Methanol Reactor. Hydrogenation of CO_2 to form CH_3OH on a Cu/ZnO/Al_2O_3 catalyst. ORIGIN := 1

This catalyst converts methanol from CO_2 (not much from CO) and H_2, and it also catalyzes the formation of CO_2 from CO via the reversible water gas shift reaction.

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There are 8 chemical species. Assign ID numbers to names. $i := 1..8$ $R := 8.314$ J/mole·K

$(CH4\ \ H2O\ \ H2\ \ CO\ \ CO2\ \ O2\ \ N2\ \ CH3OH) := (1\ \ 2\ \ 3\ \ 4\ \ 5\ \ 6\ \ 7\ \ 8)$

methanol reactor

Reaction 2r: $CO_2 + H_2 \longleftrightarrow CO + H_2O$

Reaction 5: $CO_2 + 3\,H_2 \longleftrightarrow CH_3OH + H_2O$

stoichiometric coefficients

$\nu_{2r} := (0\ \ 1\ \ -1\ \ 1\ \ -1\ \ 0\ \ 0\ \ 0)^T$

$\nu_5 := (0\ \ 1\ \ -3\ \ 0\ \ -1\ \ 0\ \ 0\ \ 1)^T$

Kinetic model parameters from Vanden Bussche & Froment, J. Catalysis, 161, 1–10 (1996), Table 2.

$K_{H2}(T) := 0.499 \cdot \exp\left(\frac{17197}{R \cdot T}\right)$ ... sqrt(K_{H2}) in Vanden Bussche & Froment

$K_{H2O}(T) := 6.62 \cdot 10^{-11} \cdot \exp\left(\frac{124119}{R \cdot T}\right)$ ... K_{H2O} in Vanden Bussche & Froment

$K_{H2OH2}(T) := 3453.38$ ... $K_{H2O}/K_8/K_9/K_{H2}$ in Vanden Bussche & Froment

$k_5(T) := 1.07 \cdot \exp\left(\frac{36696}{R \cdot T}\right)$ ... $K'_{5a} \cdot K'_2 \cdot K_3 \cdot K_4 \cdot K_{H2}$ in Vanden Bussche & Froment, in mol/s/kg catalyst

$k_{2r}(T) := 1.22 \cdot 10^{10} \cdot \exp\left(-\frac{94765}{R \cdot T}\right)$ ... k'_1 in Vanden Bussche & Froment (note the sign)

Equilibrium constants

$K_{MeOH}(T) := 10^{\frac{3066}{T} - 10.592}$ ... K_1 in Vanden Bussche & Froment

$K_{RWGS}(T) := 10^{-\frac{2073}{T} + 2.029}$ ... $1/K_3$ in Vanden Bussche & Froment

Reaction rates

methanol synthesis (Reaction 5)

$$r_5(p,T) := k_5(T) \cdot p_{CO2} \cdot p_{H2} \cdot \frac{1 - \frac{1}{K_{MeOH}(T)} \cdot \frac{p_{CH3OH} \cdot p_{H2O}}{p_{CO2} \cdot (p_{H2})^3}}{\left(1 + K_{H2OH2}(T) \cdot \frac{p_{H2O}}{p_{H2}} + K_{H2}(T) \cdot \sqrt{p_{H2}} + K_{H2O}(T) \cdot p_{H2O}\right)^3}$$

reverse WGS (Reaction 2r)

$$r_{2r}(p,T) := k_{2r}(T) \cdot p_{CO2} \cdot \frac{1 - \frac{1}{K_{RWGS}(T)} \cdot \frac{p_{CO} \cdot p_{H2O}}{p_{CO2} \cdot p_{H2}}}{1 + K_{H2OH2}(T) \cdot \frac{p_{H2O}}{p_{H2}} + K_{H2}(T) \cdot \sqrt{p_{H2}} + K_{H2O}(T) \cdot p_{H2O}}$$

Isothermal Methanol Reactor. $T := 500$ K $P := 100$ bar

$m_{cat} := 1.64$ kg catalyst per basis = 1 mole of feed to methanol reactor ⟶
need to scale up to the specified capacity later

$dndt = \nu \cdot r = \nu_{5} \cdot r_{5} + \nu_{2r} \cdot r_{2r}$

$dndt(t, n) := m_{cat} \cdot \nu_{5} \cdot r_{5}\left(\frac{n}{\sum n} \cdot P, T\right) + m_{cat} \cdot \nu_{2r} \cdot r_{2r}\left(\frac{n}{\sum n} \cdot P, T\right)$

