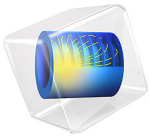


Hydrodealkylation in a Membrane Reactor

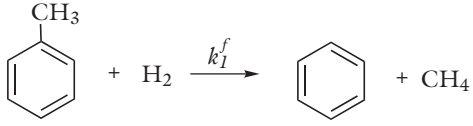
Introduction

At high temperatures and pressures, and in the presence of hydrogen, toluene can be demethylated to produce benzene. Furthermore, benzene can react reversibly to produce biphenyl. The following example illustrates the simulation of the hydrodealkylation process, carried out in a membrane reactor. This reactor arrangement allows for continuous addition of hydrogen to the process, increasing the selectivity for the desired benzene product.

The example shows how you can easily modify the predefined Plug Flow reactor type in the Reaction Engineering interface to set up a membrane reactor model. We will also learn how to create a Thermodynamic System from Thermodynamics to get different thermodynamic and physical property functions for each compound and their mixture. After all species in Reaction Engineering have been coupled to a corresponding species in the Thermodynamic system, the required species and mixture properties will automatically be created and added to the package.

Model Definition

Two important reactions occur in the thermal hydrodealkylation (HDA) of toluene. The main reaction involves toluene reacting with hydrogen to produce benzene and methane:

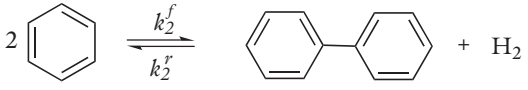


(1)

The dealkylation reaction rate is first order in the toluene concentration and half order in the hydrogen concentration:

$$r_1 = k_1 c_{C_7H_8} \sqrt{c_{H_2}}$$

At the same time, biphenyl is reversibly formed from benzene:



(2)

The rate of the coupling reaction follows the mass action law:

$$r_2 = k_2^f c_{C_6H_6}^2 - k_2^r c_{H_2} c_{C_{12}H_{10}}$$

In the above rate expressions, the rate constants follow Arrhenius type behavior:

$$k = Ae^{-\frac{E}{R_g T}}$$

The values of the frequency factors and activation energies (J/mol) are taken from the literature (Ref. 1 and Ref. 2) and are presented in Table 1.

TABLE 1: ARRHENIUS PARAMETERS.

	FREQUENCY FACTOR	ACTIVATION ENERGY
Forward reaction 1	5.67e9	228.2e3
Forward reaction 2	1e8	167.5e3
Reverse reaction 2	1e8	149.8e3

The chemical reactions given in Equation 1 and Equation 2 suggest that maintaining high concentrations of hydrogen would be beneficial to ensure a high benzene yield. Such process conditions can be achieved by using a membrane reactor. As illustrated schematically in Figure 1, hydrogen can be supplied continuously across the porous membrane.

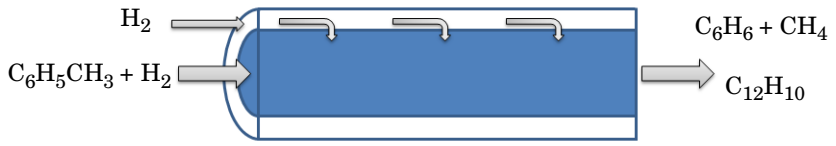


Figure 1: Hydrogen is continuously supplied to the reactor through a porous membrane.

