Appendix

I. Flowsheet & Pinch Analysis

A. Original Process: Heating and Cooling Duties

HEATING DUTIES

Heaters	ΔH [kW]	TIN [°C]	TOUT [°C]
Furnace	696.6	129	450
E31	43.1	40	75
QREB,1	95	130	130
QREB,2	286.5	150.4	150.4
QREB,3	2832	249.4	249.4
TOTAL	**3953.2**		

COOLING DUTIES

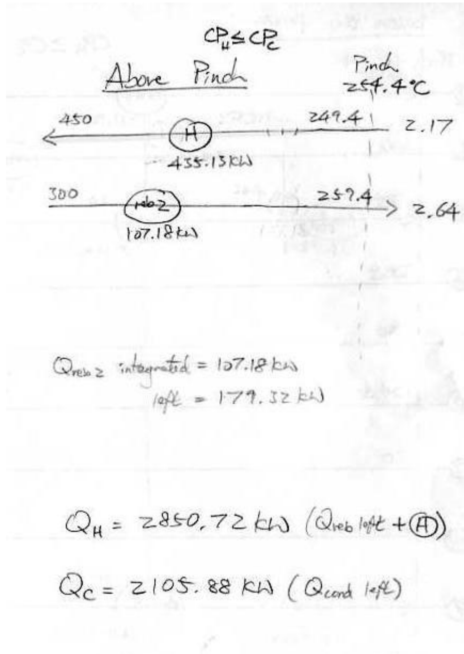
Coolers	ΔH [kW]	TIN [°C]	TOUT [°C]
E21	686.4	300	40
E32	57.4	129.9	80
E12	26.4	249.3	25
E9	336.2	183.2	80
E6	22.6	104.5	70
E4	2.2	35.5	25
E8	2	70	35
EE	29.4	80	25
QCOND,1	35.7	35.5	35.5
QCOND,2	186.8	104.5	104.5
QCOND,3	2552.7	183.2	183.2
TOTAL	**3937.8**		

B. Heat Cascade

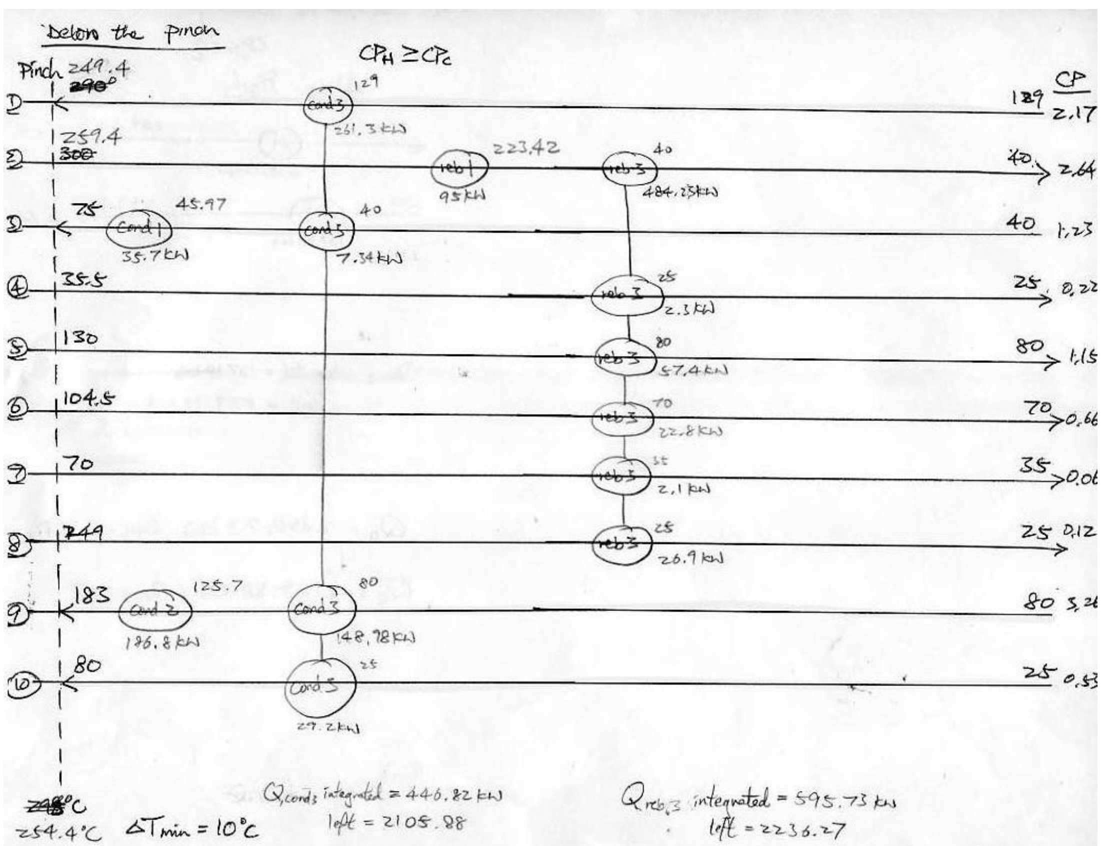
INTERVAL	TEMPERATURE [°C]	Ti+1-Ti [°C]	∑CP [kW/°C]	ΔH [kW]	S/D	CASCADE		
	455					↓	3160.12	$Q_{H,MIN}$ [kW]
1		160	-2.17	-347.2	D	-347.2		
	295					↓	2812.92	
2		40.6	0.47	19.08	S	19.08		
	254.4					↓	2832	
3		REB,3	--	-2832	D	-2832		
	254.4					↓	**0**	**PINCH**
4		10.4	0.47	4.89	S	4.89		
	244					↓	4.89	
5		56	0.59	33.04	S	33.04		
	188					↓	37.93	
6		9.8	-2.61	-25.58	D	-25.58		
	178.2					↓	12.35	
7		COND,3	--	2552.7	S	2552.7		
	178.2					↓	2565.05	
8		22.8	-2.61	-59.51	D	-59.51		
	155.4					↓	2505.54	
9		REB,2	--	-286.5	D	-286.5		
	155.4					↓	2219.04	
10		20.4	-2.61	-53.24	D	-53.24		
	135					↓	2165.8	
11		REB,1	--	-95	D	-95		
	135					↓	2070.8	
12		1	-2.61	-2.61	D	-2.61		
	134					↓	2068.19	
13		9	-0.44	-3.96	D	-3.96		
	125					↓	2064.23	
14		25.45	0.71	18.11	S	18.11		
	99.5					↓	2082.34	
15		COND,2	--	186.8	S	186.8		
	99.5					↓	2269.14	
16		14.5	1.37	19.87	S	19.87		
	85					↓	2289.01	
17		5	4.04	20.2	S	20.2		
	80					↓	2309.21	
18		5	2.81	14.05	S	14.05		
	75					↓	2323.26	
19		10	1.66	16.6	S	16.6		
	65					↓	2339.86	
20		20	1.06	21.2	S	21.2		
	45					↓	2361.06	
21		10	2.29	22.9	S	22.9		
	35					↓	2383.96	
22		4.5	-0.35	-1.575	D	-1.575		
	30.5					↓	2382.385	
23		COND,1	--	35.7	S	35.7		
	30.5					↓	2418.085	
24		0.5	-0.13	-0.065	D	-0.065		
	30					↓	2418.02	
25		10	0.34	3.4	S	3.4		
	20						2421.42	$Q_{C,MIN}$ [kW]

