

Answers: EO reactor design

2. Reaction equations

The molar flow rates are related by atom balances. The change in molar flow rate of component A over the reactor is defined as:

$$\Delta F_A = F_A - F_{A,0}$$

We have the following components:

E: 2C, 4H

EO: 2C, 4H, 1O

O₂: 2O;

CO₂: 1C, 2O

H₂O: 2H, 1O

The C-atom balance is:

$$2\Delta F_E + 2\Delta F_{EO} + \Delta F_{CO_2} = 0$$

The H-atom balance is:

$$4\Delta F_E + 4\Delta F_{EO} + 2\Delta F_{H_2O} = 0$$

The O-atom balance is:

$$\Delta F_{EO} + 2\Delta F_{O_2} + 2\Delta F_{CO_2} + \Delta F_{H_2O} = 0$$

We want to calculate ΔF_{EO} , ΔF_{CO_2} and ΔF_{H_2O} as function of ΔF_E and ΔF_{O_2} . The atom balances can be written in vector notation as follows:

$$A \begin{bmatrix} \Delta F_{EO} \\ \Delta F_{CO_2} \\ \Delta F_{H_2O} \end{bmatrix} = \begin{bmatrix} 2 & 1 & 0 \\ 4 & 0 & 2 \\ 1 & 2 & 1 \end{bmatrix} \begin{bmatrix} \Delta F_{EO} \\ \Delta F_{CO_2} \\ \Delta F_{H_2O} \end{bmatrix} = \begin{bmatrix} -2\Delta F_E \\ -4\Delta F_E \\ -2\Delta F_{O_2} \end{bmatrix}$$

From the equation above the vector $[\Delta F_{EO} \ \Delta F_{CO_2} \ \Delta F_{H_2O}]'$ can be calculated.

$$\begin{bmatrix} \Delta F_{EO} \\ \Delta F_{CO_2} \\ \Delta F_{H_2O} \end{bmatrix} = A^{-1} \begin{bmatrix} -2\Delta F_E \\ -4\Delta F_E \\ -2\Delta F_{O_2} \end{bmatrix} = \begin{bmatrix} 0.4 & 0.1 & -0.2 \\ 0.2 & -0.2 & 0.4 \\ -0.8 & 0.3 & 0.4 \end{bmatrix} \begin{bmatrix} -2\Delta F_E \\ -4\Delta F_E \\ -2\Delta F_{O_2} \end{bmatrix}$$

A^{-1} can be calculated in MatLab by the command function `inv(A)`.

Filling in the relations for ΔF_E and ΔF_{O_2} :

$$\Delta F_E = F_E - F_{E,0} = -F_{E,0} X_E$$

$$\Delta F_{O_2} = F_{O_2} - F_{O_2,0} = -F_{O_2,0} X_{O_2}$$

leads to:

$$\Delta F_{EO} = 1.2 F_{E,0} X_E - 0.4 F_{O_2,0} X_{O_2,0}$$

$$\Delta F_{CO_2} = \Delta F_{H_2O} = -0.4 F_{E,0} X_E + 0.8 F_{O_2,0} X_{O_2,0}$$

and finally to:

$$F_E = F_{E,0} (1 - X_E)$$

$$F_{O_2} = F_{O_2,0} (1 - X_{O_2})$$

$$F_{EO} = F_{EO,0} + 1.2 F_{E,0} X_E - 0.4 F_{O_2,0} X_{O_2,0}$$

$$F_{CO_2} = F_{CO_2,0} - 0.4 F_{E,0} X_E + 0.8 F_{O_2,0} X_{O_2,0}$$

$$F_{H_2O} = F_{H_2O,0} - 0.4 F_{E,0} X_E + 0.8 F_{O_2,0} X_{O_2,0}$$

3. Kinetics

A) $(\sigma'_{EO})_E$ and $(\sigma'_{EO})_{O_2}$ can be derived directly from the reaction equations. R_p and R_x are given in mol O₂ per kg_{cat} per second, so that:

$$(\sigma'_{EO})_E(T) = \frac{2R_p}{2R_p + \frac{R_x}{3}} = \frac{2k_p(T)}{2k_p(T) + \frac{k_x(T)}{3}}$$

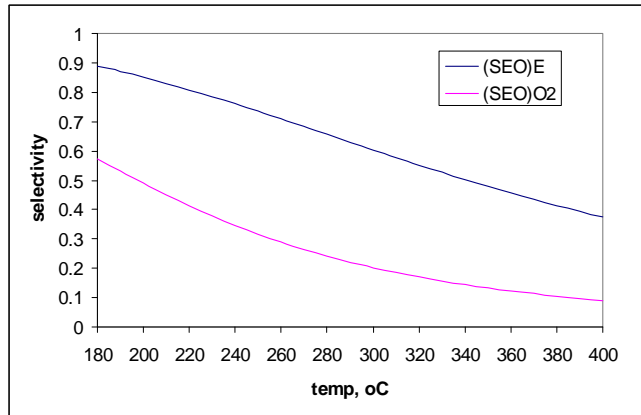
$$(\sigma'_{EO})_{O_2}(T) = \frac{R_p}{R_p + R_x} = \frac{k_p(T)}{k_p(T) + k_x(T)}$$

Because both reactions are first order in C_{O₂}, C_{O₂} cancels out from the equations.

B)

$$(\sigma'_{EO})_{O_2} = \frac{(\sigma'_{EO})_E / 2}{(\sigma'_{EO})_E / 2 + 3(1 - (\sigma'_{EO})_E)}$$

C)



4. Enthalpy of reaction

A) The enthalpy of reaction is:

$$\Delta H_r(T) = \Delta H_r(298.2K) + \Delta C_p(T - 298.2)$$

For Rp:

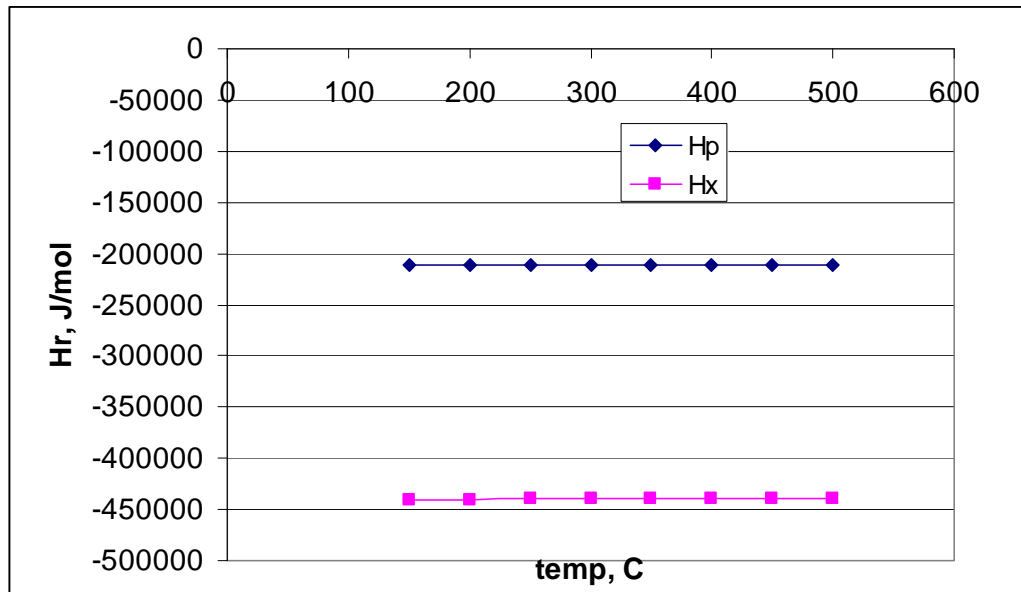
$$\Delta H_r(298.2) = 2H_{f,EO} - 2H_{f,E} - H_{f,O_2} = -2.10 \times 10^5 \text{ J / mol O}_2$$

$$\Delta C_{p_r} = 2C_{p_{f,EO}} - 2C_{p_{f,E}} - C_{p_{f,O_2}} = -4 \text{ J / (mol.K)}$$

For Rx:

$$\Delta H_r(298.2) = \frac{2}{3}H_{f,CO_2} + \frac{2}{3}H_{f,H_2O} - \frac{1}{3}H_{f,E} - H_{f,O_2} = -4.41 \times 10^5 \text{ J / mol O}_2$$

$$\Delta C_{p_r} = \frac{2}{3}C_{p_{CO_2}} + \frac{2}{3}C_{p_{H_2O}} - \frac{1}{3}C_{p_E} - C_{p_{O_2}} = 10 \text{ J / (mol.K)}$$



B)

