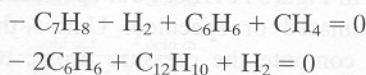


chemical reactions involving C chemical species:

$$\sum_{j=1}^C v_{ij} A_j = 0 \quad i = 1, \dots, R \quad (\text{A-III.16})$$

where A_j is the chemical formula for species j and v_{ij} is the stoichiometric coefficient for species j in reaction i (negative for reactants, positive for products). As an example, for the hydrodealkylation of toluene (Section 3.3), let the chemicals be ordered according to decreasing volatility, that is, (1) H_2 , (2) CH_4 , (3) C_6H_6 , (4) C_7H_8 , and (5) $\text{C}_{12}\text{H}_{10}$. The two reactions can be written as



and the stoichiometric coefficient matrix is

$$(v_{ij}) = \begin{array}{c} \text{H}_2 \\ \text{CH}_4 \\ \text{C}_6\text{H}_6 \\ \text{C}_7\text{H}_8 \\ \text{C}_{12}\text{H}_{10} \end{array} \begin{array}{c} \text{Reaction} \\ \begin{array}{cc} 1 & 2 \\ \left[\begin{array}{cc} -1 & 1 \\ 1 & 0 \\ 1 & -2 \\ -1 & 0 \\ 0 & 1 \end{array} \right] \end{array} \end{array}$$

Stoichiometric Reactor Models

In these models, the fractional conversion, X of key reactant k ,

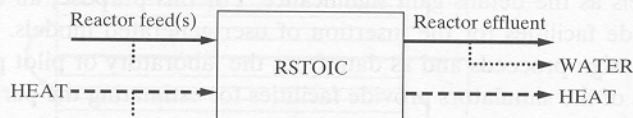
$$X_k = \frac{n_{k_{\text{in}}} - n_{k_{\text{out}}}}{n_{k_{\text{in}}}} = \frac{\Delta n_k}{n_{k_{\text{in}}}} \quad (\text{A-III.17})$$

where $n_{k_{\text{in}}}$ and $n_{k_{\text{out}}}$ are the moles of species k entering and leaving the reactor and $0 \leq X_k \leq 1$, or the extent of reaction i ,

$$\xi_i = \frac{\Delta n_{ij}}{v_{ij}} \quad j = 1, \dots, C \quad (\text{A-III.18})$$

are specified. Then, using these stoichiometric equations, the models determine the flow rates of all of the species leaving the reactor. Many of the models also include the energy balance and determine either the rate of heat transfer, to or from the reactor, or the temperature of the product stream.

In ASPEN PLUS, the RSTOIC subroutine has been prepared for this purpose. The schematic for the simulation flowsheet is



Note that several inlet streams can be mixed adiabatically to obtain an overall inlet stream. Also, two or more heat streams can be mixed similarly. In addition to the stoichiometric coefficients for the reactions, the fractional conversions of key reactants or the extents of reactions, two additional specifications are required: (1) P_{out} or $\Delta P = P_{\text{in}} - P_{\text{out}}$, and (2)

either the rate of heat transfer, Q , or T_{out} or ϕ_{out} , where ϕ_{out} is the vapor fraction of the product stream. The subroutine computes the molar flow rates of the species in the product stream and the unknown variables among T_{out} , ϕ_{out} , and Q .

EXAMPLE A-III.1

A hydrodealkylation reactor feed at 1,200°F and 494 psia consists of:

Component	lbmol/hr
Hydrogen	2,045.9
Methane	3,020.8
Benzene	46.2
Toluene	362.0
Biphenyl	1.0
Total	5,475.9

The reactions are the main and side reactions cited above, just below Eq. (A-III.16). If the conversion of toluene is 75% for the main reaction, and 2% of the benzene, both that in the feed and that produced by the main reaction, is converted to biphenyl by the side reaction, determine the reactor effluent flow rate, composition, and temperature for adiabatic operation with a 5 psi pressure drop.

SOLUTION

This example was solved with both ASPEN PLUS and CHEMCAD.

