

# Reactors

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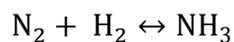
Reactions are usually the heart of the chemical processes in which relatively cheap raw materials are converted to more economically favorable products. In other cases, reactions play essential safety and environmental protection roles. In any case, proper design and operation of the reactor is required to provide the desired outcome. Such design is usually based on thermodynamics, chemical kinetics, and transport studies coupled with experience and economic considerations.

When studying chemical reactions we need to determine what are the reactants and products needed, to what extent will the reaction proceed, and how fast it will proceed. The study of such factors in addition to the detailed design of the reactor consist the chemical reaction engineering field in which process simulation can be of great help.

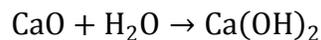
Aspen Plus provides several libraries to model reactive processes. The selection of the model depends on the amount of information available and the type of simulation.

## Reaction Classifications

There are several ways to classify a chemical reaction. For example, reactions can be classified as reversible and irreversible reactions. In reversible reactions, the reactants are converted to products at a certain rate while the products are converted to reactants at a different rate. At equilibrium, the two rates become equal. An example of reversible reaction is the formation of ammonia from hydrogen and nitrogen:



In irreversible reactions, on the other hand, the rate of conversion of products to reactants is zero. For example, the hydration of calcium oxide to form calcium hydroxide is an irreversible reaction:



Another classification of reactions is based on the phase(s) involved. In this classification, a homogeneous reaction is defined as a reaction which occurs in one phase. On the other hand, a heterogeneous reaction requires the presence of two or more phases for the reaction to take place (regardless of where the reaction is occurring). For example, the burning of methane is a homogeneous reaction since it occurs in the gas phase only. On the other hand, burning coal is a heterogeneous reaction since the presence of oxygen (gas) and coal (solid) are needed to complete the reaction.

When considering the phase of the reaction, it is important to distinguish between the phases present during a reaction and the phases in which the reaction occurs. For example, an oxygen scavenging system such as sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) solution when used to remove oxygen from a gas stream, the gas will have to dissolve in the solution for the oxygen to be removed. Thus,

while the reaction is heterogeneous (requires the presence of gas and liquid phases), the reaction occurs in the liquid phase only.

## Material Balance on Reactive Processes

For the general reaction:

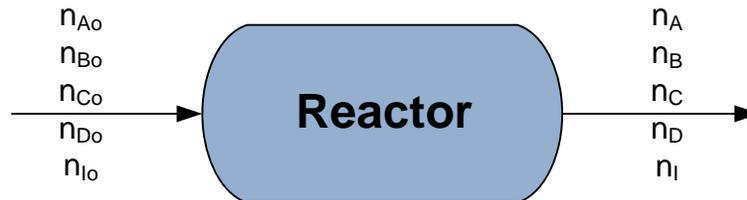
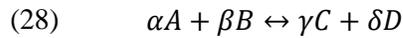


Figure 67. Simple reactor block.

occurring in the process shown in Figure 67. The amount of each component entering the system is known, and the objective is to determine the outlet composition. One approach to solve this material balance is to use the fractional conversion of one of the materials. The fraction conversion is defined as:

$$(29) \quad X_i = \frac{n_{io} - n_i}{n_{io}}$$

Of course,  $X_i$  ranges from 0 to 1. Then, the outlet of component  $i$  can be determined by rearranging Equation (29) to give:

$$(30) \quad n_i = n_{io}(1 - X_i)$$

Using stoichiometry, the outlet for other components can be calculated.