Adiabatic energy balance:

$$[F_E C_{p_E} + F_{O_2} C_{p_{O_2}}]_{in} (T_{out} - T_{in}) = F_{O_2} [-\Delta H_{r,p}(T_{out})(\sigma_{EO})_{O_2} - \Delta H_{r,x}(T_{out})(1 - (\sigma_{EO})_{O_2})]$$

$$F_{total} [f_E C_{p_E} + f_{O_2} C_{p_{O_2}}]_{in} (T_{out} - T_{in}) = F_{total} f_{O_2} [-\Delta H_{r,p}(T_{out})(\sigma_{EO})_{O_2} - \Delta H_{r,x}(T_{out})(1 - (\sigma_{EO})_{O_2})]$$

$$[f_E C_{p_E} + f_{O_2} C_{p_{O_2}}]_{in} (T_{out} - T_{in}) = f_{O_2} [-\Delta H_{r,p}(T_{out})(\sigma_{EO})_{O_2} - \Delta H_{r,x}(T_{out})(1 - (\sigma_{EO})_{O_2})]$$

For $(\sigma_{EO})_E = 1$:

$$(T_{out} - T_{in}) = f_{O_2} \frac{-\Delta H_{r,p}(T_{out})}{[f_E C_{p_E} + f_{O_2} C_{p_{O_2}}]_{in}}$$

Solving gives $T_{out} = 401.75^\circ\text{C} \rightarrow T_{ad} = 201.75^\circ\text{C}$

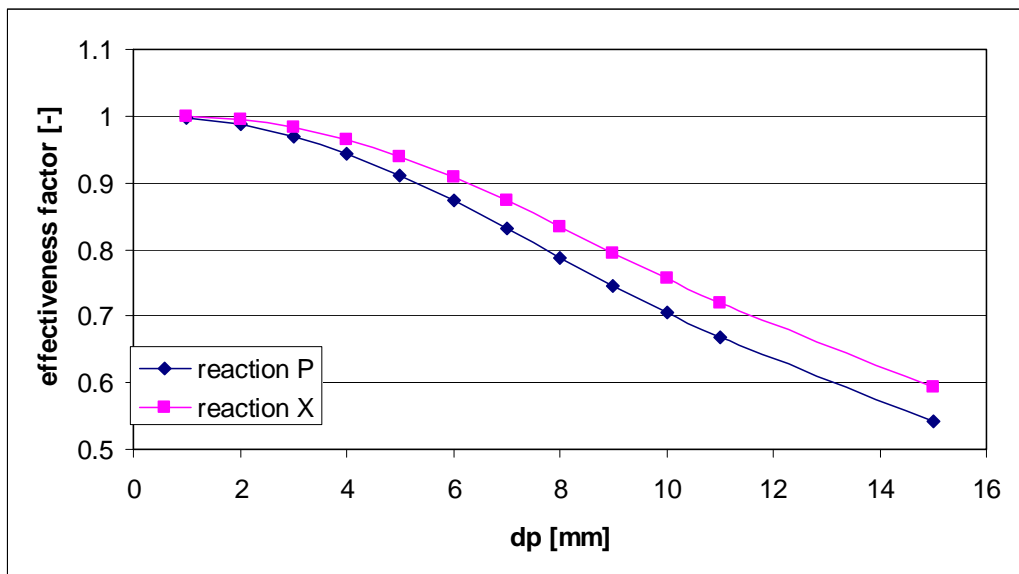
For $(\sigma_{EO})_E = 0$:

$$(T_{out} - T_{in}) = f_{O_2} \frac{-\Delta H_{r,x}(T_{out})}{[f_E C_{p_E} + f_{O_2} C_{p_{O_2}}]_{in}}$$

Solving gives $T_{out} = 617.8^\circ\text{C} \rightarrow T_{ad} = 417.8^\circ\text{C}$

5. Maximal particle size of the catalyst

With the particle model the following graph can be constructed for $T = 240\text{ }^{\circ}\text{C}$, $P=1\text{ MPa}$,
 $f_{\text{O}_2}=5\text{ vol\%}$, $f_{\text{E}}=90\text{ vol\%}$, $u=1.3\text{ m/s}$.



Concluding, the maximal particle size is 5 mm. Larger particles have an effectiveness factor smaller than 0.9.

6. Reactor model

Mathematically this reactor is described by:

$$u \frac{dC_{O_2}}{dz} = (R_p + R_x) \rho_{c,t}$$

$$u \frac{dC_E}{dz} = (2R_p + \frac{1}{3}R_x) \rho_{c,t}$$

$$u \rho_g C_p \frac{dT}{dz} = (R_p H_p + R_x H_x) \rho_{c,t} - \frac{4U}{d_t} (T - T_c)$$

The concentrations of the other components EO, CO₂ and H₂O, conversions and selectivities can be calculated with the relations derived under 2 and 3.

