# Pyrolysis of Benzene

Diphenyl ($C_{12}H_{10}$) is an important industrial intermediate. One production scheme involves the pyrolytic dehydrogenetation of benzene ($C_6H_6$) [1]. During the process, triphenyl ($C_{18}H_{14}$) is also formed by a secondary reaction.

The reactions are as follows:

(1) $$2\,C_6H_6 \rightleftarrows C_{12}H_{10} + H_2$$

(2) $$C_6H_6 + C_{12}H_{10} \rightleftarrows C_{18}H_{14} + H_2$$

Substituting the symbolic IDs A = $C_6H_6$, B = $C_{12}H_{10}$, C = $C_{18}H_{14}$ and D = $H_2$

(3) $$2\,A \rightleftarrows B + D$$

(4) $$A + B \rightleftarrows C + D$$

Murhpy, Lamb and Watson presented some laboratory data regarding these reactions originally carried out by Kassell [2]. In these experiments, liquid benzene was vaporized, heated to the reaction temperature and fed to a plug flow reactor (PFR). The product stream is condensed and analyzed for various components. The results are tabulated in Table 1.

**Table 1 the laboratory data for P = 1 atm.**

| **Temperature (°F)** | **Flow rate (lbmole/hr)** | $y_A$ | $y_B$ | $y_C$ | $y_D$ |
|---|---|---|---|---|---|
| 1400 | 0.0682 | 0.8410 | 0.0695 | 0.00680 | 0.0830 |
| 1265 | 0.0210 | 0.8280 | 0.0737 | 0.00812 | 0.0900 |
| 1265 | 0.0105 | 0.7040 | 0.1130 | 0.02297 | 0.1590 |
| 1265 | 0.0070 | 0.6220 | 0.1322 | 0.03815 | 0.2085 |
| 1265 | 0.0053 | 0.5650 | 0.1400 | 0.05190 | 0.2440 |
| 1265 | 0.0035 | 0.4990 | 0.1468 | 0.06910 | 0.2847 |
| 1265 | 0.0030 | 0.4820 | 0.1477 | 0.07400 | 0.2960 |
| 1265 | 0.0026 | 0.4700 | 0.1477 | 0.07810 | 0.3040 |
| 1265 | 0.0007 | 0.4430 | 0.1476 | 0.08700 | 0.3220 |
| 1265 | 0.0003 | 0.4430 | 0.1476 | 0.08700 | 0.3220 |


[1] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed., p.77-79, Prentice Hall, New Jersey, 1999.

[2] G.B. Murphy, G.G. Lamb, and K.M. Watson, *Trans. Am. Inst. Chem. Engrs.*, (**34**) 429, 1938.

## Additional data

Recall A = $C_6H_6$ B = $C_{12}H_{10}$ C = $C_{18}H_{14}$ D = $H_2$

**The reactor tube dimensions:**

L = 37.5 in, D = 0.5 in

**Rate laws**

$$-r_{1A} = k_{1A}\left(p_A^2 - \frac{p_B p_D}{K_{1A}}\right)$$

$$-r_{2B} = k_{2B}\left(p_A p_B - \frac{p_C p_D}{K_{2B}}\right)$$

**Specific reaction rate constants**

$$k_{1A} = A_1 \exp(-\frac{E_1}{RT})$$

$$k_{2B} = A_2 \exp(-\frac{E_2}{RT})$$

**Equilibrium constants**

$$\ln K_{1A} = A' + \frac{B'}{T} + C' \ln(T) + D'T + E'T^2$$

$$\ln K_{2B} = A'' + \frac{B''}{T} + C'' \ln(T) + D''T + E''T^2$$

**Parameter values**

| | |
|---|---|
| $E_1$ = 30190 cal/mol | $A_1$ = 7.4652E6 lbmole/h/ft$^3$/atm$^2$ |
| $E_2$ = 30190 cal/mol | $A_2$ = 8.6630E6 lbmole/h/ft$^3$/atm$^2$ |
| A’ = -19.76 | A’’ = -28.74 |
| B’ = -1692 | B’’ = 742 |
| C’ = 3.13 | C’’ = 4.32 |
| D’ = -1.63E-3 | D’’ = -3.15E-3 |
| E’ = 1.96E-7 | E’’ = 5.08E-7 |
| P = 14.69595 psi | R = 1.987 cal/mol/K |

## Exercises

a) Follow the instructions during the lab session and use the handouts to replicate the data presented in Table 1 for T = 1400 °F and P = 1 atm using Aspen Plus™. What is the percent difference between experimental and simulated mole fractions?

b) Run Aspen Plus™ simulations for different flow rates presented in Table 1 for T = 1265 °F. Compare your results to the experimental values by preparing a graph. The mole fractions should be graphed as a smooth curve for the simulated data and as hollow circles for the experimental values. Try to fit everything on one figure.

c) Calculate the number of reactor tubes (L = 219 in and D = 0.5 in) necessary to meet a production target of 8000 lbmole/day diphenyl. Simulate this case with Aspen Plus™. (Reactor temperature is kept constant at 1400 °F)

d) A simpler approach to solve this problem would be to ignore the side-reaction that produces terphenyl. Simulate this simplified case for T = 1400 °F and P = 1 atm using Aspen Plus™. What is the percent difference between experimental and simulated mole fractions?

e) Repeat part b for the simplified version.

f) Did the number of tubes change for part c? By how many?

g) Discuss the effects of simplification. Do you recommend it?

Hint:

1) Attached is the solution of the problem in polymath. It might be useful to understand the solution. Please use Aspen Plus™ to solve it. Due to the round off errors there will be slight differences in the reported answers from Polymath and Aspen Plus™!
2) In part c, use the new dimensions for one reactor tube to come up with a flow rate that would reach 60% conversion first.
3) For questions you can use the following email address: gurmen@umich.edu

# POLYMATH Results

**Aspen Plus Workshop - Pyrolysis of Benzene** 03-06-2002, Rev5.1.225

## Calculated values of the DEQ variables

| Variable | initial value | minimal value | maximal value | final value |
|---|---|---|---|---|
| V | 0 | 0 | 0.004263 | 0.004263 |
| FA | 0.0682 | 0.0568806 | 0.0682 | 0.0568806 |
| FB | 0 | 0 | 0.0048753 | 0.0048753 |
| FC | 0 | 0 | 5.229E-04 | 5.229E-04 |
| FD | 0 | 0 | 0.0059211 | 0.0059211 |
| To | 1033 | 1033 | 1033 | 1033 |
| Po | 1 | 1 | 1 | 1 |
| T | 1033 | 1033 | 1033 | 1033 |
| P | 1 | 1 | 1 | 1 |
| Ep | 1.96E-07 | 1.96E-07 | 1.96E-07 | 1.96E-07 |
| Epp | 5.08E-07 | 5.08E-07 | 5.08E-07 | 5.08E-07 |
| E1 | 3.019E+04 | 3.019E+04 | 3.019E+04 | 3.019E+04 |
| E2 | 3.019E+04 | 3.019E+04 | 3.019E+04 | 3.019E+04 |
| Dp | -0.00163 | -0.00163 | -0.00163 | -0.00163 |
| Dpp | -0.00315 | -0.00315 | -0.00315 | -0.00315 |
| Cpp | 4.32 | 4.32 | 4.32 | 4.32 |
| App | -28.74 | -28.74 | -28.74 | -28.74 |
| Bpp | 742 | 742 | 742 | 742 |
| K2B | 0.4715116 | 0.4715116 | 0.4715116 | 0.4715116 |
| F | 0.0682 | 0.0682 | 0.0682 | 0.0682 |
| R | 1.987 | 1.987 | 1.987 | 1.987 |
| Co | 4.872E-04 | 4.872E-04 | 4.872E-04 | 4.872E-04 |
| CA | 4.872E-04 | 4.063E-04 | 4.872E-04 | 4.063E-04 |
| CB | 0 | 0 | 3.483E-05 | 3.483E-05 |
| CD | 0 | 0 | 4.23E-05 | 4.23E-05 |
| CC | 0 | 0 | 3.736E-06 | 3.736E-06 |
| pA | 1 | 0.8340269 | 1 | 0.8340269 |
| pB | 0 | 0 | 0.0714852 | 0.0714852 |
| pC | 0 | 0 | 0.0076676 | 0.0076676 |
| A1 | 7.465E+06 | 7.465E+06 | 7.465E+06 | 7.465E+06 |
| A2 | 8.663E+06 | 8.663E+06 | 8.663E+06 | 8.663E+06 |
| k1A | 3.056827 | 3.056827 | 3.056827 | 3.056827 |
| k2B | 3.547288 | 3.547288 | 3.547288 | 3.547288 |
| pD | 0 | 0 | 0.0868203 | 0.0868203 |
| Ap | -19.76 | -19.76 | -19.76 | -19.76 |
| Bp | -1692 | -1692 | -1692 | -1692 |
| Cp | 3.13 | 3.13 | 3.13 | 3.13 |
| K1A | 0.3167343 | 0.3167343 | 0.3167343 | 0.3167343 |
| r1A | -3.056827 | -3.056827 | -2.0664335 | -2.0664335 |
| r2B | 0 | -0.2064831 | 0 | -0.2064831 |
| rA | -3.056827 | -3.056827 | -2.2729167 | -2.2729167 |
| rB | 1.5284135 | 0.8267336 | 1.5284135 | 0.8267336 |
| rC | 0 | 0 | 0.2064831 | 0.2064831 |
| rD | 1.5284135 | 1.2396999 | 1.5284135 | 1.2396999 |

## ODE Report (RKF56)

Differential equations as entered by the user

[1] d(FA)/d(V) = rA
[2] d(FB)/d(V) = rB
[3] d(FC)/d(V) = rC
[4] d(FD)/d(V) = rD

Explicit equations as entered by the user

[1] To = 1033
[2] Po = 1

```
[3]  T = To
[4]  P = Po
[5]  Ep = 1.96e-7
[6]  Epp = 5.08e-7
[7]  E1 = 30190
[8]  E2 = 30190
[9]  Dp = -1.63e-3
[10]  Dpp = -3.15e-3
[11]  Cpp = 4.32
[12]  App = -28.74
[13]  Bpp = 742
[14]  K2B = exp(App + Bpp/T + Cpp*ln(T) + Dpp*T + Epp*T^2)
[15]  F = FA + FB + FC + FD
[16]  R = 1.987
[17]  Co = Po/R/To
[18]  CA = Co*(FA/F)*(P/Po)*(To/T)
[19]  CB = Co*(FB/F)*(P/Po)*(To/T)
[20]  CD = Co*(FD/F)*(P/Po)*(To/T)
[21]  CC = Co*(FC/F)*(P/Po)*(To/T)
[22]  pA = CA*R*T
[23]  pB = CB*R*T
[24]  pC = CC*R*T
[25]  A1 = 2.68e9/359
[26]  A2 = 3.11e9/359
[27]  k1A = A1*exp(-E1/R/T)
[28]  k2B = A2*exp(-E2/R/T)
[29]  pD = CD*R*T
[30]  Ap = -19.76
[31]  Bp = -1692
[32]  Cp = 3.13
[33]  K1A = exp(Ap + Bp/T + Cp*ln(T) + Dp*T + Ep*T^2)
[34]  r1A = - k1A * (pA^2 - pB*pD/K1A)
[35]  r2B = - k2B * (pA*pB - pC*pD/K2B)
[36]  rA = r1A+r2B
[37]  rB = r2B-r1A/2
[38]  rC = -r2B
[39]  rD = -r1A/2-r2B
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Comments

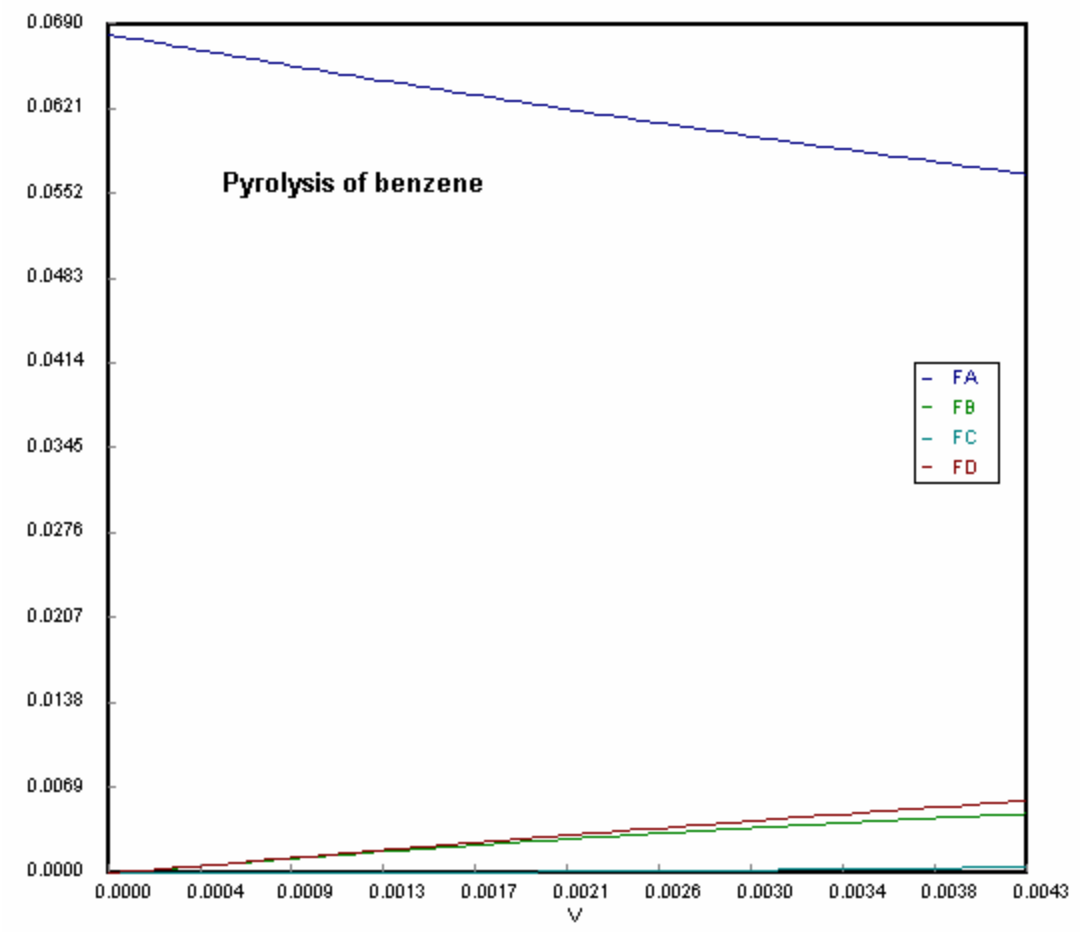
```
[1]  d(FA)/d(V) =   rA
       lbmole/h/ft^3
[2]  d(FB)/d(V) =   rB
       lbmole/h/ft^3
[3]  d(FC)/d(V) =   rC
       lbmole/h/ft^3
[4]  d(FD)/d(V) =   rD
       lbmole/h/ft^3
[5]  To =  1033
       K
[6]  Po =  1
       atm
[7]  T =  To
       K (isothermal)
[8]  P =  Po
       atm (isobaric, no pressure drop)
[11]  k1A = A1*exp(-E1/R/T)
        lbmole/h/ft^3/atm^2
[12]  k2B = A2*exp(-E2/R/T)
        lbmole/h/ft^3/atm^2
```

[13] r1A = - k1A * (pA^2 - pB*pD/K1A)
*lbmole/h/ft^3/atm^2*
[14] r2B = - k2B * (pA*pB - pC*pD/K2B)
*lbmole/h/ft^3/atm^2*
[15] rA = r1A+r2B
*lbmole/h/ft^3/atm^2*
[16] rB = r2B-r1A/2
*lbmole/h/ft^3/atm^2*
[17] rC = -r2B
*lbmole/h/ft^3/atm^2*
[18] rD = -r1A/2-r2B
*lbmole/h/ft^3/atm^2*
[19] F = FA + FB + FC + FD
*lbmole/h (Total molar flow rate)*
[20] Co = Po/R/To
*lbmole/ft^3*
[21] CA = Co*(FA/F)*(P/Po)*(To/T)
*lbmole/ft^3*
[22] CB = Co*(FB/F)*(P/Po)*(To/T)
*lbmole/ft^3*
[23] CD = Co*(FD/F)*(P/Po)*(To/T)
*lbmole/ft^3*
[24] CC = Co*(FC/F)*(P/Po)*(To/T)
*lbmole/ft^3*
[25] pA = CA*R*T
*atm*
[26] pB = CB*R*T
*atm*
[27] pC = CC*R*T
*atm*
[28] pD = CD*R*T
*atm*
[29] A1 = 2.68e9/359
*lbmole/h/ft^3/atm^2*
[30] A2 = 3.11e9/359
*lbmole/h/ft^3/atm^2*
[31] E1 = 30190
*cal/gmole*
[32] E2 = 30190
*cal/gmole*
[33] R = 1.987
*cal/gmole/K*
[34] Ap = -19.76
*for the 1st equilibrium constant*
[39] App = -28.74
*for the 2nd equilibrium constant*

Independent variable
variable name : V
initial value : 0
final value : 0.004263

Precision
Step size guess. h = 0.000001
Truncation error tolerance. eps = 0.000001

General
number of differential equations: 4
number of explicit equations: 39


Pyrolysis of benzene
0.0690
0.0621
0.0552
0.0483
0.0414
0.0345
0.0276
0.0207
0.0138
0.0069
0.0000
0.0000
0.0004
0.0009
0.0013
0.0017
0.0021
0.0026
0.0030
0.0034
0.0038
0.0043
V
FA
FB
FC
FD