The species mass balance for hydrogen in the membrane reactor is given by:

$$\frac{\mathrm{d}F_{\mathrm{H_2}}}{\mathrm{d}V} = R_{\mathrm{H_2}} + f_{\mathrm{H_2}}$$

where F is the molar flow rate (SI unit: mol/s) in the reactor, V is the reactor volume (SI unit: m^3), R is the species rate expression (SI unit: $\mathrm{mol/(m^3 \cdot s)}$), and f is the molar flow rate per unit volume (SI unit: $\mathrm{mol/(m^3 \cdot s)}$) across the membrane. The velocity of the hydrogen gas across the porous membrane can be described by Darcy's law:

$$u = K(p_{\mathrm{shell}} - p_{\mathrm{reactor}})$$

where K (SI unit: $\mathrm{m^3/(N \cdot s)}$) is a proportionality constant, p_{shell} (SI unit: Pa) is the gas pressure on the shell side of the membrane, and p_{reactor} (SI unit: Pa) the pressure on the reactor side. The molar flow rate per unit volume across the membrane then becomes:

$$f_{H_2} = uac_{shell}$$

Above, a is the membrane surface area per unit volume (SI unit: m^2/m^3), and c_{shell} is the concentration of hydrogen (SI unit: mol/m^3) on the shell side.

Except for hydrogen, the other chemical species in the reactor do not pass through the membrane and their material balances thus follow the standard plug flow equations:

$$\frac{dF_i}{dV} = R_i \tag{3}$$

The adiabatic energy balance for the reactor is given by:

$$\sum_i F_i C_{mix} \frac{dT}{dV} = Q + Q_{mem} \tag{4}$$

In Equation 4, C_{mix} represents the mixture (reacting system) molar heat capacity (SI unit: J/(mol·K)), and Q denotes the heat due to chemical reaction (SI unit: $J/(m^3 \cdot s)$):

$$Q = -\sum_j H_j r_j$$

where H_j is the heat produced by reaction j, calculated from:

$$H_j = \sum_i \nu_{ij} h_j \tag{5}$$

In Equation 5 h_i represents the species partial molar enthalpy (SI unit: J/mol) and ν_{ij} the stoichiometric coefficients.

The last term in the energy balance accounts for the energy transfer associated with the flow of hydrogen across the membrane:

$$Q_{mem} = f_{H_2} h_{H_2}$$

The Reaction Engineering interface automatically sets up and solves Equation 3 and Equation 4 when you select the predefined Plug-flow reactor type. To adjust the default model to account for hydrogen entering the reactor through the membrane, the flow term f_H has to be specified and included into the hydrogen material balance.

Solving the energy balance, Equation 4, requires the input of mixture molar heat capacities C_{mix} (SI unit: J/(mol·K)), and the partial molar enthalpies, h_i (SI unit: J/mol), of the

reacting species. In this example, these thermodynamic properties are calculated from the thermodynamic system.

Results and Discussion

In a first simulation, the reactor is assumed to be a standard tubular reactor, that is, without hydrogen entering through the reactor circumference. The reactor is fed with equal molar flows (10 mol/s) of hydrogen and toluene. At the inlet the reactant gas is held at 1200 K and 2 atmospheres. The result is shown in Figure 2.

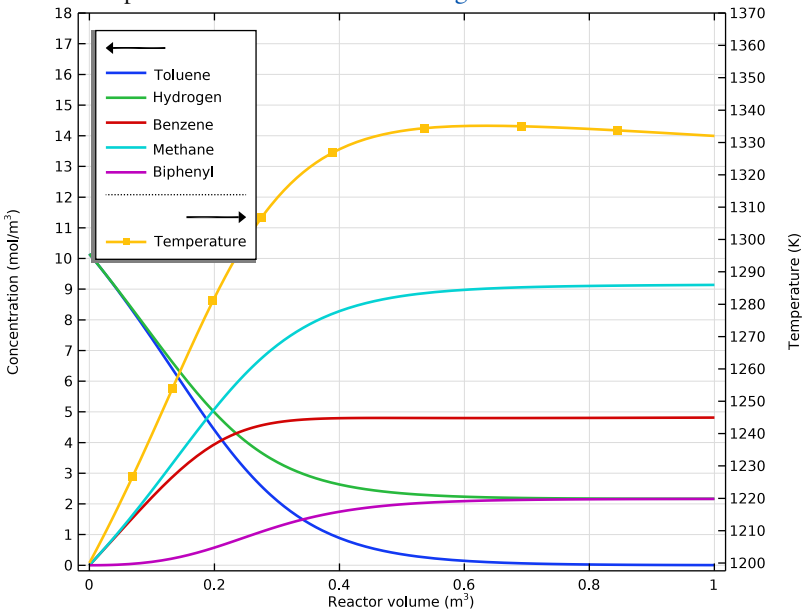


Figure 2: Concentration (mol/m^3) and temperature (K) as function of reactor volume (m^3) for a tubular reactor design.