ASPEN PLUS SOLUTION

The RSTOIC subroutine is applicable. It permits the specification of one or more reactions, which can occur simultaneously or in series. For the previous specifications, the series option applies. Also, the extent or conversion of a limiting reactant must be specified. For the main reaction, the stoichiometric ratio of hydrogen to toluene is 1 : 1. The mole ratio of hydrogen to toluene in the reactor feed is $2,045.9/362.0 = 5.65$. Therefore, toluene is the limiting reactant and a conversion of 0.75 is specified. Because the only reactant in the side reaction is benzene, it is the limiting reactant with a conversion (after the main reaction occurs) of 0.02. The effluent temperature depends on the heat of reaction. It is not necessary to provide this value because all enthalpies in ASPEN PLUS are referred to the elements, using built-in heats of formation.

Using RSTOIC, with effluent specifications of 489 psia and 0 heat duty, and with the Peng–Robinson equation of state for thermodynamic properties, the following results are obtained, where both reactor feed and effluent are found to be vapor:

Effluent temperature: 1,264.5°F

Effluent component flow rates:

Component	lbmol/hr
Hydrogen	1,777.577
Methane	3,292.300
Benzene	311.346
Toluene	90.500
Biphenyl	4.177
Total	5,475.900

Note that the 4.177 lbmol/hr of biphenyl in the effluent is obtained from a 2% conversion of benzene following the main reaction, or from $46.2 + 0.75(362.0) = 317.7$ lbmol/hr of benzene.

CHEMCAD SOLUTION

The REAC model is applicable. However, it only allows one reaction. Therefore, two REAC blocks are used in series, the main reaction in the first block and the side reaction in the second

block. Enthalpies in CHEMCAD are also referred to the elements. Therefore, it is not necessary to specify heats of reaction.

The results for the effluent flow rate and composition leaving the second REAC block are identical to those for ASPEN PLUS. The effluent temperature of 1264.95°F differs by only 0.45°F from ASPEN PLUS. ■

Equilibrium Reactor Models

Most simulators provide two models for calculating chemical equilibrium. In addition, simultaneous phase equilibrium can also be requested. The first model is based on the use of chemical equilibrium constants for specified stoichiometric reactions. This is the classic method taught to undergraduate chemical engineers in a thermodynamics course. In ASPEN PLUS, this model is REQUIL. The second model is based on the minimization of Gibbs free energy. The reactions are not specified, but the possible products are. In ASPEN PLUS, the second model is RGIBBS.

It would seem that for simplicity or usefulness the second model would be preferred, because when using this model, an independent set of chemical reactions need not be specified. Hence, the designer is not concerned with identifying the principal reactions that take place. Since most reactors are designed to emphasize desired reactions and curtail or exclude undesired reactions, the chemical reactions that take place in the reactor are usually known by the time the reactor is to be designed. Thus, the first model may be preferred, with the second model being useful for preliminary exploration of the thermodynamic possibilities. To make the second model more useful, it is possible to place restrictions on certain possible reactions. The following example illustrates the considerably different results that can be obtained from the two methods.

For the reactor feed in Example A-III.1, compute the component flow rates and temperature for adiabatic conditions with a 5 psi pressure drop at chemical and phase equilibrium, assuming the validity of the Peng-Robinson equation of state.

SOLUTION

The first method is applied by using the REQUIL model in ASPEN PLUS. The stoichiometries of both the main and side reactions are specified. ASPEN PLUS computes the chemical equilibrium constants as a function of temperature from built-in free energies of formation. The second method is applied by using the RGIBBS model in ASPEN PLUS. With this model, no restrictions are placed on the possible reactions and the possible components in the reactor effluent are only those in the reactor feed. In both cases, the possibility of vapor and liquid phases in the effluent at equilibrium is considered by specifying two effluent phases.

