Reactions

Workshop

This module demonstrates the HYSYS philosophy for building reactions within a simulation. HYSYS defines reactions within the context of the Fluid Package. This is important for a number of reasons:

- By associating reactions with the fluid system rather than a specific "reactor" unit operation, the user is free to model reactions anywhere they might take place: in flash tanks, tray sections, reboilers etc., as well as in reactors. Reactions are defined and simply *attached* to the equipment piece.
- By defining the reactions up front in the fluid system, the reactions need only be defined once, rather than each time a reactor unit is built. Additionally, any changes to the basic reaction data are updated throughout the model automatically.
- By separating the reaction definitions from the unit operations or model topology, component and reaction data may be saved out as an independent file for use in another case. The user can then create a reaction library or database for future use, thereby eliminating a repetitive task, reducing engineering time and working more efficiently.

This module presents Steam-Methane Reforming.

Learning Objectives

Once you have completed this section, you will be able to:

- Define reactions in HYSYS
- Model Conversion and Equilibrium reactors in HYSYS.

Prerequisites

Before beginning this section you need to know how to:

- Create a Fluid Package
- Add streams
- Add Unit Operations

Reactions and Reactors

There are five different types of reactors that can be simulated with HYSYS. By using combinations of these five reactors, virtually any reactor can be modelled within HYSYS. The five reactor types are:
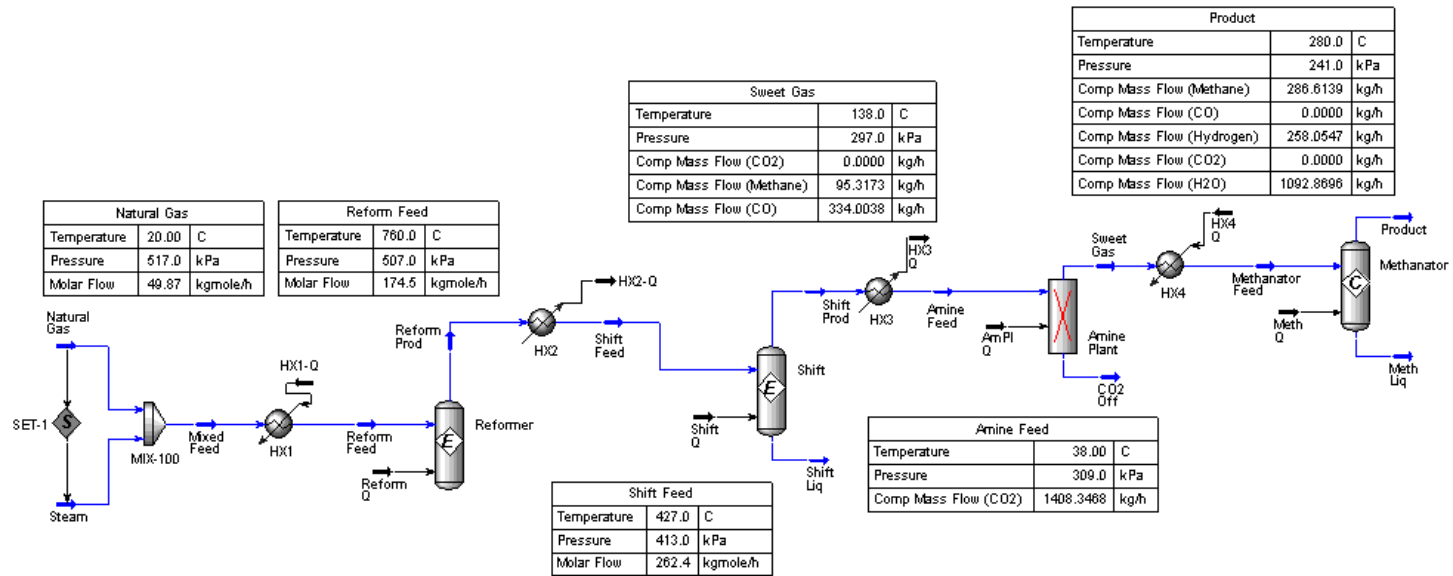
Note that Kinetic, Kinetic RevEqb, and Langmuir-Hinshelwood reactions can only be modelled in the CSTR, PFR and Separator.