A second model simulates the membrane reactor, with a continuous supply of hydrogen through the membrane. Figure 3 shows the corresponding concentration distributions.

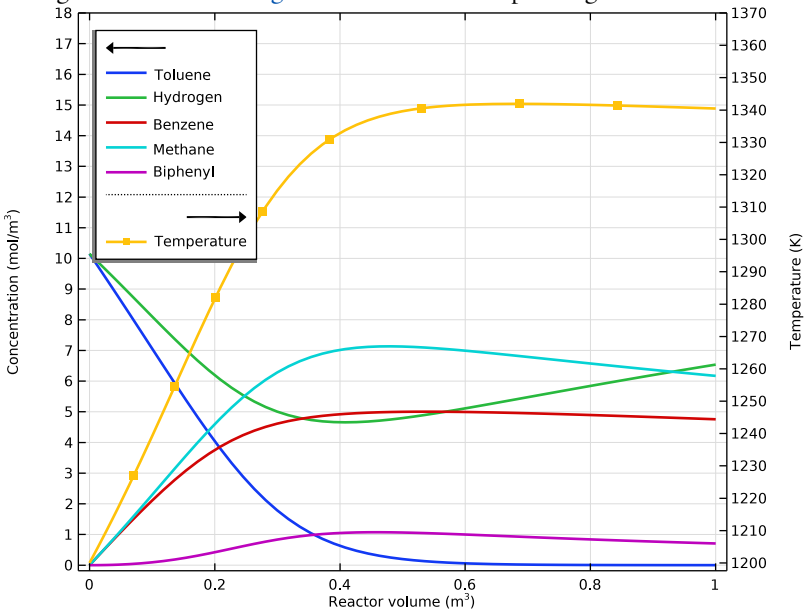


Figure 3: Concentration (mol/m^3) and temperature (K) as function of reactor volume (m^3) for a membrane reactor design with a continuous supply of hydrogen.

The biphenyl concentration is reduced versus that obtained from the first model. Clearly, the membrane reactor produces benzene with greater selectivity. However, note that this comparison is somewhat lacking in this particular model, the total amount of added hydrogen differs due to the flow across the membrane being an additional source. A more elaborate model, with irreversible reactions leading to unwanted byproducts, would however exhibit differences even after compensating for different amounts of hydrogen.

References

1. K.C. Hou and H.B. Palmer, "The Kinetics of Thermal Decomposition of Benzene in a Flow System," *J. Phys. Chem.*, vol. 69, no. 3, pp. 863–868, 1965.

2. S.E. Shull and A.N. Hixson, *I&EC Process Design and Development*, vol. 5, p. 147, 1966.

Application Library path: `Chemical_Reaction_Engineering_Module/Thermodynamics/membrane_hda`

Note: This model is included in the booklet *Introduction to Thermodynamic Properties*.

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport>Reaction Engineering (re)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Stationary Plug Flow**.

6 Click **Done**.

REACTION ENGINEERING (RE)

In this model, a **Thermodynamic System** will be created from **Thermodynamics**. The **Thermodynamic System** includes all thermodynamic properties (such as enthalpy, entropy, etc) which are needed in the simulation of reacting system. The properties from **Thermodynamics** are coupled to **Reaction Engineering** automatically.

