

Methane Reforming

Demonstration Problem

Revision 0; October 14, 2008

Reference: Wang Shuyan et. al., Simulation of effect of catalytic particle clustering on methane steam reforming in a circulating fluidized bed reformer, Chemical Engineering Journal 139 (2008) 136–146.

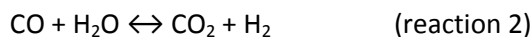
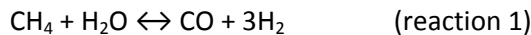
Purpose and Overview

Steam reforming of methane (conversion of CH₄ into syngas: CO and H₂) is of interest for applications such as fuel cells, conversion of natural gas to liquid fuels, etc. Similar reactors are of interest for coal-to-liquid (CTL) and biofuel synthesis applications.

A simple demonstration problem has been developed in SINDA/FLUINT, using both the Sinaps© nongeometric (sketchpad) GUI and the Thermal Desktop© with FloCAD© geometric (CAD-based) GUI. Since both sets of models are available for inspection and for use as a starting point or template, only brief descriptions are included in this document as general guidance. A basic understanding of SINDA/FLUINT modeling is assumed.

Reaction Kinetics

Two simultaneous reactions of five species are considered:



Reaction 2 is the water-gas shift (WGS) reaction.

The referenced paper (Shuyan, et. al.) contains the reaction kinetics used in this problem, based on the presence of Haldor Topsoe Ni/Mg Al₂O₄ spinel catalytic particles. Because of the demonstrative nature of this problem, the details of the catalyst are neglected: the catalyst is assumed to operate at full activity.

Shuyan lists formulae for forward reaction rates for these reactions,¹ using equilibrium constants as the basis for estimating reverse rates. Assuming full catalytic activity, the current reaction rate can be calculated as a function of temperature, pressure, and partial pressures. The temperature dependencies for both the reaction rate constants and the equilibrium constants are exponential functions of an Arrhenius form.

¹ Specifically, equations 8, 9, 11, 12, 13, and 15-20.

Notes on Fluid Properties

In SINDA/FLUINT, each species is assigned a letter identifier:

| Species | Symbol | Letter ID |
|-------------------------|------------------|-----------|
| Methane | CH ₄ | M |
| Water | H ₂ O | W |
| Carbon monoxide (“gas”) | CO | G |
| Hydrogen | H ₂ | H |
| Carbon dioxide | CO ₂ | C |

Water may be a condensable (two-phase) fluid. However, in this case the temperatures will always be high enough such that the liquid phase will never occur.² Therefore, either a perfect gas (8000 series fluid) or a real gas (“NEVERLIQ” 6000 series fluid) could have been used. Versions of such files are available (<http://www.crtech.com/properties.html>) that were built from the NIST program REFPROP, perhaps subsequently simplified to a perfect gas using the SINDA/FLUINT PR8000 utility.

Unfortunately, the NIST database does not extend to sufficiently high temperatures for CO, CH₄, and H₂. For example, the upper temperature limit for CO is only 500K in the current version of REFPROP.

Therefore, properties for all five gases were generated using NASA’s free CEA chemical equilibrium program combined with a C&R utility for converting outputs to FPROP DATA format.³ While this interface is intended to prepare fluids representing equilibrium reacting mixtures with variable molecular weights, the ‘only’ mode in CEA can be used to produce properties for single constituents with constant molecular weights. Therefore, despite the resulting generalized 6000 series “real gas” fluid tables, it should be noted that the actual properties reflect CEA’s intrinsic assumption of perfect gases. Heat of formation (HFORM) and diffusion volume (DIFV) information were then added to these fluid files, noting that CEA uses the heat of formation as the basis of the enthalpy at 25°C. The heat of formation of water is therefore diminished by the heat of vaporization to reflect the all-gas nature of this CEA-derived fluid file. (For a full two-phase water description, the uncorrected heat of formation should instead be applied, since a liquid state exists at standard temperature and pressure.)

Reactor Design

An intentionally generic and simplified plug-flow reactor (PFR) is assumed.

Inclusion of the solid catalyst particles could take several forms – as a packed bed of stationary particles held in place by structured catalysts supports, free-flowing with the gas transport, or other configurations – but inclusion of the catalysts in any form overshadows the illustrative intent of this demonstration problem. The chosen scenario focuses on how to incorporate the reaction kinetics into SINDA/FLUINT.

² If temperatures below the dew point are included, a full two-phase description of water should be used instead. Indeed, such a description (<http://www.crtech.com/properties.html>) was used as part of the validation effort when temperatures as low as 25°C were used as a feed temperature.