The Matlab mode is given below

```
function [conO2, conE, seo_E, YE, L, ntube, total_tube_volume, total_hft_area,
UU, Tmax]=eo_reactor
%
%

clear all
%
%
global rho_cat u C Cpe UU Tc Hp Hx dt dp

%the variables below can be changed in the simulations----
%-----variables-----
EO_P=50000; %ton/year - production of EO
Xo2=0.4; %-, conversion of O2
u=1.3; %m/s - superficial gas velocity == constant
Tin=225; %C - inlet temperature
P=1e6; %Pa - pressure == constant
fo2=0.07; %vol. fraction - vol. f. O2 in the feed
fe=1-fo2; %vol. fraction - vol. f. E in the feed - the feed contains only O2 and E
dp=4e-3; %m - diameter of the catalyst particles
dtube=2; %inch - tube diameter, only 1, 2 and 3 inch can be selected
%-----
%-----fixed parameters-----
R=8.314; %J/(mol.K) - gas constant
rho_cat=850; %kg_cat/m3_reactor - density of the catalyst
```

```

Cpe=65; %J/(mol.K) - Cp of ethylene
Me=28e-3; %kg/mol - molar mass of ethylene
Meo=44e-3; %kg/mol - molar mass of ethylene oxide
Hp=-2.11e5; %J/mol O2 - enthalpy of Rp
Hx=-4.42e5; %J/mol O2 - enthalpy of Rx
IG=0.04; %W/(m.K) - conductivity of the reaction mixture
IC=0.22; %W/(m.K) - conductivity of the used catalyst
visc=1.5e-5; %Pa.s - viscosity of the reaction mixture
eps=0.45; %- - porosity (gas fraction) of the packed bed
%-----

%-----derived variables-----
Tin=Tin+273.2; % changing Tin from C to K
Tc=Tin; %K - coolant temp equals the inlet temp
C=P/(R*Tc); %mol/m3 - molar concentration of the whole mixture == constant
CO2_0=fo2*C; %mol/m3 - O2 con at z=0
CE_0=fe*C; %mol/m3 - E con at z=0
Lspan=[0:0.01:50]; %axial points at which output is generated
init=[CO2_0 CE_0 Tin]'; %initial vector for solving the set of odes
if dtube == 1
    dt = 24.3e-3; %m - inner tube diameter in m
    dto = 25.4e-3; %m - outer diamter in m
end
if dtube == 2
    dt = 49.3e-3;
    dto = 2*25.4e-3;
end
if dtube == 3
    dt = 73.7e-3;
    dto = 3*25.4e-3;
end
%-----

%-----heat transfer model-----
%----- Dixon for the overall heat transfer coefficient
%the overall heat transfer coefficient is determined at the inlet
%conditions
REp=C*Me*dp*u/visc; %- - particle Reynolds number
It=C*Cpe*dp*u/(8*(2-(1-2*dp/dt)^2)); %W/(m.K) - turbulent (flowing) radial
conductivity of the bed
p1=IG/IC; %- - ratio IG/IC
CC=1.25; %constant assuming cylindrical particles
B=CC*((1-eps)/eps)^1.11;
A=2/(1-p1*B)*((1-p1)*B/(1-p1*B)^2*log(1/(B*p1))-(B+1)/2-(B-1)/(1-p1*B));
I0=IG*(0.67*eps+(1-eps)^0.5*A); %W/(m.K) - radial non flowing conductivity of
the bed

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```

ltotal=l0+lt; %W/(m.K) - total radial conductivity of the bed
a_wall=1.5*REp^-0.25*ltotal/dp; %W/(m2.K) - heat transfer coefficient inside the
tube
BI=a_wall*dt/2/ltotal; %-, Biot number
Uinv=1/a_wall+dt/2/(3*ltotal)*((BI+3)/(BI+4)); %1/U, according to Dixon
UU=1/Uinv; %W/(m2.K) - overall heat transfer coefficient (based on inner tube
diameter)
%UU=0.95*UU
%-----

%-----calling the ode solver-----
options=odeset('RelTol',1e-6,'AbsTol',1e-9,'NormControl','on');
[z,x]=ode45(@der_eo,Lspan,init,options);
%-----

%-----output variables-----
%-----Axial profiles
n=20/0.01+1; %- - number of points in axial out variables
cono2=(CO2_0-x(2:n,1))/CO2_0; %conversion of O2 as function of the reactor
length
cone=(CE_0-x(2:n,2))/CE_0; %conversion of E as function of the reactor length
ceo=-0.4*cono2*CO2_0+1.2*cone*CE_0; %concentration EO as function of the
reactor length
s=1./((cone*CE_0)./ceo); %EO selectivity based on E as function of the reactor
length
temp=x(2:n,3); %temp as function of the reactor length
Tmax=max(temp)-273.2;;

%----values at the end of the reactor
i=find(cono2 >= Xo2); %- finding the length at which the set conversion level is
reached
a=i(1);
L=z(a); %length
seo_E=s(a); %ethylene oxide selectivity based on E
conO2=cono2(a); % oxygen conversion
conE=cone(a); % ethylene conversion
YE=conE*seo_E; % EO yield
area=1/4*3.14159*dt^2; %m2 - area based in internal diameter
areaO=1/4*3.14159*dto^2; %m2 - area based in external diameter
EO_production=u*area*CE_0*YE*Meo*3600*8000; %kg EO per tube per year
ntube=EO_P*1e3/EO_production; %number of tubes required for the set
production rate
total_tube_volume=ntube*areaO*L; %m3, total tube volume
total_htf_area=3.14159*dto*L*ntube; % total heat transfer area