1 In the **Reaction Engineering** toolbar, click **Thermodynamics** and choose **Thermodynamic System**.

First, select a phase state for the Thermodynamic System.

SELECT SYSTEM

1 Go to the **Select System** window.

Select phases **Vapor-liquid**.

2 From the **Phase** list, choose **Vapor-liquid**.

3 Click **Next** in the window toolbar.

Select species hydrogen, methane, benzene, toluene and biphenyl.

SELECT SPECIES

1 Go to the **Select Species** window.

2 In the **Species** list, select **hydrogen (1333-74-0, H2)**.

3 Click + **Add Selected**.

4 In the **Species** list, select **methane (74-82-8, CH4)**.

5 Click + **Add Selected**.

6 In the **Species** list, select **benzene (71-43-2, C6H6)**.

7 Click + **Add Selected**.

8 In the **Species** list, select **toluene (108-88-3, C7H8)**.

9 Click + **Add Selected**.

10 In the **Species** list, select **biphenyl (92-52-4, C12H10)**.

11 Click + **Add Selected**.

12 Click **Next** in the window toolbar.

SELECT THERMODYNAMIC MODEL

1 Go to the **Select Thermodynamic Model** window.

2 Click **Finish** in the window toolbar.

GLOBAL DEFINITIONS

Vapor-Liquid System 1 (pp1)

Create a mixture function for enthalpy of formation to introduce a heat source used later in **Reaction Engineering**.

1 In the **Model Builder** window, under **Global Definitions>Thermodynamics** right-click **Vapor-Liquid System 1 (pp1)** and choose **Mixture Property**.

SELECT PROPERTIES

1 Go to the **Select Properties** window.

2 In the list, select **Enthalpy of formation (J/mol)**.

3 Click **Add Selected**.

4 Click **Next** in the window toolbar.

SELECT PHASE

1 Go to the **Select Phase** window.

2 Click **Next** in the window toolbar.

SELECT SPECIES

1 Go to the **Select Species** window.

2 Click **Add All**.

3 Click **Next** in the window toolbar.

MIXTURE PROPERTY OVERVIEW

1 Go to the **Mixture Property Overview** window.

2 Click **Finish** in the window toolbar.

GLOBAL DEFINITIONS

Enthalpy of formation 1 (EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor1 1, EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor1 1_Dtemperature, EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor1 1_Dpressure)
Change the function name to `hF_mixture`.

1 In the **Model Builder** window, under **Global Definitions>Thermodynamics>Vapor-Liquid System 1 (pp1)>Mixture>Vapor** click **Enthalpy of formation 1 (EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor 1 1, EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor1 1_Dtemperature, EnthalpyF_benzene_biphenyl_hydrogen_methane_toluene_Vapor1 1_Dpressure)**.

2 In the **Settings** window for **Mixture Property**, type `hF_mixture` in the **Function name** text field.

Load model parameters by importing their definitions from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `membrane_hda_parameters.txt`.

DEFINITIONS

Add variable definitions from a text file.

Variables 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `membrane_hda_variables.txt`.

Note that some expressions use functions in **Thermodynamics** and variables defined in the **Reaction Engineering** interface. These variables need to be specified with the scope of the **Reaction Engineering** node. For example, `re.T` specifies the temperature variable defined by the **Reaction Engineering** node with the identifier `re`.

REACTION ENGINEERING (RE)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Reaction Engineering (re)**.

2 In the **Settings** window for **Reaction Engineering**, locate the **Reactor** section.

3 From the **Reactor type** list, choose **Plug flow**.

4 Locate the **Energy Balance** section. From the list, choose **Include**.

5 In the Q text field, type `Q_mem`.

This accounts for the heat transferred into the reactor due to the flow across the membrane.

6 Click to expand the **Mixture Properties** section. In the p text field, type `p_reactor`.

Reaction 1

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `C6H5CH3+H2=>C6H6+CH4`.