³ <http://www.crtech.com/EQfluids.html>

Temperatures, pressures, inlet flows, and dimensions may be changed parametrically in the model, with a subset of possible parametric settings used for the baseline runs shown in the table below.

| Parameter | Register Name | Value | Units | Comment |
|--|---|---------------------|----------------|---|
| Reactor length | <i>length</i> | 1 | m | (Arbitrary choice.) Longer lengths might be considered as needed to bring the outlet conditions closer to the equilibrium condition |
| Reactor hydraulic diameter | <i>diam</i> | 0.008 | m | (Arbitrary choice) |
| Reactor flow area | <i>area</i> | 4.e-4 | m ² | Undefined fins or slit shape is assumed, as needed to provide adequate heat transfer area |
| Inlet temperature | <i>temp_in</i> | 800 | °C | (Arbitrary choice, but representative of typical applications.) |
| Wall temperature | Assumed equal to the inlet | 800 | °C | Inlet and wall temperatures are assumed to be equal, but can be independently adjusted if need be |
| Inlet flow rate | <i>moles_in</i> | 0.03e-3 | kmol/s | (Arbitrary choice) |
| Inlet mole fractions of CH ₄ , H ₂ O and other inlet stream constituents, plus excess steam fraction beyond stoichiometric | <i>mol_in_m</i> , <i>mol_in_w</i> , <i>SteamX</i> | 0.5, 0.5, 3.0 | - - - | Stoichiometric (equal mole fractions) plus 2 times more steam. Use SteamX=1.0 for stoichiometric feed rates. |
| Outlet pressure | <i>pres</i> | 101325. | Pa | This indirectly sets the reactor pressure due to the small pressure drop through the reactor |

A Refresher: Modeling Reactions in SINDA/FLUINT

The rate of creation of mass of any species i is designated $XMDOT_i$ in SINDA/FLUINT, with the caveat that $\sum_i XMDOT_i = 0$: there is no net generation or loss of total mass as a result of a chemical reaction. A species that is being consumed will have a negative $XMDOT$, and a species that is being produced will have a positive $XMDOT$. Since this model uses metric units, $XMDOT$ has units of kg/s (lb_m/hr would be the units in the English system).

When $XMDOTs$ are nonzero, the code will automatically calculate and apply a corrective heat of reaction (QCHEM) based on the fluid properties (heats of formation and enthalpy basis). If each fluid uses the heat of formation as the enthalpy basis at STP, this corrective QCHEM term is zero.

When the desired concentration of one or more species is known (e.g., when either the equilibrium concentration or the reaction/combustion efficiency is known), the EQRATE utility can be used to generate $XMDOT$ values, perhaps obeying one or more chemical reactions (supplied as stoichiometric numbers). For example, preliminary CEA runs could have generated equilibrium state predictions (perhaps as functions of temperature), which could have been used as inputs to the EQRATE utility.

If instead only the rate of reaction is known (as is the case in this example), then EQRATE is not applicable and the XMDOT values should instead be calculated explicitly by the user in user logic block FLOGIC 0 at the start of each solution interval (i.e., time step or steady state relaxation step). The XMDOT value for each species i will be the sum of all the reactions in which it participates.

The resulting set of XMDOT values is assumed to be constant (along with the corresponding QCHEM) over the next solution interval. In other words, the species production and extinction rates are based on the temperatures and pressures at the start of the interval, and are not implicitly adjusted for temperature or pressure changes that are about to occur.⁴

A significant restriction on chemical reactions is that they can only apply to *tanks* (control volumes), and not to *junctions* (massless/volumeless state points). Noting that the main solution routine STEADY (aka “FASTIC”) treats tanks temporarily as junctions, this means that steady-state solutions can only be achieved using STDSTL (pseudo-transient integration toward a time-independent state). This in turn means that, unlike most steady-state analyses, chemical reaction steady-state solutions are dependent on initial guesses (especially species fractions).

Reactor Model

The source of gases is represented by two *plena*: one (reactor.1000) representing a stoichiometric mixture of methane and steam, and another (reactor.1100) representing excess steam that can be added to the reactor. The mixture ratio within plenum reactor.1000 is set using registers (e.g., *mol_in_w* for steam, *mol_in_m* for methane) based on mole fractions, which are then converted into gas mass fractions (XG_i for each species i as represented by the register *xin_m*, *xin_w*, *xin_h*, *xin_c*, and *xin_g*). Note that while *xin_c* and *xin_g* are both zero (no inflowing CO₂ or CO), *xin_h* is nonzero: it is set to a very small value. An extremely small amount of hydrogen is added simply to avoid the need to deal with the mathematical singularity caused by the presence of the partial pressure of hydrogen in the denominator of the rate equations.

There are many ways to represent the inlet conditions. For example, the mass fractions on a single plenum could be set. Alternatively, N *plena* could be used for each of the N species involved, setting the mass or volumetric flow rate of each species being injected.

In this case, a single *SetFlow* (SINDA/FLUINT MFRSET connector) is applied from each plenum, with the ratio of the flow rates being controlled via the *SteamX* register: *SteamX*=1 for stoichiometric flow, 2 for twice the steam required, etc. The steady-state case (named “PFR”) is run at *SteamX*=1: stoichiometric inlet conditions, or equal molar flows of methane and steam, with zero excess steam flow added from plenum reactor.1100.

⁴ By default, SINDA/FLUINT *does* implicitly reduce reactions for reactants that are present in low concentrations and that vanish during the solution interval, as described in the User’s Manual. In other words, XMDOTs can be an implicit function of concentration, but they are assumed independent of temperature and pressure *during* each solution interval. Normally, they are adjusted in a stair-step fashion *between* solution intervals according to calculations in user logic.