- **Conversion** - given the stoichiometry of all the reactions occurring and the conversion of the base component, calculates the composition of the outlet stream.
- **Equilibrium** - determines the composition of the outlet stream given the stoichiometry of all reactions occurring and the value of equilibrium constant (or the temperature dependant parameters that govern the equilibrium constant) for each reaction.
- **Gibbs** - evaluates the equilibrium composition of the outlet stream by minimizing the total Gibbs free energy of the effluent mixture.
- **CSTR** - computes the conversion of each component entering the reactor. The conversion in the reactor depends on the rate expression of the reactions associated with the reaction type.
- **PFR** - assumes that the reaction streams pass through the reactor in plug flow in computing the outlet stream composition, given the stoichiometry of all the reactions occurring and a kinetic rate constant for each reaction.

Note: The required input is different depending on the type of reactor that is chosen. CSTR and PFR reactors must have kinetic rate constants (or the formula to determine the kinetic rate constant) as inputs, as well as the stoichiometry of the reactions. All of the reactor types, except for the Gibbs type, must have the reaction stoichiometry as inputs.

Reactions can also occur in the Tank, Separator, and Three Phase Separator Unit Operations if a reaction set is attached.

Process Overview

Natural Gas		
Temperature	20.00	C
Pressure	517.0	kPa
Molar Flow	49.87	kgmole/h

Reform Feed		
Temperature	760.0	C
Pressure	507.0	kPa
Molar Flow	174.5	kgmole/h

Sweet Gas		
Temperature	138.0	C
Pressure	297.0	kPa
Comp Mass Flow (CO2)	0.0000	kg/h
Comp Mass Flow (Methane)	95.3173	kg/h
Comp Mass Flow (CO)	334.0038	kg/h

Product		
Temperature	280.0	C
Pressure	241.0	kPa
Comp Mass Flow (Methane)	286.6139	kg/h
Comp Mass Flow (CO)	0.0000	kg/h
Comp Mass Flow (Hydrogen)	258.0547	kg/h
Comp Mass Flow (CO2)	0.0000	kg/h
Comp Mass Flow (H2O)	1092.8696	kg/h

Shift Feed		
Temperature	427.0	C
Pressure	413.0	kPa
Molar Flow	262.4	kgmole/h

Amine Feed		
Temperature	38.00	C
Pressure	309.0	kPa
Comp Mass Flow (CO2)	1408.3468	kg/h

Steam-Methane Reformer

Steam reformation of methane is often undertaken in conjunction with processes which require large amounts of hydrogen – for instance hydrotreating, ammonia production, or any process which may utilise such a synthesis gas. Successive reaction stages take advantage of thermodynamics and catalysts to enhance the production of hydrogen at the expense of the by-product gases carbon monoxide and dioxide. Finally, remaining carbon oxides are converted back into methane as completely as possible to minimise CO and CO_2 carryover into the downstream process.

In the course of this problem, we will use two of the reactor types in HYSYS to simulate the reactors in the steam reformation train: the **Conversion** and **Equilibrium** reactors.

Building the Simulation

Defining the Simulation Basis

For this simulation we will use the Peng Robinson EOS with the following components: **methane**, **carbon monoxide**, **carbon dioxide**, **hydrogen** and **water**. The Fluid Package that you defined can be renamed to Steam-C1 reformer.

Adding the Reactions

The reactions which take place in this simulation are:

Reaction Name	Reaction
Reform1	$CH_4 + H_2O \longrightarrow CO + 3H_2$
Reform2	$CO + H_2O \longrightarrow CO_2 + H_2$
Shift1	$CO + H_2O \longleftrightarrow CO_2 + H_2$
Meth1	$CO + 3H_2 \longrightarrow H_2O + CH_4$

Reactions in HYSYS are added in a manner very similar to the method used to add components to the simulation:

1.   Open the Fluid Package and select the **Rxns** tab. Press the *Simulation Basis Mgr* button to open component selection view. Here, we will select the components that we will have use in our reactions.