In the example in Figure 67, if the conversion of  $A$  is known ( $X_A$ ), then the outlet flow rates can be written as:

$$(31)a \quad n_A = n_{Ao}(1 - X_A)$$

$$(31)b \quad n_B = n_{Bo} \left( 1 - \frac{\beta}{\alpha} X_A n_{Ao} \right)$$

$$(31)c \quad n_C = n_{Co} \left( 1 + \frac{\gamma}{\alpha} X_A n_{Ao} \right)$$

$$(31)d \quad n_D = n_{Do} \left( 1 + \frac{\delta}{\alpha} X_A n_{Ao} \right)$$

Alternatively, the extent of reaction can be used. The extent of reaction can be viewed as a hypothetical product for which one molecule (or mole) is produced each time a reaction event occurs. The extent of reaction ( $\xi$ ) is used to define the output from the reaction using the following expression:

$$(32) \quad n_i = n_{io} + \sum v_{ij} \xi_j$$

where a summation is used to account for the presence of multiple reactions (denoted by the subscript  $j$ ), and  $\nu_{ij}$  denotes the stoichiometric coefficient of component  $i$  in reaction  $j$ . Thus, for the above system, the outlet flow rates can be written as:

$$(33)a \quad n_A = n_{Ao} - \alpha\xi$$

$$(33)b \quad n_B = n_{Bo} - \beta\xi$$

$$(33)c \quad n_C = n_{Co} - \gamma\xi$$

$$(33)d \quad n_D = n_{Do} - \delta\xi$$

Both the conversion and extent of reaction are based on stoichiometry and requires knowledge of the exact reaction(s) taking place.

In some cases, detailed information about the reaction is available and different approaches need to be taken that does not require exact knowledge of the reaction. For example, reactions involving non-conventional materials, such as crude oil and food stuffs, it can be difficult to write a set of chemical reactions describing the system. In such cases, general knowledge of the reactants and products present and quantities produced can be employed. The reaction yield, defined as:

$$(34) \quad \text{Yield} = \frac{\text{amount of product produced}}{\text{amount of feed}}$$

Since the stoichiometry is unknown, yield must be provided for each product. If, however, yield is used with reaction where stoichiometry is determined, the yields can all be related through the stoichiometric coefficients.

In all of the above analysis information is needed about the final product (conversion,  $\xi$ , or yield). If such information is not available a different approach may be followed. Consider for example the reversible reaction in Equation (28), with an equilibrium constant  $K$ . The equilibrium constant is defined from thermodynamics as:

$$(35) \quad K = \prod_i \left( \frac{\hat{f}_i}{f_i^o} \right)^{\nu_i}$$

where  $f_i$  refers to the fugacity of component  $i$ , and  $K$  is equal to:

$$(36) \quad K = \exp\left(-\frac{\Delta G^o}{RT}\right)$$

and:

$$(37) \quad \Delta G^o = \sum_i \nu_i G_i^o$$

which is the stoichiometric weighted difference between the products and reactants. Thus, once the reaction stoichiometry is known, we can calculate the equilibrium constant and the equilibrium conversion (*i.e.*, material balance) of each species. Notice here that the equilibrium

constant is affected by the temperature based on the value of  $\Delta G^o$  and  $T$  in the denominator of the exponential argument in Equation (36).

In cases where information on the stoichiometry is unknown and, especially, if phases changes accompany the reaction an approach based on minimizing the Gibbs free energy of the whole mixture can be used. In this approach, the total Gibbs energy of all components (reactants, products, and inerts) is minimized. For example, the Gibbs energy for an ideal mixture is given by:

$$(38) \quad G_{mix} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

which, for two components system, is minimized as:

$$(39) \quad \frac{\partial G_{mix}}{\partial x_1} = G_1 - G_2 + RT \ln \left( \frac{x_1}{1 - x_1} \right)$$

This derivative is set to zero to find the minimum  $G_{mix}$ . A similar approach can be applied for more complex systems with multiple phases.

## Reaction Kinetics

Reactors are usually designed based on rate considerations. Two commonly used reactors are the CSTR (continuous stirred tank reactor) and the PFR (plug flow reactor). These reactors provide enough residence time for the reaction to take place with satisfactory conversion. In such reactors, the reaction rate expression must be known determined.