```



```

%-----

%-----plots-----
figure(1)
subplot(1,3,1)
plot(z(2:n),temp-273.2)
xlabel('reactor length, m');
ylabel('temperature, C');

subplot(1,3,2)
plot(z(2:n),cono2)
xlabel('reactor length, m');
ylabel('oxygen conversion, -');

subplot(1,3,3)
plot(z(2:n),s)
xlabel('reactor length, m');
ylabel('selectivity (Seo)e, -');

%-----

%-----defining the differential equations-----
function der=der_eo(z,x);

global rho_cat u C Cpe UU Tc Hp Hx dt dp

der=zeros(3,1);
kp=35.2*exp(-7200/x(3)); %mole o2 per kg cat per sec;
kx=74.1e3*exp(-10800/x(3)); %mole o2 per kg cat per sec;
effp=1; %- - effectiveness factor Rp,
effx=1; %- - effectiveness factor Rx,

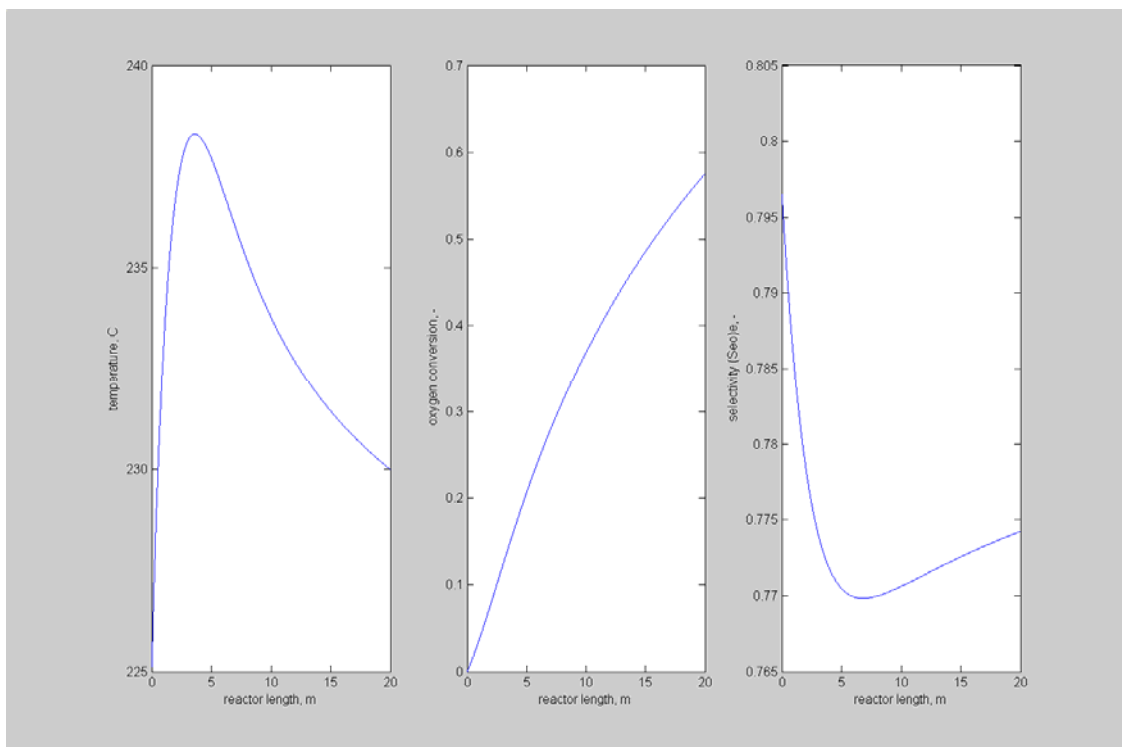
der(1)=-(effp*kp+effx*kx)*x(1)*rho_cat/u; %mol balance O2:  $u \frac{dCo_2}{dz} = -(effp \cdot kp \cdot co_2 - effx \cdot kx \cdot co_2) \cdot rho\_cat$ 
der(2)=-(2*effp*kp+(1/3)*effx*kx)*x(1)*rho_cat/u; %mol balance E:  $u \frac{dCE}{dz} = -(2 \cdot effp \cdot kp \cdot co_2 - 1/3 \cdot effx \cdot kx \cdot co_2) \cdot rho\_cat$ 
der(3)=(-kp*effp*x(1)*rho_cat*Hp-kx*effx*x(1)*rho_cat*Hx-4*UU/dt*(x(3)-Tc))/(u*C*Cpe);