2. Press the *Add Comps* button, and ensure that the *FPkg Pool* radio button is selected. Press the *Add This Group of Components* button. This moves the entire component list over to the Selected Reaction Components group.
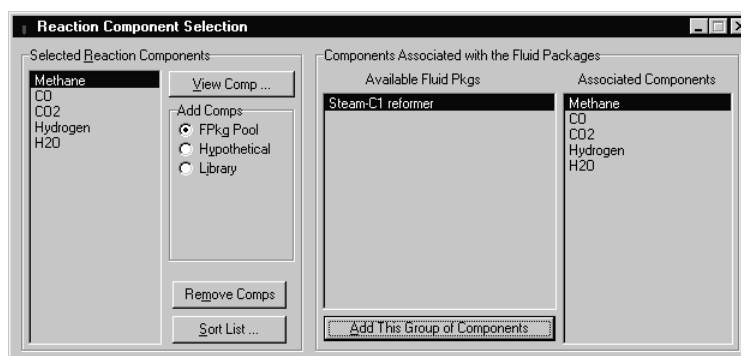
3. Return to the **Simulation Basis Manager** view and press the *Add Rxn* button. Choose **Equilibrium** as the type from the displayed list.

4. Press the *Add Reaction* button and enter the necessary information as shown:
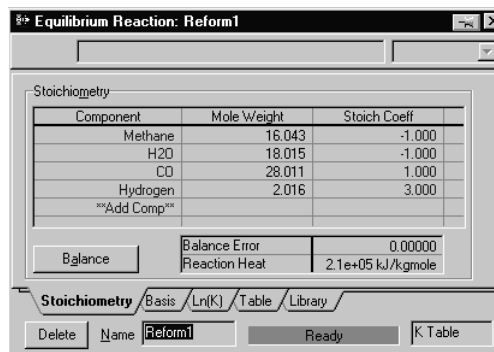
This has defined the stoichiometry of the first reaction:

$$CH_4 + H_2O ---> CO + 3H_2$$
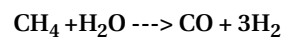
Note that reactants are defined with negative coefficients and products have positive coefficients; this is the HYSYS standard. All reactions must be defined this way.

5. Move to the **Basis** tab and click the *K vs T Table* radio button.

6.   On the **Table** tab, enter the following values:

Temperature, °C (°F)	Keq
595°C (1100°F)	0.5
650°C (1200°F)	3
705°C (1300°F)	14
760°C (1400°F)	63
815°C (1500°F)	243
870°C (1600°F)	817

7.   Add the second **Equilibrium** reaction by selecting the reaction type as **Equilibrium**.

$$CO + H_2O \text{ ---> } CO_2 + H_2$$
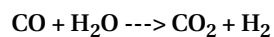
8.   For reaction 2, proceed as above and enter the following values for the **Equilibrium Constant**:

Temperature, °C (°F)	Keq
675°C (1250°F)	1.7
705°C (1300°F)	1.5
730°C (1350°F)	1.3
760°C (1400°F	1.2
790°C (1450°F)	1.1
815°C (1500°F)	1.0

The name of this reaction can be changed to **Reform 2**.

In the absence of a catalyst and at **430** °**C** (**800°F**), the rate of reaction number 1 in the Shift Reactor is negligible, and reaction number 2 becomes the only reaction.

HYSYS contains a library of some of the most commonly encountered chemical reactions with their Equilibrium Constants. For the Shift Reactor, you will use the library values for the Equilibrium Constant.

9. Add the third **Equilibrium** reaction by selecting the reaction type as **Equilibrium**. On the **Library** tab, highlight the reaction with the form $CO + H_2O = CO_2 + H_2$. Press the *Add Library Rxn* button. This adds the reaction and all of the reaction's data to the simulation.

10. Rename the reaction **Shift1**.

11. Add a **Conversion** reaction for the reverse of reaction number 1. The reaction is:

$$CO + 3H_2 \text{ ---> } H_2O + CH_4$$
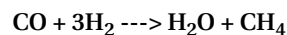
12. Move to the **Basis** tab and enter **CO** as the **Base Component** and **100** as the **% Conversion**.

13. Rename this reaction **Meth1**.

Adding the Reaction Sets

Reaction Sets may contain more than one Reaction. There is limited flexibility for the mixing of reaction types within a Reaction Set.

