ChE445_Seminar4_Winter2020

February 4, 2020

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Multiple reactions in an ideal isothermal reactor. Reactor descriptors

Q1. Multiple reactions. The following gas-phase reactions were carried out in an isothermal PFR without pressure drop:

Rxn1). $3A \rightarrow B + C$; $\quad -r_{1A} = k_{1A}C_A$; $\;k_{1A} = 7min^{-1}$

Rxn2). $2C + A \rightarrow 3D$; $\quad r_{2D} = k_{2D}C_A^2C_C$; $k_{2D} = 10000dm^6mol^{-2}min^{-1}$

Rxn3). $4D + 3C \rightarrow 3E$; $\;r_{3E} = k_{3E}C_DC_C$; $k_{3E} = 8000dm^3mol^{-1}min^{-1}$

The total concentration of pure A entering the reactor is $0.2mol/dm^3$, and entering volumetric flow rate is $10dm^3/min$. Find reactor volume to achieve maximum yield of D. Find STY and integral reactor selectivity at the point of maximum D yield. A similar problem and its solution can be found in the online resources accompanying the book by Fogler: http://umich.edu/~elements/06chap/frames.htm (go to "Learning Resources" $\rightarrow$ "Summary Notes" $\rightarrow$ scroll down to Example C: gas phase PFR, no pressure drop).

Answer:

Mole Balance for each species in the PFR:

$$\frac{dF_A}{dV} = r_A;\;\; \frac{dF_B}{dV} = r_B;\;\; \frac{dF_C}{dV} = r_C;\;\; \frac{dF_D}{dV} = r_D;\;\; \frac{dF_E}{dV} = r_E$$

B.C.: At $V_0 = 0$, all $F_{i0} = 0$ except for $F_{A0} = C_{A0}Q_0 = 0.2 * 10 = 2mol/min$

Rate Laws:

$$r_j = \sum r_{ij}$$

Where j is the species and i is the reaction number.

$$r_A = r_{1A} + r_{2A};\quad r_B = r_{1B};\quad r_c = r_{1c} + r_{2c} + r_{3c};\quad r_D = r_{2D} + r_{3D};\quad r_E = r_{3E}$$

$$-r_{1A} = -k_{1A}C_A;\quad k_{1A} = 7min^{-1}$$

$$r_{2D} = k_{2D}C_A^2C_C;\quad k_{2D} = 10000dm^6mol^{-2}min^{-1}$$

$$r_{3E} = k_{3E}C_DC_C;\quad k_{3E} = 8000dm^3mol^{-1}min^{-1}$$

Reaction rate connections.

Rxn1).

$$\frac{r_{1A}}{-3} = \frac{r_{1B}}{+1} = \frac{r_{1C}}{+1}$$

$$r_{1B} = \frac{-r_{1A}}{3}$$

$$r_{1C} = \frac{-r_{1A}}{3}$$

Rxn2).

$$\frac{r_{2C}}{-2} = \frac{r_{2A}}{-1} = \frac{r_{2D}}{+3}$$

$$r_{2A} = -1/3 r_{2D}$$

$$r_{2C} = -2/3 r_{2D}$$

Rxn3).

$$\frac{r_{3D}}{-4} = \frac{r_{3C}}{-3} = \frac{r_{3E}}{+3}$$

$$r_{3C} = -r_{3E}$$

$$r_{3D} = -4/3 r_{3E}$$

Stoichiometry Constant T and P

$$C_A = C_{T0}\frac{F_A}{F_T}; \quad C_C = C_{T0}\frac{F_C}{F_T}; \quad C_D = C_{T0}\frac{F_D}{F_T}$$

$$C_{T0} = 0.2 mol/dm^3$$

$$F_T = F_A + F_B + F_C + F_D + F_E$$

$$\frac{dF_A}{dV} = r_{1A} + r_{2A} = -k_{1A}C_A - 1/3(k_{2D}C_A^2 C_C) = -7C_A - (10000C_A^2 C_C)/3$$