C. Process Network

1. Above Pinch

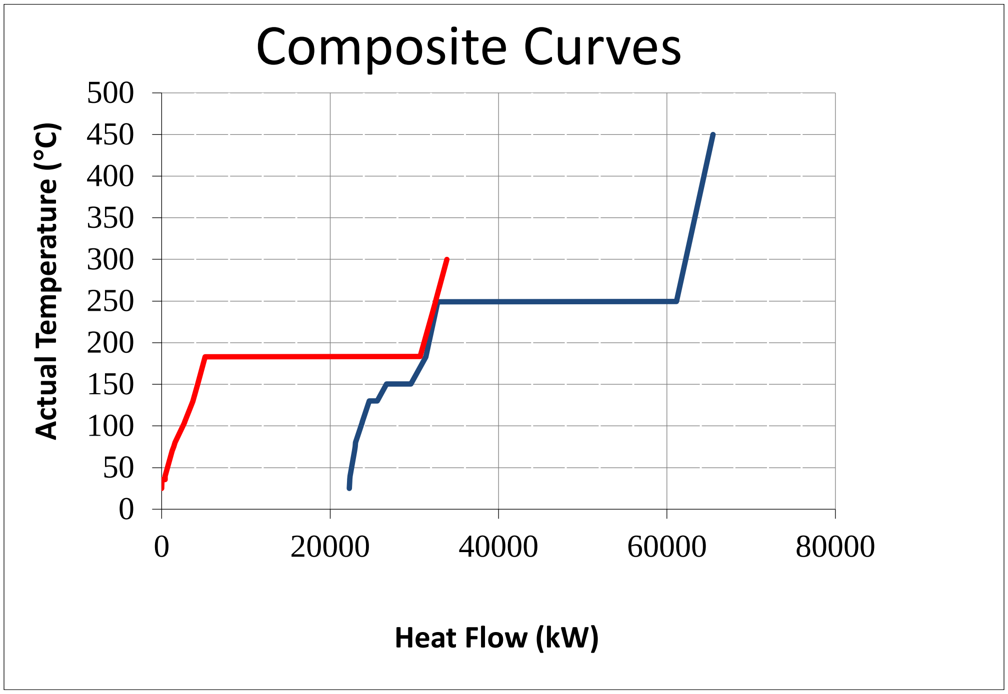


2. Below Pinch

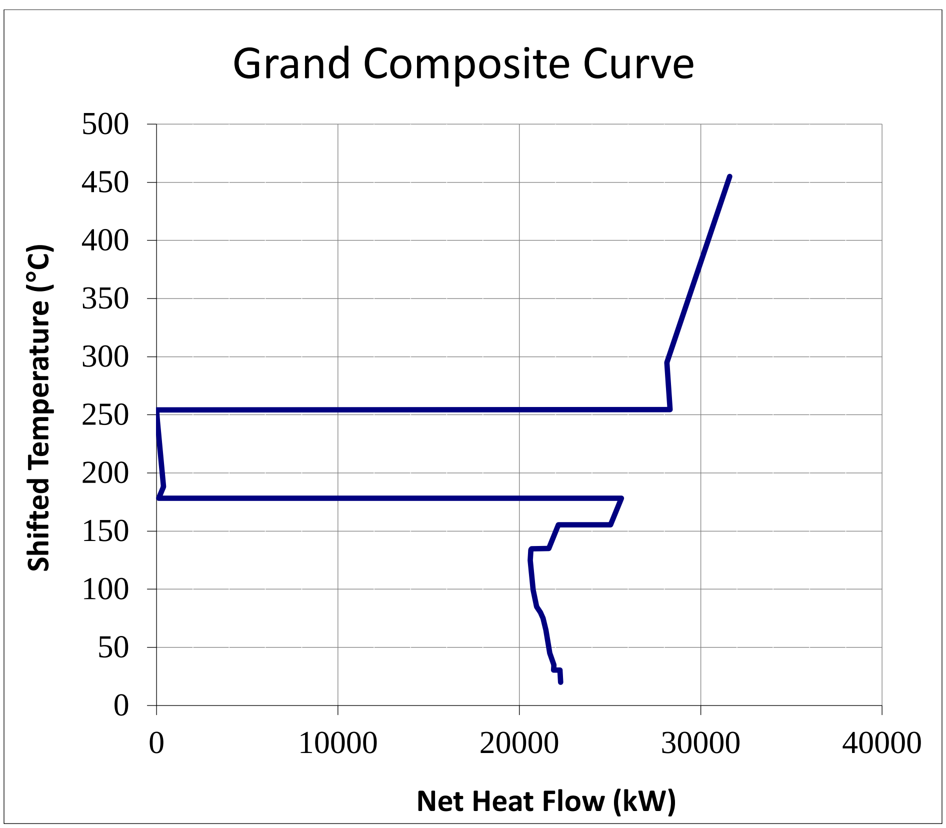


D. Composite Curves & Steam Generation

1. Hot and Cold Composite Curves



2. Grand Composite Curve



3. Steam Generation

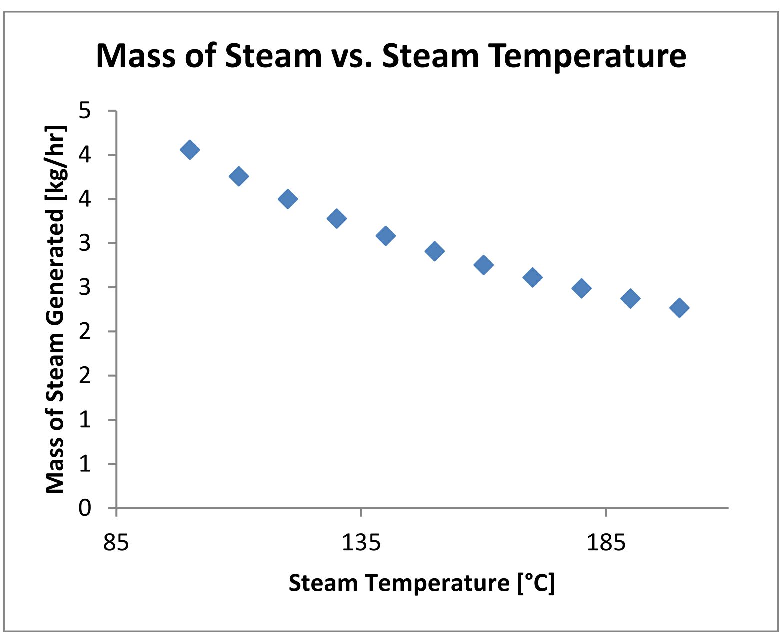
The amount of steam that was able to be generated from the process was calculated using the waste heat from the process below the pinch. Since the maximum amount of heat generated was 22281 kW, this would be the amount of heat available to generate steam. The amount of steam generated is related to the waste heat by the equation: $Q = m_1 \Delta H_{vap} + m_2 C_p \Delta T$, where Q is the heat from the process, m_1 is the mass of steam that can be generated, ΔH_{vap} is the heat of vaporization, C_p is