The results of the two calculations are as follows:

Effluent Conditions	REQUIL	RGIBBS
Temperature, °F	1,284.2	1,627.1
Phases present	Vapor	Vapor
Flow rates, lbmol/hr:		
Hydrogen	1,695.868	583.396
Methane	3,376.918	4,112.804
Benzene	390.163	224.459
Toluene	5.882	33.725
Biphenyl	7.087	12.364
Total	5,475.918	4,966.748

The results of the two methods are drastically different. For REQUIL, the results are comparable to those of the previous example. At equilibrium, the conversion of toluene is 90.68%, compared to the specification of 75% in the previous example. The conversion of benzene to biphenyl at equilibrium is 1.51%, which is somewhat lower than the specification of 2% in the previous example. Since the main and side reactions are equimolar in reactants and products, there is no change in total moles per hour for REQUIL. Because of the higher conversion of toluene, the effluent temperature of 1,284.2°F is somewhat higher than the 1,264.5°F of the previous example.

The results from RGIBBS show a considerably higher outlet temperature and a much higher conversion of hydrogen. The effluent composition cannot be explained in terms of just the main and side reactions cited previously because the rate of disappearance of toluene is not equal to the rate of appearance of methane. In fact, much more methane appears than toluene disappears. The results can be explained if a third reaction occurs:



However, the likelihood of this reaction occurring is small because of the large numbers of hydrogen molecules involved, which would require a very complicated mechanism of elementary reactions. The RGIBBS model could be applied by ruling out this third reaction, but that requires that it be determined from the results in the previous table. This is not always a simple determination. Thus, for cases in which the reactions that take place are known, REQUIL is a better choice for determining equilibrium conditions. Note that REQUIL computes the same results as RGIBBS when any three independent reactions are specified. In general, the number of independent chemical reactions, R , is $C - \rho$, where C is the number of chemical species and ρ is the rank of the atom matrix [see Eq. (A-IV.15)]. ■

Kinetic Reactor Models

All steady-state simulation programs contain at least two kinetic reactor models: one for the plug-flow tubular reactor (PFTR or PFR) and one for the continuous-stirred-tank reactor (CSTR or CFSTR). Both models require the user to provide rate equations for the chemical reactions. The model can be used for either of two modes: (1) to compute the reactor volume for a specific conversion, or (2) to compute the conversion for a specified reactor volume.

PFTR Model

The PFTR model in ASPEN PLUS is RPLUG. It is a rigorous one-dimensional, plug-flow model that neglects axial dispersion. Thus, there are no radial gradients of temperature, composition, or pressure; and mass transfer by diffusion does not occur in the axial direction. Operation of the reactor can be adiabatic, isothermal, or nonadiabatic, nonisothermal. For the latter, heat transfer to or from the reacting mixture occurs along the length of the reactor.

Consider the case of an adiabatic operation with one chemical reaction. A mole balance for the limiting reactant, A , can be written as:

$$F_{A0} \frac{dX}{dV} = -r_A\{X, T\} \quad (\text{A-III.19})$$

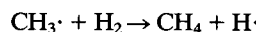
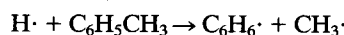
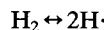
where F_{A0} is the molar flow rate of A entering the reactor, X is the fractional conversion of A , V is the reactor volume, and r_A is the rate of reaction of A written as a function of fractional conversion and temperature. Because ASPEN PLUS computes enthalpies referred to the elements, the heat of reaction is handled automatically, and the energy balance for adiabatic operation becomes simply:

$$H\{X, T\} = H\{X = 0, T = T_0\} \quad (\text{A-III.20})$$

where H is the enthalpy flow rate of the reacting mixture, energy/unit time, and T_0 is the entering temperature. The balances are solved by numerical integration. The following example illustrates the use of RPLUG for sizing the hydrodealkylation reactor considered in the previous two examples.

