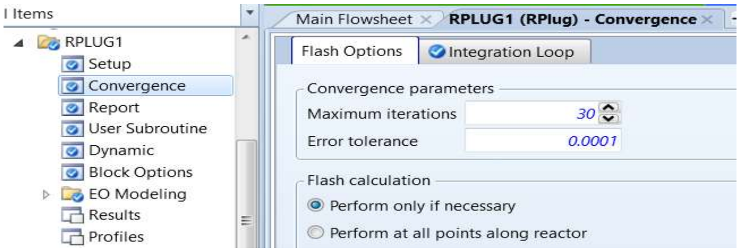
Table 3.3 summarizes the recommended RCSTR mass-balance convergence algorithms for polyolefin process simulation.

Table 3.3 Recommendations for RCSTR mass-balance convergence algorithms

Polyolefin Polymerization Kinetics	**RCSTR Mass-Balance Convergence Algorithm**
1. Free radical polymerization (Chapter 4: LDPE, EVA; Chapter 7, PS) [16,19]	Use Broyden for homopolymerization, assuming pseudo steady state approximation (PSSA); otherwise, use Newton.
2. Ziegler-Natta polymerization (Chapter 5: HDPE, PP, LLDPE); and ionic polymerization (Chapter 7: SBS) [17,19]	Use Newton with estimates. If this fails, initialize with integration. Reduce the default trace scaling factor of 0.0001 (see Figure 3.12) by a factor of 10 if trouble persists. Change the stabilization strategy from "dogleg" to "line search".

3.7 RPLUG/RBATCH Convergence

The convergence calculations of both RPLUG and RBATCH are essentially similar. They use a variable-step Gear integration scheme [5] to solve the mass, energy, and polymer attribute conservation equations. For RPLUG, we integrate along the reactor length, and for RBATCH, we integrate along the time axis. Figure 3.19 shows the identical "flash options" for both RPLUG and RBATCH.

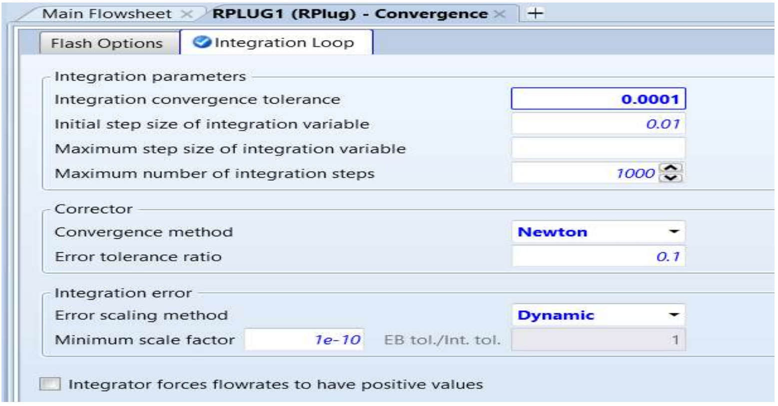


Convergence parameters
Maximum iterations 30
Error tolerance 0.0001

Flash calculation
● Perform only if necessary
○ Perform at all points along reactor

Figure 3.19 Flash options for both RPLUG and RBATCH

Figure 3.20 illustrates the "integration loop" of RPLUG.



Integration parameters
Integration convergence tolerance 0.0001
Initial step size of integration variable 0.01
Maximum step size of integration variable
Maximum number of integration steps 1000

Corrector
Convergence method Newton
Error tolerance ratio 0.1

Integration error
Error scaling method Dynamic
Minimum scale factor 1e-10 EB tol./Int. tol. 1

☐ Integrator forces flowrates to have positive values

Figure 3.20 Integration loop of RPLUG.

For both RPLUG and RBATCH, the solver algorithm of mass, energy and polymer attribute conservation calculations is called *the corrector*. Two corrector methods are available to RPLUG and RBATCH: (1) *Direct* - direct substitution method; and (2) *Newton* method. In general, Newton method is best performance with polymerization kinetics; but for problems with a large number of variables, the direct method is faster. Aspen Plus online help suggests trying both methods to see which is faster for a specific problem.

In Figure 3.20, we see an "*initial step size of integration variables*" of 0.01. If the solver cannot converge the equations with this step size, it will cut the step size by a factor of ten. This process will repeat up to six time. If the solver still cannot converge, the reactor calculation fails with an error message "*solver cannot converge with minimum step size*". When this occurs, we recommend reducing the initial step size to as low as 1E-4.

Figure 3.20 also shows a "*maximum number of integration steps*" of a default value of 1000. For kinetics with fast reactions involving trace components, especially when the corrector uses the direct substitution method, Aspen Plus online help recommends increasing the maximum number of integration steps from 1000 to 5000. If more than 5000 steps are required for convergence, try replacing the corrector method to Newton.

We see in Figure 3.20 that for RPLUG, a default "*error tolerance ratio*" of 0.1. This means that the corrector tolerance is 1E-5, that is, 0.1 times the integration convergence tolerance (set at 0.0001). For some problems, especially those involving RPLUG with heat-transfer calculations, the error tolerance ratio may be higher than 0.1, but it should always be less than 1. For RBATCH, we do *not s*ee the entry of error tolerance ratio within the integration loop, but it has a hidden default value of 0.1.

Like RCSTR, RPLUG and RBATCH solve the mass, energy and polymer attribute conservation equations using scale factors discussed in Section 3.6.2. In Figure 3.20, we see the entry of *error scaling method*. Both RPLUG and RBATCH have two options: (1) *Static* scaling factors based on the feed steam conditions and they are held constant throughout the integration process; and (2) *Dynamic* scaling factors, which are updated at each integration step based on previous variable values. In Figure 3.20, we see in the integration loop of RPLUG an entry of "*minimum scale factor*" with a default value of 1E-10. When running RPLUG simulation, we may encounter an error message of "integration error: maximum number of integration steps is reached". This may happen with dynamic scaling when a variable value becomes so small that small absolute error becomes large, scaled errors. The solution is to increase *the minimum scale factor* from the default value of 1E-10 to 1E-5.

This concludes our general discussion of guidelines for reactor convergence tips. In an application involving dynamic data, Sharma et al. [10] demonstrated the use of RBatch to simulate polymer data, facilitating advanced data analysis. In Chapters 4 to 7, we illustrate the applications of these guidelines to specific industrial polymerization reactors with different polymerization kinetics, and discuss the practical guidelines for flowsheet convergence involving reactors, separators, and other units.

3.8 Data Fit (Simulation Data Regression)

In Section 2.7, we discussed the data regression (DRS) tool to estimate thermophysical properties and pure component and binary interaction parameters for property methods. Aspen Plus has another useful tool for simulation data regression, called *data fit*. We can use it to: (1) estimate unknown model parameters (e.g., reaction kinetic parameters, heat transfer coefficients, separation efficiencies, etc.); (2) reconcile measured data; and (3) estimate unknown model parameters and reconcile measured data simultaneously.