4 Locate the **Rate Constants** section. Select the **Use Arrhenius expressions** check box.

5 In the A^{f} text field, type `5.67e9[1/s]`.

6 In the E^{f} text field, type `228.2e3`.

7 Locate the **Reaction Rate** section. From the list, choose **User defined**.

8 Find the **Volumetric overall reaction order** subsection. In the **Forward** text field, type `1`.

9 In the r_j text field, type `re.kf_1*re.c_C6H5CH3*(re.c_H2/1[mol/m^3])^0.5`.

Change the default kinetic expression by modifying the reaction order for hydrogen.

Reaction 2

1 In the **Reaction Engineering** toolbar, click  **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `2C6H6<=>C12H10+H2`.

4 Locate the **Rate Constants** section. Select the **Use Arrhenius expressions** check box.

5 In the A^{f} text field, type `1e8`.

6 In the E^{f} text field, type `167.5e3`.

7 In the A^{r} text field, type `1e8`.

8 In the E^{r} text field, type `149.8e3`.

Additional Source 1

You will now add an **Additional Source** feature to **Reaction Engineering** to the membrane reactor model.

1 In the **Reaction Engineering** toolbar, click  **Additional Source**.

2 In the **Settings** window for **Additional Source**, locate the **Additional Rate Expression** section.

3 In the **Volumetric species** table, enter the following settings:

Species	Additional rate expression (mol/(m^3*s))
H2	`f_H2`

The `f_H2` term corresponds to the flow of hydrogen across the membrane.

Initial Values 1

The plug flow reactor requires you to input the inlet molar flow.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **General Parameters** section.

3 In the $T_{0,\mathrm{in}}$ text field, type `T_inlet`.

4 Locate the **Volumetric Species Initial Values** section. In the table, enter the following settings:

Species	Molar flow rate (mol/s)
C6H5CH3	10
H2	10

Couple all species in **Reaction Engineering** to corresponding species in the created **Thermodynamic System**. For a coupled species, its thermodynamic properties will be set automatically to the coupled Thermodynamic System. When all species in **Reaction Engineering** are coupled (fully coupled), the properties of the reacting system (heat capacity, molar volume, etc) will be calculated from the Thermodynamic System.

5 In the **Model Builder** window, click **Reaction Engineering (re)**.

6 In the **Settings** window for **Reaction Engineering**, locate the **Mixture Properties** section.

7 Select the **Thermodynamics** check box.

8 Locate the **Species Matching** section. In the table, enter the following settings:

Species	From Thermodynamics
C12H10	C12H10
C6H5CH3	C7H8
C6H6	C6H6
CH4	CH4
H2	H2

In the present example the total reactor volume is 1 m^3, so default solver settings can be used.

TUBULAR REACTOR

You have now set up a model for a nonisothermal tubular reactor. For the tubular reactor, the **Additional Source** feature is disabled. First solve this model and review the results, then move on to study the related membrane reactor model with the **Additional Source** feature.

1 In the **Model Builder** window, right-click **Study 1** and choose **Rename**.

2 In the **Rename Study** dialog box, type `Tubular reactor` in the **New label** text field.

3 Click **OK**.

Step 1: Stationary Plug Flow

1 In the **Model Builder** window, under **Tubular reactor** click **Step 1: Stationary Plug Flow**.

2 In the **Settings** window for **Stationary Plug Flow**, locate the **Physics and Variables Selection** section.

3 Select the **Modify model configuration for study step** check box.

4 In the tree, select **Component 1 (comp1)>Reaction Engineering (re)>Additional Source 1**.

5 Right-click and choose **Disable**.

6 In the **Model Builder** window, click **Tubular reactor**.

7 In the **Settings** window for **Study**, locate the **Study Settings** section.

8 Clear the **Generate default plots** check box.

9 In the **Home** toolbar, click **Compute**.

RESULTS

1D Plot Group 1

In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

Global 1

Right-click **1D Plot Group 1** and choose **Global**.