One of the most common reaction rates is the power law expression. This law can be written as:

$$(40) \quad r = k \underbrace{\left( \frac{T}{T_{ref}} \right)^\alpha \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right]}_{\text{Kinetic factor}} \underbrace{\prod_i (K_i^D C_i)^{\beta_i}}_{\text{Driving force}}$$

Where the concentration is multiplied by a temperature dependent factor ( $K_i^D$ ), which represents a weighing factor for the dependence of the reaction rate on the different components concentrations. The exponent ( $\beta_i$ ) can be equal to the stoichiometric coefficient, and in such case the rate is termed an elementary, or it can differ.

In many cases, a catalyst is used to enhance the reaction. In such cases, the adsorption of the different materials on the catalyst can be an important process that affects the reaction rate. In such cases, the reaction rate of Equation (40) must be modified to take into account the adsorption effect. One of the most commonly used reaction rates for such cases is the Langmuir-Hinshelwood-Hougen-Watson (LHHW). The reaction rate with the LHHW model is similar to that in Equation (40) except for the addition of an adsorption term as a denominator, *i.e.*:

$$(41) \quad \text{Rate} = \frac{(\text{kinetic factor})(\text{driving force})}{\text{adsorption term}}$$

The adsorption term is given by:

$$(42) \quad \text{Adsorption term} = \sum K_i \prod (C_j)^{\nu_j}$$

Once the kinetics is known, the reactor design can be made based on material balance. For an ideal CSTR reactor, the residence time ( $\tau$ ) required for the reaction is given by:

$$(43) \quad \tau = \frac{V}{v} = \frac{C_{A0} X_A}{-r_A}$$

For an ideal PFR reactor, the residence time is given by:

$$(44) \quad \tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

## Heat of Reaction

Energy balances on reactors are coupled with material balances to determine the heating or cooling requirements. Here, the energy balance is similar to that for non-reactive system except for the addition of the heat of reaction term. The heat of reaction is defined as:

$$(45) \quad \Delta H_{rxn} = \sum \nu_i H_{f,i}^o$$

where  $H_{f,i}^o$  is the heat of formation for the reactants and products and  $\nu_i$  is the stoichiometric coefficient (negative for the reactants and positive for the products). For example, the energy balance for CSTR with a single reaction is given by:

$$(46) \quad -\Delta H_{rxn} r_A V + q \sum_i c_i (H_{if} - H_i) + \dot{Q} = 0$$

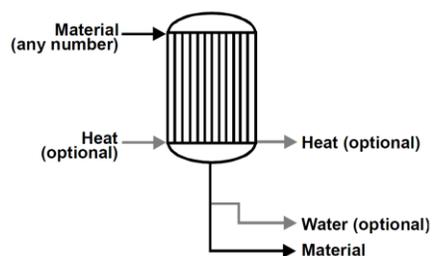
where  $c_i$  is the concentration of component  $i$  and  $\dot{Q}$  is the external heating or cooling to the reactor. Similar expression can be written for the PFR.

## Reactor Modeling in Aspen Plus

There are seven blocks for reaction modeling in Aspen that can perform calculations based on the stoichiometry, yield, equilibrium, and Gibbs minimization, plus the kinetics models for CSTR and PFR. In addition, a batch model is available for batch reactors.

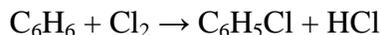
### RStoic

When the reaction stoichiometry is known but information on kinetics is not available (or not important). The block must have one or more feed streams, one required output stream. Optional connections are the water decant and input and output heat streams. The connectivity for this block is shown in the figure to the right.



The input form for this block is shown in Figure 68. Two specifications must be made either to the outlet stream conditions or the heat duty of the reactor. The form allows specification of the valid phases inside the reactor. The reactions can be defined in the **Setup | Reactions** tab by

defining a New reaction and entering the reactants and products with their stoichiometric coefficients as shown in Figure 69. In this figure, an example has been input for the reaction:



The stoichiometric coefficients are automatically adjusted to be negative for the reactants and positive for the products. The form also defines the completion of the reaction through either the extent of reaction or the fractional conversion of any reactant.