$$\frac{dF_B}{dV} = r_{1B} = k_{1A}C_A/3$$

$$\frac{dF_C}{dV} = r_{1c} + r_{2c} + r_{3c} = 1/3k_{1A}C_A - 2k_{2D}C_A^2 C_C/3 - k_{3E}C_D C_C = 7C_A/3 - 20000C_A^2 C_C/3 - 8000C_D C_C$$

$$\frac{dF_D}{dV} = r_{2D} + r_{3D} = k_{2D}C_A^2 C_C + k_{3E}C_D C_C = 10000C_A^2 C_C + 8000C_D C_C$$

$$\frac{dF_E}{dV} = r_{3E} = k_{3E}C_D C_C = 8000C_D C_C$$

Applying any ODE solver at $V = 0.664L$, $F_{Dmax} = 0.146\frac{mol}{min}$

$$STY = \frac{mol_D}{time.V_{reactor}} = \frac{0.146}{0.664} = 0.22\frac{mol}{min.L} = 13\frac{kmol_D}{m^3.h}$$

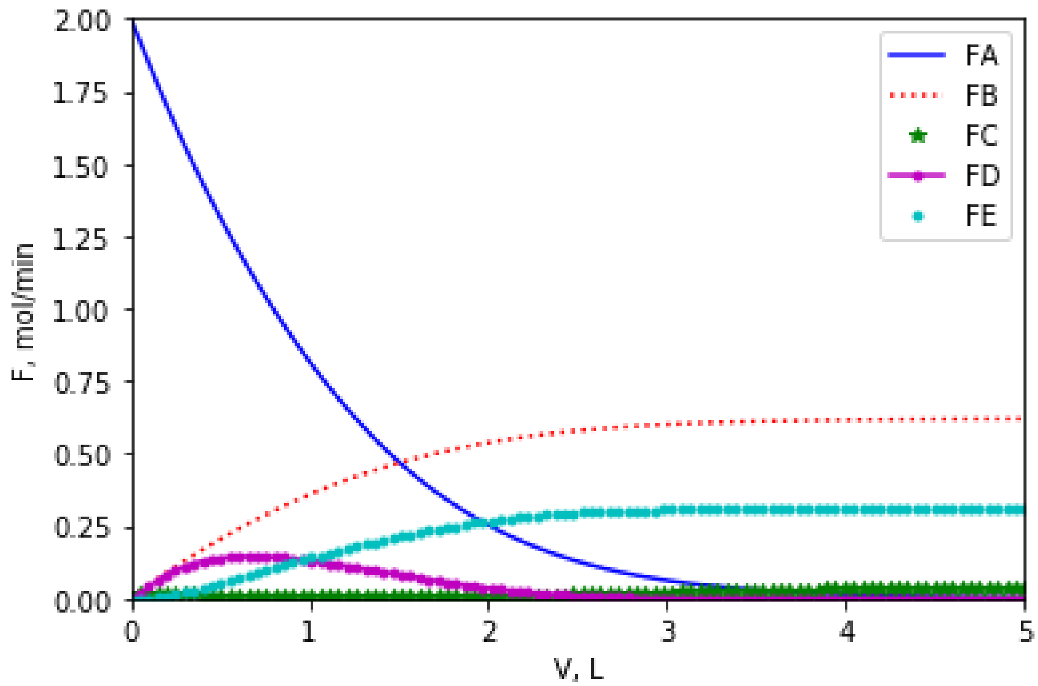
$$S_D = \frac{F_D}{F_D + F_B + F_C + F_E} = \frac{0.146}{0.146 + 0.26 + 0.01 + 0.08} = 29\%$$

