A COMSOL Interface to Cape-Open Compliant Physical and Thermodynamic Property Packages

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Abstract

COMSOL version 3.5 [Ref. 1] features a CAPE-OPEN thermodynamic and physical properties interface, enabling COMSOL products to access property calculations from CAPE-OPEN compliant physical property packages. The interface supports both CAPE-OPEN Thermo 1.1 and CAPE-OPEN Thermo 1.0 standards. External property packages are accessed through COMSOL Script®, allowing for compound constant import, single-phase, two-phase, pressure-dependent, and temperature-dependent property calculations, as well as for equilibrium computations. Such external calculations can subsequently be directly imported to the graphical user interfaces of COMSOL Multiphysics® and COMSOL Reaction Engineering Lab®.

In this paper, two reactor models are presented to exemplify the use of the new interface. The first model treats a steady-state membrane reactor simulated under plug-flow conditions. The second model deals with a three-dimensional reactor where fluid flow, temperature, and composition are simulated for time and space dependency.

Introduction

COMSOL Multiphysics is a modeling environment where you readily couple computational fluid dynamics (CFD) to heat and mass transfer, including reaction kinetics. The software sets up and solves the equations describing time- and space-dependent reacting systems in 1D, 2D, 2D-axisymmetry, and 3D, allowing for detailed and accurate simulation of chemical engineering processes.

The Reaction Engineering Lab is COMSOL's environment for chemical reaction engineering and kinetics modeling. The software sets up and solves models of ideal reactor systems, such as perfectly mixed batch and semi-batch systems, continuous stirred tank reactors (CSTRs), and plug-flow reactors. Working with chemical kinetics and reaction engineering problems is made easy as the software features automatically generated kinetics as well as the capability to validate and calibrate reaction models through parameter estimation.

When creating models for chemical engineering applications, the COMSOL software helps you set up the proper differential equations, describing flow, energy and mass transport. To complete the model set up, user input is required for a number of thermodynamic and physical properties. The quality of these inputs influences the accuracy as well as validity range of the model. This is where interfacing with CAPE-OPEN compliant thermodynamic and physical property packages becomes important.

The following sections introduce the COMSOL/CAPE-OPEN interface and illustrate how it can be used to perform detailed and accurate simulations in COMSOL Multiphysics and Reaction Engineering Lab.

The Command Line Interface

COMSOL Script is COMSOL's command line environment for script programming. It features an interface to CAPE-OPEN compliant property packages, so that external physical and thermodynamic property calculations can be used in COMSOL Multiphysics and Reaction Engineering Lab.
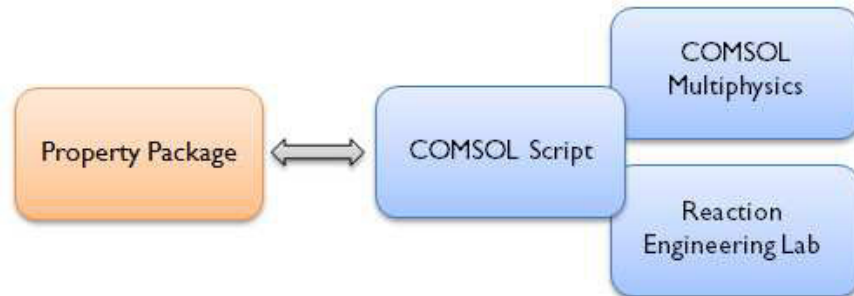

Figure 1: COMSOL Script provides the interface between COMSOL software and CAPE-OPEN compliant property packages.

The interface supports both CAPE-OPEN Thermo 1.1 and CAPE-OPEN Thermo 1.0 standards [Ref. 2]. It consists of 25 Script commands in total. The functions let you, for instance:

- Inspect and select available property packages.
- Inspect and select available property functions.
- Evaluate property functions and plot the results.

In the example below, the CAPE-OPEN interface will be used to calculate the heat capacity of air as a function of temperature.

capepackmanagers
This function lists all CAPE-OPEN package managers available on your system:

```
[managers index]=capepackmanagers

index =
'OATS (CAPE-OPEN 1.0)            (1)'
'OATS.PropertyPackageManager     (2)'
'COCO_TEA.ThermoPack             (3)'
'COCO_TEA.PropertyPackManager    (4)'
'CCOTS (CAPE-OPEN 1.0)           (5)'
'CCOTS.PropertyPackageManager    (6)'
```