- *Equilibrium and Kinetic reactions can be within a single reaction set*
- *Conversion reactions cannot be in the same set as other reaction types*

Once all three reactions are entered and defined, you can create reaction sets for each type of reactor.

1. On the **Reactions** page of the Simulation Basis Manager, press the *Add Set* button. Name the first Set **Reformer Rxn Set**, and add **Reform1** and **Reform2**.

Reactions are added by highlighting the **<empty>** field in the **Active List** group, and selecting the desired reaction from the drop down list. The

view should look like this after you have finished:
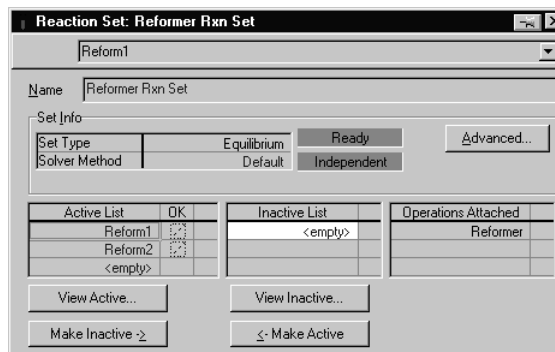
2.   Create two more reaction sets with the following information:

Name	Active List
Shift Rxn Set	Shift1
Methanator Rxn Set	Meth1

Attaching Reaction Sets to the Fluid Package

After the three reaction Sets have been created, they must be added to
the current fluid package in order for HYSYS to use them.

1.   On the **Reactions** page of the **Simulation Basis Manager** view,
highlight the **Reformer Rxn Set** and press the *Add to FP* button.
2.   Select the only available Fluid Package and press the *Add Set to
Fluid Package* button.
3.   Repeat Steps 1 and 2 to add all three reaction sets (Reformer, Shift
and Methanator).

Once all three reaction sets are added to the Fluid Package, you can
enter the Simulation Environment and begin constructing the
simulation.

Adding the Unit Operations

Add the Feed Streams

Create two new material streams with the following information:

In This Cell...	Enter...
Conditions	
Name	Natural Gas
Temperature	20°C (70°F)
Pressure	520 kPa (75 psia)
Mass flow	800 kg/h (1765 lb/hr)
Composition	
Mass Fraction CH_4	1.0

Name	Steam
Temperature	180°C (360°F)
Pressure	965 kPa (140 psia)
Composition	
Mass Fraction H_2O	1.0

Add a Mixer
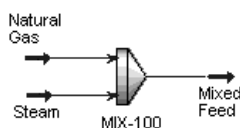
In This Cell...	Enter...
Connections	
Name	Mix-100
Inlet	Natural Gas / Steam
Outlet	Mixed Feed

On the **Parameters** page, select the *Set Outlet to Lowest Inlet* radio button.

Add a Heater

A Heater is needed to heat the feed to the reaction temperature.

Add a **Heater** with the following information:

| Pressure Drop | 10.00 | kPa |
| Product Temperature | 760.0 | C |
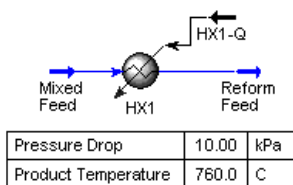
In This Cell...	Enter...
Connections	
Name	HX1
Inlet	Mixed Feed
Energy	HX1-Q
Outlet	Reform Feed
Parameters	
Delta P	10 kPa (1.5 psi)
Worksheet	
Reform Feed, Temperature	760°C (1400°F)

Add a Set Operation

A Set operation is needed to fix the steam rate relative to the methane feed rate.

Add a **Set** operation with the following information:

Natural
Gas

SET-1

Steam
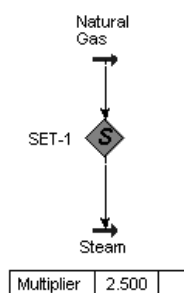
| Multiplier | 2.500 | |

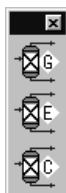| In This Cell...	Enter...
Connections	
Name	SET-1
Target Object	Steam, Molar Flow
Source	Natural Gas
Parameters	
Multiplier	2.5
Offset	0.0 kgmole/h (0.0 lbmole/hr)

The Reform Feed stream should now be completely defined.