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%energy balance:

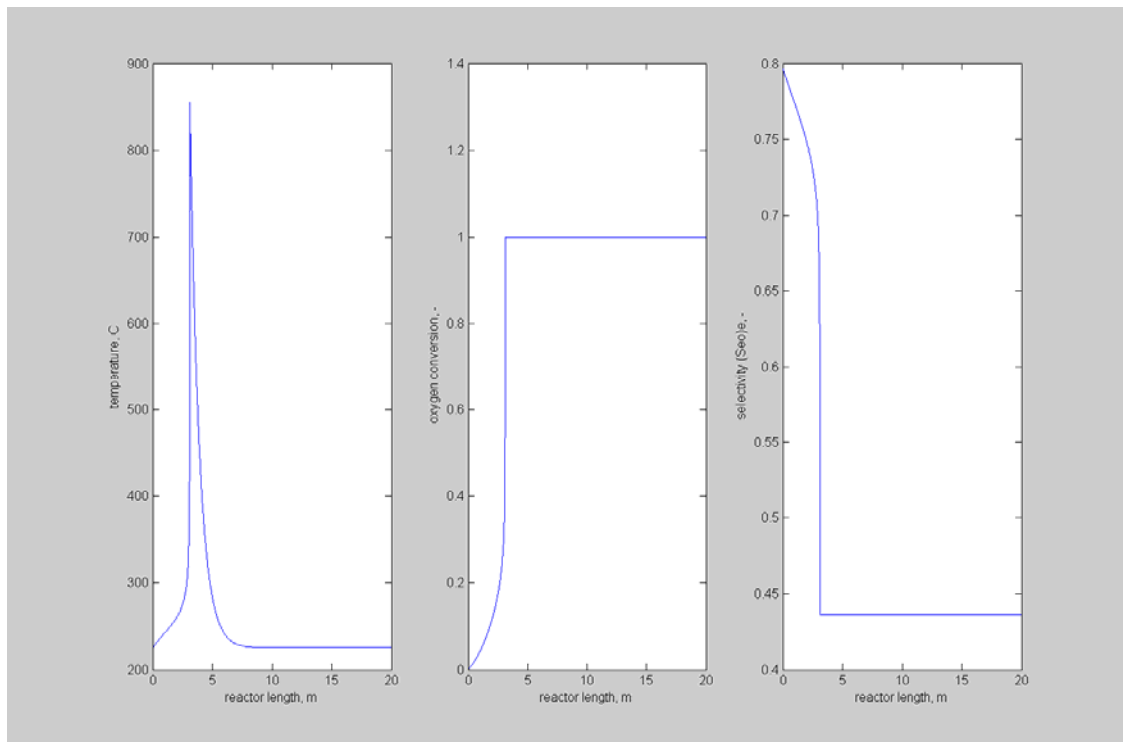
$$\rho(uC_p) \frac{dT}{dz} = (-\text{effp} \cdot k_p \cdot \text{co}_2 \cdot H_p - \text{effx} \cdot k_x \cdot \text{co}_2 \cdot H_x) \cdot \rho_{\text{cat}} - 4 \cdot U/dt \cdot (T - T_c)$$

A) The curve of T versus the reactor length shows a maximum that is called the 'hot spot'. At the hot spot dT/dz (dT/dX_{O_2}) is zero and heat production through the exothermic reactions equals the heat removal via the wall.

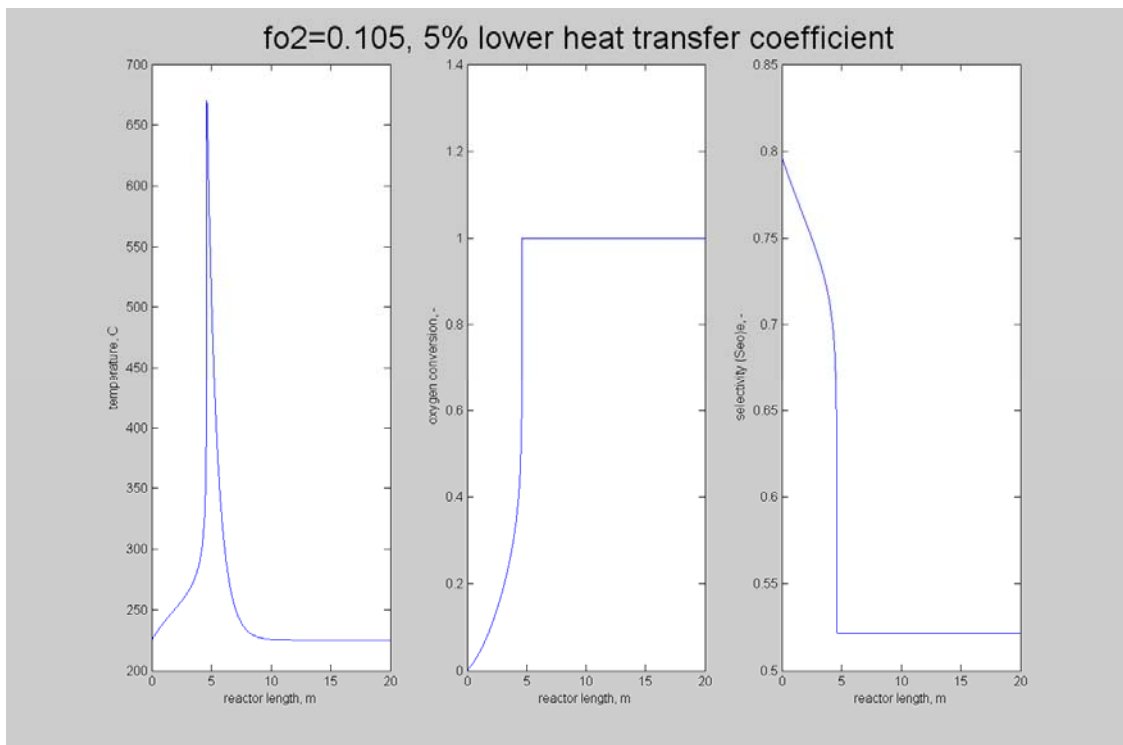
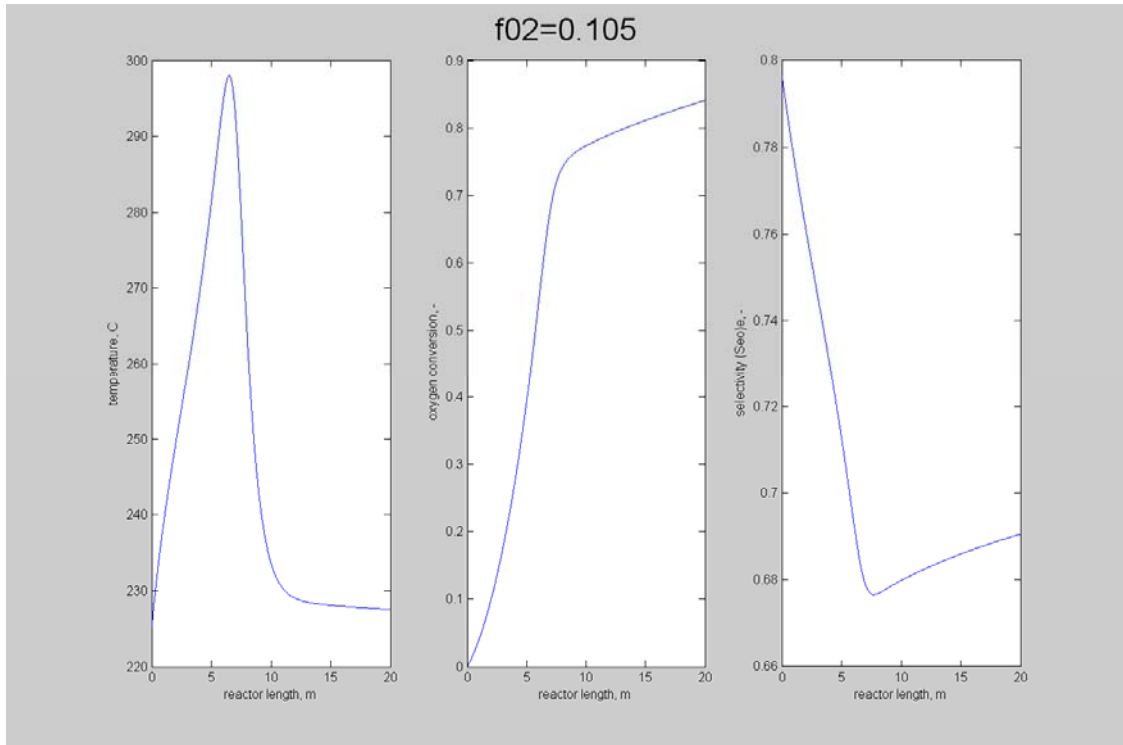


Not in all cases the profiles will be given, only the ones that are particularly interesting. The overall results are presented in table 4.

F) For $f_{O_2}=0.12$ the temperature increases very rapidly at some point along the reactor length. In this trajectory, the temperature continues to increase until all oxygen has been consumed. This behavior is called “run away”. With the mathematical model we can conveniently investigate under which conditions the system shows run away behavior.