Assign the desired manager to a variable:

```
myManager=managers{4}

myManager =
'COCO_TEA.PropertyPackManager'
'COCO Thermodynamics for Engineering Applications'
'COCO_TEA.PropertyPackManager'
'Property Package Manager version 1.1'
```

capepacks

The property packages supported by the selected property package manager can be found using the function 'capepacks':

```
packageNames=capepacks(myManager)

packageNames =
'C1_C2'
'C1_C2 (EOS)'
'n-depropanizer'
'alkanes'
'HDA'
'Water-nButanol-UNIQUAC'
'ethane production'
'toluene_hda'
'steam_reformer'
```

capecreatepack

This function sets up a connection to a property package, allowing you to use it from the Script prompt. Here, the property package 'steam_reformer' is chosen and assigned the name 'myPackage':

```
capecreatepack(myManager,'steam_reformer','myPackage')
```

capepackdata

Properties that can be obtained from the package are given by the function 'capepackdata'. As an example, the following lines of code list the compounds and single phase properties available:

```
[info,compounds,phases,constantProps,TdepProps,PdepProps,
singlePhaseProps,twoPhaseProps] = capepackdata('myPackage');

capecompids(compounds)
ans =
'Propane'
'Water'
'Hydrogen'
'Carbon dioxide'
'Air'

singlePhaseProps
singlePhaseProps =
```

```
'density'
'density.Dmoles'
'density.DmolFraction'
'density.Dpressure'
'density.Dtemperature'
'enthalpy'
'enthalpy.Dmoles'
'enthalpy.DmolFraction'
'enthalpy.Dpressure'
'enthalpy.Dtemperature'
'heatCapacityCp'
'heatCapacityCp.Dmoles'
'heatCapacityCp.DmolFraction'
'heatCapacityCp.Dpressure'
'heatCapacityCp.Dtemperature'
'logFugacityCoefficient'
'logFugacityCoefficient.Dmoles'
'logFugacityCoefficient.DmolFraction'
'logFugacityCoefficient.Dpressure'
'logFugacityCoefficient.Dtemperature'
'thermalConductivity'
'thermalConductivity.Dmoles'
'thermalConductivity.DmolFraction'
'thermalConductivity.Dpressure'
'thermalConductivity.Dtemperature'
'viscosity'
'viscosity.Dmoles'
'viscosity.DmolFraction'
'viscosity.Dpressure'
'viscosity.Dtemperature'
```

From the package you can access compound constants as well as set up function objects (functors) for single-phase, two-phase, pressure-dependent, and temperature-dependent property calculations, as well as for equilibrium calculations. Each type of function object is created with its own command. Here, a function object is set up for a single phase property.

capefunc1phase

The following lines create the function object 'Cp_ht' for the heat capacity of air, which is a single-phase property:

```
capefunc1phase('Cp_ht','myPackage','heatcapacitycp','vapor','air)
ans =

'Functor name: Cp_ht'
'Property package: myPackage'
'Type: Single phase property calculation'
'Compounds: Air'
'Arguments: [Temperature/[K], Pressure/[Pa]]'
'Phase: Vapor (type: Vapor)'
'Properties: heatcapacitycp/[J/(mol*K)]'
```

Above, the description of the function object lists the input and return arguments.

capeeval

Once the function object is created, it can be evaluated using the 'capeeval' command. The following lines evaluate 'Cp_ht' for a range of temperatures:

```
T=[300:50:1000];
p=1e5*ones(15,1)';
cp=capeeval('Cp_ht',T,p);
plot(T,cp)
```
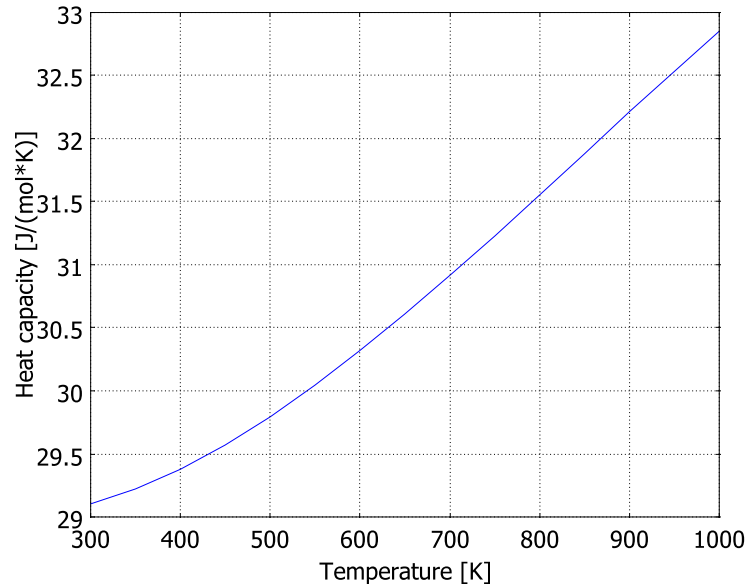

Figure2: Heat capacity of air as function of temperature.