the specific heat capacity, m_2 is the mass of water that is not steam, and ΔT is the temperature change of the leftover water.

Excel's Solver function was used in order to maximize the mass of water using the amount of heat available. The following table shows the results for different temperatures. A resulting graph was also made to show the amount of steam that can be generated at different temperatures.

$Q=m_1H_{lat}+m_2C_p(T-Ts)$

T_2=	**25**	**°C**

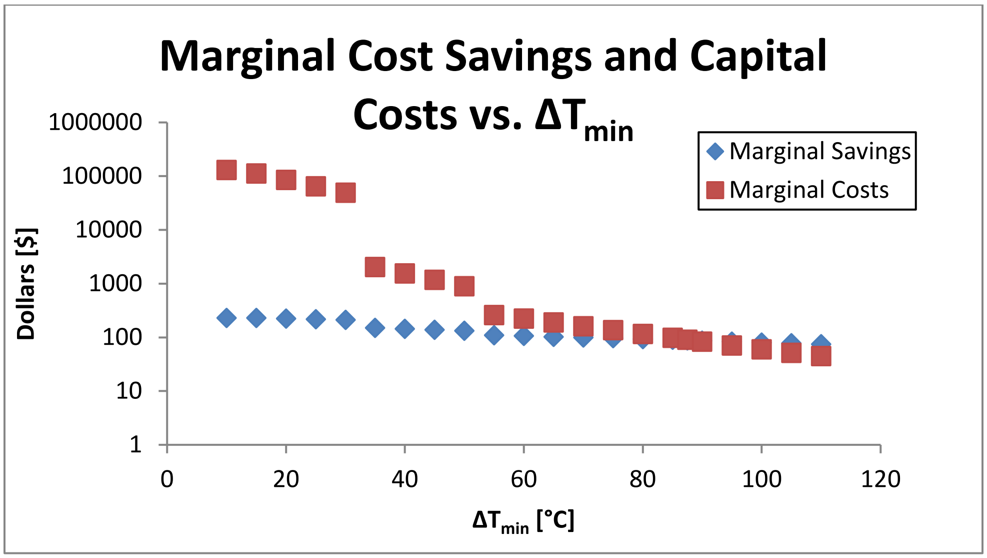
m_1 [kg/hr]	m_2 [kg/hr]	T [°C]	Q [kW]
1	1	100	5498.95
2	2	100	10997.9
4	4	100	21995.8
4.04	4.06	100	22281
3.76	3.76	110	22281
3.50	3.50	120	22281
3.28	3.28	130	22281
3.08	3.08	140	22281
2.91	2.91	150	22281
2.75	2.75	160	22281
2.61	2.61	170	22281
2.49	2.49	180	22281
2.37	2.37	190	22281
2.27	2.27	200	22281