Global 2

In the **Model Builder** window, right-click **1D Plot Group 1** and choose **Global**.

Concentration and Temperature profile, tubular reactor

1 In the **Settings** window for **1D Plot Group**, type `Concentration and Temperature profile, tubular reactor` in the **Label** text field.

2 Locate the **Plot Settings** section.

3 Select the **x-axis label** check box. In the associated text field, type `Reactor volume (m<sup>3</sup>)`.

4 Select the **y-axis label** check box. In the associated text field, type `Concentration (mol/m<sup>3</sup>)`.

5 Select the **Two y-axes** check box.

6 In the table, select the **Plot on secondary y-axis** check box for **Global 2**.

7 Select the **Secondary y-axis label** check box. In the associated text field, type `Temperature (K)`.

Concentration

1 In the **Model Builder** window, under **Results>Concentration and Temperature profile, tubular reactor** click **Global 1**.

2 In the **Settings** window for **Global**, type `Concentration` in the **Label** text field.

3 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
re.c_C6H5CH3	mol/m^3	Concentration
re.c_H2	mol/m^3	Concentration
re.c_C6H6	mol/m^3	Concentration
re.c_CH4	mol/m^3	Concentration
re.c_C12H10	mol/m^3	Concentration

4 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.

5 In the table, enter the following settings:

Legends
Toluene
Hydrogen
Benzene
Methane
Biphenyl

6 Click to expand the **Coloring and Style** section. From the **Width** list, choose **2**.

Temperature

1 In the **Model Builder** window, under **Results>Concentration and Temperature profile, tubular reactor** click **Global 2**.

2 In the **Settings** window for **Global**, type `Temperature` in the **Label** text field.

3 Locate the **y-Axis Data** section. Click **Clear Table**.

4 In the table, enter the following settings:

Expression	Unit	Description
re.T	K	Temperature

5 Locate the **Coloring and Style** section. From the **Width** list, choose **2**.

6 Find the **Line markers** subsection. From the **Marker** list, choose **Point**.

7 From the **Positioning** list, choose **Interpolated**.

8 In the **Concentration and Temperature profile, tubular reactor** toolbar, click **Plot**.

9 Click **Plot**.

10 Locate the **Legends** section. From the **Legends** list, choose **Manual**.

11 In the table, enter the following settings:

Legends
Temperature

Concentration and Temperature profile, tubular reactor

1 In the **Model Builder** window, click **Concentration and Temperature profile, tubular reactor**.

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **None**.

4 Locate the **Axis** section. Select the **Manual axis limits** check box.

5 In the **y maximum** text field, type `18`.

6 In the **Secondary y maximum** text field, type `1370`.

7 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

8 In the **Concentration and Temperature profile, tubular reactor** toolbar, click **Plot**.

ADD STUDY

1 In the **Home** toolbar, click **Add Study** to open the **Add Study** window.

2 Go to the **Add Study** window.

3 Find the **Studies** subsection. In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces>Stationary Plug Flow**.

4 Click **Add Study** in the window toolbar.

5 In the **Home** toolbar, click **Add Study** to close the **Add Study** window.

MEMBRANE REACTOR

1 In the **Model Builder** window, click **Study 2**.

2 In the **Settings** window for **Study**, type `Membrane reactor` in the **Label** text field.

Note: the **Additional Source** feature is included in membrane reactor model.

3 Locate the **Study Settings** section. Clear the **Generate default plots** check box.

4 In the **Home** toolbar, click **Compute**.

RESULTS

Concentration and Temperature profile, membrane reactor

1 In the **Model Builder** window, right-click **Concentration and Temperature profile, tubular reactor** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Concentration and Temperature profile, membrane reactor` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Membrane reactor/ Solution 2 (sol2)**.

4 In the **Concentration and Temperature profile, membrane reactor** toolbar, click **Plot**.