Data fit is an efficient nonlinear regression tool that allows the user to determine statistically acceptable model parameters from constant, or time-varying, or temperature-dependent laboratory measurements, or from matching the process simulation to plant targets. We can use either point data or time-profile data for regression. We need to define the data with reconciled input variables and a standard deviation. We estimate the model parameters using the data within the specified range [6].

The least-square regression objective function that the data fit minimizes is as follows:

$$f = \min_{X_p, X_{ri}} \frac{1}{2} \sum_{i=1}^{N_{set}} (W_i \times (\sum_{j=1}^{N_{expi}} (\sum_{i=1}^{N_{ri}} \left(\frac{X_{mri} - X_{ri}}{\sigma_{X_{mri}}}\right)^2 + \sum_{m=1}^{N_{rr}} \left(\frac{X_{mrr} - X_{rr}}{\sigma_{X_{mrr}}}\right)^2))) \qquad (3.1)$$

subject to $$X_{plb} \leq X_p \leq X_{pub}\ ,\ X_{rilb} \leq X_{ri} \leq X_{riub} \qquad (3.2)$$

where:

N_{set} = Number of datasets specified for regression

N_{expi} = Number of experiments in dataset i

N_{ri} = Number of reconciled input variables

N_{rr} = Number of measure output variables

W_i = Weight for each dataset *i* for regression

X_p = Vector of varied parameters

X_{mri} = Measured values of the reconciled input variables

X_{ri} = Calculated values of the reconciled input variables

X_{mrr} = Measured values of the output variables

X_{rr} = Calculated values of the output variables

σ = Standard deviation specified for the measured variables

Since the model parameter estimation is a complex regression problem, we can vary some numerical parameters within the data fit to speed up the convergence calculations. We vary *the maximum algorithm iterations* and *the maximum number of passes* through the process flowsheet which are required to compute the residuals. We specify *a bound factor* which gives the upper and lower bounds for variables by multiplying by the standard deviation. We also specify *the absolute sum of squares objective function tolerance*, so that the problem converges whenever the objective function value is less than the tolerance value.

The tool performs the least-square regression using a *trust region algorithm* for parameter estimation. Specifically, the algorithm maintains an estimate of the diameter of a region, called *the trust region*, about the current estimate of the vector of varied values in which it can predict the behavior of the least-squares objective function. If an adequate model is found within the trust region, the region is expanded; if the model is a poor approximation, then the trust region is contracted. The tool also provides certain handles to implement the regression with the trust region optimization algorithm.

Sharma et al. [9] utilized this regression strategy to estimate the kinetics of polyolefin processes. Similarly, McNeeley et al. [11] employed the regression tool to estimate the kinetics of nylon depolymerization.

3.9 Workshop 3.1 Data Fit of Kinetic Parameters for Styrene Polymerization Using Concentration Profile Data

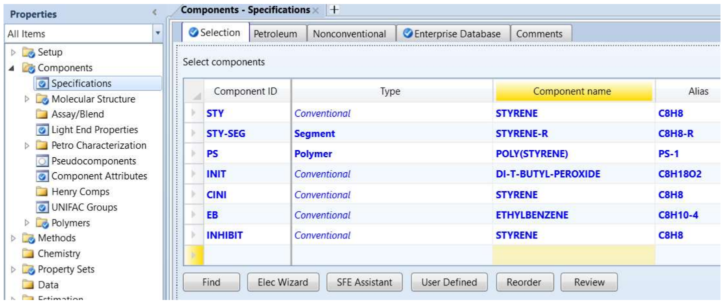
3.9.1 Objective

The objective of this workshop is to demonstrate the steps involved in applying data fit tool to regress kinetic parameters for *simplified* styrene bulk polymerization by thermal initiation [7,8]. This is an example of free radical polymerization, which we discuss detail in Chapters 4 for LDPE and EVA (ethylene-vinyl-acetate copolymer), and in Chapter 6 for polystyrene (PS). For this workshop, we begin with a simplified simulation model for PS, explain the completed steps, and then demonstrate the step-by-step application of the data fit tool in order to regress the kinetic parameters of the polymerization reactions based on time-dependent evolution of PS concentration in a batch reactor. Our starting simulation file for the workshop is: ***WS 3.1 Data Fit_Profile Data_PS.bkp.***

3.9.2 A Simplified Kinetic Model for Styrene Polymerization

We open the starting simulation file and go to the Properties environment. The Setup folder shows that this example uses a unit set METCBAR built from a MET unit set by changing the temperature unit from K to °C, and pressure unit from atm to bar, as demonstrated previously in Figure 1.7a.

Next, we go to the Components folder, and see the following specifications:



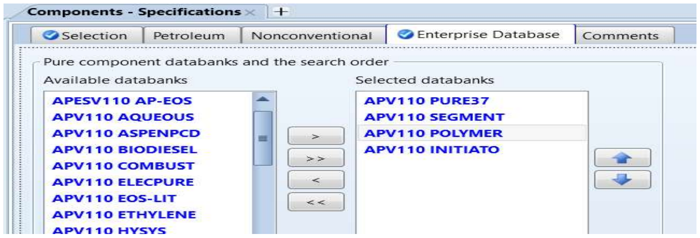
Select components

Component ID	Type	Component name	Alias
STY	*Conventional*	STYRENE	C8H8
STY-SEG	Segment	STYRENE-R	C8H8-R
PS	Polymer	POLY(STYRENE)	PS-1
INIT	*Conventional*	DI-T-BUTYL-PEROXIDE	C8H18O2
CINI	*Conventional*	STYRENE	C8H8
EB	*Conventional*	ETHYLBENZENE	C8H10-4
INHIBIT	*Conventional*	STYRENE	C8H8

Figure 3.21 Component specifications

Here, STY and STE-SEG are styrene monomer, and styrene segment (repeat type). PS is the polystyrene product. INIT is the chain initiator, di-t-butyl-peroxide (DTBP), which is available within the Aspen Polymers initiator databank. CINI is a co-initiator, which is a *hypothetical* component required to activate the thermal initiator reaction in the free radical polymerization kinetic model of Aspen Polymers. EB (ethylbenzene) is a chain-transfer agent to control the molecular weight. INHIBIT is an inhibitor, which is represented by STY.

We click on the “Enterprise Database” button displayed in Figure 3.21 to ensure that we have included databanks for pure components, segments, polymers and initiators for this example. See Figure 3.22.



Available databanks
APESV110 AP-EOS
APV110 AQUEOUS
APV110 ASPENPCD
APV110 BIODIESEL
APV110 COMBUST
APV110 ELECPURE
APV110 EOS-LIT
APV110 ETHYLENE
APV110 HYSYS

Selected databanks
APV110 PURE37
APV110 SEGMENT
APV110 POLYMER
APV110 INITIATO

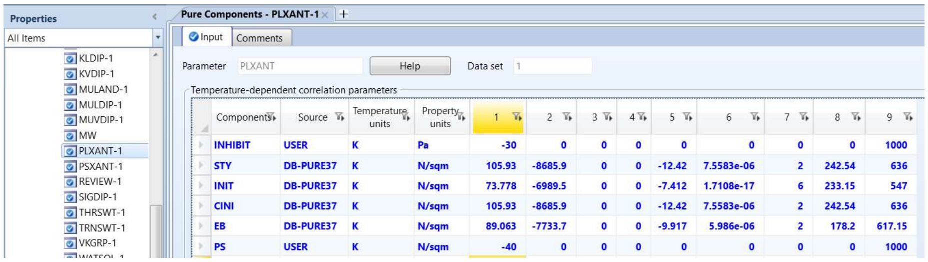
Figure 3.22 Specified enterprise databases

Next, we follow the path: Properties -> Components -> Polymers -> (1) Segments: segment ID = STY-SEG, type = Repeat; and (2) Polymers: Polymer ID: Choose “PS”; Built-in attribute group: Choose “Free radical selection”.

This workshop uses the POLYNRTL property method discussed in Section 2.2.4. Follow the path: Properties -> Methods -> Specifications -> Global -> Method name: Choose POLYNRTL.

Next, we click on the “Review” bottom displayed in Figure 3.21 to call up the pure component parameters. We see the resulting pure component parameters by following the path: Properties-> Methods -> Parameters -> Pure Components.

To ensure that PS has an extremely small liquid vapor pressure and does not vaporize, we enter the first temperature-dependent parameter for the extended Antoine correlation for liquid vapor pressure (PLXANT-1) for PS as -40. See Figures 3.23. To see the specific equation for the PLXANT correlation, click on the “Help” button displayed in Figure 3.23 to see the extended Antoine correlation.



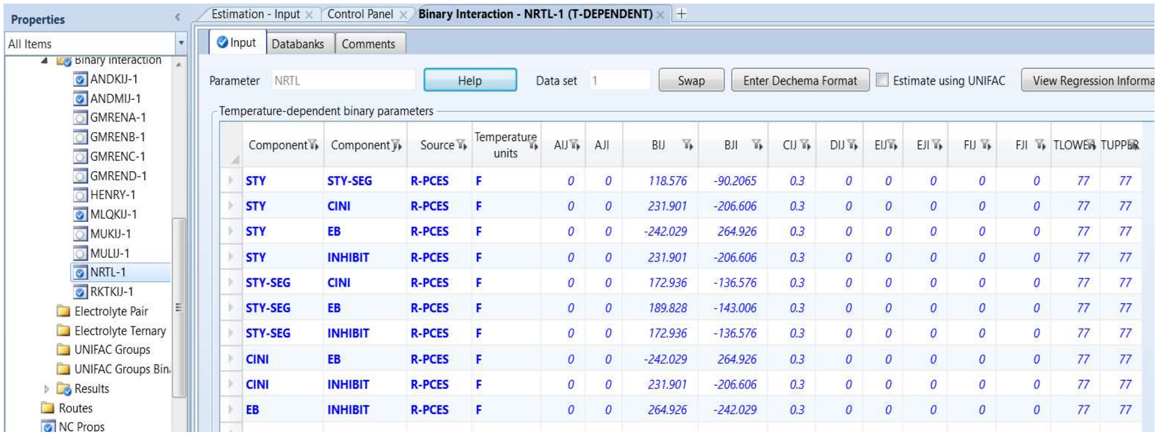
Parameter: PLXANT
Data set: 1

Temperature-dependent correlation parameters

Components	Source	Temperature units	Property units	1	2	3	4	5	6	7	8	9
INHIBIT	USER	K	Pa	-30	0	0	0	0	0	0	0	1000
STY	DB-PURE37	K	N/sqm	105.93	-8685.9	0	0	-12.42	7.5583e-06	2	242.54	636
INIT	DB-PURE37	K	N/sqm	73.778	-6989.5	0	0	-7.412	1.7108e-17	6	233.15	547
CINI	DB-PURE37	K	N/sqm	105.93	-8685.9	0	0	-12.42	7.5583e-06	2	242.54	636
EB	DB-PURE37	K	N/sqm	89.063	-7733.7	0	0	-9.917	5.986e-06	2	178.2	617.15
PS	USER	K	N/sqm	-40	0	0	0	0	0	0	0	1000

Figure 3.23 Specification of user parameter for liquid vapor pressure correlation for PS

Following Section 2.3, Workshop 2.1, we estimate all the missing binary interaction parameters for the POLYNRTL model using the UNIFAC group contribution method. We follow the path to see the estimated parameters: Properties -> Methods -> Parameter -> Binary Interactions -> NRTL-1 (see Figure 3.24). After this estimation, we follow the path to discontinue this estimation step in the next simulation: Properties -> Estimation -> Input -> Setup -> Estimation options: choose “Do not estimate any parameters”.



Parameter NRTL

Data set 1

☐ Estimate using UNIFAC

Temperature-dependent binary parameters

Component	Component	Source	Temperature units	AIJ	AJI	BIJ	BJI	CIJ	DIJ	EIJ	EJI	FIJ	FJI	TLOWER	TUPPER
STY	STY-SEG	R-PCES	F	0	0	118.576	-90.2065	0.3	0	0	0	0	0	77	77
STY	CINI	R-PCES	F	0	0	231.901	-206.606	0.3	0	0	0	0	0	77	77
STY	EB	R-PCES	F	0	0	-242.029	264.926	0.3	0	0	0	0	0	77	77
STY	INHIBIT	R-PCES	F	0	0	231.901	-206.606	0.3	0	0	0	0	0	77	77
STY-SEG	CINI	R-PCES	F	0	0	172.936	-136.576	0.3	0	0	0	0	0	77	77
STY-SEG	EB	R-PCES	F	0	0	189.828	-143.006	0.3	0	0	0	0	0	77	77
STY-SEG	INHIBIT	R-PCES	F	0	0	172.936	-136.576	0.3	0	0	0	0	0	77	77
CINI	EB	R-PCES	F	0	0	-242.029	264.926	0.3	0	0	0	0	0	77	77
CINI	INHIBIT	R-PCES	F	0	0	231.901	-206.606	0.3	0	0	0	0	0	77	77
EB	INHIBIT	R-PCES	F	0	0	264.926	-242.029	0.3	0	0	0	0	0	77	77

Figure 3.24 Estimated POLYNRTL binary interaction parameters

Next, we go to the simulation environment, and see the flowsheet of the RBATCH reactor in Figure 3.25.