All products are at the same reactor point $= 0.664$

[2]:
```python
from scipy.integrate import odeint
import matplotlib.pyplot as plt
```

```python
import numpy as np

CA0=0.2
Q0=10.
FA0=CA0*Q0 # mol/min

V=np.linspace(0.,5.,100)
FA=np.zeros(len(V))
FB=np.zeros(len(V))
FC=np.zeros(len(V))
FD=np.zeros(len(V))
FE=np.zeros(len(V))

F=[FA,FB,FC,FD,FE]

def fun(F,V):
        k1=7.
        k2=10000.
        k3=8000.
        CT0=0.2 #mol/dm^3
        FT=F[0]+F[1]+F[2]+F[3]+F[4]
        Ca=CT0*F[0]/FT
        Cc=CT0*F[2]/FT
        Cd=CT0*F[3]/FT
        dFdV= [-k1*Ca-k2*pow(Ca,2)*Cc/3., k1*Ca/3., k1*Ca/3.-2.*k2*pow(Ca,2)*Cc/
 ↪3.-k3*Cd*Cc, k2*pow(Ca,2)*Cc-4.*k3*Cd*Cc/3., k3*Cd*Cc]
        return dFdV

        #dFAdV=-k1*CA-k2*CA^2*CC/3                   #r1A+r2A
        #dFBdV=k1*CA/3                               #r1B
        #dFCdV=k1*CA/3-2*k2*CA^2*CC/3-k3*CD*CC       #r1C+r2C+r3C
        #dFDdV=k2*CA^2CC-4*k3*CD*CC/3                #r2D+r3D
        #dFEdV=k3*CD*CC                              #r3E

init_F= [FA0,0,0,0,0]
FS=odeint(fun,init_F,V)

plt.plot(V, FS[:,0], 'b-', label='FA')
plt.plot(V, FS[:,1], 'r:', label='FB')
plt.plot(V, FS[:,2], 'g*', label='FC')
plt.plot(V, FS[:,3], 'm.-', label='FD')
plt.plot(V, FS[:,4], 'c.', label='FE')

plt.xlabel('V, L')
plt.ylabel('F, mol/min')
plt.legend(loc="upper right")
plt.ylim(0, 2.0)
```

```
plt.xlim(0, 5.0)
plt.show()
```



[3]:
```
print(max(FS[:,3]))
result=np.where(FS[:,3] == np.amax(FS[:,3]))
print(result[0])
print(V[result[0]])
```

```
0.14593829696802288
[13]
[0.65656566]
```

[4]:
```
STY=max(FS[:,3])/V[result[0]] #\frac{kmol_D}{m^3.h}$
S_D=100.*FS[result[0],3]/
 ↪(FS[result[0],1]+FS[result[0],2]+FS[result[0],3]+FS[result[0],4])
print("STY=", STY*100)
print("S_D=", S_D)
#All products are at the same reactor point $= 0.664$
```

```
STY= [22.22752523]
S_D= [29.57249593]
```

Q2. Some PBR descriptors: WHSV, LHSV and GHSV.

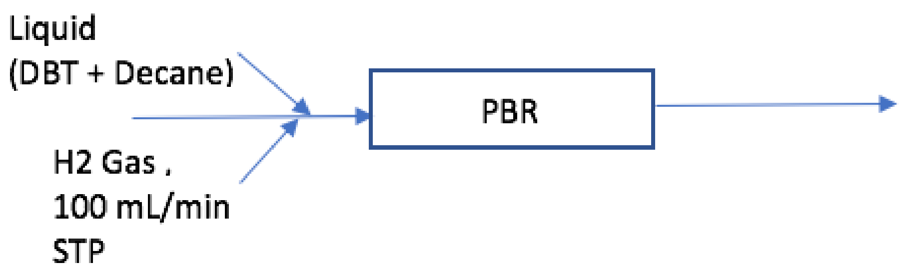
Hydrodesulfurization (HDS) of dibenzothiophene (DBT) was performed over a Co-Mo/Al2O3 catalyst $(0.09g)$ at $5.0MPa$ and 300^oC.

$0.5wt\%$ DBT solution in n-decane was fed by a pump at $0.05cc/min$. Liquid decane density is $0.73g/cc$. Hydrogen was fed at $10sccm$ (standard cubic centimeters per minute). The liquid feed is completely vaporized under the reaction conditions. The catalyst (alumina) density is $4g/cm^3$, the bed porosity is 0.2. Internal cross-sectional area of the reactor tube is $0.8cm^2$. Assume ideal gas.

a). Calculate Weight Hourly Space Velocity (WHSV).

b). Find Liquid Hourly Space Velocity(LHSV) and Gas Hourly Space Velocity(GHSV).

c). Find superficial and interstitial (true) linear velocity of hydrogen at the bed entrance



PFR.png

Liquid: $0.5wt\%$ DBT in decane.