Function objects set up in COMSOL Script can be used together with the 'capeeval' command directly in the graphical user interface of COMSOL Multiphysics as well as Reaction Engineering Lab, thus providing accurate thermodynamic and property calculations to these simulation environments. The following two examples illustrate this important aspect.

Modeling Example – Hydrodealkylation of Toluene

This modeling example illustrates the use of the CAPE-OPEN interface in a Reaction Engineering Lab simulation. The complete model documentation can be accessed through the COMSOL website [Ref. 3].

Introduction

In the thermal hydrodealkylation (HDA) of toluene, benzene is formed from toluene, and may further react to reversibly produce biphenyl.

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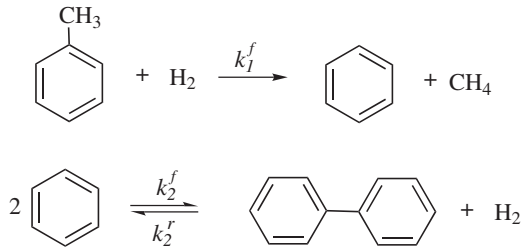
Kinetic parameters for these reactions are reported in the literature [Ref. 4, Ref. 5]. The chemical reactions formulas suggest that maintaining high concentrations of hydrogen would be beneficial to ensure a high benzene yield. Such process conditions can be achieved using a membrane reactor. As illustrated schematically in Figure 3, hydrogen can be supplied continuously across the porous membrane.
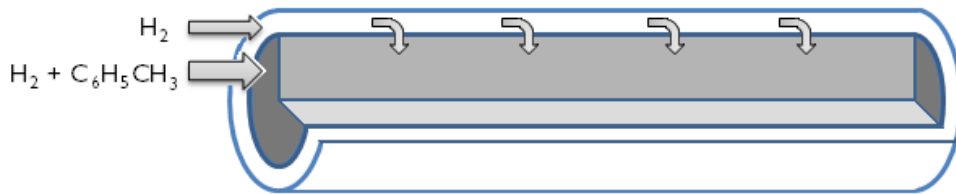

Figure 3: Hydrogen is continuously supplied to the reactor through a porous membrane.

Model Equations

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

$$\frac{dF_i}{dV} = R_i + f_i$$

where F_i is the species molar flow rate (mol/s), V is the reactor volume (m^3), R_i is the species rate expression (mol/(m^3·s)), and f_i is the molar flow rate per unit volume (mol/(m^3·s)) across the membrane, applicable to permeable species. The adiabatic energy balance for the reactor is given by:

$$\sum_i F_i Cp_i \frac{dT}{dV} = Q + Q_{mem}$$

Above, Cp_i represents the species molar heat capacity (J/(mol·K)), and Q denotes the heat due to chemical reaction (J/(m^3·s)):

$$Q = -\sum_j H_j r_j$$

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

$$H_j = \sum_i v_{ij} h_j$$

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The calculations are set up and solved using the predefined plug-flow reactor type.

Thermodynamic property calculations

Solving the energy balance requires the input of molar heat capacities, Cp_i (J/(mol·K)), and the molar enthalpies, h_i (J/mol), of the reacting species. These thermodynamic properties are calculated using the CAPE-OPEN compliant property package manager TEA [Ref. 6]. Other property packages containing the appropriate species and property functions could of course also be used.