Add the Steam Reformer

An Equilibrium Reactor will be used to simulate the Steam Reformer.

General Reactors button

From the Object Palette, click **General Reactors**. Another palette appears with three reactor types: **Gibbs**, **Equilibrium** and **Conversion**. Select the **Equilibrium Reactor**, and enter it into the PFD. Make the following connections:

General Reactors palette

In This Cell...	Enter...
Connections	
Name	Reformer
Inlet	Reform Feed
Vapour Outlet	Reform Prod
Liquid Outlet	Reform Liq
Energy	Reform Q
Parameters	
DeltaP	70 kPa (10 psi)

1. On the **Parameters** page, select the *Heating* radio button for the Duty.
2. On the **Worksheet** tab, set the temperature of **Reform Prod** to **760°C (1400°F)**.
3. On the **Reactions** tab, select the **Reformer Rxn Set** as the Reaction Set. This will automatically connect the proper reactions to this Reactor and the Reactor will solve.
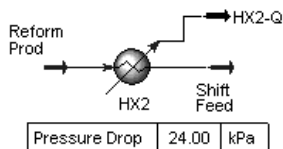
> *What is the % conversion of Methane?* _____
>
> *How much CO and H_2 were produced in the reaction; i.e. what is the molar flowrate of these two compounds in the reactor's product stream?* _____ & _____

Add a Cooler

Add a Cooler to cool the stream **Reform Prod** down to the Shift Reactor's temperature. Enter the connections with the following information:
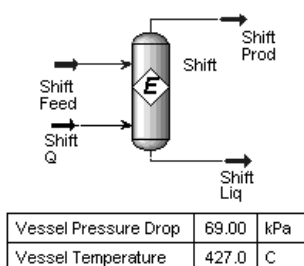

In This Cell...	Enter...
Connections	
Name	HX2
Inlet	Reform Prod
Energy	HX2-Q
Outlet	Shift Feed
Parameters	
Delta P	24 kPa (3.5 psi)
Worksheet	
Shift Feed	427°C (800°F)

Add the Shift Reactor

Another Equilibrium Reactor will be used to model the Shift Reactor.

Add an Equilibrium Reactor with the following data:

| Vessel Pressure Drop | 69.00 | kPa |
| Vessel Temperature | 427.0 | C |

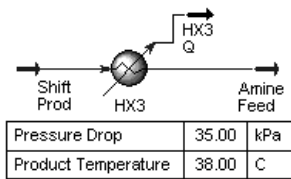| In This Cell...	Enter...
Connections	
Name	Shift
Inlet	Shift Feed
Vapour Outlet	Shift Prod
Liquid Outlet	Shift Liq
Energy	Shift Q
Parameters	
Delta P	70 kPa (10 psi)
Worksheet	
Shift Prod, Temperature	430°C (800°F)

1. On the **Parameters** page, choose the *Cooling* radio button for the Duty.
2. On the **Reactions** tab, select **Shift Rxn Set** as the Reaction Set. This will automatically connect the proper reactions to this reactor.

What is the % conversion of CO in this reactor? _____

Add a Cooler

Add a **Cooler** to cool the stream Shift Prod down to the Amine Plant's temperature (the Amine Plant will be added next). Make the connections as follows:

In This Cell...	Enter...
Connections	
Name	HX3
Inlet	Shift Prod
Energy	HX3-Q
Outlet	Amine Feed
Parameters	
Delta P	35 kPa (5 psi)
Worksheet	
Amine Feed, Temperature	38°C (100°F)