E. Parameters for Cost Analysis

Efficiency of Coal Power Plants [%]	30%
1 kW·hr/yr	4.37 metric tons Coal
Coal Cost per ton	$60.00
1 Ton Coal	1.83 Tons of CO_2 Emissions

F. Marginal Cost Savings for ΔT_{min}



II. Reactor Design

A. Equations and Derivations

1. CSTR Equations

$$C_{mx,0} - C_{mx} = -\frac{dC_{mx}}{d\tau} \cdot \tau = -\tau\left(-k_1 C_{mx} - k_3 {C_{mx}}^2\right)$$

$$C_{px,0} - C_{px} = -\frac{dC_{px}}{d\tau} \cdot \tau = -\tau\left(k_1 C_{mx} - k_2 C_{px}\right)$$

$$C_{ox,0} - C_{ox} = -\frac{dC_{ox}}{d\tau} \cdot \tau = -\tau\left(k_2 C_{px}\right)$$

$$C_{d,0} - C_d = -\frac{dC_d}{d\tau} \cdot \tau = -\tau\left(k_3 {C_{mx}}^2\right)$$

2. CSTR in Series

$$C_{mx,2} - C_{mx} = 2\tau\left(-k_1 C_{mx} - k_3 {C_{mx}}^2\right)$$
$$C_{px,2} - C_{px} = 2\tau\left(k_1 C_{mx} - k_2 C_{px}\right)$$
$$C_{ox,2} - C_{ox} = 2\tau\left(k_2 C_{px}\right)$$
$$C_{d,2} - C_d = 2\tau\left(k_3 {C_{mx}}^2\right)$$

3. PFTR Equations

$$\frac{dC_{mx}}{dt} = -k_1 C_{mx} - k_3 {C_{mx}}^2$$
$$\frac{dC_{px}}{dt} = k_1 C_{mx} - k_2 C_{px}$$
$$\frac{dC_{ox}}{dt} = k_2 C_{px}$$
$$\frac{dC_d}{dt} = k_3 {C_{mx}}^2$$

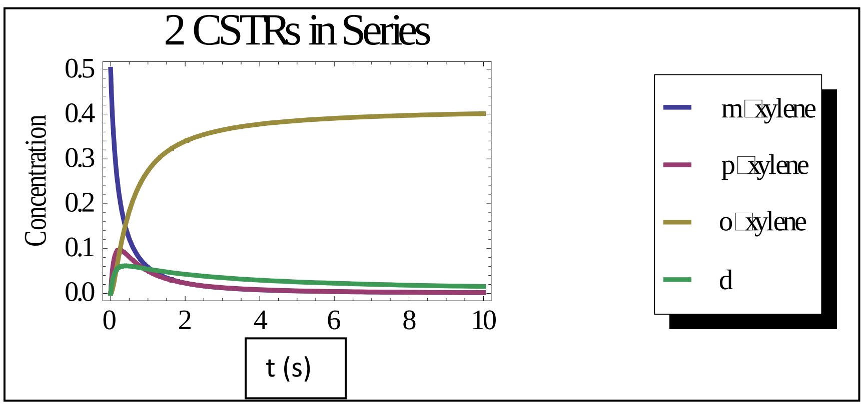
a. Initial Conditions

$$C_{mx}[t = 0] = 0.5\ mol/L$$
$$C_{px}[t = 0] = 0\ mol/L$$
$$C_{ox}[t = 0] = 0\ mol/L$$
$$C_d[t = 0] = 0\ mol/L$$

B. Reactor Systems Results

The following graphs and tables show the concentration profiles, optimal residence times, optimal volumes, and concentrations for the given optimal residence times for the less desirable reactor systems.

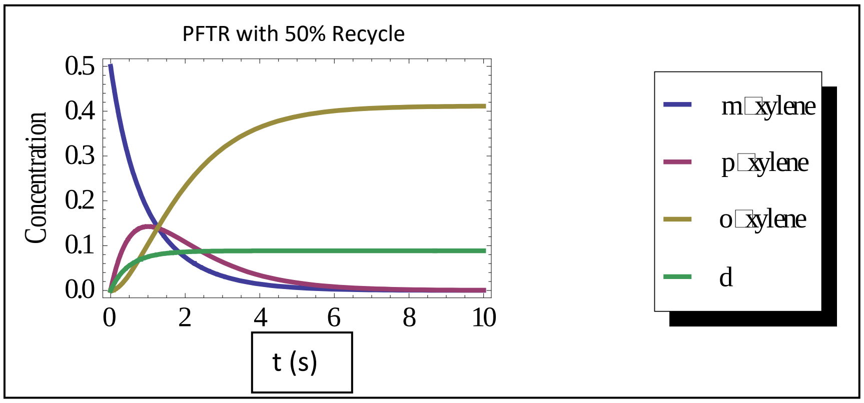
1. Two CSTRs in Series



2 CSTRs in Series

$\tau_{OPTIMAL}$ [s]	0.238
F [L/s]	1
$V_{OPTIMAL}$ [L]	0.238
$C_{p\text{-}xylene}$ [mol/L]	0.097
$C_{m\text{-}xylene}$ [mol/L]	0.215
$C_{o\text{-}xylene}$ [mol/L]	0.092
C_d [mol/L]	0.059

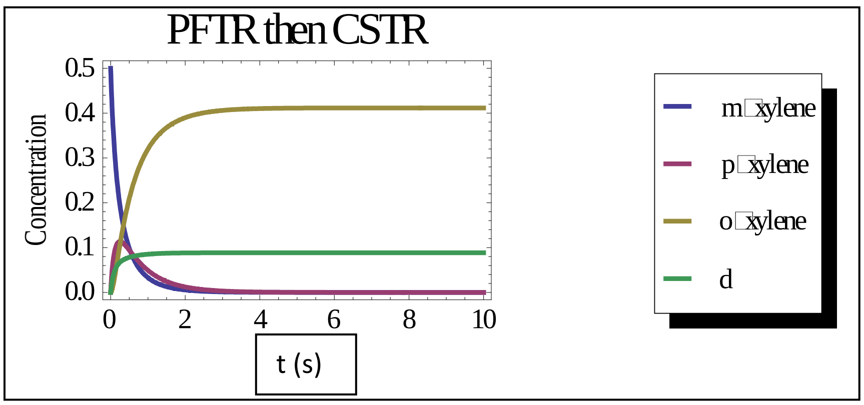
2. PFTR with 50% Recycle Stream



PFTR with 50% Recycle

$\tau_{OPTIMAL}$ [s]	1.007
F [L/s]	1
$V_{OPTIMAL}$ [L]	1.007
$C_{p\text{-xylene}}$ [mol/L]	0.143
$C_{m\text{-xylene}}$ [mol/L]	0.178
$C_{o\text{-xylene}}$ [mol/L]	0.104
C_d [mol/L]	0.075

3. PFTR and CSTR in Series



PFTR then CSTR in Series

$\tau_{OPTIMAL}$ [s]	0.250
F [L/s]	1
$V_{OPTIMAL}$ [L]	0.250
$C_{p\text{-xylene}}$ [mol/L]	0.113
$C_{m\text{-xylene}}$ [mol/L]	0.194
$C_{o\text{-xylene}}$ [mol/L]	0.107
C_d [mol/L]	0.067

C. Mathematica Code

The following sections show the Mathematica codes written to calculate and graph the concentration profiles and optimal residence times for each of the reactor systems.

1. Single CSTR

```
"SINGLE CSTR";

Clear[k1,k2,k3,Cao]
Solve[Ca-Cao==t*(-k1*Ca-k3*Ca^2),Ca]
Solve[Cb==t*(Ca-k2*Cb),Cb]
Solve[Cc==t*k2*Cb,Cc]
Solve[Cd==t*k3*Ca^2,Cd]
```

$\{\{Ca \to \frac{-1-\sqrt{1+4 Ca0 k3 t}}{2 k3 t}\},\{Ca \to \frac{-1+\sqrt{1+4 Ca0 k3 t}}{2 k3 t}\}\}\{\{Cb\to(Ca*t)/(1+k2*t)\}\}$

$\{\{Cc\to Cb*k2*t\}\}$

$\{\{Cd\to Ca^2*k3*t\}\}$

```
k1=1.2;
k2=1.5;
k3=1.1;
Cao=0.5;
```

```
CaCSTR[t_]= -1/(2*k3*t) - Sqrt[1+4Ca0*k3*t]/(2*k3*t) ;
CbCSTR[t_]=(t*CaCSTR[t])/(1+k2*t);
CcCSTR[t_]=CbCSTR[t]*k2*t;
CdCSTR[t_]=(CaCSTR[t]^2)*k3*t;


Needs["PlotLegends`"];

Plot[{CaCSTR[t],CbCSTR[t],CcCSTR[t],
CdCSTR[t]},{t,0,10},PlotRange→All,PlotLegend→{"m-xylene", "p-xylene",
"o-xylene", "d"}, LegendPosition→{1.1,-0.4}, Frame→True,
PlotStyle→{Thick}, PlotLabel→Style["Single
CSTR",16],FrameLabel→{"τ","Concentration"}]

"Single CSTR Information"
"p-xylene"FindMaximum[CbCSTR[t],{t,0.1}]
"m-xylene" CaCSTR[0.737584]
"o-xylene" CcCSTR[0.737584]
"d" CdCSTR[0.737584]

{0.0841698 p-xylene,{p-xylene (t□0.737584)}}
0.24037 m-xylene
0.0931235 o-xylene
0.0468777 d
```

2. CSTRs in Series

```
Solve[Ca2-Ca== 2*t*(-k1*Ca2-k3*Ca2^2),Ca2]
Solve[Cb2-Cb==2* t*(Ca2-k2*Cb2),Cb2]
Solve[Cc2-Cc==2* t*k2*Cb2,Cc2]
Solve[Cd2-Cd== 2*t*k3*Ca2^2,Cd2]
```

$$\left\{\left\{\mathrm{Ca2} \to \frac{-1-2\mathrm{k1}t-\sqrt{8\mathrm{Ca0k3}t+(1+2\mathrm{k1}t)^2}}{4\mathrm{k3}t}\right\},\left\{\mathbf{Ca2} \to \frac{-1-2\mathrm{k1}t+\sqrt{8\mathrm{Ca0k3}t+(1+2\mathrm{k1}t)^2}}{4\mathrm{k3}t}\right\}\right\}$$

$$\left\{\left\{\mathrm{Cb2} \to \frac{\mathrm{Cb0}+2\mathrm{Ca2}t}{1+2\mathrm{k2}t}\right\}\right\}$$

$$\{\{\mathrm{Cc2} \to \mathrm{Cc0}+2\mathrm{Cb2k2}t\}\}$$

$$\{\{\mathrm{Cd2} \to \mathrm{Cd0}+2\mathrm{Ca2}^2\mathrm{k3}t\}\}$$

```
CaCSTRseries[t_]=Ca2[t] - 2Ca2[t] * k1 * t - 2Ca2[t]^2 * k3 * t;
CbCSTRseries[t_]=(CbCSTR[t]+2*CaCSTRseries[t]*t)/(1+2*k2*t);
CcCSTRseries[t_]=2*t*k2*CbCSTRseries[t]+CcCSTR[t];
CdCSTRseries[t_]=CdCSTR[t]+2*k3*t*CaCSTRseries[t]^2;

Needs["PlotLegends`"];

Plot[{CaCSTRseries[t],CbCSTRseries[t],CcCSTRseries[t],CdCSTRseries[t]},
{t,0,10}, PlotRange→All, PlotLegend→{"m-xylene", "p-xylene", "o-
xylene", "d"}, LegendPosition→{1.1,-0.4}, Frame→True,
PlotStyle→{Thick}, PlotLabel→Style["2 CSTRs in
Series",16],FrameLabel→{"t","Concentration"}]

"p-xylene"FindMaximum[CbCSTRseries[t],{t,0.1}]
"m-xylene" CaCSTRseries[0.23795964192427874`]
```

```
"o-xylene" CcCSTRseries[0.23795964192427874`]
"d" CdCSTRseries[0.23795964192427874`]

{0.0968018 p-xylene,{p-xylene (t→0.23796)}}
0.215132 m-xylene
0.091778 o-xylene
0.0585727 d
```

3. Single PFTR

```
"SINGLE PFTR";
ClearAll["Global`"]
k1=1.2;
k2=1.5;
k3=1.1;

Solution1=NDSolve[{Ca'[t]==-k1*Ca[t]-k3*Ca[t]^2, Ca[0]==0.5}, Ca,
{t,0,20}];
CaPFTR[t_]=Ca[t]/.Flatten[Solution1];

Solution2=NDSolve[{Cb'[t]==k1*CaPFTR[t]-k2*Cb[t],Cb[0]==0}, Cb,
{t,0,20}];
CbPFTR[t_]=Cb[t]/.Flatten[Solution2];

Solution5=NDSolve[{Cc'[t]== k2*CbPFTR[t], Cc[0]== 0},Cc,{t,0,20}];
CcPFTR[t_]=Cc[t]/.Flatten[Solution5];

Solution4=NDSolve[{Cd'[t]==k3*CaPFTR[t]^2, Cd[0]==0}, Cd, {t,0,20}];
CdPFTR[t_]=Cd[t]/.Flatten[Solution4];

Needs["PlotLegends`"];

Plot[{CaPFTR[t],CbPFTR[t],CcPFTR[t],CdPFTR[t]}, {t,0,10},
PlotLegend→{"m-xylene", "p-xylene", "o-xylene", "d"},
LegendPosition→{1.1,-0.4}, PlotRange→All,Frame□True,
PlotStyle→{Thick}, PlotLabel→Style["Single
PFTR",16],FrameLabel→{"t","Concentration"}]

FindMaximum[CbPFTR[t],{t,0}]
"m-xylene" CaPFTR[0.6712070200182012`]
"o-xylene" CcPFTR[0.6712070200182012`]
"d" CdPFTR[0.6712070200182012`]

{0.142602,{t→0.671207}}
0.178254 m-xylene
0.103886 o-xylene
0.0752573 d
```

4. PFTR with Recycle

```
"PFTR with Recycle"
ClearAll["Global`"]
k1=1.2;
k2=1.5;
k3=1.1;
R=0.5;
```

```
Solution1=NDSolve[{Ca'[t] == (-k1*Ca[t]-k3*Ca[t]^2)/(1+R), Ca[0] ==0.5},
Ca, {t,0,20}];
CaPFTR[t_]=Ca[t]/.Flatten[Solution1];

Solution2=NDSolve[{Cb'[t] == (k1*CaPFTR[t]-k2*Cb[t])/(1+R),Cb[0] ==0},
Cb, {t,0,20}];
CbPFTR[t_]=Cb[t]/.Flatten[Solution2];

Solution5=NDSolve[{Cc'[t] == (k2*CbPFTR[t])/(1+R), Cc[0] ==
0},Cc,{t,0,20}];
CcPFTR[t_]=Cc[t]/.Flatten[Solution5];

Solution4=NDSolve[{Cd'[t] == (k3*CaPFTR[t]^2)/(1+R), Cd[0] ==0}, Cd,
{t,0,20}];
CdPFTR[t_]=Cd[t]/.Flatten[Solution4];

Needs["PlotLegends`"];

Plot[{CaPFTR[t],CbPFTR[t],CcPFTR[t],CdPFTR[t]}, {t,0,10},
PlotLegend→{"m-xylene", "p-xylene", "o-xylene", "d"},
LegendPosition→{1.1,-0.4}, PlotRange→All,Frame→True,
PlotStyle→{Thick}, PlotLabel→Style["PFTR with 50%
Recycle",16],FrameLabel→{"t","Concentration"}]

FindMaximum[CbPFTR[t],{t,0}]
"m-xylene" CaPFTR[1.0068105301519739`]
"o-xylene" CcPFTR[1.0068105301519739`]
"d" CdPFTR[1.0068105301519739`]

{0.142602,{t→1.00681}}
0.178254 m-xylene
0.103886 o-xylene
0.0752573 d
```