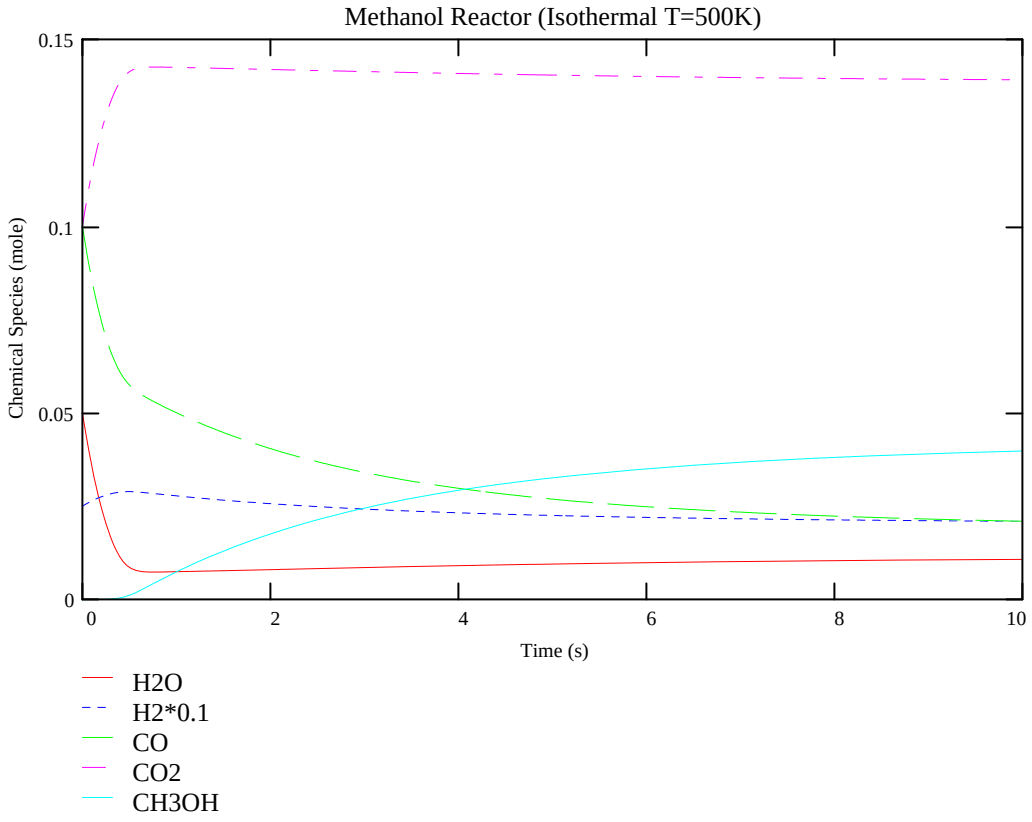
I.C.

$$n_{init} := \begin{pmatrix} CH4 & H2O & H2 & CO & CO2 & O2 & N2 & CH3OH \\ 0 & 0.05 & 0.25 & 0.1 & 0.1 & 0 & 0.5 & 0 \end{pmatrix} \qquad n_{init} := \left(n_{init}^{T}\right)^{\langle 2 \rangle}$$

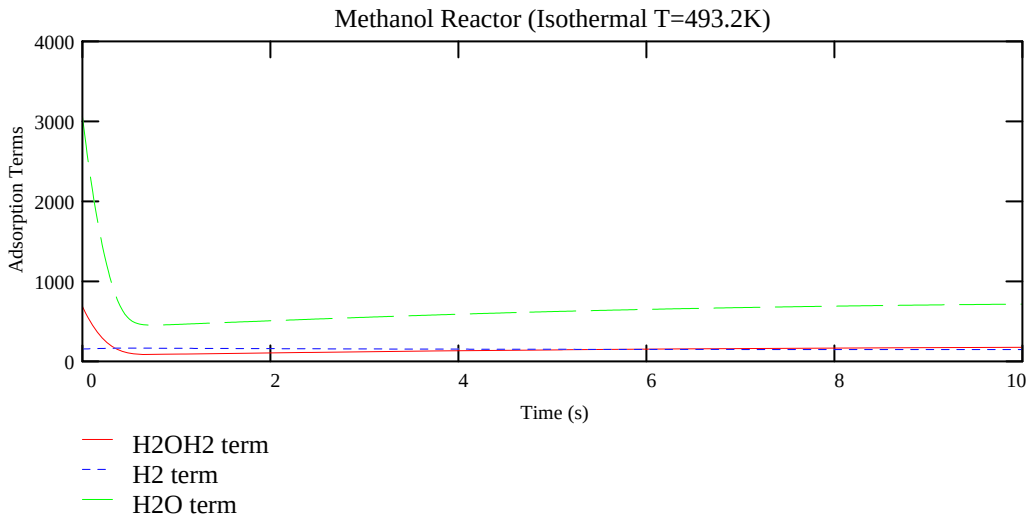
Call a routine to solve ODE in $nstep := 1000$ steps from t=0 to $t_f := 10$ sec $final := nstep + 1$