The profiles for $f_{O_2}=0.105$ are given below and shows no real run away behavior, just a high maximal temperature. If the heat transfer coefficient drops only 5%, a run away occurs. This means that $=0.105$ is not a save operating point.



The criteria of Froment yield the following for the base case:

$$T_m = \frac{E_{act}}{R} 0.5 \left[1 - \sqrt{1 - \frac{4RT_c}{E_{act}}} \right], \text{ K}$$

$$\frac{E_{act}}{R} = 10800 \text{ K}$$

$$T_c = 225^\circ\text{C} = 498.2 \text{ K}$$

$$T_m = 523.6 \text{ K}$$

and

$$\Delta T_{ad} = (T_m - T_c) \left(1 + \sqrt{\frac{N_c}{e} + \frac{N_c}{e}} \right), \text{ K}$$

$$N_c = \frac{4U}{d_t k_v(T_c) \rho_g C_{p_g}}, \text{ -}$$

$$e = 2.718281828$$

$$U = 315 \text{ W} / (\text{m}^2 \cdot \text{K})$$

$$\rho_g C_{p_g} = \frac{P}{RT_{in}} C_{p_E} = 15692.77 \text{ J} / (\text{m}^3 \cdot \text{K})$$

$$d_t = 49.3 \cdot 10^{-3} \text{ m}$$

$$k_v(T_c) = 74.1 \cdot 10^3 e^{\frac{-10800}{498.2}} \cdot 850 = 0.024242844 \text{ 1/s}$$

$$\Delta T_{ad} = 778.9 \text{ K}$$

With ΔT_{ad} the inlet concentration of oxygen can be calculated:

$$f_{O_2} = \frac{\Delta T_{ad} C_{p_E}}{-\Delta H_X} \approx 0.115$$

This fraction is in fair agreement with the results from the numerical model.