5. PFTR then CSTR

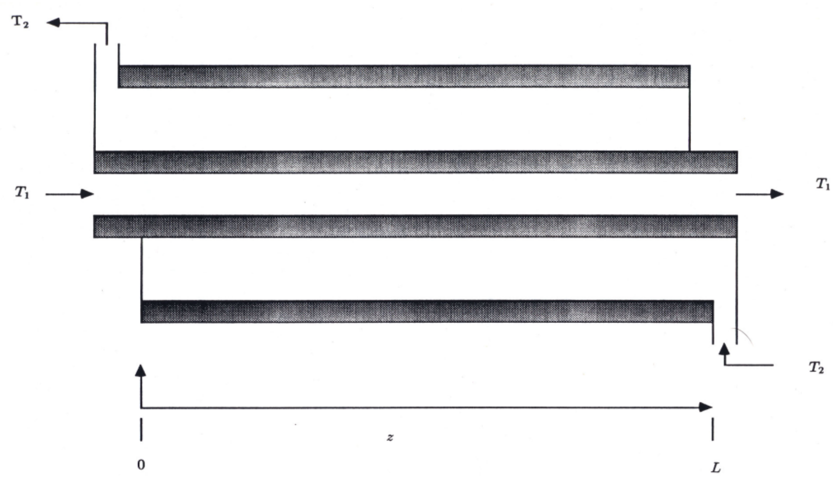
```
"PFTR then CSTR";
ClearAll["Global`"]

k1=1.2;
k2=1.5;
k3=1.1;
Cao=0.5;

Solution1=NDSolve[{Ca'[t] ==-k1*Ca[t]-k3*Ca[t]^2, Ca[0] ==0.5}, Ca,
{t,0,20}];
CaPFTR[t_]=Ca[t]/.Flatten[Solution1];
Plot[CaPFTR[t], {t,0,20}, PlotRange→All];

Solution2=NDSolve[{Cb'[t] ==k1*CaPFTR[t]-k2*Cb[t],Cb[0] ==0}, Cb,
{t,0,20}];
CbPFTR[t_]=Cb[t]/.Flatten[Solution2];
"Plot[CbPFTR[t],{t,0,20}, PlotRange□All]";

Solution3=NDSolve[{Cc'[t] == k2*CbPFTR[t], Cc[0] == 0},Cc,{t,0,20}];
CcPFTR[t_]=Cc[t]/.Flatten[Solution3];
```

```
Solution4=NDSolve[{Cd'[t] ==k3*CaPFTR[t]^2, Cd[0] ==0}, Cd, {t,0,20}];
CdPFTR[t_]=Cd[t]/.Flatten[Solution4];
Plot[CdPFTR[t],{t,0,20},PlotRange→All];

Needs["PlotLegends`"];

Plot[{Ca2[t],Cb2[t],Cc2[t],
Cd2[t]},{t,0,10},PlotRange→All,PlotLegend→{"m-xylene", "p-xylene", "o-
xylene", "d"}, LegendPosition→{1.1,-0.4}, Frame→True,
PlotStyle→{Thick}, PlotLabel→Style["PFTR then
CSTR",16],FrameLabel→{"t","Concentration"}]

FindMaximum[Cb2[t],{t,0,0.1}]
"m-xylene" Ca2[0.250464]
"o-xylene" Cc2[0.250464]
"d" Cd2[0.250464]

{0.11303,{t→0.250464}}
0.193716 m-xylene
0.106646 o-xylene
0.0672002 d
```

III. Heat Exchanger Dynamics

A. Shell and Tube Heat Exchanger Schematic

The following figure shows the schematic of a shell and tube heat exchanger with a counter current stream. The equation shows the equations used for the numerical solution.



Heat Exchanger Schematic with Natural Variables

$$T1_{i,j+1} = \left(1 - \frac{vl}{m} - \Phi_1 lv\right) T1_{i,j} + \frac{vl}{m} T1_{i-1,j} + \Phi_1 lv * T2_{i,j+1}$$

The following tables show the data and parameters that was input to the Excel program for the numerical solution.

Input Data		
Stream		
$T_{i, in}$	80.00	°C
C_v (heat capacity)	2	
G	2	kg/
v (velocity)	1.5	m/s
Disturbance	0	°C
Length of Disturbance	0	t
$T_{2, in}$	322.5	°C
Exchanger		
U	0.7	
S	1	
L	3.048	meters

Parameters	
Exact/Numerical Integration	
H_{hot}= (U*S*L)/($C_{p2}G_2$)	0.53
L	3.048
v (velocity)	1.5000
l (time step)	0.0100
m (z step)	0.0500
vl/m	0.3000
H_{hot}/L	0.1750
Φ=(H_{hot}/L)*l*v	0.0026