$tn := rkfixed(n_{init}, 0, t_f, nstep, dndt)$ $t := 1 .. final$ $time := tn^{\langle 1 \rangle}$ $n := submatrix(tn, 1, final, 2, 9)$

$\Sigma n_t := \sum\left(n^{T}\right)^{\langle t \rangle}$ $y_{t,i} := \frac{n_{t,i}}{\Sigma n_t}$ $p := y \cdot P$ $n_f := \left(n^{T}\right)^{\langle final \rangle}$ $n_f^{T} = (\ 0 \quad 0.0108 \quad 0.2096 \quad 0.021 \quad 0.1392 \quad 0 \quad 0.5 \quad 0.0398\ )$



Comparison of different adsorption terms



Let us integrate without the K_{H2OH2} term

$$r_{5.approx}(p,T) := k_5(T)\cdot p_{CO2}\cdot p_{H2}\cdot \frac{1-\frac{1}{K_{MeOH}(T)}\cdot\frac{p_{CH3OH}\cdot p_{H2O}}{p_{CO2}\cdot\left(p_{H2}\right)^3}}{\left(1+K_{H2}(T)\cdot\sqrt{p_{H2}}+K_{H2O}(T)\cdot p_{H2O}\right)^3}$$

$$r_{2r.approx}(p,T) := k_{2r}(T)\cdot p_{CO2}\cdot \frac{1-\frac{1}{K_{RWGS}(T)}\cdot\frac{p_{CO}\cdot p_{H2O}}{p_{CO2}\cdot p_{H2}}}{1+K_{H2}(T)\cdot\sqrt{p_{H2}}+K_{H2O}(T)\cdot p_{H2O}}$$

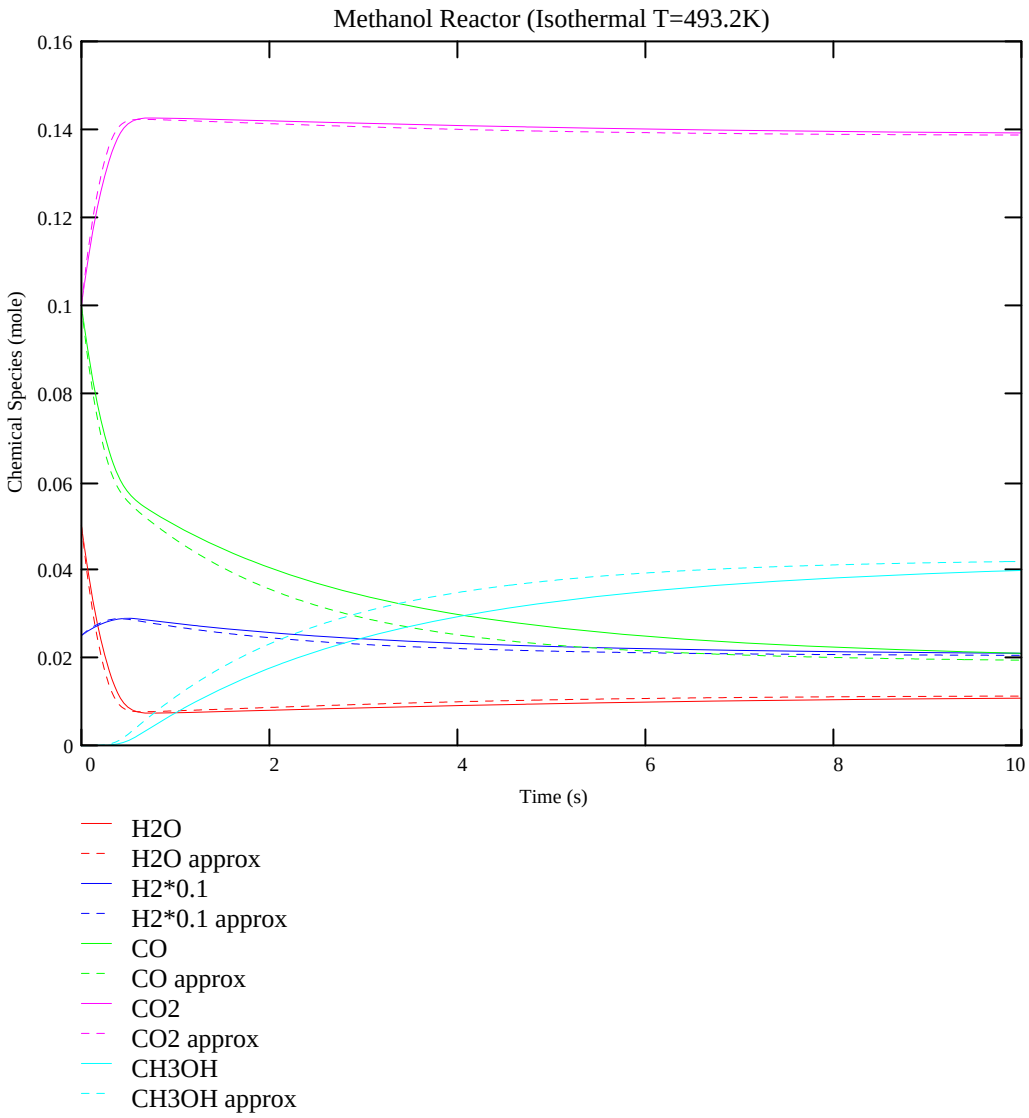
$$dndt(t,n) := m_{cat}\cdot\nu_5\cdot r_{5.approx}\left(\frac{n}{\sum n}\cdot P,T\right)+m_{cat}\cdot\nu_{2r}\cdot r_{2r.approx}\left(\frac{n}{\sum n}\cdot P,T\right)$$

I.C.

$$n_{init} := \begin{pmatrix} CH4 & H2O & H2 & CO & CO2 & O2 & N2 & CH3OH \\ 0 & 0.05 & 0.25 & 0.1 & 0.1 & 0 & 0.5 & 0 \end{pmatrix} \qquad n_{init} := \left(n_{init}^{T}\right)^{<2>}$$

Call a routine to solve ODE in $nstep := 1000$ steps from t=0 to $t_f := 10$ sec $final := nstep + 1$

$$tn := rkfixed\left(n_{init},0,t_f,nstep,dndt\right) \qquad t := 1\,..\,final \qquad time := tn^{<1>} \qquad n_{approx} := submatrix(tn,1,final,2,9)$$



$$n_{approx.f} := \left(n_{approx}^{T}\right)^{\langle final \rangle}$$

$$n_{approx.f} = \begin{bmatrix} 0.0000 \\ 0.0113 \\ 0.2050 \\ 0.0194 \\ 0.1387 \\ 0.0000 \\ 0.5000 \\ 0.0418 \end{bmatrix}$$

Kinetic model parameters #3 for Cu/ZnO/Al_2O_3 catalyst, from Lu, Teng, Xiao, Chemical Engineering Science, 59, 5455-5464, 2004. Eqns 8-19.

$k_5(T) := 35.45 \cdot \exp\left(-\frac{17069}{R \cdot T}\right)$ mol/s/g catalyst, pressure in bar, K_1 in Lu et al..

$k_2(T) := 7.3976 \cdot \exp\left(-\frac{20436}{R \cdot T}\right)$ mol/s/g catalyst, pressure in bar, K_3 in Lu et al..

$K_{H2}(T) := 0.249 \cdot \exp\left(\frac{34394}{R \cdot T}\right)$

$K_{CO2}(T) := 1.02 \cdot 10^{-7} \cdot \exp\left(\frac{67400}{R \cdot T}\right)$

$K_{CO}(T) := 7.99 \cdot 10^{-7} \cdot \exp\left(\frac{58100}{R \cdot T}\right)$

$K_{MeOH}(T) := \exp\left(\frac{4213}{T} - 5.752 \cdot \ln(T) - 1.707 \cdot 10^{-3} \cdot T + 2.682 \cdot 10^{-6} \cdot T^2 - 7.232 \cdot 10^{-10} \cdot T^3 + 17.6\right)$ ... K_{P1} in Lu et al.