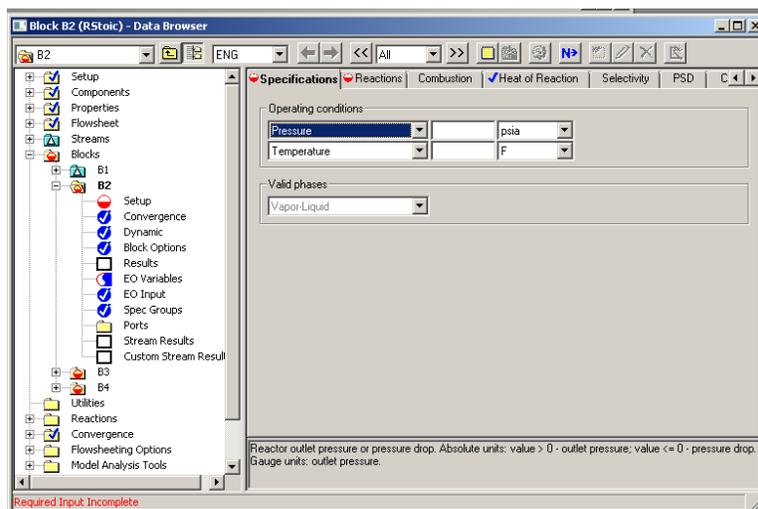


Figure 68. Input form for the RStoic block.

Multiple reactions can be defined in the **Reactions** form. The option "Reactions occur in series", if checked, will cause the calculations to proceed in the order the reactions are entered. If the option is not selected, the reactions will be taken to occur in parallel.

If the reaction involved is a combustion reaction, the **Setup | Combustion** tab can be used. In this case, no reaction needs to be defined, and the simulation will assume complete combustion of all carbon, hydrogen, sulfur, and nitrogen. Components containing atoms other than C, H, S, or N will be ignored. When the combustion is selected, make sure to add the combustion

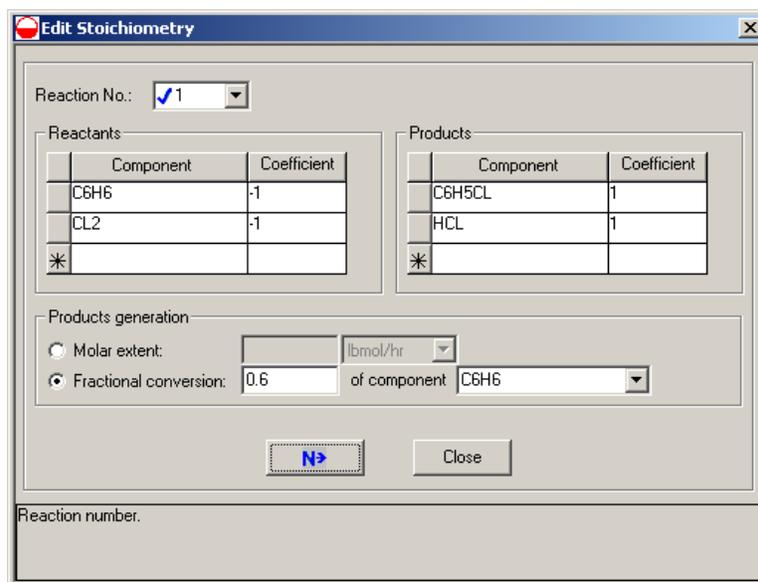


Figure 69. Edit Stoichiometry form used for entering the reaction information.

products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ , and  $\text{NO}$  or  $\text{NO}_2$ ).