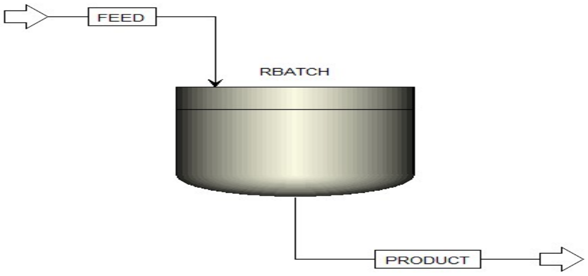
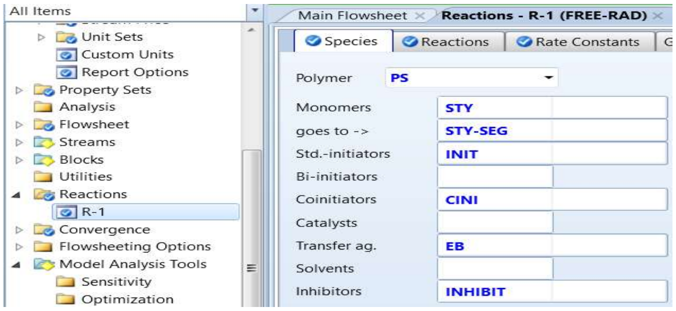


Figure 3.25 RBATCH reactor for WS 3.1

The FEED steam is at 100°C and 4.5 bar, and the component mass flow rates (kg/hr) are: STY= 1000; INIT= CINIT = 1; EB = 5; and INHIBIT= 0.5.

We discuss in more detail in Chapter 4 about the kinetics of free-radical polymerization. To create our reaction set, we follow the path: Simulation -> Reactions -> New -> Create New ID ->Enter ID = R-1; Select Type: Free-Rad.-> OK -> Species specification -> See Figure 3.26.



Polymer PS

Monomers STY

goes to -> STY-SEG

Std.-initiators INIT

Bi-initiators

Coinitiators CINI

Catalysts

Transfer ag. EB

Solvents

Inhibitors INHIBIT

Figure 3.26 Reaction specie specifications.

For this workshop, we generate the reactions by following the path: Simulation -> Reactions -> Reaction R-1a -> Species specification (Figure 3.2) -> Reactions -> Click on “Generate Reactions” button -> Nine reactions listed in Figure 3.27, which includes: (1) initiator decomposition (Init-Dec) (2) special thermal initiation (Init-Sp); (3) chain initiation (Chain-Ini); (4) chain propagation (Propagation); (5) chain transfer to monomer (Chat-Mon); (6) chain transfer to chain-transfer agent (Chain-Agent); (7) termination by disproportionation (Term-Dis); (8) chain termination by combination (Term-Comb); and (9) inhibition by inhibition agent (Inhibition).

Reaction	Reactants		Products	Active	Delete
1) Init-Dec	Init	->	e.n.R* + a.A + b.B	☑	✗
2) Init-Sp	Sty + Cini	->	P1[Sty-Seg] + a.A + b.B	☑	✗
3) Chain-Ini	Sty + R*	->	P1[Sty]	☑	✗
4) Propagation	Pn[Sty] + Sty	->	Pn+1[Sty]	☑	✗
5) Chat-Mon	Pn[Sty] + Sty	->	(1-f).Dn + f.Dn= + P1[Sty]	☑	✗
6) Chat-Agent	Pn[Sty] + Eb	->	Dn + R*	☑	✗
7) Term-Dis	Pn[Sty] + Pm[Sty	->	Dn + (1-f).Dm + f.Dm=	☑	✗
8) Term-Comb	Pn[Sty + Pm[Sty]	->	Dn+m	☑	✗
9) Inhibition	Pn[Sty] + Inhibit	->	Dn	☑	✗

Figure 3.22 The generated reaction set for styrene polymerization by thermal initiation.

In Section 4.2, we will give detailed explanations of each type of free-radical reactions. For the current workshop, we focus only on a simplified reaction set by deleting reactions 1 and 7 and enter the initial set of rate constants as the initial values for kinetic parameter regression by the data-fit tool. Figure 3.28 shows the initial rate constants for the remaining seven reactions.

Type	Comp 1	Comp 2	Pre-Exp	Act-Energy	Act-Volume	Ref. Temp.	No. Rads [n]	TDB fraction [f]	Gel Effect
			1/hr	kcal/kmol	cc/mol	C			
INIT-SP	STY	CINI	3.6e-07	27000	0	115			0
CHAIN-INI	STY		3.6e+06	7000	0	115			0
PROPAGATION	STY	STY	3.6e+06	7000	0	115			0
CHAT-MON	STY	STY	900	12500	0	115		1	0
CHAT-AGENT	STY	EB	396	7000	0	115			0
TERM-COMB	STY	STY	5.4e+11	1500	0	115			0
INHIBITION	STY	INHIBIT	3.6e+08	2000	0	115			0

Figure 3.28 Initial rate constants for WS3.1

We note that the reaction rate constants listed in Figure 3.23 have the following standard Arrhenius form:

$$k = k_0 * e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)} \qquad (3.3)$$

where k_o is the pre-exponential factor, E is the activation energy, R is the ideal gas constant, and T is the temperature of the reaction system and T_r is the reference temperature.

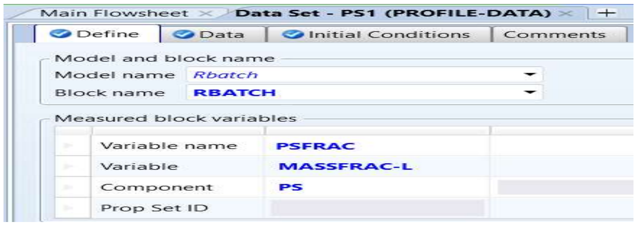
3.9.3 Datasets

Our isothermal experimental data from RBATCH include the time evolution of the liquid-phase mass fraction of PS (PSFRAC). See Table 3.4.

Table 3.4 Time evolution of liquid-phase mass fraction of PS

Data Set	PS1	PS2	PS3
Time, hr	PSFRAC	PSFRAC	PSFRAC
0	0	0	0
0.5	0.00799	0.000366	0.00041
1	0.015	0.000806	0.000861
1.5	0.0227	0.00123	0.00127
2	0.0316	0.00163	0.00178
2.5	0.038	0.00211	0.00205
3	0.0466	0.00249	0.00265
3.5	0.0506	0.00294	0.00304
4	0.061	0.0033	0.00358
4.5	0.064	0.00388	0.00389
5	0.0759	0.0043	0.0046

We create the datasets by following the path: Simulation -> Model Analysis Tools -> Data Fit -> Dataset -> New -> Enter ID = PS1; Select type = Profile-data -> OK -> (1) Define: See Figure 3.29; (2) Data: See Figure 3.30 for dataset PS1 in Table 3.4. Repeat this path to enter datasets PS2 and PS3.