$K_{WGS}(T) := 10^{\frac{2167}{T} - 0.5194 \cdot \log(T) + 1.037 \cdot 10^{-3} \cdot T - 2.331 \cdot 10^{-7} \cdot T^2 - 1.2777}$ ... K_{P3} in Lu et al.

$K_{WGS}(T) := \exp\left[\ln(10) \cdot \left(\frac{2167}{T} - 0.5194 \cdot \log(T) + 1.037 \cdot 10^{-3} \cdot T - 2.331 \cdot 10^{-7} \cdot T^2 - 1.2777\right)\right]$

methanol synthesis (Reaction 5)

$$r_5(p,T) := k_5(T) \cdot \frac{p_{CO2} \cdot p_{H2} \cdot \left[1 - \frac{1}{K_{MeOH}(T)} \cdot \frac{p_{CH3OH} \cdot p_{H2O}}{p_{CO2} \cdot (p_{H2})^3}\right]}{\left(1 + K_{CO2}(T) \cdot p_{CO2} + K_{CO}(T) \cdot p_{CO} + \sqrt{K_{H2}(T) \cdot p_{H2}}\right)^3}$$

forward WGS (Reaction 2)

$$r_2(p,T) := k_2(T) \cdot \frac{p_{H2O} - \frac{1}{K_{WGS}(T)} \cdot \frac{p_{CO2} \cdot p_{H2}}{p_{CO}}}{1 + K_{CO2}(T) \cdot p_{CO2} + K_{CO}(T) \cdot p_{CO} + \sqrt{K_{H2}(T) \cdot p_{H2}}}$$

Isothermal Methanol Reactor. $T := 500$ K $P := 100$ bar

$m_{cat} := 1640$ g catalyst; this roughly corresponds to an initial void fraction of a=0.5 and catalyst density of ρ=2000kg/m^3 at T=500K & P=50bar (numbers chosen for easy calculation; may be a what-if)

$V := \frac{R \cdot T}{50 \cdot 10^5}$ $V = 8.314 \cdot 10^{-4}$ m^3/mole reactant $2000 \cdot V = 1.663$ kg/mole reactant

dndt=ν·r=$\nu_5 \cdot r_5 + \nu_2 \cdot r_2$ $\nu_2 := -\nu_{2r}$

$dndt(t,n) := m_{cat} \cdot \nu_5 \cdot r_5\left(\frac{n}{\sum n} \cdot P, T\right) + m_{cat} \cdot \nu_2 \cdot r_2\left(\frac{n}{\sum n} \cdot P, T\right)$

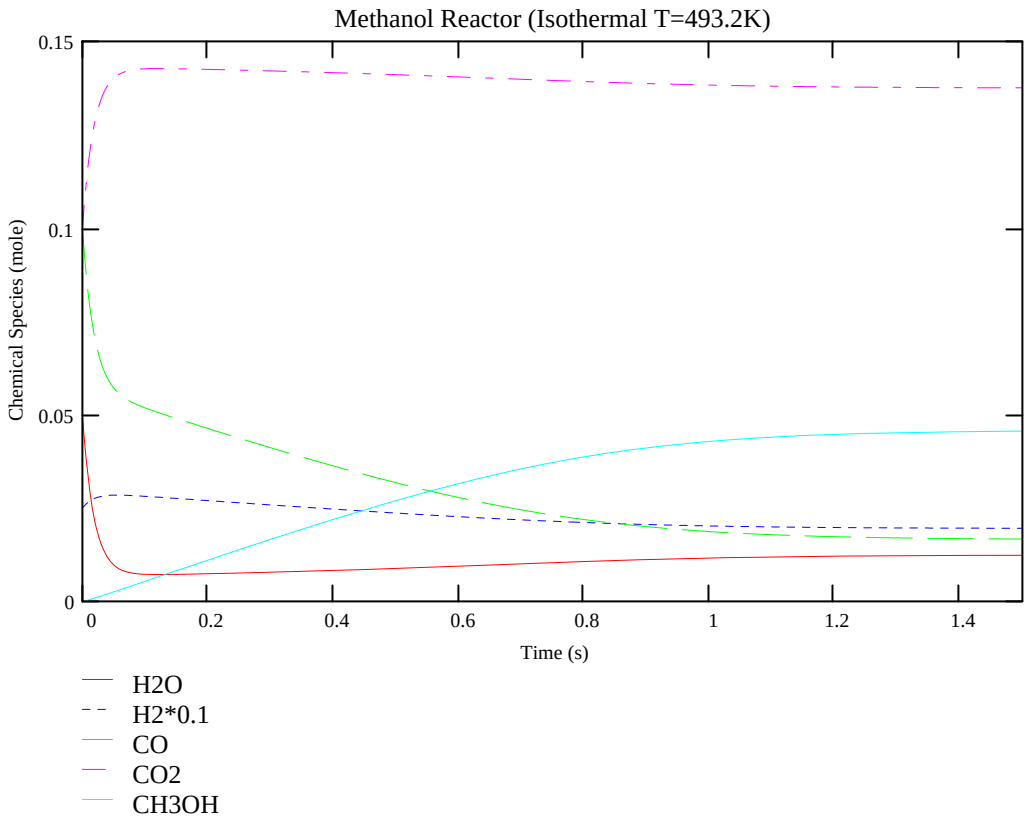
I.C.