Assume density = density of decane

a).

WHSV=LWHSV+GWHSV

$LWHSV = \frac{\dot{m}(DBT+Decane)}{W_{cat}} = \frac{0.05[ccLiq.feed.min^{-1}]*0.73[g/cc]*60}{0.09[g]} = 24.33[h^{-1}]$

Gas flow rate: $PQ = FRT$

Q=100 cm$^{3.min}${-1} at Standard Temperature & Pressure (STP)

$\dot{m}_{h_2} = \frac{100cm^3.min^{-1}*10^5Pa*60min.h^{-1}}{8.314[m^3PaK^1mol^1]*10^6[cm^3.m^{-3}]*273.15K} * 2g.mol^{-1}[MWofH2] = 0.53g/h$

$WHSV = \frac{2.19[L]+0.53[G]}{0.09[gCat]} = 30.2h^{-1}$

b).

$V_{bed} = \frac{m_{bed}}{\rho_{bed}} = \frac{m_{cat}}{\rho_{cat}(1-\Phi_{bed})} = \frac{0.09g}{4(1-0.2)} = 0.028$

$LHSV = \frac{Q_{l0}(STP)}{V_{cat.bed}} = \frac{0.05[cc.min^{-1}]*60}{0.028} = 107[h^{-1}]$ Feed from pump

$GHSV(H_2) = \frac{Q_0(STP)}{V_{cat.bed}} = \frac{100sccm*60}{0.028} = 214285.7h^{-1}$

c).

$u_s = \frac{Q_0(rxn)}{A_c}$

$Q_0(rxn) = Q_0(STP) * \frac{T(rxn)}{T(STP)} * \frac{P(STP)}{P(rxn)} = 100(sccm) * 60(min/h) * \frac{573K}{273.15}\frac{0.1MPa}{5MPa} = 252\frac{cm^3}{h}$

$u_s = \frac{252}{0.8} = 314\frac{cm}{h}$

True (interstitial velocity): $u_i = \frac{u_s}{\Phi_{bed}} = \frac{315}{0.2} = 1573\frac{cm}{h}$

[5]:
```
Ql0=0.05 #DBT+Decane cc Liq. feed.min^{-1}
Pstp = 0.1  #MPa
Tstp = 273.15 #K
Prxn = 5.0 #
```

```
Trxn = 573.15 #K
rol = 0.73 #Liquid decane density, /
w_cat = 0.09 # catalyst weight
rho_cat = 4. # catalyst (alumina) density, /^3
phi_bed =0.2
R = 8.314 #[m^3PaK^{1}mol^{1}]
MW_H2 = 2 #g.mol^{-1}, [MW of H2]
Qg0 = 100 #Vol. flow rate of Hydrogen was fed  (standard cubic centimeters per␣
↪minute, sccm)
Ac = 0.8  #Internal cross-sectional area of the reactor tube is, cm^2

LWHSV = Ql0*rol*60/w_cat #h^{-1}
GWHSV =((Qg0*1000000*Pstp*60)*MW_H2/(R*1000000*Tstp))/w_cat #=0.53 g/h$
WHSV=LWHSV+GWHSV
```

[6]:
```
WHSV
```

[6]: 30.204541943495986

[7]:
```
rho_bed=rho_cat*(1-phi_bed)
V_bed=w_cat/rho_bed

LHSV=Ql0*60/V_bed # Feed from pump, h^{-1}
GHSV=Qg0*60/V_bed #h^{-1}
```

[8]:
```
GHSV
```

[8]: 213333.33333333334

[9]:
```
Qg0rxn=Qg0*60*(Trxn/Tstp)*(Pstp/Prxn)   # cm^3/h
us=Qg0rxn/Ac
ui=us/phi_bed  #True (interstitial velocity)
```

[10]:
```
us
```

[10]: 314.74464579901155

[ ]:
```

```