Add the Amine Plant

Add a **Component Splitter** to model the Amine Plant. The purpose of this Splitter is only to remove the CO_2 present in the flow. The connections are shown below:
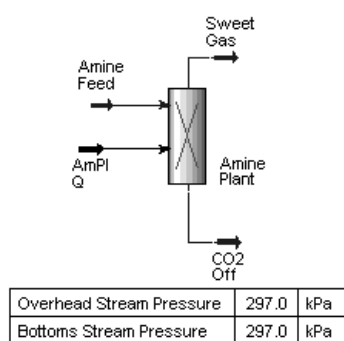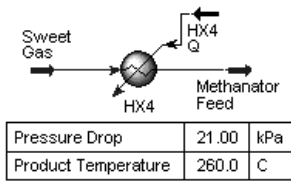
In This Cell...	Enter...
Connections	
Name	Amine Plant
Inlet	Amine Feed
Overhead Outlet	Sweet Gas
Energy Stream	AmPl Q
Bottoms Outlet	CO2 Off
Parameters	
Overhead Pressure	297 kPa (43 psia)
Bottoms Pressure	297 kPa (43 psia)
Worksheet	
Sweet Gas, Temperature	138°C (280°F)

Overhead Stream Pressure	297.0	kPa
Bottoms Stream Pressure	297.0	kPa

On the **Splits** page, specify the **Fraction to Overhead** as **1.0** for **Methane**, **CO**, **Hydrogen** and **H₂O**. The "Fraction to Overhead" for the CO_2 must be **0**; this will force all CO_2 to the bottom and all other components to the top.

Add a Heater

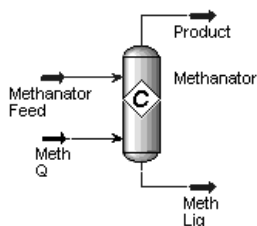A Heater is needed to heat the feed to the Methanator Reactor
temperature.

Add a **Heater** with the following information:

In This Cell...	Enter...
Connections	
Name	HX4
Inlet	Sweet Gas
Energy	HX4-Q
Outlet	Methanator Feed
Parameters	
Delta P	21 kPa (3 psi)
Worksheet	
Methanator Feed, Temperature	260°C (500°F)

Pressure Drop	21.00	kPa
Product Temperature	260.0	C

Add the Methanator Reactor

Add a **Conversion** Reactor with the following connections:

In This Cell...	Enter...
Connections	
Name	Methanator
Inlet	Methanator Feed
Vapour Outlet	Product
Liquid Outlet	Meth Liq
Energy	Meth Q
Parameters	
Delta P	35 kPa (5 psi)
Worksheet	
Product, Temperature	280°C (536°F)

Vessel Pressure Drop	35.00	kPa
Product Temperature	280.0	C

On the **Reactions** tab, choose the **Methanator Rxn Set** from the **Reaction Set** drop down menu.

What is the % conversion of CO? _____

How much Methane was produced in this reactor? _____

Save your case!

# Analysing the Results

Using the Case Study

The Case Study tool allows you to monitor the steady state response of key process variables to changes in your process. You select independent variables to change and dependent variables to monitor. HYSYS varies the independent variables one at a time, and with each change, the dependent variables are calculated.

To illustrate the Case Study tool's capabilities, imagine the following scenario: your boss approaches you one day and asks you to comment on the affects of varying the amount of Steam to the process on the flow of CO2 entering the Amine Plant and the flow of methane leaving the Methanator Reaction. He or she wants to compare steam flow rates of 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 times that of the natural gas. The bad news is he or she wants the information first thing tomorrow morning (and you have a tee time in one hour). The good news is, you can use the Case Study tool in HYSYS to generate these numbers and still make your tee time!
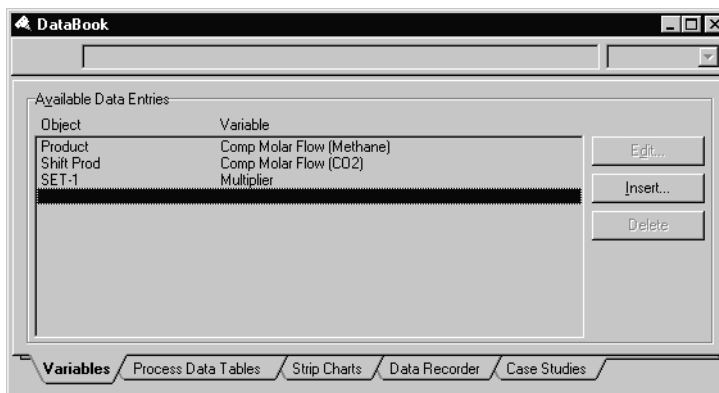
1.   From the **Tools** menu select **Databook**, or use the **<Ctrl><D>** Hot Key, to open the **Databook**.
2.   On the **Variables** tab, press the *Insert* button to open the **Variable Navigator**.
3.   Select **Shift Prod** as the object, **Comp Molar Flow** as the variable, and **CO2** as the variable's specific.