$$n_{init} := \begin{pmatrix} CH4 & H2O & H2 & CO & CO2 & O2 & N2 & CH3OH \\ 0 & 0.05 & 0.25 & 0.1 & 0.1 & 0 & 0.5 & 0 \end{pmatrix} \qquad n_{init} := \left(n_{init}^{T}\right)^{<2>}$$

Call a routine to solve ODE in $nstep := 1000$ steps from t=0 to $t_f := 1.5$ $final := nstep + 1$

$tn := rkfixed(n_{init}, 0, t_f, nstep, dndt)$ $t := 1 .. final$ $time := tn^{<1>}$ $n := submatrix(tn, 1, final, 2, 9)$

$\Sigma n_t := \sum\left(n^{T}\right)^{<t>}$ $y_{t,i} := \frac{n_{t,i}}{\Sigma n_t}$ $p := y \cdot P$ $n_f := \left(n^{T}\right)^{<final>}$ $n_f^{T} = (0 \quad 0.0124 \quad 0.1963 \quad 0.0168 \quad 0.1376 \quad 0 \quad 0.5 \quad 0.0456)$



Let us approximate the K_{MeOH} & K_{WGS} terms

$$K_{MeOH}(T) := \exp\left(\frac{4213}{T} - 18.043\right)$$

$$K_{WGS}(T) := \exp\left[\ln(10)\cdot\left(\frac{2167}{T} - 2.212\right)\right]$$

methanol synthesis (Reaction 5)

$$r_{5.approx}(p,T) := k_5(T)\cdot\frac{p_{CO2}\cdot p_{H2}\cdot\left[1 - \frac{1}{K_{MeOH}(T)}\cdot\frac{p_{CH3OH}\cdot p_{H2O}}{p_{CO2}\cdot\left(p_{H2}\right)^3}\right]}{\left(1 + K_{CO2}(T)\cdot p_{CO2} + K_{CO}(T)\cdot p_{CO} + \sqrt{K_{H2}(T)\cdot p_{H2}}\right)^3}$$

forward WGS (Reaction 2)

$$r_{2.approx}(p,T) := k_2(T)\cdot\frac{p_{H2O}-\frac{1}{K_{WGS}(T)}\cdot\frac{p_{CO2}\cdot p_{H2}^{7}}{p_{CO}}}{1+K_{CO2}(T)\cdot p_{CO2}+K_{CO}(T)\cdot p_{CO}+\sqrt{K_{H2}(T)\cdot p_{H2}}}$$