EXAMPLE A-III.3**Toluene Hydrodealkylation Reactor**

An adiabatic reactor is to be designed for the specifications in Example A-III.1. From the results of that example and Example A-III.2, we can neglect the kinetics of the backward reaction for the main reaction and assume the main reaction is irreversible. Also, because the equilibrium conversion of benzene to biphenyl is so small, we can neglect the kinetics of the side reaction. For the main reaction, laboratory studies have shown that in the absence of a catalyst, the following free-radical chain reaction mechanism applies:



If local equilibrium is achieved rapidly in the first step and the second step is the slow or controlling step, the reaction rate is proportional to the product of the toluene concentration and the square root of the hydrogen concentration. The laboratory kinetic data for temperatures in the range of 500°C (932°F) to 900°C (1,652°F) and pressures from 1 to 250 atm are correlated by the reaction-rate equation:

$$-\frac{dc_{\text{toluene}}}{dt} = 6.3 \times 10^{10} \exp\left(-\frac{52,000}{RT}\right) c_{\text{toluene}} c_{H_2}^{1/2}$$

where concentrations are in mol/L (same as kmol/m³), time is in sec, and the activation energy is in cal/mol. Assuming plug flow with no axial dispersion, use RPLUG to determine a cylindrical process-vessel reactor with a length-to-diameter ratio of 6. Use the Peng–Robinson equation of state to estimate the thermophysical properties for this vapor–phase reaction.

SOLUTION

The RPLUG model can handle multiple reactions, but the kinetics must be specified for each reaction. Unfortunately, the kinetics are not known for the side reaction, but it occurs only to a small extent. For the reactor effluent computed from the RPLUG model to be identical to the result for the RSTOIC model obtained in Example A-III.1, the reactor feed can be modified by letting the side reaction take place before the feed enters the reactor. Then the side reaction will not occur in the RPLUG model. To do this, the RSTOIC result shows that 4.177 – 1.000 = 3.177 lbmol/hr of biphenyl is produced. Thus, the side reaction also produces 3.177 lbmol/hr of hydrogen, and uses 2(3.177) = 6.354 lbmol/hr of benzene. Therefore, the feed to the RPLUG model becomes:

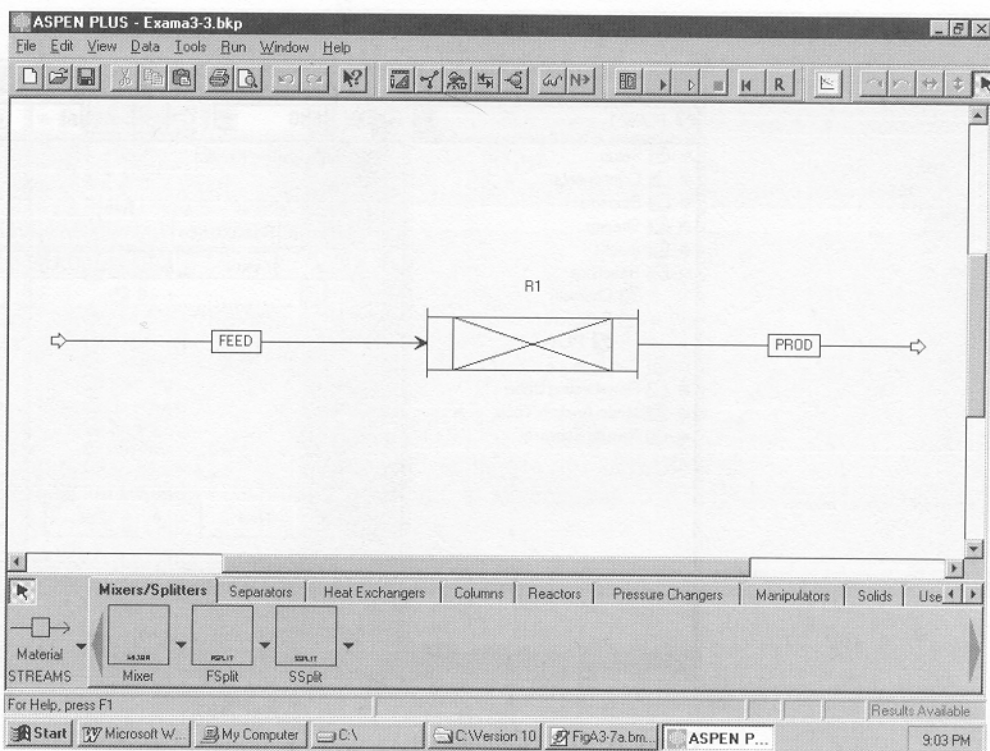
Component	lbmol/hr
Hydrogen	2,049.077
Methane	3,020.8
Benzene	39.846
Toluene	362.0
Biphenyl	4.177
Total	5,475.9