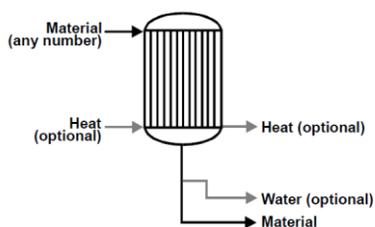
The heat of reaction can be calculated or input in the **Setup | Heat of Reaction** tab. The heat of reaction will not be used in the calculations but will be presented in the **Results** sheet. The heat of reaction will be calculated based on the reaction of 1 mole of a reference component (reactant). The temperature, pressure, and phase for the calculations must be specified.

Other options are available in the RStoic **Setup** form such as the calculations of the selectivity for multiple reactions and options for working with non conventional streams.

Consider for example the benzene chlorination reaction shown previously. If 100 kmol/hr of an equimolar amounts of chlorine and benzene at 70 °C and 2 bar are fed to an RStoic reactor in which 80% conversion of benzene is achieved. No pressure drop and no temperature changes occur. The **Results** form gives information about the outlet stream conditions and heat duty of the reactor, phase equilibrium, heat of reactions (if selected).

### RYield

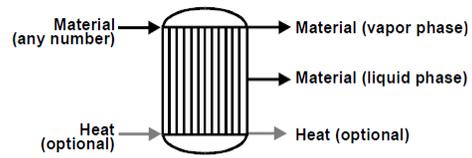
The second block in the Reactors library, RYield, performs the calculations based on the yield. The block takes similar streams as that for the RStoic block, as shown in the figure to the right. This block does not require exact information about the stoichiometry or kinetics. Similar input to that of RStoic is needed here for the exit stream. The output of the reaction is defined based on the yield in the **Setup | Yield** form shown in Figure 70. The yield is defined as mole or mass of each component per total mass input to the block. Inert components can be defined in the same form and will not be included in the yield calculations. No heat of reaction can be calculated here because the stoichiometry of the reaction is not known. Another option to enter the yield is through the component mapping option. If this option is selected in the **Yield** form, the **Setup | Comp. Mapping** form becomes available. In this form, the combination (lumping) or breaking (de-lumping) of reactants (with their weight fraction) to form products is input for each material.



If we want to repeat the previous example, we can define the yield as shown in Figure 70. Similar results to that obtained in the RStoic is displayed in the **Results** form.

## REquil

When one or more reactions involved are equilibrium reaction, the REquil block can be used. The block requires knowledge of the reaction stoichiometry, and performs chemical and phase equilibrium reactions. Unlike the previous blocks, the REquil block has a vapor and liquid phase product streams (both are required). The only required information for this block is the output stream and the reaction. With this input, all the required calculations are made based on thermodynamics calculations as described in page 97. The equilibrium constant for the reaction will be calculated and presented in the **Results | Keq** form. The constant will be calculated at the outlet stream conditions. If the equilibrium constant needs to be estimated at a different temperature than the that of the reactor, input can be made in the Temperature approach field of the Edit Stoichiometry window show in Figure 71. If the extent of a reaction is known and no equilibrium calculations are need the Molar extent can be defined directly in the Edit Stoichiometry window as well.



**Edit Stoichiometry**

Reaction No.:

Reactants				Products			
Component	Coefficient	Solid		Component	Coefficient	Solid	
CL2	-1	No		HCL	1	No	
BENZENE	-1	No		CB	1	No	
*				*			

Products generation:

Molar extent:  kmol/hr

Temperature approach:  C

Extent estimate:  kmol/hr

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Reaction number.

Yield options:

Component yields		
Component	Basis	Yield
CL2	Mole	10
BENZENE	Mole	10
HCL	Mole	40
CB	Mole	40
*		

Inert Components:

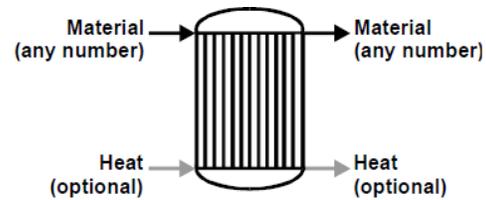
Results Available with Warnings

Figure 70. Defining the yield for RYield reactor.