*Both the independent and the dependent variables are added to the Databook from the **Variables** tab.*
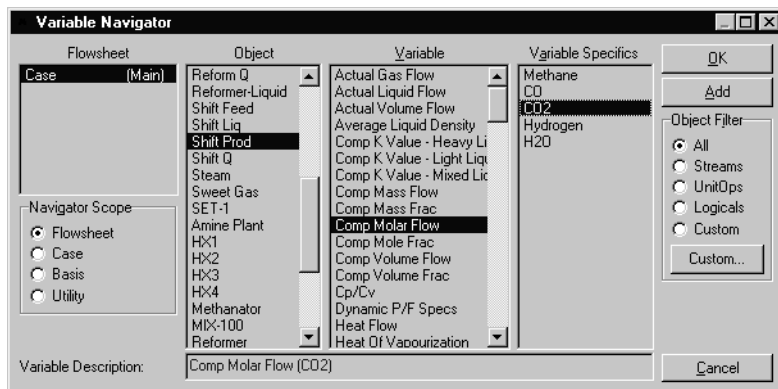
4. Add the two remaining variables as shown below: **Product** and **SET-1**.

5. Switch to the **Case Studies** tab.

6. Press the *Add* button to add a new Case Study.

7. Select the **Multiplier** of **SET-1** as the **Independent Variable**, and select the remaining two variables as the **Dependant Variables**.

Only user supplied variables can be selected as Independent Variables
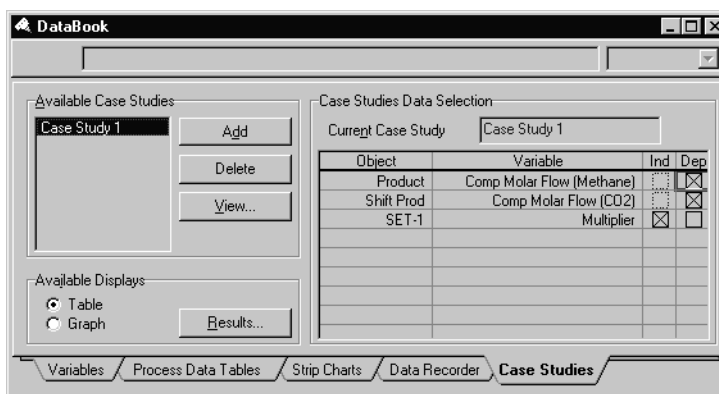
8.   Press the *View* button to setup the Case Study.
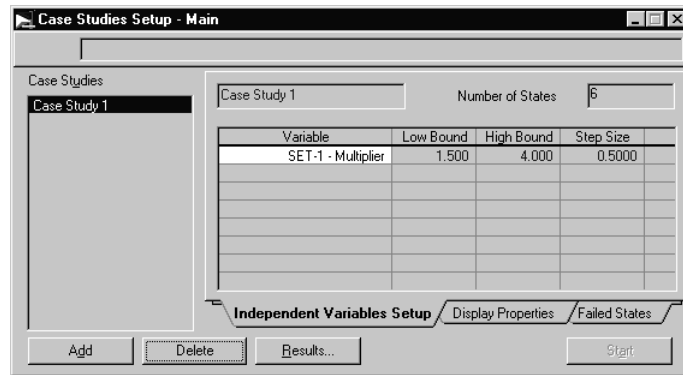
9.   Enter values for **Low Bound, High Bound,** and **Step Size** of **1.5, 4.0** and **0.5** respectively.