The RPLUG model requires the user to specify the length and diameter of the plug-flow tubular reactor. For this example, the fractional conversion of toluene is fixed and the length and diameter of the reactor are to be determined. To accomplish this with ASPEN PLUS, a design

specification is applied as follows. For a plug-flow reactor, the conversion of the limiting reactant is a function of reactor volume. Thus, any ratio of reactor length to diameter can be used to make the calculation with RPLUG. From Example A-III.1, using the RSTOIC model, the specified conversion of 75% of the toluene in the feed results in a flow rate of 90.5 lbmol/hr of toluene in the reactor effluent. Let the reactor diameter be fixed at 10 feet. Use a design specification to vary the reactor length to obtain the 90.5 lbmol/hr of toluene in the effluent.

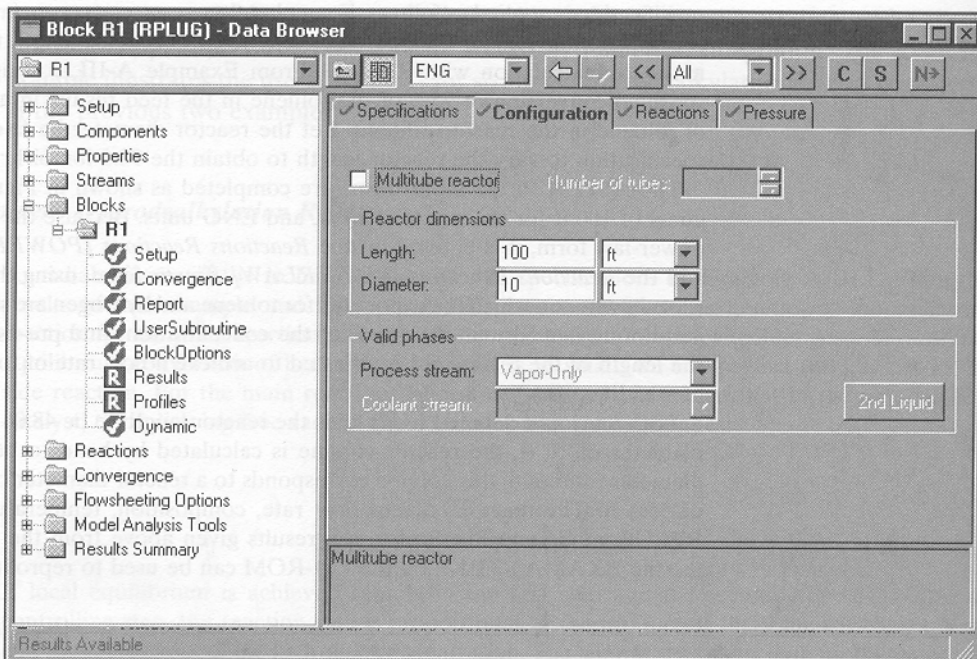
The ASPEN PLUS input forms are completed as shown in Figure A-III.7, using an initial guess of 100 ft for the reactor length, and ENG units. Because the kinetic rate expression is a power-law form, it is entered on the *Reactions Reactions [POWERLAW]-Stoichiometry* form and the *Reactions Reactions [POWERLAW]-Kinetic* form, using the *Edit Reaction* dialog box (not shown—on which the exponents for toluene and hydrogen are set to 1 and 0.5, respectively) and noting that SI units are used for the concentrations and pre-exponential factor. Note that the length of the reactor R1 is adjusted to achieve a flow rate of toluene in the PROD stream of 90.5 lbmol/hr.