The previous example can be repeated with the REquil block. The results show that most of the reactants are consumed in this system. The equilibrium constant for the reaction at 70 °C is  $2.16 \times 10^{19}$  showing a large favorability of the forward reaction as indicated by the consumption of the reactants.

## RGibbs

The fourth block provides reaction calculations without the need for detailed stoichiometry or yield. The calculations are based on minimizing the Gibbs energy for the system as discussed in page 98. The block takes one or more input and one or more output streams, and an optional heat



input and/or output streams. The input form requires two variable specifications. The block can be used to calculate phase and/or chemical equilibrium, and allows constraining the equilibrium value with specific heat duty and/or temperature approach in the **Setup | Specifications** form. If restricted equilibrium is selected, reactions can be defined for the system. The block also allows specifying the number of phases, which components present in each phase, and how to distribute the phase on the outlet streams (when multiple output streams are used) in the **Setup | Products** and **Setup | Assign Streams** forms. Inert components can be defined in the **Setup | Inerts** form. The setup form for the RGibbs block is shown in Figure 72.

Figure 72. The RGibbs Setup form.

Repeating the previous example with the RGibbs block gives close results to that in the previous examples. The **Results** form gives information on the outlet conditions and reactor duty, and information on the outlet phases and compositions as defined in the **Setup** form.

## RCSTR and RPlug

When rigorous simulation of reactors is needed, the RCSTR and RPlug are used. These two blocks perform simulation of ideal reactors operated under specific conditions. For the CSTR, two design variables are needed (pressure and temperature or heat duty), specification of the valid phases, and a reactor specification. For the plug reactor, a specification is needed for the type of the reactor (specific temperature, adiabatic, or cooled). Depending on the type choice, the required specification will vary: temperature or temperature profile, no specifications are needed,

or heat transfer coefficient. The configuration for the reactor is input in the **Setup | Configuration** form which includes the reactor geometry. The pressure drop can be specified in the **Setup | Pressure** form.

In both the RCSTR and RPlug, specifications for the catalyst can be made in the **Setup | Catalyst** form. Catalyst specification will be used to calculate species generation when the basis for the reaction rate is given in weight catalyst. In addition, pressure drop calculations will depend on the catalyst specifications when Ergun's equation is used.

Unlike the previous blocks, detailed information on the reaction and its kinetics must be input for these blocks. The reactions are defined in the **Reactions** folder. Two types of reactions present: chemistry (used for ions forming systems) and reactions (for reactions in general). Only the second type will be discussed here. New reactions can be defined by going the **Reactions | Reactions** folder and click the New... button. The Create new ID window appears where you can input a reaction name and select its type. The available reaction types cover a wide range of kinetics expression for general reactions, polymerization reactions, and reactive distillation applications. The General type provides options for common reaction kinetics including power law, equilibrium, and LHHW.

For example, the benzene chlorination reaction described in the previous examples have a kinetics of the form:

$$(47) \quad r = 0.001C_{Cl_2}C_{Ben}$$

where  $C_{Cl_2}$  and  $C_{Ben}$  are the concentrations in  $\text{kmol/m}^3$ , and the rate is given in  $\text{kmol/m}^3\cdot\text{s}$ . The reacting phase is the liquid phase. Define a new reaction (named CLBZ) as a general reaction of the power law type, and input the information as shown in Figure 73.

To use the reaction in the RCSTR and RPlug reactions, go back to the **Setup | Reactions** form and add the reaction to the Selected reaction sets.