Model and block name

Model name: Rbatch

Block name: RBATCH

Measured block variables

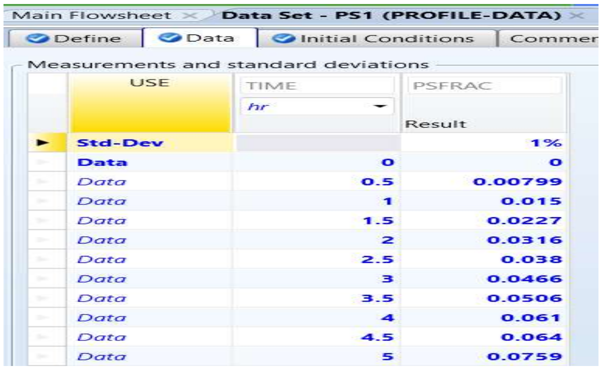
Variable name: PSFRAC

Variable: MASSFRAC-L

Component: PS

Prop Set ID:

Figure 3.29 Defining the time evolution of the liquid-phase mass fraction of PS as dataset PS1



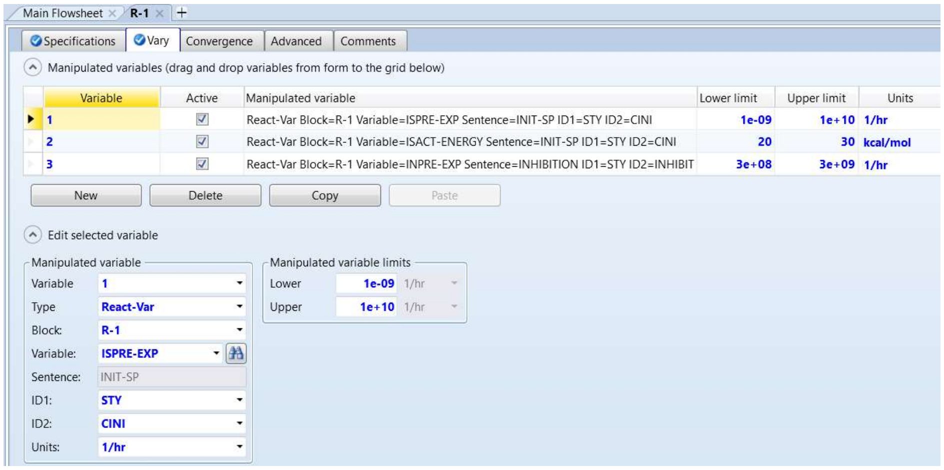
Measurements and standard deviations

USE	TIME hr	PSFRAC Result
Std-Dev		1%
Data	0	0
Data	0.5	0.00799
Data	1	0.015
Data	1.5	0.0227
Data	2	0.0316
Data	2.5	0.038
Data	3	0.0466
Data	3.5	0.0506
Data	4	0.061
Data	4.5	0.064
Data	5	0.0759

Figure 3.30 Dataset PS1

3.9.4 Simulation Data Regression (Data Fit)

To define a simulation regression run, we follow the path: Simulation -> Model Analysis Tools-> Data Fit -> Regression -> New -> Enter ID: R-1 -> OK -> Specifications: (1) Active: yes; (2) Select datasets to be regressed: PS1, PS2 and PS3; (2) Vary: New-> See Figure 3.31. Variable 1 (ISPRE-EXP, pre-exponential factor for special initiation reaction); Variable 2 (ISACT-Energy, activation energy of special initiation reaction); Variable 3 (INPRE-EXP, pre-exponential factor of inhibition reaction). Define Variable 2 and Variable 3 in the same way as Variable 1.



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

Variable	Active	Manipulated variable	Lower limit	Upper limit	Units
1	☑	React-Var Block=R-1 Variable=ISPRE-EXP Sentence=INIT-SP ID1=STY ID2=CINI	1e-09	1e+10	1/hr
2	☑	React-Var Block=R-1 Variable=ISACT-ENERGY Sentence=INIT-SP ID1=STY ID2=CINI	20	30	kcal/mol
3	☑	React-Var Block=R-1 Variable=INPRE-EXP Sentence=INHIBITION ID1=STY ID2=INHIBIT	3e+08	3e+09	1/hr

Edit selected variable

Manipulated variable

Variable	1
Type	React-Var
Block:	R-1
Variable:	ISPRE-EXP
Sentence:	INIT-SP
ID1:	STY
ID2:	CINI
Units:	1/hr

Manipulated variable limits

Lower	1e-09	1/hr
Upper	1e+10	1/hr

Figure 3.31 Manipulated variables (“Vary”) of simulation data regression R-1

Figure 3.32 shows the *default* convergence parameters for data fit:

(1) Maximum algorithm iterations: Controls the number of regression iterations. 50 runs are more than enough (the current run converges in 5 iterations).

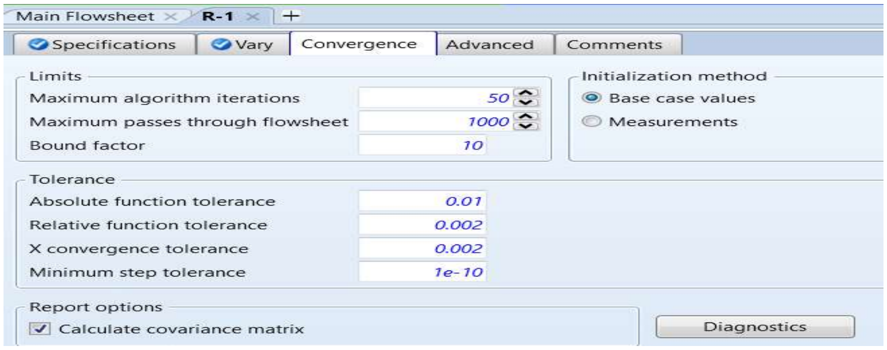
(2) Maximum passes through the flowsheet: For problems with many variables and experiments, increase the number of passes.

(3) Absolute (objective) function tolerance: Usually the default value of 0.01 is too low.

(4) Relative function tolerance: Stop iterating when the predicted relative change in the objective function falls below the specified value; the default of 0.002 is very tight. Typically, a value of 0.01 (or 1%) is sufficient.

(5) X convergence tolerance: Stop iterating when the predicted maximum relative change in any variable is below the specified value; the default value of 0.002 is very tight

(6) Minimum step tolerance: Controls “solution may be suboptimal message”. The default value is very conservative.



Limits

Maximum algorithm iterations	50
Maximum passes through flowsheet	1000
Bound factor	10

Initialization method

● Base case values

○ Measurements

Tolerance

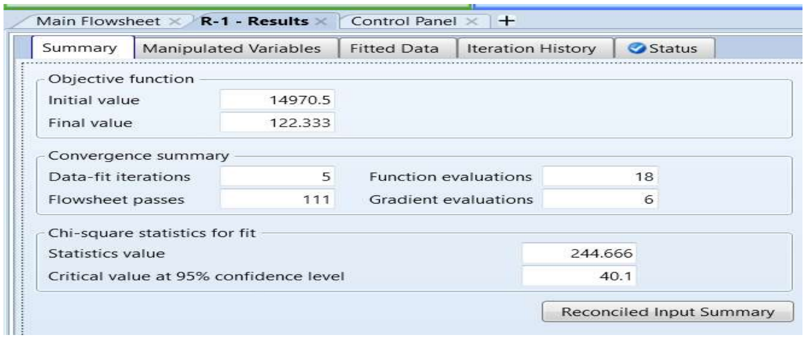
Absolute function tolerance	0.01
Relative function tolerance	0.002
X convergence tolerance	0.002
Minimum step tolerance	1e-10

Report options

☑ Calculate covariance matrix

Figure 3.32 Default convergence parameters for data fit.