As mentioned above, the property calculations are accessed by setting up the appropriate function object in COMSOL Script and then using these objects together with the 'capeeval' command. Figure 4 shows how the 'capeeval' function calls can be entered directly in the graphical user interface of Reaction Engineering Lab, making it straight forward to include the property calculations in the simulations. The graphics also show that dependent variables of the Reaction Engineering Lab model, here T and p_reactor, serve as inputs to the property function calls.
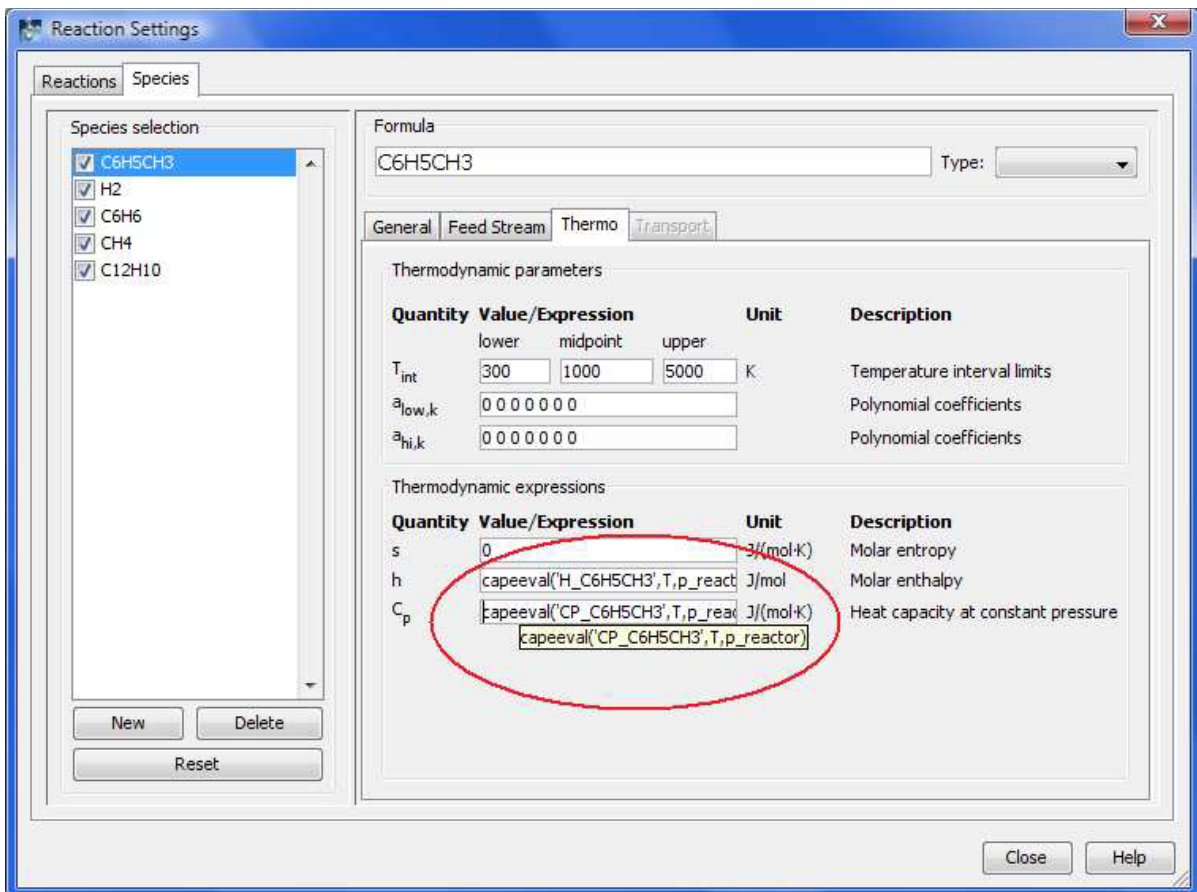

Figure 4: Capeeval function calls can be made directly from the graphical user interface. The input arguments T and p_reactor are dependent variables of the Reaction Engineering Lab model.

Results

Two simulations were performed to evaluate the difference between a standard tubular reactor design and a corresponding membrane reactor. Figure 5 shows the molar flow rates of the reacting species as a function of the reactor volume. Clearly, the membrane reactor produces benzene with greater selectivity.
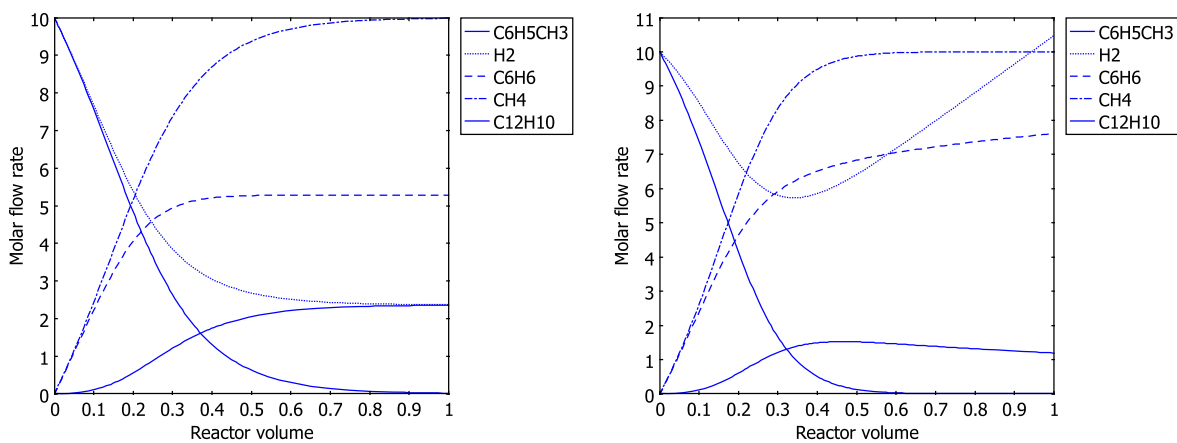