10.   Press the *Results* button to view the calculations.
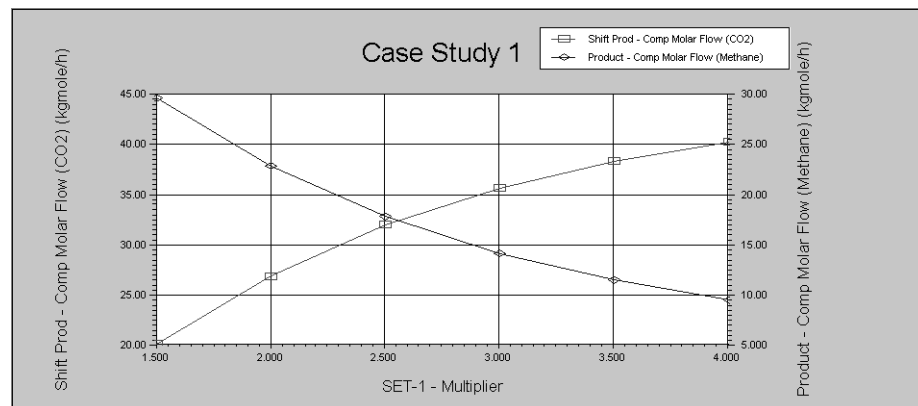
Exercise

Using the Adjust Operation

In this exercise, we will use the Adjust operation in HYSYS to determine what temperature in the **Shift 1** reactor will produce a molar ratio of hydrogen to methane of 10:1 in the final product.

The **Adjust** operation in HYSYS is similar to a "steady state controller." It will manipulate one process variable (this variable must be specifiable) until another variable is equal to a set target value. In this case, we will manipulate the temperature of the outlet stream from the Shift 1 reactor until the desired molar ratio is achieved in the final product.

Normally, the target variable can be selected using the variable navigator; however, this is not the case here. The molar ratio of methane to hydrogen is not a normal process variable; therefore, we must use the Spreadsheet operation to calculate this value and transfer its value to another location that can be selected using the variable navigator.

The process for doing this will be given here:

1.   Create a new stream and name it: **Dummy Stream.** We do not need to enter any data for this stream; its sole purpose will be to hold a value from the spreadsheet and make it available to the Adjust operation.
2.   Add a **Spreadsheet** operation to the flowsheet. We need to import two variable into this spreadsheet. There are several ways to do this; for this exercise, only one method will be illustrated, but keep in mind that this is only one possibility.
3.   Right click on any spreadsheet cell (an example would be B1). From the menu that appears, select **Import Variable**, and use the variable navigator to choose the Mole Fraction of **Hydrogen** in the **Product** stream.
4.   In another spreadsheet cell (say B2) import the Mole Fraction of **Methane** of the same stream.
5.   In a third spreadsheet cell, enter the ratio formula. If you used cells B1 and B2 in the two steps above, the ratio formula will look like this: **+B1/B2**. The current value of this ratio should be around 7.

6.   Now, we can export this value as any variable owned by the **Dummy Stream**. Right click on cell that contains the ratio formula, and select **Export Formula Result** from the menu. Use the variable navigator to choose a suitable location for the molar ratio. For this example, we can use **Temperature**.

Notice that the type of variable is not important when exporting to the dummy stream. You should be aware that there could be problems if you tried to exceed the natural limits of the variable type. For example, do not try to export a value greater than 1 or less than 0 into the vapour fraction.

7.   Add the **Adjust** operation to the flowsheet. Make the following connections:

In This Cell...	Enter...
Adjust Variable	Shift Prod - Temperature
Target Variable	Dummy Stream - Temperature
Specified Target Value	10

8.   On the **Parameters** tab, enter the following information:

In This Cell...	Enter...
Method	Secant (default)
Tolerance	0.01
Step Size	25
Maximum Iterations	30

9.   Press the *Start* button to begin the calculations. The progress of the calculations can be seen on the **Monitor** tab.

> *What is the reactor temperature that produces the desired molar ratio? _____*

Save your case!

Challenge

A new application of the **Product** stream has been found. However, it requires that the amount of methane in the stream be less than 1% of the amount of hydrogen. In other words, the molar ratio must be increased to 100.

What happens when the Specified Target Value is changed to 100? _____

What else can be changed to improve the composition of the Product stream? Hint: look at the beginning of this process; remember that the products of a process are influenced by the inputs. _____

Change the multiplier of the Set-100 operation to 5. Is the Adjust operation now able to converge with a target value of 100? _____