We follow the path: Simulation -> Model analysis tools -> Data fit -> Regression -> Results -> Summary. See Figure 3.33. Here, we look for reasonable improvement from the initial value (14970.5) to the final value (122.333) of the objective function. Theoretically speaking, the statistical value of Chi-square should be less than the 95% confidence critical value; however, this rarely happens in real regressions.



Objective function

Initial value	14970.5
Final value	122.333

Convergence summary

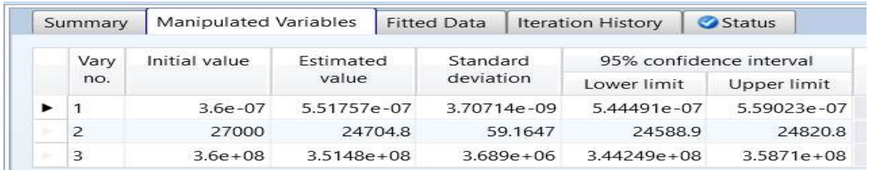
Data-fit iterations	5	Function evaluations	18
Flowsheet passes	111	Gradient evaluations	6

Chi-square statistics for fit

Statistics value	244.666
Critical value at 95% confidence level	40.1

Figure 3.33 Summary of simulation regression results.

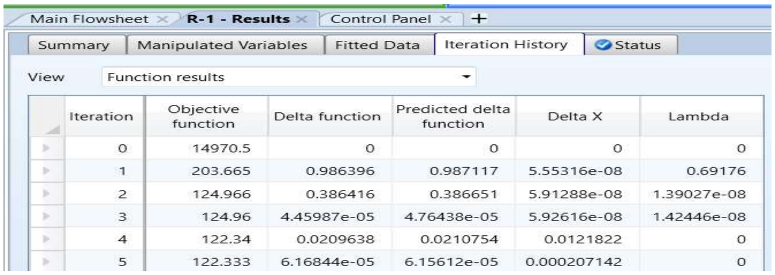
Next, we check the resulting manipulated variables shown in Figure 3.34. Here, we look for tighter bounds between the lower and upper limits of the 95% confidence interval. Wide bounds indicate loose fits. Also, make sure that estimated value is reasonably larger than the standard deviation.



Vary no.	Initial value	Estimated value	Standard deviation	95% confidence interval	
				Lower limit	Upper limit
1	3.6e-07	5.51757e-07	3.70714e-09	5.44491e-07	5.59023e-07
2	27000	24704.8	59.1647	24588.9	24820.8
3	3.6e+08	3.5148e+08	3.689e+06	3.44249e+08	3.5871e+08

Figure 3.34 Estimated manipulated variable values and standard deviations

A review of the iteration history will also give useful insights. Figure 3.35 shows a good progress between iterations in terms of the "objective function" value, and of the actual relative difference between the previous and current values of the objective function (called "delta function"). Interested readers may search Aspen Plus online help for "Data fit regression results iteration history sheet" for explanations of other tabulated results in the figure.

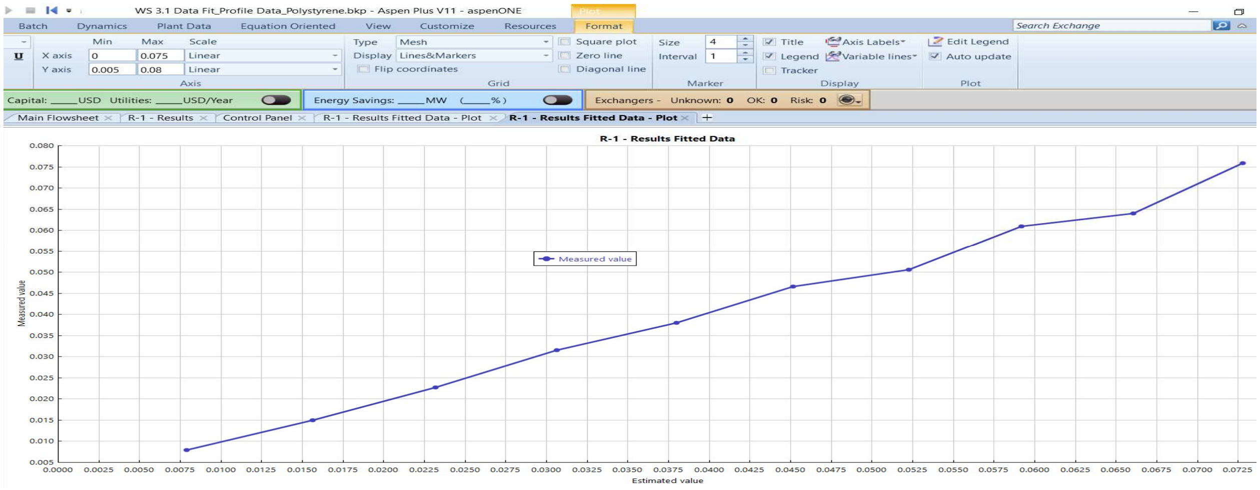


View: Function results

Iteration	Objective function	Delta function	Predicted delta function	Delta X	Lambda
0	14970.5	0	0	0	0
1	203.665	0.986396	0.987117	5.55316e-08	0.69176
2	124.966	0.386416	0.386651	5.91288e-08	1.39027e-08
3	124.96	4.45987e-05	4.76438e-05	5.92616e-08	1.42446e-08
4	122.34	0.0209638	0.0210754	0.0121822	0
5	122.333	6.16844e-05	6.15612e-05	0.000207142	0

Figure 3.35 Iteration history of data fit run.

Lastly, we may compare the estimated and measured values by following the path: Regression R-1 -> Results -> Fitted Data -> Plot: Choose Custom. X Axis – estimated values; Y Axis – measured value -> OK. See the initial plot in Figure 3.361 -> Plot: Format. Choose Squared plot and Diagonal line -> see the improved plot in Figure 3.37.


WS 3.1 Data Fit_Profile Data_Polystyrene.bkp - Aspen Plus V11 - aspenONE

X axis: Min 0, Max 0.075, Scale Linear
Y axis: Min 0.005, Max 0.08, Scale Linear
Type: Mesh
Display: Lines&Markers
Size: 4
Interval: 1
☐ Square plot
☐ Zero line
☐ Diagonal line
☐ Flip coordinates
☑ Title
☑ Legend
☐ Tracker
☐ Edit Legend
☑ Auto update

Capital: _____USD Utilities: _____USD/Year
Energy Savings: _____MW (_____%)
Exchangers - Unknown: 0 OK: 0 Risk: 0

Figure 3.36 The initial plot of estimated value versus measured value. Note the Format options of Squared plot and Diagonal line at the top.

