Combining HAZOP with Dynamic Process Model Development for Safety Analysis

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The Needs

- Process hazards analysis is an essential part of the process design activity. In the US OSHA (Occupational Health and Safety Administration) regulations require that major chemical plants perform process hazards analysis on a regular basis.

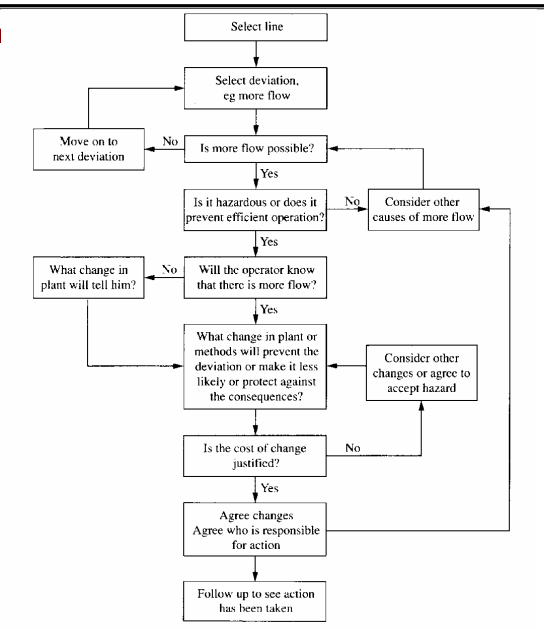
- HAZOP (Hazard and Operability Analysis) is a widely used procedure for process hazards analysis. It is carried out by a multidisciplinary team of experts in a *qualitative* manner.

- HAZOP is often followed by a detailed hazard analysis (HAZAN) where the *probability* for the occurrence of catastrophic events is evaluated.

The Needs

- HAZOP and HAZAN cannot provide *quantitative* answers regarding the *magnitude* of the deviations that will lead to severe consequences, nor the *time it takes* to reach a "no return" stage of an accident after the deviation has occurred, or the *action* that can be taken in order *to prevent* the accident.
- Dynamic simulation in emergency conditions can provide quantitative assessment of the consequences of abnormal operating conditions.
- HAZAN and Dynamic Simulation are compatible as both require *division of the process into small sections*.

A Typical Flow Diagram of a HAZOP (Kletz, 1999)



Operability Analysis for Part of an Olefin Dimerization Unit (Lawley, 1974)

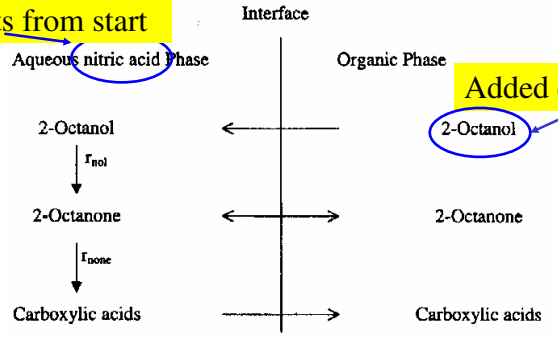
Guide Word	Deviation	Possible Causes	Consequences	Action Required
NONE	No flow	(1) No hydrocarbon available at intermediate storage.	Loss of feed to reaction section and reduced output. Polymer formed in heat exchanger under no flow conditions.	(a) Ensure good communications with intermediate storage operator. (b) Install low level alarm on settling tank LIC.
		(2) J1 pump fails (motor fault, loss of drive, impeller corroded away etc).	As for (1)	Covered by (b)
		(3) Line blockage, isolation valve closed in error, or LCV fails shut.	As for (1)	Covered by (b)
			J1 pump overheats	(c) Install kickback on J1 pumps. (d) Check design of J1 pump strainers.
		(4) Line fracture	As for (1)	Covered by (b)
			Hydrocarbon discharged into area adjacent to public highway.	(e) Institute regular patrolling & inspection of transfer line.
MORE OF	More flow	(5) LCV fails open or LCV bypass open in error.	Settling tank overfills	(f) Install high level alarm on LIC and check sizing of relief opposite liquid overfilling. (g) Institute locking off procedure for LCV bypass when not in use.
			Incomplete separation of water phase in tank, leading to problems on reaction section.	(h) Extend J2 pump suction line to 12" above tank base.
	More pressure	(6) Isolation valve closed in error or LCV closes, with J1 pump running.	Transfer line subjected to full pump delivery or surge pressure.	(j) Covered by (c) except when kickback blocked or isolated. Check line, FQ and flange ratings, and reduce stroking speed of LCV if necessary. Install a PG upstream of LCV and an independent PG on settling tank.
		(7) Thermal expansion in an isolated valved section due to fire or strong sunlight.	Line fracture or flange leak.	(k) Install thermal expansion relief on valved section (relief discharge route to be decided later in study).
	More temperature	(8) High intermediate storage temperature.	Higher pressure in transfer line and settling tank.	(l) Check whether there is adequate warning of high temperature at intermediate storage. If not, install.
LESS OF	Less flow	(9) Leaking flange or valved stub not blanked and leaking.	Material loss adjacent to public highway.	Covered by (e) and the checks in (j).
	Less temperature	(10) Winter conditions	Water sump and drain line freeze up	(m) Lag water sump down to drain valve, and steam trace drain valve and drain line downstream
PART OF	High water concentration in stream	(11) High water level in intermediate storage tank.	Water sump fills up more quickly. Increased chance of water phase passing to reaction section.	(n) Arrange for frequent draining off of water from intermediate storage tank. Install high interface level alarm on sump.