For example, define a CSTR with  $0.5 \text{ m}^3$  volume where the reaction is taking place in the liquid phase only. Once the simulation is executed, the **Results** page gives about the reactor duty, phases, and residence time. We can also use the same reaction with a RPlug block for a PFR having a specified exit temperature of  $70 \text{ }^\circ\text{C}$ , zero pressure drop, 5.22 m length, 0.35 m diameter, and reaction in liquid phase only. The **Results** page gives similar information to that of the RCSTR.

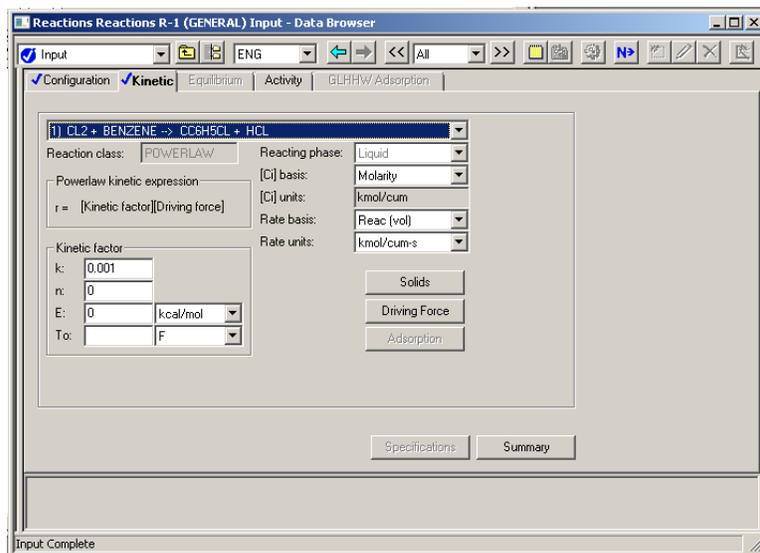
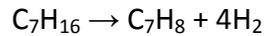


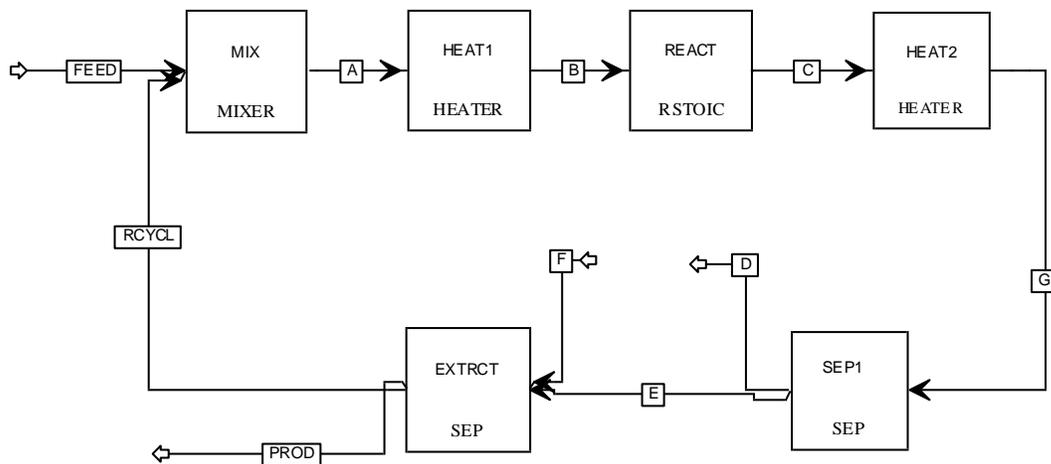
Figure 73. Defining power law kinetics for the benzene chlorination reaction.