Toluene disproportionation flowsheet

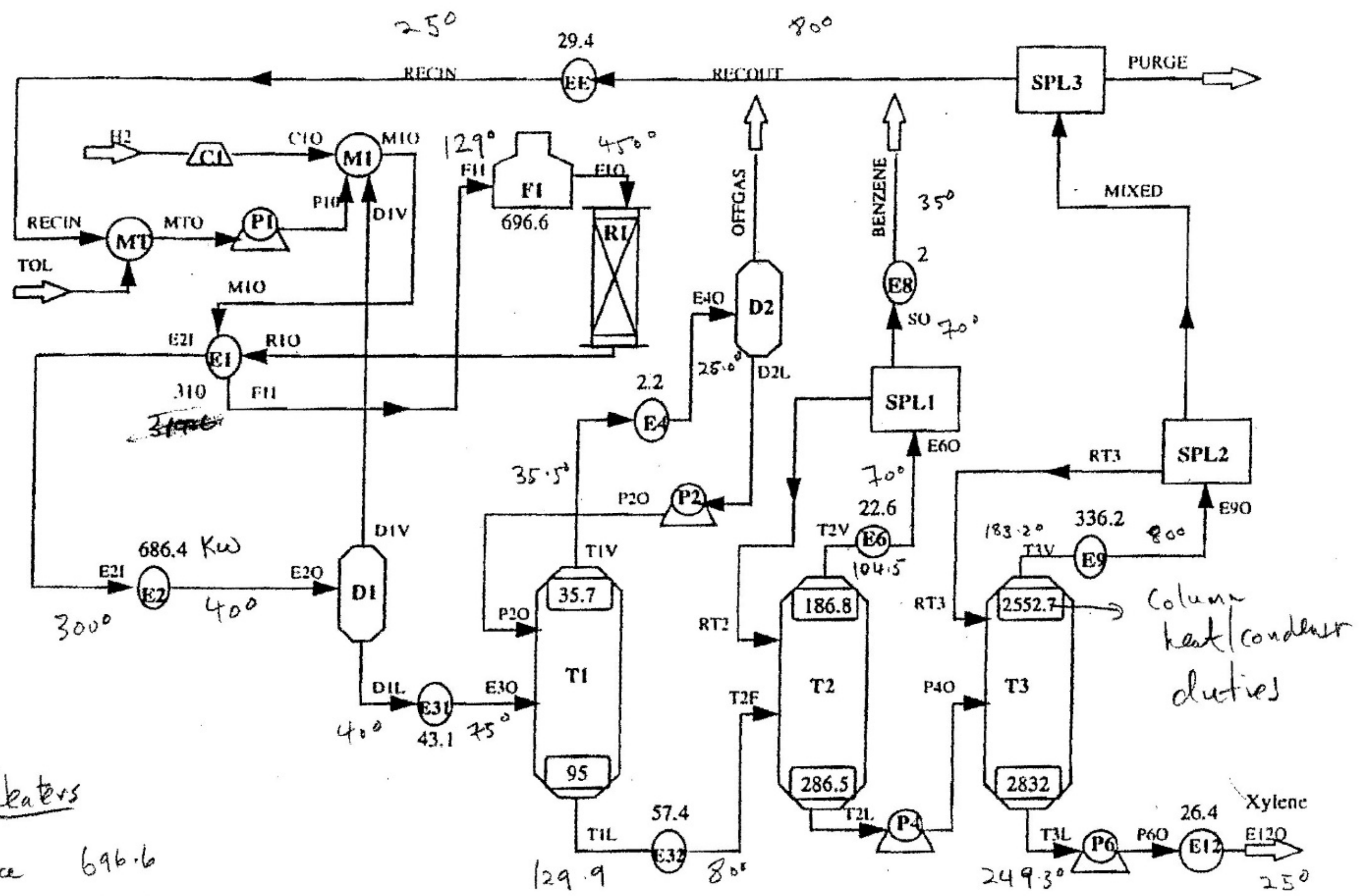


Figure 1
Process Flowsheet before Heat Integration

Heaters

urnace	696.6
E31	43.1
$Q_{reb,1}$	95
$Q_{reb,2}$	286.5
$Q_{reb,3}$	2832
	3953.2

Coolers

E21	686.4
E32	57.4
E12	26.4
E9	336.2
E6	22.6
E4	2.2
E8	2
EE	29.4

$Q_{cond,1} = 35.7$

$Q_{cond,2} = 186.8$

$Q_{cond,3} = 2552.7$

3937.8

Toluene Disproportionation.

Design Flowsheet Data.

Flowrate (kmol/hr)	H2	TOL	MTO	M10	F11	F10	R10	E21	E20	DIV	DIL
Toulene	0	10.9	16.16	17.07	17.07	17.07	9.35	9.35	9.35	0.92	8.43
Benzene	0	0	3.42	4.24	4.24	4.24	8.10	8.10	8.10	0.82	7.28
Xylene	0	0	3.32	3.45	3.45	3.45	7.31	7.31	7.31	0.12	7.18
Hydrogen	2.00	0	0	82.00	82.00	82.00	82.00	82.00	82.00	80.00	2.00
Total Flow	2.00	10.90	22.90	106.76	106.76	106.76	106.76	106.76	106.76	81.86	24.90
Temp (C)	25.0	25.0	25.0	35.5	129.0	450.0	450.0	300.0	40.0	40.0	40.0
Pres (bar)	1.0	1.0	1.0	10.0	10.0	35.0	35.0	35.0	10.0	10.0	10.0
Enthalpy (kW)	0.0	36.4	78.0	116.5	431.1	1127.7	1128.5	813.9	127.4	33.6	94.2
Flowrate (kmol/hr)	**E30**	**T1V**	**E40**	**Offgas**	**D2L**	**T1L**	**T2F**	**T2V**	**E60**	**SO**	**BEN-ZENE**
Toluene	8.43	0	0	0	0	8.43	8.43	0	0	0	0
Benzene	7.28	0.50	0.50	0.22	0.28	7.06	7.06	2.34	2.34	1.58	1.58
Xylene	7.18	0	0	0	0	7.18	7.18	0	0	0	0
Hydrogen	2.00	2.00	2.00	2.00	0	0	0	0	0	0	0
Total Flow	24.90	2.50	2.50	2.22	0.28	22.68	22.68	2.34	2.34	1.58	1.58
Temp (C)	75.0	35.5	25.0	20.0	20.0	129.9	80.0	104.5	70.0	70.0	35.0
Pres (bar)	1.5	1.0	1.0	1.0	1.0	2.0	0.5	2.0	2.0	2.0	1.0
Enthalpy (kW)	137.3	11.8	9.5	5	3.7	188.6	131.2	58.6	36	24.2	22.1
Flowrate (kmol/hr)	**RT2**	**T2L**	**T3L**	**E120**	**T3V**	**E90**	**RT3**	**Mixed**	**Purge**	**Rec-out**	**Recin**
Toulene	0	8.43	0	0	10.81	10.81	2.38	8.43	3.17	5.26	5.26
Benzene	0.77	5.48	0	0	7.03	7.03	1.55	5.48	2.06	3.42	3.42
Xylene	0	7.18	1.86	1.86	6.83	6.83	1.5	5.33	2.01	3.32	3.32
Hydrogen	0	0	0	0	0	0	0	0	0	0	0
Total Flow	0.77	21.10	1.86	1.86	24.68	24.68	5.43	19.24	7.24	12.00	12.00
Temp (C)	70.0	150.3	249.3	25.0	183.2	80.0	80.0	80.0	80.0	80.0	25.0
Pres (bar)	2.0	3.0	1.0	1.0	5.0	2.0	2.0	2.0	2.0	2.0	1.0
Enthalpy (kW)	11.8	184.2	13.6	-12.8	482.3	146.0	32.2	113.9	42.9	71.0	41.6

Table 1
Mass and Energy Balances