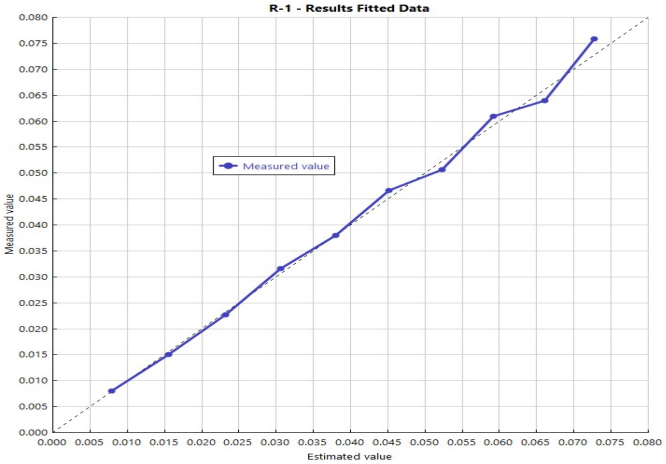


Figure 3.37 versus measured data.

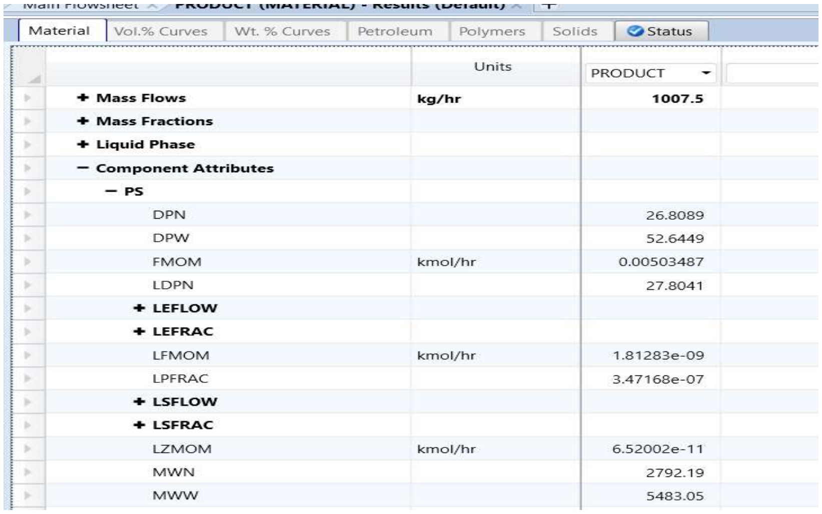
This concludes the current workshop. We save the simulation file as ***WS 3.1 Data Fit_Profile Data.bkp***.

3.10 Workshop 3.2 Data Fit of Kinetic Parameters for Styrene Polymerization Using Point Data

3.10.1 Objective:

The objective of the current workshop is to continue our previous PS workshop and demonstrates how to apply data fit tool to regress kinetic parameters for the product stream from the RBATCH reactor to meet the required MWN and MWW values at the end of batch polymerization. The dataset for data fit run includes only single values of MWN and MWW, which are called *point dataset*.

We use the same simulation file as WS3.1 and re-save it as ***WS 3.2 Data Fit_ Point Data_PS. Bkp***. We follow the path: Simulation -> Streams -> Product -> Result -> Component Attributes -> MWN = 2792.19, and MWW = 5483.05 (see Figure 3.38). Our task is to find the appropriate pre-exponential factors for rate constants for chain propagation reaction and chain-transfer-to-monomer reaction to produce a PS product with MWN =2800 and MWW = 5500.

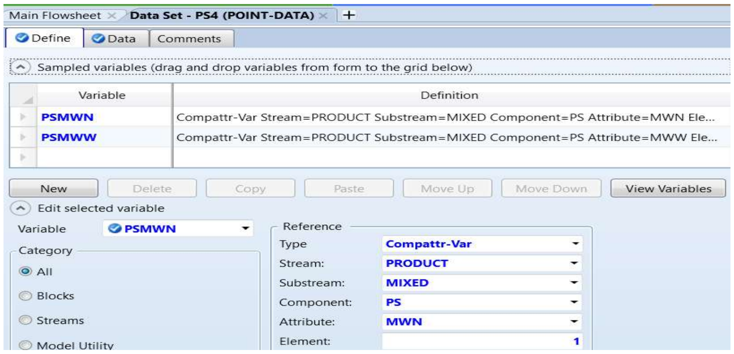


	Units	PRODUCT
+ Mass Flows	**kg/hr**	**1007.5**
+ Mass Fractions		
+ Liquid Phase		
− Component Attributes		
− PS		
DPN		26.8089
DPW		52.6449
FMOM	kmol/hr	0.00503487
LDPN		27.8041
+ LEFLOW		
+ LEFRAC		
LFMOM	kmol/hr	1.81283e-09
LPFRAC		3.47168e-07
+ LSFLOW		
+ LSFRAC		
LZMOM	kmol/hr	6.52002e-11
MWN		2792.19
MWW		5483.05

Figure 3.38 Product polymer attributes: MWN and MWW values

3.10.2 Dataset

We create the dataset by following the path: Simulation -> Model Analysis Tools -> Data Fit -> Dataset -> New -> Enter ID = PS4; Select type = Point-data -> OK -> (1) Define: Variable PSMWN See Figure 3.39 for MWN of PS product stream; repeat the same step to define variable PSMWW for MWW of PS product stream; (2) Data: See Figure 3.40 for dataset PS4.



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

Variable	Definition
PSMWN	Compattr-Var Stream=PRODUCT Substream=MIXED Component=PS Attribute=MWN Ele...
PSMWW	Compattr-Var Stream=PRODUCT Substream=MIXED Component=PS Attribute=MWW Ele...