## Exercise 1: Toluene Production

A fresh feed of 20 lbmol/hr of pure *n*-heptane at 77 °F and 1 atm is combined with a solvent recycle from an extractor and heated to 425 °F at 1 atm. The hot stream is fed into a reactor in which the following reaction occurs:



The conversion based on *n*-heptane is 15%. The products of reaction are cooled to 180 °F, after which the hydrogen is completely separated from the reactor products in the first separator. A feed of 100 lbmol/hr of benzene at 180 °F and 1 atm is combined with the remaining products of reaction to extract the toluene. All of the toluene and benzene leave as the product of the process. The unreacted *n*-heptane is recycled to the mixer. A sketch of the process is given below. Use the RStoic model for the reactor, and Chao-Seader property method.



### Questions:

14. What is the overall conversion of the process?

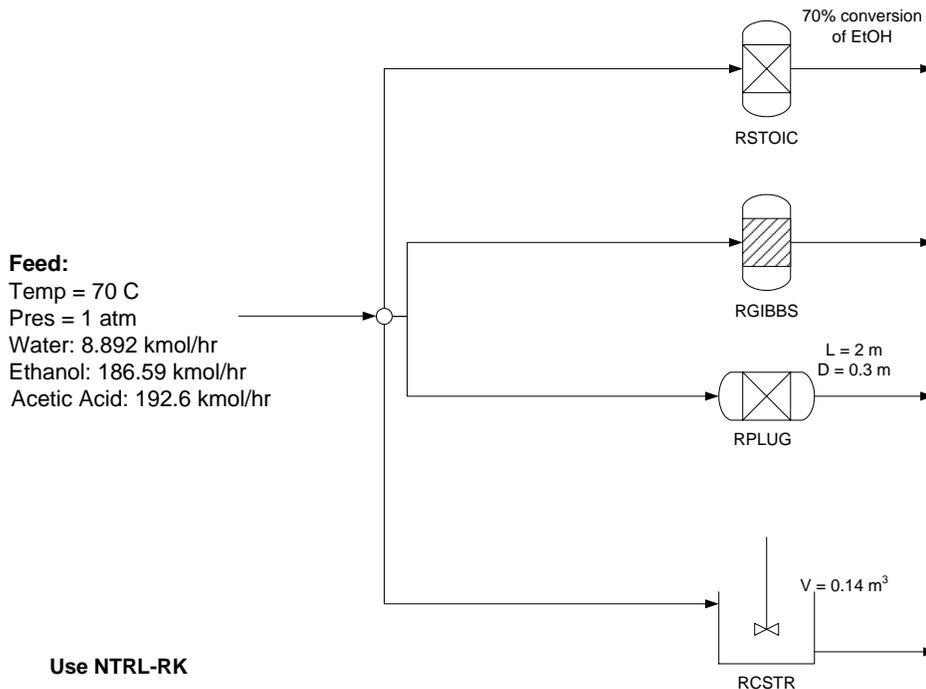
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## Exercise 2: Different Reactor Types

Using the conditions listed below and in the figure to prepare your simulation: the reactor conditions are 70 °C and 1 atm. The reaction taking place is:



Which has a first order with respect to each of the reactants in the reaction (second order overall). The reaction rate is expressed with an Arrhenius type relation:  $k = k_0 \cdot e^{-E/RT}$  with a forward Reaction pre-exp. factor of  $1.9 \times 10^8$ , and activation energy of  $5.95 \times 10^7$  J/kmol. The reverse reaction has a pre-exp. factor of  $5.0 \times 10^7$  and activation energy of  $5.95 \times 10^7$  J/kmol. The reactions occur in the liquid phase, and composition basis is Molarity. (*Hint: Check that each reactor is considering both Vapor and Liquid as Valid phases.*) Setup a simulation as shown in the flowsheet below.



### Questions:

1. What is the kmol/hr of ethyl acetate from each reactor:

RSTOIC: ..... RGIBBS: .....

RPLUG: ..... RCSTR: .....

2. Calculate the conversion of ethanol for each reactor:

RSTOIC: ..... RGIBBS: .....

RPLUG: ..... RCSTR: .....

3. Plot the composition profile for each component in the PFR reactor as a function of distance.