Figure 5: Molar flow rates (mol/s) as function of reactor volume (m^3) for a tubular reactor (left) and a membrane reactor (right). The membrane reactor produces more of the desired benzene product.

Modeling Example – Steam Reformer

The following modeling example illustrates the use of the CAPE-OPEN interface in a COMSOL Multiphysics simulation. The complete model documentation can be accessed through the COMSOL website [Ref. 3].

Introduction

Figure 6 shows a steam reforming unit that supplies hydrogen to a fuel cell stack. The reformation chemistry occurs in the porous catalytic bed. Energy supplied by heating tubes drives the endothermal reaction system. The reactor is enclosed in an insulating jacket.
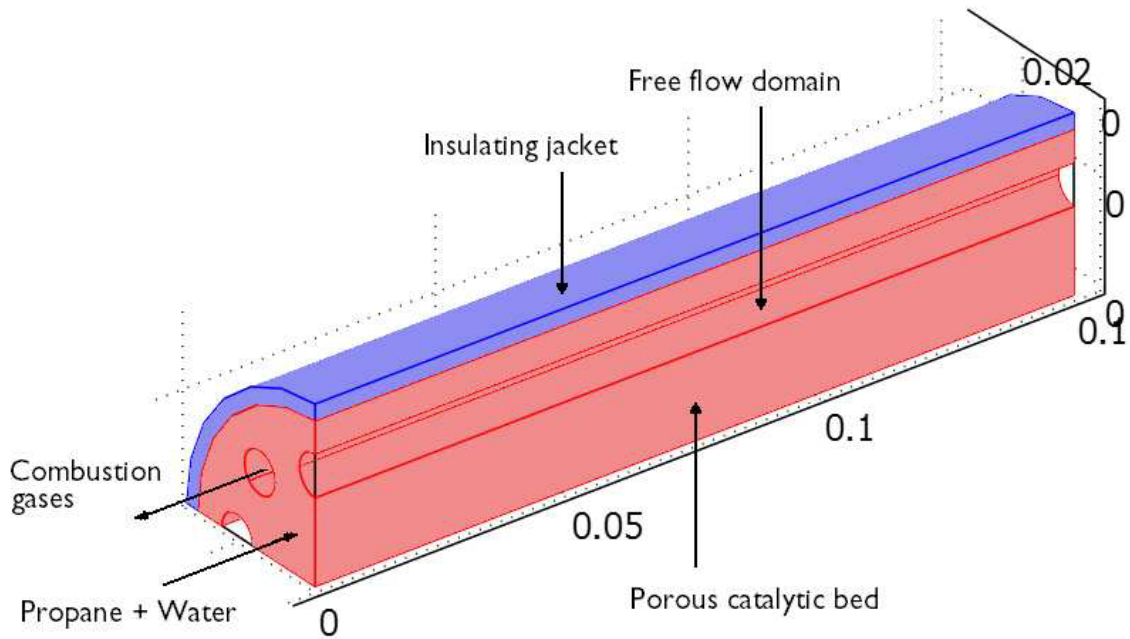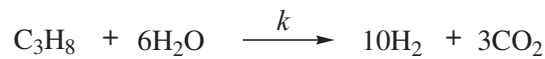
Figure 6: Steam reformer unit with catalytic bed, heating tubes, and insulating jacket. Making use of symmetry, the modeling domain is reduced to a quarter of the full geometry.

In the reformer, water and propane react to form hydrogen and carbon dioxide:

$$C_3H_8 \ + \ 6H_2O \ \xrightarrow{\ k\ } \ 10H_2 \ + \ 3CO_2$$

A rate equation proposed by Gateau has been used [Ref. 7].