With this input data, RPLUG finds the reactor length to be 48.06 ft. For the specified reactor diameter of 10 ft, the reactor volume is calculated by hand to be 3,774 ft³. For a length to diameter ratio of 6, this volume corresponds to a reactor diameter of 9.3 ft and a reactor length of 55.8 ft. The reactor effluent flow rate, composition, temperature, and pressure from the RPLUG model are identical to the results given above from the RSTOIC model. Note that the file EXAMA3-3.BKP on the CD-ROM can be used to reproduce these results. ■

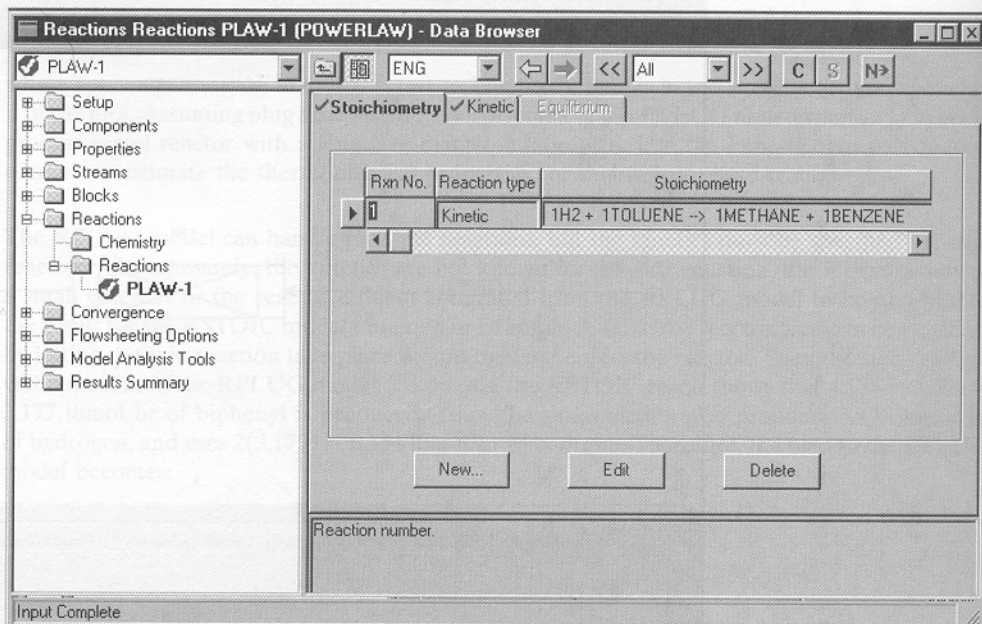


(a)

Figure A-III.7 PFTR simulation: (a) simulation flowsheet; (b) reactor parameters (*Block [RPLUG] Configuration* form); (c) reaction definition (*Reactions Reactions [POWERLAW] Stoichiometry* form); (d) reaction kinetics (*Reactions Reactions [POWERLAW] Kinetic* form); (e) *Design-Spec Define* form; (f) *Design-Spec Spec* form; (g) *Design-Spec Vary* form.



(b)



(c)

Figure A-III.7 (Continued)

Reactions Reactions PLAW-1 (POWERLAW) - Data Browser

PLAW-1

ENG

Stoichiometry Kinetic Equilibrium

1) 1H₂ + 1TOLUENE → 1METHANE + 1BENZENE

Reacting phase: Liquid

Power Law kinetic expression

$$r = k T^n e^{-E/RT}$$

k: 6.3E+10

n: 0

E: 52000 cal/mol

[C] basis: Molarity

Edit reactions

Solids

Input Complete

(d)

Design-Spec DS-1 - Data Browser

DS-1

ENG

Define Spec Vary Fortran Declarations

Fortran variable	Definition
TOL2	MOLE-FLOW Stream=PROD Substream=MIXED Component=TOLUEN