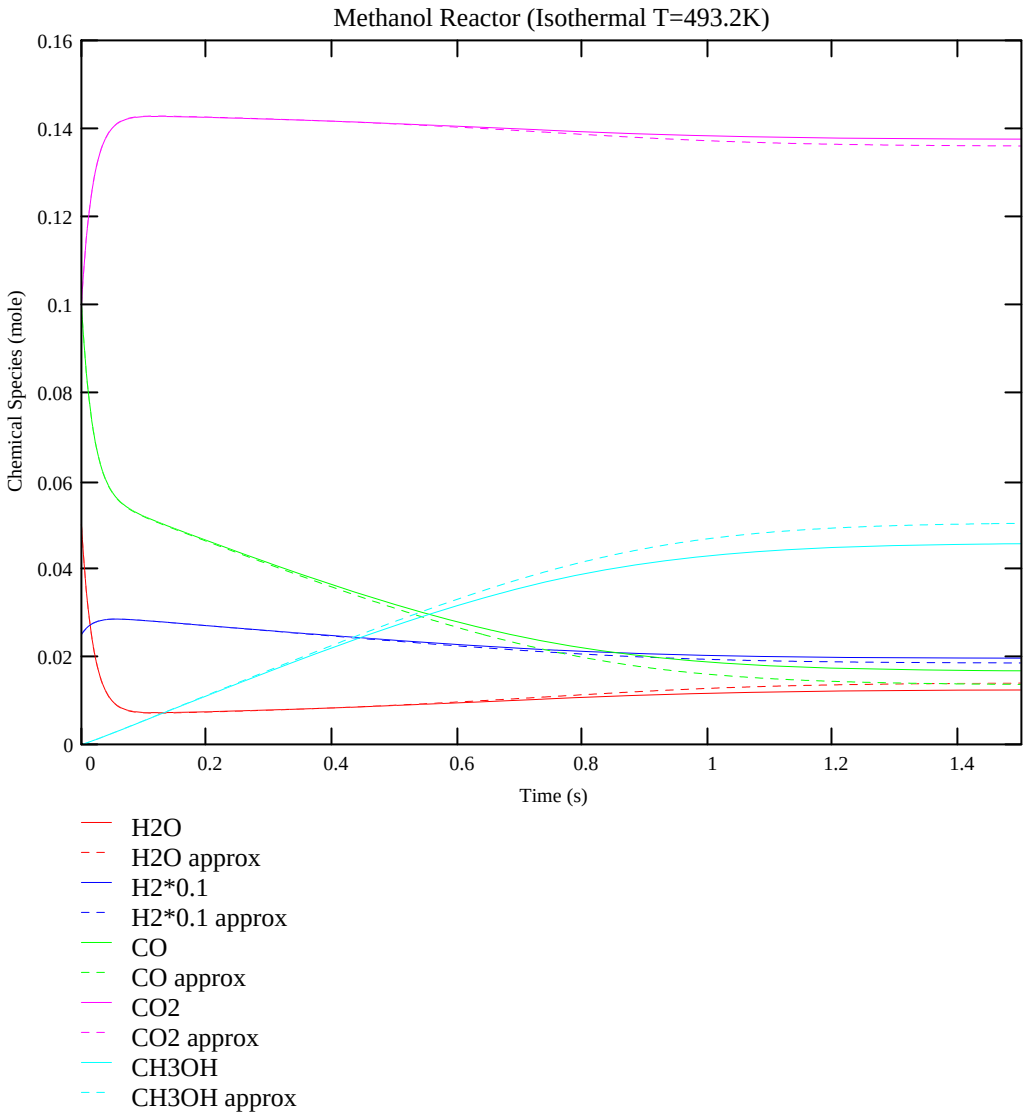
$$dndt(t,n) := m_{cat}\cdot\nu_5\cdot r_{5.approx}\left(\frac{n}{\sum n}\cdot P,T\right)+m_{cat}\cdot\nu_2\cdot r_{2.approx}\left(\frac{n}{\sum n}\cdot P,T\right)$$

I.C.

$$n_{init} := \begin{pmatrix} CH4 & H2O & H2 & CO & CO2 & O2 & N2 & CH3OH \\ 0 & 0.05 & 0.25 & 0.1 & 0.1 & 0 & 0.5 & 0 \end{pmatrix} \qquad n_{init} := \left(n_{init}^{T}\right)^{<2>}$$

Call a routine to solve ODE in $nstep := 1000$ steps from t=0 to $t_f := 1.5$ sec $\quad final := nstep + 1$

$$tn := rkfixed\left(n_{init},0,t_f,nstep,dndt\right) \qquad t := 1 .. final \qquad time := tn^{<1>} \qquad n_{approx} := submatrix(tn,1,final,2,9)$$



$$n_{approx.f} := \left(n_{approx}^{T}\right)^{<final>}$$

$$n_{approx.f} = \begin{bmatrix} 0.0000 \\ 0.0139 \\ 0.1855 \\ 0.0137 \\ 0.1361 \\ 0.0000 \\ 0.5000 \\ 0.0503 \end{bmatrix}$$