Edit selected variable

Variable: **PSMWN**

Category

● All

○ Blocks

○ Streams

○ Model Utility

Reference

Type: **Compattr-Var**

Stream: **PRODUCT**

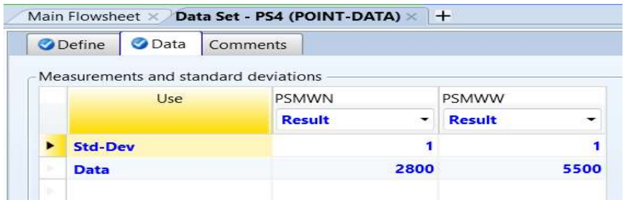
Substream: **MIXED**

Component: **PS**

Attribute: **MWN**

Element: 1

Figure 3.39 Defining point-data variables PSMWN and PSMWW



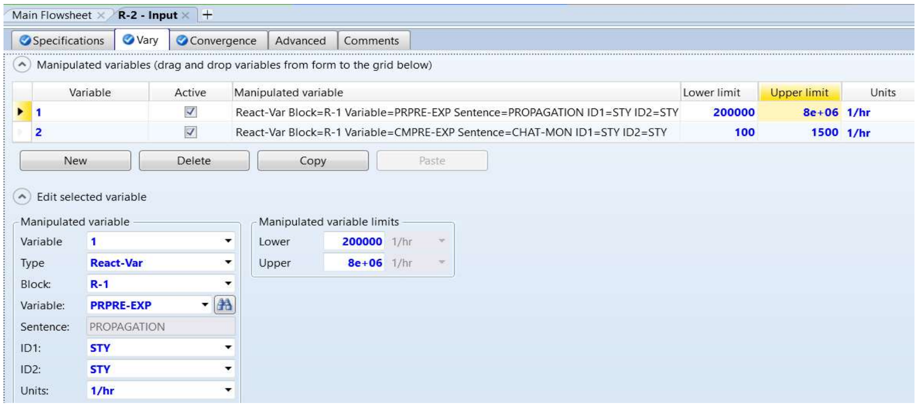
Measurements and standard deviations

Use	PSMWN **Result**	PSMWW **Result**
Std-Dev	1	1
Data	**2800**	**5500**

Figure 3.40 Specification of point dataset PS4

3.10.3 Simulation Data Regression (Data Fit)

To define a simulation regression run, we follow the path: Simulation -> Model Analysis Tools-> Data Fit -> Regression -> New -> Enter ID: R-2 -> OK -> Specifications: (1) Active: yes; (2) Select datasets to be regressed: PS4; (2) Vary: New-> See Figure 3.41. Variable 1 (PRPRE-EXP, pre-exponential factor for chain propagation); Variable 2 (CMPRE-EXP, pre-exponential factor of chain transfer to monomer). Define Variable 2 in the same way as Variable 1.



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

Variable	Active	Manipulated variable	Lower limit	Upper limit	Units
1	☑	React-Var Block=R-1 Variable=PRPRE-EXP Sentence=PROPAGATION ID1=STY ID2=STY	200000	8e+06	1/hr
2	☑	React-Var Block=R-1 Variable=CMPRE-EXP Sentence=CHAT-MON ID1=STY ID2=STY	100	1500	1/hr

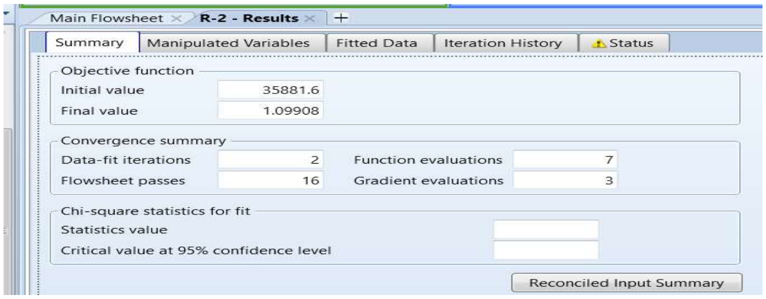
Edit selected variable

Manipulated variable
Variable: 1
Type: React-Var
Block: R-1
Variable: PRPRE-EXP
Sentence: PROPAGATION
ID1: STY
ID2: STY
Units: 1/hr

Manipulated variable limits
Lower: 200000 1/hr
Upper: 8e+06 1/hr

Figure 3.41 Manipulated variables for simulation data regression R-2

Before we run regression R-2, we need to deactivate the previous regression run R-1 by following the path: Simulation -> Model Analysis Tools -> Data Fit -> Regression -> R-1 -> Specifications: Cancel the "Active" entry. We then run regression R-2 through the control panel. Figure 3.42 shows the regression objective function drops from 355881.6 to 1.09908 within two iterations.



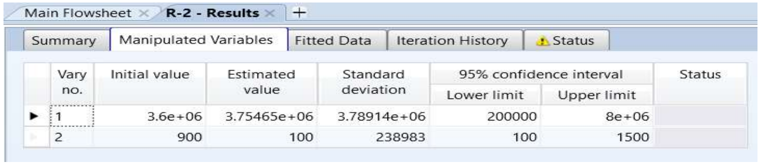
Objective function
Initial value: 35881.6
Final value: 1.09908

Convergence summary
Data-fit iterations: 2
Function evaluations: 7
Flowsheet passes: 16
Gradient evaluations: 3

Chi-square statistics for fit
Statistics value
Critical value at 95% confidence level

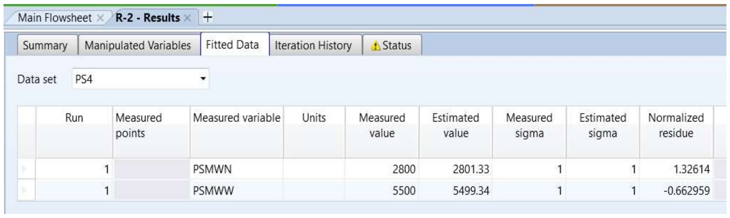
Figure 3.42 Summary of simulation regression results

Figure 3.43 illustrates that the standard deviation for the estimated kinetic parameters is large. We note this is due to the regression of 2 variables using 2 datapoints. From a technical standpoint, the regression should be able to perfectly fit the data and a standard deviation should not exist, but one does exist due to variable 2 being at its lower bound. This workshop is simply a demonstration of how to use the data fit tool. Real data fit problems should rely on more datapoints for fitting. For 'n' variables, a minimum of 'n' datapoints are required and 'n+1' datapoints are required for a standard deviation to exist. Results that are statistically significant require a number of datapoints that is at least an order of magnitude greater than the number of regressed variables. Figures 3.44 and 3.45 show where you can compare fitted data to regression estimated data and objective function iteration results.



Vary no.	Initial value	Estimated value	Standard deviation	95% confidence interval		Status
				Lower limit	Upper limit	
1	3.6e+06	3.75465e+06	3.78914e+06	200000	8e+06	
2	900	100	238983	100	1500	

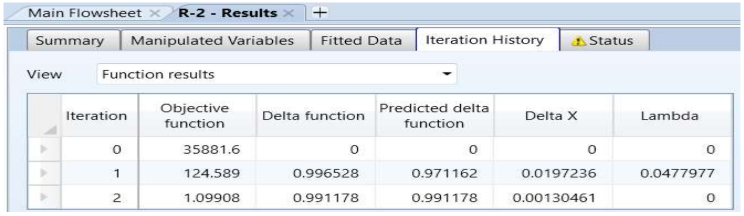
Figure 3.43 Estimated manipulated variables and standard deviations



Data set PS4

Run	Measured points	Measured variable	Units	Measured value	Estimated value	Measured sigma	Estimated sigma	Normalized residue
1		PSMWN		2800	2801.33	1	1	1.32614
1		PSMWW		5500	5499.34	1	1	-0.662959

Figure 3.44 Comparison of measured value and estimated value.



View Function results

Iteration	Objective function	Delta function	Predicted delta function	Delta X	Lambda
0	35881.6	0	0	0	0
1	124.589	0.996528	0.971162	0.0197236	0.0477977
2	1.09908	0.991178	0.991178	0.00130461	0

Figure 3.45 The objective function drops significantly within two iterations.

We conclude the current workshop and save the simulation file as: ***WS 3.2 Data Fit_ Point Data_PS. Bkp***. This chapter is published with Wiley publication in the book *Integrated Process Modeling, Advanced Control and Data Analytics for Optimizing Polyolefin Manufacturing by Liu & Sharma.* [12-23]

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