Nevertheless, the maximal oxygen fraction according to the criteria gives runaway behavior according to the model.

Table 4. Simulation results. Figures in red indicate run away or that one of the design criteria is not met.

parameter	unit	CASE A	CASE B	CASE C	CASE D	CASE E	CASE F	CASE G	CASE H	CASE I	CASE J
X_{O_2}	-	0.4001	0.4001	0.5001	0.4005	0.4003	0.4179	0.4006	0.4002	0.4000	0.4001
X_E	-	0.0281	0.0280	0.0352	0.0258	0.0354	0.0406	0.0233	0.0246	0.0287	0.0273
$(\sigma_{EO})_E$	-	0.7711	0.7694	0.7728	0.7327	0.7527	0.6385	0.6814	0.7103	0.7802	0.7593
Y_E	-	0.0217	0.0215	0.0272	0.0189	0.0266	0.0259	0.0158	0.0175	0.0224	0.0208
Tube length	m	11.18	10.910	15.720	6.480	8.560	3.070	3.350	2.340	18.760	9.370
Nr. of tubes	Nr.	3270.6	3289.5	2599.8	1676.1	2715.8	2887.1	4603.8	8777.5	2164.9	1137.3
Tube volume	m ³	74.111	72.740	82.833	49.529	47.118	17.965	31.259	41.630	82.315	21.599
Tube area	m ²	5835.5	5727.6	6522.3	2600	3710.1	1414.5	2461.4	3277.9	6481,5	1700.7
U	W/(m ² .K)	315.44	303.56	315.44	297.50	315.44	315.44	307.98	169.075	428.43	763.77
T_{max}	°C	238.31	239.13	238.31	261.91	247.81	854.71	295.03	460.31	233.623	244.23