

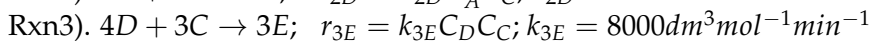
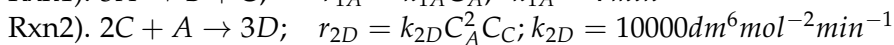
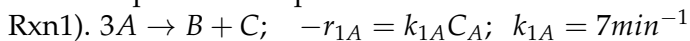
# ChE445\_Seminar4\_Winter2020

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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:



The total concentration of pure  $A$  entering the reactor is  $0.2\text{mol}/\text{dm}^3$ , and entering volumetric flow rate is  $10\text{dm}^3/\text{min}$ . 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" → "Summary Notes" → scroll down to Example C: gas phase PFR, no pressure drop).

**Answer:**

**Mole Balance** for each species in the PFR:

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

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

**Rate Laws:**

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

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

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

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

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

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

**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

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

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

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

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

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

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

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

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

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

$$STY = \frac{\text{mol}_D}{\text{time} \cdot V_{\text{reactor}}} = \frac{0.146}{0.664} = 0.22 \frac{\text{mol}}{\text{min} \cdot L} = 13 \frac{\text{kmol}_D}{\text{m}^3 \cdot h}$$

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

All products are at the same reactor point = 0.664

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

```

import numpy as np

CT0=0.2 #mol/dm3
CA0=0.2 #
Q0=10. #
FA0=CA0*Q0 # mol/min
k1=7.
k2=10000.
k3=8000.

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
    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*CA2*CC/3          #r1A+r2A
    #dFBdV=k1*CA/3                     #r1B
    #dFCdV=k1*CA/3-2*k2*CA2*CC/3-k3*CD*CC #r1C+r2C+r3C
    #dFDdV=k2*CA2*CC-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], 'b*', label='FC')
plt.plot(V, FS[:,3], 'r*', label='FD')
plt.plot(V, FS[:,4], 'b.', label='FE')

```

```
plt.xlabel('V')
plt.ylabel('mol/min')

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]
```

```
[2]: 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 $= 0.664$
```

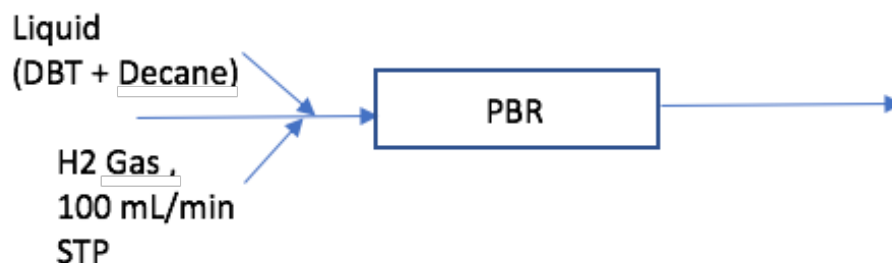
```
STY= [22.22752523]
S_D= [29.57249593]
```

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

Hydrodesulfurization (HDS) of dibenzothiophene (DBT) was performed over a Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (0.09g) at 5.0MPa and 300°C.

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 100sccm (standard cubic centimeters per minute). The liquid feed is completely vaporized under the reaction conditions. The catalyst (alumina) density is 4g/cm<sup>3</sup>, the bed porosity is 0.2. Internal cross-sectional area of the reactor tube is 0.8cm<sup>2</sup>. Assume ideal gas.

- Calculate Weight Hourly Space Velocity (WHSV).
- Find Liquid Hourly Space Velocity(LHSV) and Gas Hourly Space Velocity(GHSV).
- 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).

$$WHSV = LWSHV + GWSHV$$

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

Gas flow rate:  $PQ = FRT$

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

$$\dot{m}_{H_2} = \frac{100 \text{ cm}^3 \cdot \text{min}^{-1} * 10^5 \text{ Pa} * 60 \text{ min} \cdot \text{h}^{-1}}{8.314 [m^3 \text{ Pa K}^{-1} \text{ mol}^{-1}] * 10^6 [cm^3 \cdot m^{-3}] * 273.15 \text{ K}} * 2 \text{ g} \cdot \text{mol}^{-1} [MW \text{ of } H_2] = 0.53 \text{ g/h}$$

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

b).

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

$$LHSV = \frac{Q_{10}(STP)}{V_{cat,bed}} = \frac{0.05[cc \cdot \text{min}^{-1}] * 60}{0.028} = 107[h^{-1}] \text{ Feed from pump}$$

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

c).

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

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

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

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

```
[3]: Q10=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

LWSHV = Q10*rol*60/w_cat #h^{-1}
GWSHV = ((Qg0*1000000*Pstp*60)*MW_H2/(R*1000000*Tstp))/w_cat #=0.53 g/h$
WHSV=LWSHV+GWSHV
```

[4]: WHSV

[4]: 30.204541943495986

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

LHSV=Q10*60/V_bed # Feed from pump, h^{-1}
GHSV=Qg0*60/V_bed #h^{-1}
```

[6]: GHSV

[6]: 213333.33333333334

[7]: QgOrxn=Qg0\*60\*(Trxn/Tstp)\*(Pstp/Prxn) # cm<sup>3</sup>/h  
us=QgOrxn/Ac  
ui=us/phi\_bed #True (interstitial velocity)

[8]: us

[8]: 314.74464579901155

[ ]: