4.3 ADIABATIC OPERATION OF A TUBULAR REACTOR FOR CRACKING OF ACETONE

4.3.1 Concepts Demonstrated

Calculation of the conversion and temperature profiles in an adiabatic tubular reactor.

4.3.2 Numerical Methods Utilized

Solution of simultaneous ordinary differential equations.

4.3.3 Excel Options and Functions Demonstrated

Use of POLYAMATH and the POLYMATH ODE Solver Add-In for Excel to solve differential equations.

4.3.4 Problem Definition

The irreversible, vapor-phase cracking of acetone (A) to ketene (B) and methane (C) that is given by the reaction

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4$$

is carried out adiabatically in a tubular reactor. The reaction is first order with respect to acetone and the specific reaction rate can be expressed by

$$\ln k = 34.34 - \frac{34222}{T} \quad \textbf{(4-26)}$$

where k is in s^{-1} and T is in K. The acetone feed flow rate to the reactor is 8000 kg/hr, the inlet temperature is $T = 1150$ K and the reactor operates at the constant pressure of $P = 162$ kPa (1.6 atm). The volume of the reactor is 4 m^3.

4.3.5 Equations and Numerical Data

The material balance equations for the plug-flow reactor are given by

$$\frac{dF_A}{dV} = r_A \quad \textbf{(4-27)}$$

$$\frac{dF_B}{dV} = -r_A \quad \textbf{(4-28)}$$

$$\frac{dF_C}{dt} = -r_A \quad \textbf{(4-29)}$$

where F_A, F_B and F_C are flow rates of acetone, ketene and methane in g-mol/s, respectively and r_A is the reaction rate of A in g-mol/$m^3 \cdot$s. The reaction is first order with respect to acetone, thus

$$r_A = -kC_A \tag{4-30}$$

where C_A is the concentration of acetone in g-mol/m^3. For a gas phase reactor, using the appropriate units of the gas constant, the concentration of the acetone in g-mil/m^3 is obtained by

$$C_A = \frac{1000 y_A P}{8.31 T} \tag{4-31}$$

The mole fractions of the various components are given by

$$y_A = \frac{F_A}{F_A + F_B + F_C} \qquad y_B = \frac{F_B}{F_A + F_B + F_C} \qquad y_C = \frac{F_C}{F_A + F_B + F_C} \tag{4-32}$$

The conversion of acetone can be calculated from

$$x_A = \frac{F_{A0} - F_A}{F_{A0}} \tag{4-33}$$

An enthalpy (energy) balance on a differential volume of the reactor yields

$$\frac{dT}{dV} = \frac{-r_A(-\Delta H)}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \tag{4-34}$$

where ΔH is the heat of the reaction at temperature T (in J/g-mol) and C_{pA}, C_{pB} and C_{pC} are the molar heat capacities of acetone, ketene and methane (in J/g-mol·K). Fogler[3] provides the following equations for calculating the heat of reaction and the molar heat capacities.

$$\Delta H = 80770 + 6.8(T - 298) - 0.00575(T^2 - 298^2) - 1.27 \times 10^{-6}(T^3 - 298^3) \tag{4-35}$$

$$C_{pA} = 26.6 + 0.183T - 45.86 \times 10^{-6} T^2 \tag{4-36}$$

$$C_{pB} = 20.04 + 0.0945T - 30.95 \times 10^{-6} T^2 \tag{4-37}$$

$$C_{pC} = 13.39 + 0.077T - 18.71 \times 10^{-6} T^2 \tag{4-38}$$

(a) Calculate the flow-rates (in g-mol/s) and the mole fractions of acetone, ketene and methane along the reactor. Use POLYMATH to calculate and plot the conversion and reactor temperature (in K) versus volume.

(b) The conversion in the reactor in part (a) is very low in adiabatic operation because the reactor content cools down very quickly. It is suggested that feeding nitrogen along with the acetone might be beneficial in maintaining a higher temperature. Modify the POLYMATH equation set to enable adding nitrogen to the feed, transfer the equations to Excel and compare the final conversions and temperatures for the cases where 28.3, 18.3, 8.3, 3.3 and 0.0 g-mol/s nitrogen is fed into the reactor (the total molar feed rate is 38.3 g-mol/s in all the cases).

4.3.6 Solution(Partial)

The POLYMATH ordinary differential equations solver is used for solving this problem. Equations (4-26) to (4-38) and other needed equations can be entered into POLYMATH without any significant changes. Note that these equations can be entered in any order as they will be ordered during the problem solution. The feed flow rate to the reactor F_{A0} has to be specified in units of g-mol/s. The molecular weight of acetone (58 g/g-mol) is used for this conversion. The complete POLYMATH problem is summarized in Table 4–8.

Table 4–8 Equation Input to the POLYMATH Ordinary Differential Equation Solver - File **P4-03A.POL**

Line	Equation, # Comment
1	d(FA)/d(V) = rA # Differential mass balance on acetone
2	d(FB)/d(V) = -rA # Differential mass balance on ketene
3	d(FC)/d(V) = -rA # Differential mass balance on methane
4	d(T)/d(V) = (-deltaH) * (-rA) / (FA * CpA + FB * CpB + FC * CpC) # Differential enthalpy balance
5	XA = (FA0 - FA) / FA0 # Conversion of acetone
6	rA = -k * CA # Reaction rate in mol/m3-s
7	P = 162 # Pressure kPa
8	FA0 = 38.3 # Feed rate of acetone in mol/s
9	CA = yA * P * 1000 / (8.31 * T) # Concentration of acetone in mol/m3
10	yA = FA / (FA + FB + FC) # Mole fraction of acetone
11	yB = FB / (FA + FB + FC) # Mole fraction of ketene
12	yC = FC / (FA + FB + FC) # Mole fraction of methane
13	k = 8.2E14 * exp(-34222 / T) # Reaction rate constant in s-1
14	deltaH = 80770 + 6.8 * (T - 298) - .00575 * (T ^ 2 - 298 ^ 2) - 1.27e-6 * (T ^ 3 - 298 ^ 3)
15	CpA = 26.6 + .183 * T - 45.86e-6 * T ^ 2
16	CpB = 20.04 + 0.0945 * T - 30.95e-6 * T ^ 2
17	CpC = 13.39 + 0.077 * T - 18.71e-6 * T ^ 2
18	FB(0) = 0 # Feed rate of ketene in mol/s
19	FA(0) = 38.3 # Feed rate of acetone in mol/s
20	FC(0) = 0 # Feed rate of methane in mol/s
21	T(0) = 1035 # Inlet reactor temperature in K
22	V(0) = 0 # Reactor volume in m3
23	V(f) = 4

The POLYMATH solution that is summarized in Table 4–9 indicates that the inlet temperature of 1035 K is reduced to 907.54 K within the reactor as the reaction is endothermic. Consequently the specific reaction rate, k, and the reaction rate with respect to acetone, $-r_A$, are reduced by more that two orders of magnitude. This results in a low conversion of the acetone, only 15.7%.

Table 4–9 POLYMATH Results for Problem 4.3 (a)

	Variable	Initial value	Minimal value	Maximal value	Final value
1	CA	18.83535	12.68959	18.83535	12.68959
2	CpA	166.8786	154.9084	166.8786	154.9084
3	CpB	84.69309	80.3113	84.69309	80.3113
4	CpC	73.04238	67.86058	73.04238	67.86058
5	deltaH	7.876E+04	7.876E+04	7.977E+04	7.977E+04
6	FA	38.3	28.44647	38.3	28.44647
7	FA0	38.3	38.3	38.3	38.3
8	FB	0	0	9.853527	9.853527
9	FC	0	0	9.853527	9.853527
10	k	3.580818	0.0344545	3.580818	0.0344545
11	P	162.	162.	162.	162.
12	rA	-67.44594	-67.44594	-0.4372133	-0.4372133
13	T	1035.	907.5422	1035.	907.5422
14	V	0	0	4.	4.
15	xA	0	0	0.2572723	0.2572723
16	yA	1.	0.5907454	1.	0.5907454
17	yB	0	0	0.2046273	0.2046273
18	yC	0	0	0.2046273	0.2046273

(b) The addition of the inert gas nitrogen to the reactor feed requires the addition of an equation for heat capacity of nitrogen and modification to the energy balance.

$$C_{pN} = 6.25 + 0.00878\,T - 2.1\times10^{-8}\,T^2 \qquad \textbf{(4-39)}$$

$$\frac{dT}{dV} = \frac{-r_A(-\Delta H)}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC} + F_N C_{pN}} \qquad \textbf{(4-40)}$$

It is also necessary to add an equation that allows the molar flow rate of nitrogen, F_N, to be calculated when the feed rate of acetone, F_{A0}, is specified.

$$F_N = 38.3 - F_{A0} \qquad \textbf{(4-41)}$$

Additionally the equations for the mole fractions need to be modified to include the molar flow rate of nitrogen. Also the initial condition on the differential equation for F_{A0} must be specified with the current initial condition. The modified POLYMATH program for F_{A0} = 10 kg-mol/s shown in Figure 4–18 can be automatically exported to Excel with either pressing the F4 key or clicking the mouse on the Excel icon from the Differential Equation Solver window.

```
Differential Equations: 4 | Auxiliary Equations: 15 | ✓ Ready for solution

d(FA)/d(V) = rA # Differential mass balance on acetone
d(FB)/d(V) = -rA # Differential mass balance on ketene
d(FC)/d(V) = -rA # Differential mass balance on methane
d(T)/d(V) = (-deltaH) * (-rA) / (FA * CpA + FB * CpB + FC * CpC + FN * CpN) # Differential enthalpy balance
XA = (FA0-FA)/FA0 # Conversion of acetone
rA = -k * CA # Reaction rate in kg-mole/m3-s
FA0 = 10 # Feed rate of acetone in kg-mol/s
FN = 38.3 - FA0 # Feed rate of nitrogen in kg-mol/s
P = 162 # Pressure kPa
CA = yA * P * 1000 / (8.31 * T) # Concentration of acetone in k-mol/m3
yA = FA / (FA + FB + FC + FN) # Mole fraction of acetone
yB = FB / (FA + FB + FC + FN) # Mole fraction of ketene
yC = FC / (FA + FB + FC + FN) # Mole fraction of methane
k = 8.2E14 * exp(-34222 / T) # Reaction rate constant in s-1
deltaH = 80770 + 6.8 * (T - 298) - .00575 * (T ^ 2 - 298 ^ 2) - 1.27e-6 * (T ^ 3 - 298 ^ 3)# Heat of reaction in J/mol-K
CpA = 26.6 + .183 * T - 45.86e-6 * T ^ 2 # Heat capacity of acetone in J/mol-K
CpB = 20.04 + 0.0945 * T - 30.95e-6 * T ^ 2 # Heat capacity of ketene in J/mol-K
CpC = 13.39 + 0.077 * T - 18.71e-6 * T ^ 2 # Heat capacity of methane in J/mol-K
CpN = 6.25 + 8.78e-3 * T - 2.1e-8 * T ^ 2 # Heat capacity of nitrogen in J/mol-K
FB(0) = 0 # Feed rate of ketene in kg-mol/s
FA(0) = 10 # Feed rate of acetone in kg-mol/s
FC(0) = 0 # Feed rate of methane in kg-mol/s
T(0) = 1035 # Inlet reactor temperature in K
V(0) = 0 # Reactor volume in m3
V(f) = 4
```

Figure 4–18 The Revised POLYMATH Program Ready for Export to Excel - File **P4-03A.**

The revised Excel worksheet as automatically generated from the POLYMATH program is shown in Figure 4–19.

	A	B	C	D	E	F
1	**POLYMATH DEQ Migration Document**					
2		**Variable**	**Value**		***Polymath Equation***	***Comments***
3	Explicit Eqs	XA	0		*XA=(FA0-FA)/FA0*	*Conversion of acetone*
4		rA	-17.60990721		*rA=-k * CA*	*Reaction rate in kg-mole/*
5		FA0	10		*FA0=10*	*Feed rate of acetone in kg*
6		FN	28.3		*FN=38.3 - FA0*	*Feed rate of nitrogen in kg*
7		P	162		*P=162*	*Pressure kPa*
8		CA	4.917845344		*CA=yA * P * 1000 / (8.31 * T)*	*Concentration of acetone*
9		yA	0.261096606		*yA=FA / (FA + FB + FC + FN)*	*Mole fraction of acetone*
10		yB	0		*yB=FB / (FA + FB + FC + FN)*	*Mole fraction of ketene*
11		yC	0		*yC=FC / (FA + FB + FC + FN)*	*Mole fraction of methane*
12		k	3.580817609		*k=8.2E14 * exp(-34222 / T)*	*Reaction rate constant in*
13		deltaH	78758.21631		*deltaH=80770 + 6.8 * (T - 298) - .00575 * (T ^ 2 - 29*	*Heat of reaction in J/mol-*
14		CpA	166.8786215		*CpA=26.6 + .183 * T - 45.86e-6 * T ^ 2*	*Heat capacity of acetone*
15		CpB	84.69308625		*CpB=20.04 + 0.0945 * T - 30.95e-6 * T ^ 2*	*Heat capacity of ketene ir*
16		CpC	73.04238025		*CpC=13.39 + 0.077 * T - 18.71e-6 * T ^ 2*	*Heat capacity of methane*
17		CpN	15.31480428		*CpN=6.25 + 8.78e-3 * T - 2.1e-8 * T ^ 2*	*Heat capacity of nitrogen*
18	Integration Vars	FA	**10**		*FA(0)=10*	*Differential mass balance*
19		FB	**0**		*FB(0)=0*	*Differential mass balance*
20		FC	**0**		*FC(0)=0*	*Differential mass balance*
21		T	**1035**		*T(0)=1035*	*Differential enthalpy balan*
22	ODE Eqs	d(FA)/d(V)	**-17.60990721**		*d(FA)/d(V) = rA*	
23		d(FB)/d(V)	**17.60990721**		*d(FB)/d(V) = -rA*	
24		d(FC)/d(V)	**17.60990721**		*d(FC)/d(V) = -rA*	
25		d(T)/d(V)	**-659.7507676**		*d(T)/d(V) = (-deltaH) * (-rA) / (FA * CpA + FB * CpB + FC * CpC + FN * CpN)*	
26	Indep Var	V	**0**		*V(0)=0 ; V(f)=4*	

Figure 4–19 Generated Excel Problem as Exported from POLYMATH - File **P4-03B.XL**

The Excel version of this problem separates the set of equations and data into four categories (see column A in Figure 4–19). Rows 3 to 17 contain explicit algebraic equations and constants. The initial values for the variables that are defined by differential equations are included in rows 18 to 21. The differential equations are defined in rows 22 to 25, and the initial value for the independent variable is specified in row 26.

The names of the variables are shown in column B, and the Excel formulas of the equations are included in column C. Column E presents the equations as they were entered into POLYMATH. The POLYMATH comments are also copied into column F. It should be emphasized that only the formulas in column C are used for calculations.

The POLYMATH ODE_Solver Add-In is used for solving the equations. It can be found in the "Tools" dropdown menu. Before using the ODE solver it should be checked that in the list of Add-Ins the "Ode_Solver" is marked as active and the "Solver Add-In" is not marked (non-active) as the two Add-Ins may interfere with each other in some versions of Excel.

Selection of the POLYMATH ODE from the "Tools" menu brings up the communication box shown in Figure 4–20. Pressing the "Reload" button will automatically enter the problem into the ODE_Solver communication box. Otherwise, the ranges of the cells of the initial values and the differential equations must be entered as well as the address of the cell that contains the initial value of the independent variable and the final value (numerical) of the independent variable. Checking of the "Show Report" will place the solution output in a new worksheet. The "Intermediate Cells to Store" will output the vector of specified cells during the numerical integration.

When "Solve" is clicked, the POLYMATH ODE_Solver will start changing the independent variable value until it reaches its final value. During this process the values of the problem variables will be calculated and updated. At the

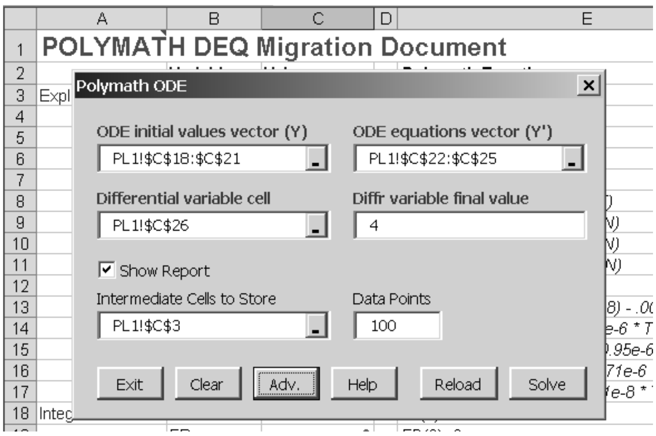

Figure 4–20 POLYMATH ODE_Solver Add-In Communication Box

18	Integration Vars	FA	6.864475993	FA(0)=10	Differential mass balance (
19		FB	3.135524007	FB(0)=0	Differential mass balance (
20		FC	3.135524007	FC(0)=0	Differential mass balance (
21		T	911.8567009	T(0)=1035	Differential enthalpy balanc
22	ODE Eqs	d(FA)/d(V)	-0.145866418	d(FA)/d(V) = rA	
23		d(FB)/d(V)	0.145866418	d(FB)/d(V) = -rA	
24		d(FC)/d(V)	0.145866418	d(FC)/d(V) = -rA	
25		d(T)/d(V)	-6.011513678	d(T)/d(V) = (-deltaH) * (-rA) / (FA * CpA + FB * CpB + FC * CpC + FN * CpN)	
26	Indep Var	V	4	V(0)=0 ; V(f)=4	

Figure 4–21 Final Values of Some of the Variables (Feed Flow Rate of Nitrogen is 28.3 g-mol/s)

end of the integration, the final values of the problem variables will be displayed. Some of those values for this problem are shown in Figure 4–21.

The "Show Report" option in the ODE solver communication box (see Figure 4–20) automatically creates a new worksheet that includes the table of initial, minimal, maximal and final values of the integration variables. Additionally a table of the values of the problem variables versus the independent variable is generated for the integration range. The number of data points displayed in the table of the detailed results is the number shown in the "Data Points" field of the communication box. If there is a need to include additional variables in the report, their cell range must be specified in the "Intermediate Cells to Store" field. In this case the value of x_A is of interest, so cell C3 was added to the list of variables to be stored.

The resulting "Report", automatically created on a new worksheet and partially shown in Figure 4–22, provides the initial, maximal, minimal and final values of V (cell C26 from the problem worksheet), F_A, F_B, F_C and T (cells C18, C19, C20 and C21) and x_A (cell C3). Note that the names of the variables are not normally displayed as they are not essential components of the problem definition in Excel, but they have been added to the spreadsheet for clarity.

	A	B	C	D	E	F	G
1	**POLYMATH Report DEQ**						
2	Ordinary Differential Equations (RKF45).						
3							
4	**Calculated values of DEQ variables**						
5		Variable	Initial	Minimal	Maximal	Final	
6	1	C26 or V	0	0	4	4	
7	2	C18 or FA	10	6.864476	10	6.864476	
8	3	C19 or FB	0	0	3.135524	3.135524	
9	4	C20 or FC	0	0	3.135524	3.135524	
10	5	C21 or T	1035	911.8567	1035	911.8567	
11	6	C3 or xA	0	0	0.313552	0.313552	

Figure 4–22 Partial View of DEQ Report Worksheet for F_{A0} = 10

A comparison of the results when pure acetone is fed to the reactor (Table 4–9) with the case when 10 g-mol/s acetone and 28.3 mol/s of nitrogen are fed into the reactor (Figure 4–22) shows that the addition of the nitrogen increases the conversion from x_A = 0.257 to x_A = 0.314. However, this increase comes at the

27	Intermediate data points						
28		t	FA	FB	FC	T	xA
29	1	0	10	0	0	1035	0
30	2	0.083061	9.186783	0.813217	0.813217	1004.17	0.077327
31	3	0.134176	8.934929	1.065071	1.065071	994.4717	0.102389
32	4	0.181147	8.76353	1.23647	1.23647	987.8297	0.119473
33	5	0.209688	8.677067	1.322933	1.322933	984.4662	0.128097
34	6	0.241688	8.591675	1.408325	1.408325	981.1358	0.136688
35	7	0.305688	8.447931	1.552069	1.552069	975.51	0.151889
36	8	0.337688	8.386281	1.613719	1.613719	973.0897	0.158358
37	9	0.369688	8.329929	1.670071	1.670071	970.8734	0.164247
38	10	0.401688	8.278062	1.721938	1.721938	968.8301	0.16965
39	11	0.465688	8.185344	1.814656	1.814656	965.1694	0.179268
40	12	0.497688	8.143562	1.856438	1.856438	963.5164	0.183588

Figure 4–23 Partial View of DEQ Report Worksheet Showing Intermediate Data Points for FA0 = 10 - File **P4-03B.XLS**

expense of almost fourfold reduction of the flow rates of the reactant and the products.

The tabular results of the Excel "Report" are shown in Figure 4–23 where variables have been entered to replace cell addresses in line 28 for clarity. This Excel table can be used to prepare temperature and conversion profile plots for the reactor (see Figures 4–24 and 4–25). It can be seen that even with the addition of the nitrogen the main part of the reaction is carried out in the first quarter (1 m^3 volume) of the reactor where the conversion reaches x_A = 0.23. In the additional 75% of the volume the conversion only increases to x_A = 0.314.

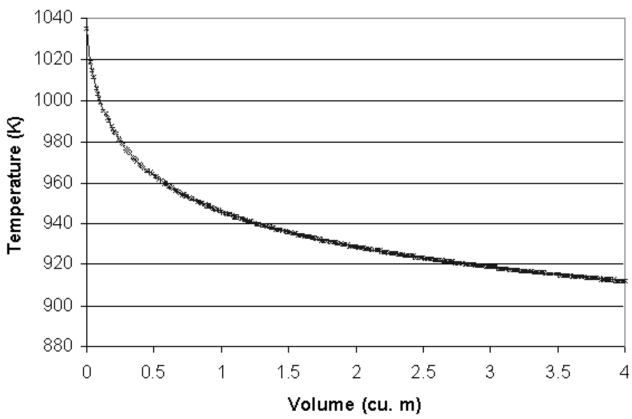

Figure 4–24 Temperature Profile in the Reactor for F_N = 28.3 g-mol/s - File **P4-03B.XLS**

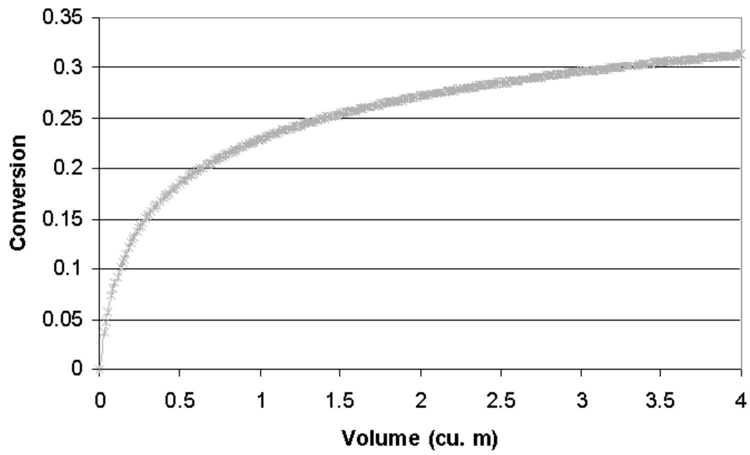

Figure 4–25 Conversion Profile in the Reactor for $F_N = 28.3$ g-mol/s - File **P4-03B.XLS**

The problem solution files are found in directory CHAPTER 4 and designated **P4-03A.POL**, **P4-03B.POL**, and **P4-03B.XLS**.