Model Equations

The flow of gaseous species through the reformer bed is given by Darcy's Law:

$$\nabla \cdot (\rho(-\frac{\kappa}{\eta}\nabla p)) = 0$$

The flow of heating gas in the tubes is described by the weakly compressible Navier-Stokes equations at steady-state:

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot (-p\mathbf{I} + \eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - (2\eta/3 - \kappa_{dv})(\nabla \cdot \mathbf{u})\mathbf{I})$$
$$\nabla \cdot (\rho \mathbf{u}) = 0$$

In the equations above, ρ denotes the fluid density (kg/m^3), η the viscosity (Pa·s), $\mathbf{u}$ represents the velocity (m/s) and p is the pressure (Pa). κ_{dv} denotes the dilational viscosity (Pa·s), and κ is the permeability of the porous medium (m^2).

The energy transport in the reactor is described by convection and conduction equations of the form:

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$$\nabla \cdot (-k\nabla T) + \rho Cp\mathbf{u} \cdot \nabla T = Q$$

Above, T is the temperature (K), and k is the thermal conductivity (W/(m·K)). Q (W/m³) is the heat source due to chemical reaction, dependent on the reaction rate:

$$Q = \Delta Hr$$

The mass-balance equations for the model are the Maxwell-Stefan diffusion and convection equations at steady state:

$$\nabla \cdot (\rho w_i \mathbf{u} - \rho w_i \sum_j D_{ij} (\nabla x_j + (x_j - w_j)\frac{\nabla p}{p}) - D_i^T \frac{\nabla T}{T}) = R_i$$

In the equations above, w_i denotes the mass fraction of species i, x_j is the molar fraction of species j, and D_{ij} is the ij component of the multicomponent Fick diffusivity (m²/s). D^T denotes the generalized thermal diffusion coefficient kg/(m·s), and R_i the reaction rate (kg/(m³·s)).

The system of partial differential equations is set up and solved in COMSOL Multiphysics using predefined modeling interfaces.

Physical property calculations

The transport equations just outlined require a number of physical property inputs. For the reacting gas in the reformer bed, the model makes use of property functions for the density, viscosity and heat capacity. These properties all depend on the gas phase temperature, pressure and composition. The combustion gases in the heating tubes are assumed to have the temperature and pressure dependent properties of air. The gas density, viscosity, thermal conductivity, and heat capacity are required for proper solution of the flow and energy transport equations.

Once again, the physical property calculations are handled by a CAPE-OPEN compliant property package (Ref. 6) accessed through the CAPE-OPEN interface of COMSOL Script. The function objects for physical properties created in Script are used together with the 'capeeval' command directly in the graphical user interface of COMSOL Multiphysics. As illustrated in Figure 7, dependent variables of the Multiphysics model, e.g. p, T, and w_i, serve as inputs to the property function calls.
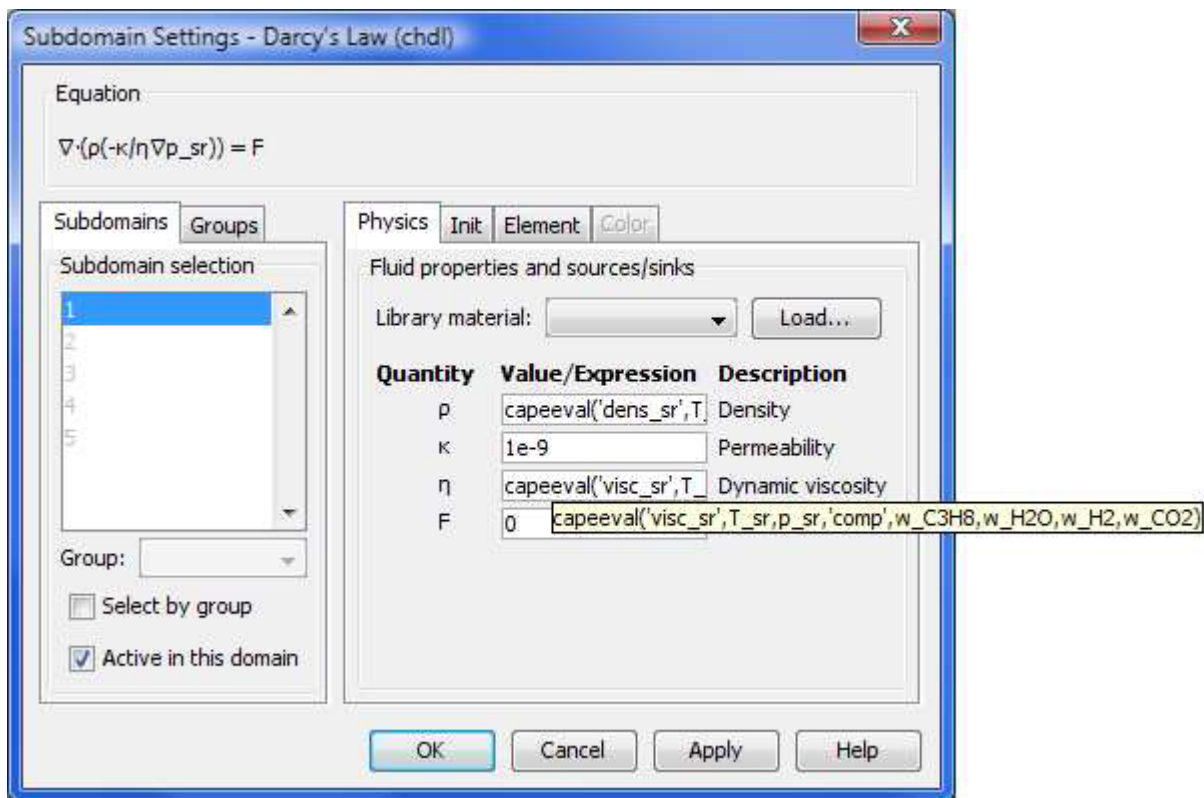
Figure7: Capeeval function calls can be made directly from the graphical user interface. Note that the input arguments are dependent variables of the Multiphysics model.

Results

Solving the coupled model equations provides the flow, temperature and species distributions in the 3D modeling domain. For example, Figure 8 shows the temperature field in the reformer bed and the heating tubes. The energy exchange between the heating tubes and the reformer bed is clearly illustrated. The gas of the heating tubes enters at 900 K and exits with an average temperature of 690 K. The reacting gas in the reformer bed enters at 700 K, goes through a minimum, and finally exits with an average temperature of 821 K.
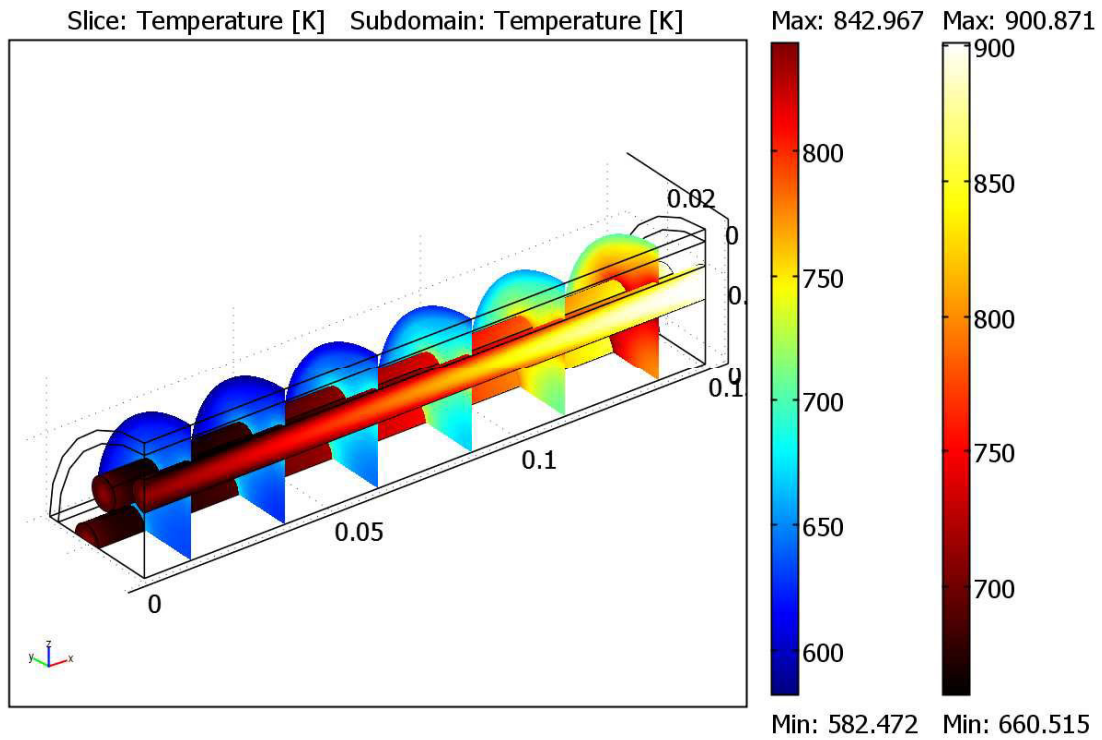
Figure 8: Temperature distributions in the reformer system, including the reformer bed, heating tubes and insulating jacket.