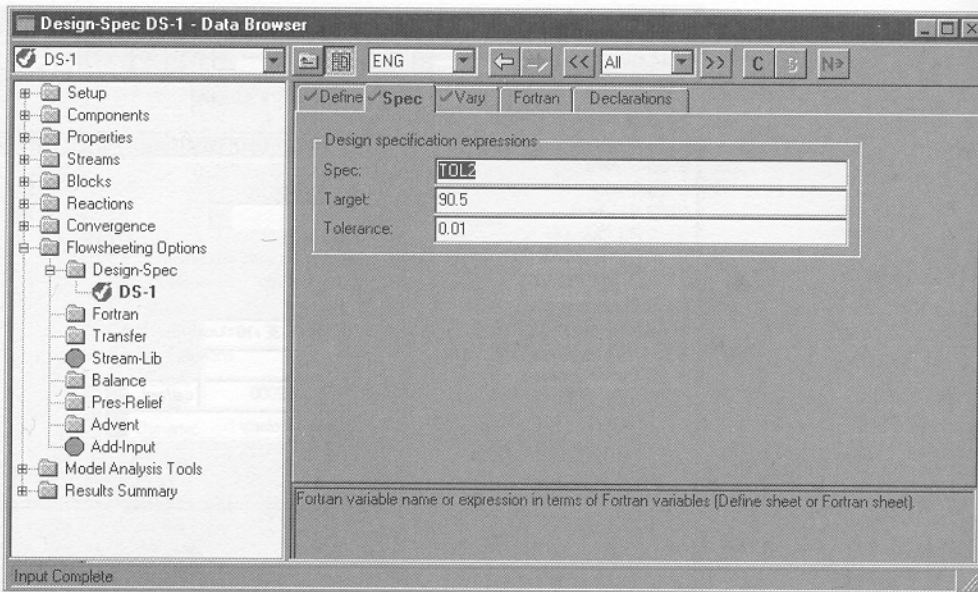
New... Edit Delete

Fortran variable name. The Fortran variable will be used to represent the sampled variable in the Fortran statements.

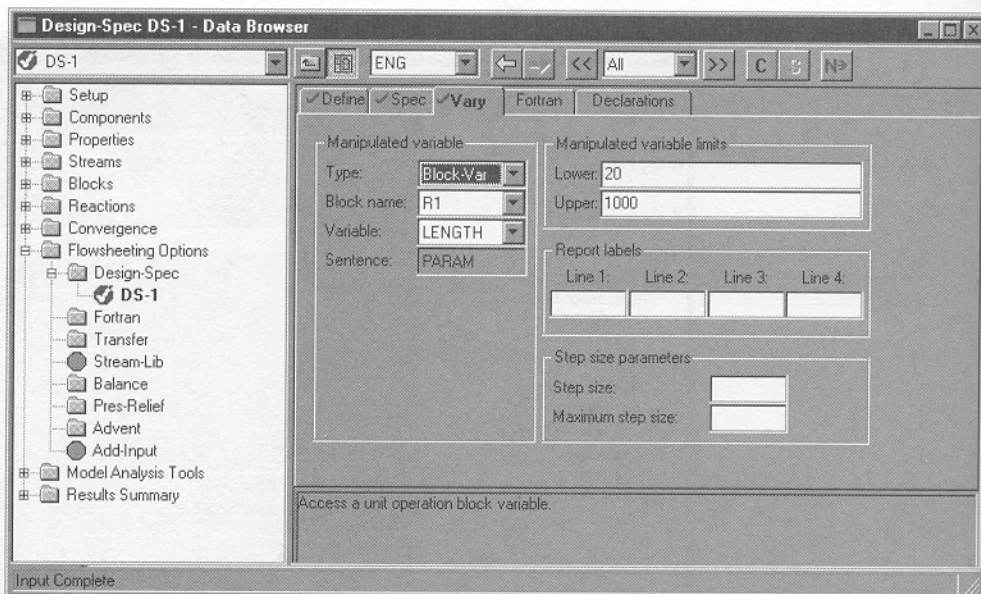
Input Complete

(e)

Figure A-III.7 (Continued)



(f)



(g)

Figure A-III.7 (Continued)

CSTR Model

The CSTR model in ASPEN PLUS is RCSTR. It assumes perfect mixing, and hence, the effluent composition and temperature are taken to be identical to the composition and temperature in the reactor. The forms for using the model are similar to those for RPLUG. To use RCSTR, the user must specify the reactor volume. To compute the reactor volume for a specified conversion, a design specification is applied.