It is of course also possible to plot the various property functions calculated by the external property package. As an example, Figure 9 shows the density variations in the reformer bed. The density decreases along the reactor length as an effect of chemical reaction, and to a lesser extent due to increasing temperature.
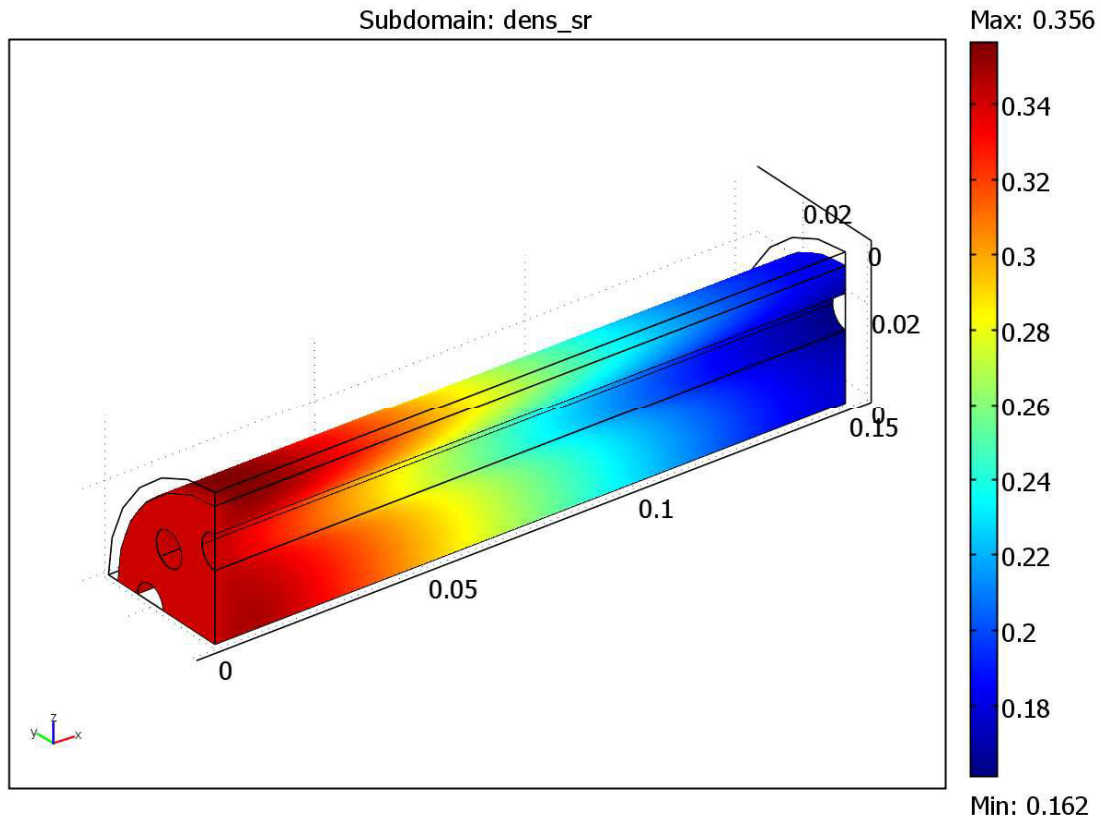
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Figure 9: Density of the reacting gas in the reformer bed.

Summary

COMSOL version 3.5 features a CAPE-OPEN thermodynamic and physical properties interface, supporting both CAPE-OPEN Thermo 1.1 and CAPE-OPEN Thermo 1.0 standards. The interface enables COMSOL Multiphysics and Reaction Engineering Lab to access property calculations from CAPE-OPEN compliant physical property packages to perform advanced and accurate chemical engineering simulations.

References

1.   see www.comsol.com/products
2.   see www.colan.org/index-3.html
3.   see www.comsol.com/showroom
4.   K.C. Hou and H.B. Palmer (1965), The Journal of Physical Chemistry, vol. 69, p. 863.
5.   S.E. Shull and A.N. Hixson (1966), I&EC Process Design and Development, vol. 5, p. 147.
6.   see www.cocosimulator.org
7.   P.Gateau (2007), Design of Reactors and Heat Exchange Systems to Optimize a Fuel Cell Reformer, Proceedings of the COMSOL Users Conference 2007, Grenoble.