Dynamic Simulation in Emergency Conditions

- Building a dynamic model of a *large-scale process* is considered a very demanding, difficult and even an *infeasible task.*
- In the HAZOP framework, dynamic models of separate (relatively small) sections of the process are needed.
- Dynamic simulation is helpful in determining the "*Consequences*" and the "Actions Required".
- Exothermic reactions are probably the most critical processes with respect to safety considerations.

Nitric Acid oxidation of 2-octanol in a Semi-Batch Reactor (van Woezik and Westerterp)

Presents from start



$$A + B \xrightarrow{r_1} P + 2B$$

$$P + B \xrightarrow{r_2} X$$

A - 2- octanol, *P* - 2-octanone , *X* – undesired oxydation products

B - nitrosonium ion, causes an autocatalytic behavior

Semi-batch Reactor Model Representation in Polymath Format (1)

Equations are entered in order and format most appropriate for documentation purposes

The program is also used as model documentation

No.	Equation	Explanation
1	t(0) = 0.0001	Starting time
2	t(f) = 72000	Final time (s)
3	d(Np)/d(t) = (r1 - r2) * Vr0 / (1 - Epsd)	Mole balance for 2-octanone (P)
4	Np(0) = 0	Number of moles of 2-octanone (P) at t = t0
5	d(Nx)/d(t) = r2 * Vr0 / (1 - Epsd)	Mole balance for carboxylic acids (X)
6	Nx(0) = 0	Number of moles of carboxylic acids (X) at t = t0
7	r1 = k1 * CaOrg * CbAq * (1 - Epsd)	Reaction rate of a and b to p[kmol/m3/s]
8	r2 = k2 * CpOrg * CbAq * (1 - Epsd)	Reaction rate of p and b to x[kmol/m3/s]
9	Vr0 = 1.5	Initial volume in a reactor [m3]
10	Epsd = Vdos1 / (Vdos1 + Vr0)	Volume fraction of dispersed phase
11	k1 = maA1 * exp(-E1perR / Tr - m1 * H)	Specific reaction rate 1
12	k2 = mpA2 * exp(-E2perR / Tr - m2 * H)	Specific reaction rate 2
13	CaOrg = (Theta * NaF - Np - Nx) / (Vdos1 * Theta)	Concentr of a in org phase [kmole/m3]
14	CpOrg = Np / (Vdos1 * Theta)	Concentr. of (P) in org phase [kmol/m3]
15	CbAq = (Np + Y * NaF) / Vr0	Concentr. of (B) in aq. phase [kmole/m3]
16	Vdos1 = 0.6	Final volume of the dose [m3]
17	maA1 = 10 ^ 5	Pre-exponential factor reaction 1 [m3/kmol/s]
18	mpA2 = 10 ^ 10	Pre-exponential factor reaction 2[m3/kmol/s]
19	E1perR = 11300	Activation temperature reaction 1 [K]
20	E2perR = 12000	Activation tempetature reaction 2 [K]
21	m1 = 6.6	Hammett's reaction rate coeff. reaction 1
22	m2 = 2.2	Hammett's reaction rate coeff. reaction 2
23	H = -.6221 - 3.7214 * wt - 1.5714 * wt ^ 2	Hammett's acidity function
24	Theta = If (t <= tdos) Then (t / tdos) Else (1)	Dimensionless time up to t=tdos
25	NaF = Vdos1 * RhoOctan / MwOctan	Total amount of 2-octanol (a) fed [kmol]

Semi-batch Reactor Model Representation in Polymath Format (2)

No.	Equation	Explanation
26	Y = 0.035	Initial concentr. of nitrosonium ion Y=Nb0/NaF
27	wt = Nn * Mw / (Vr0 * RhoAcid)	Mass concentr. of nitric acid sol [%/100%]
28	tdos = 36000	dosing time [s], 10h
29	RhoOctan = 820.7	Density of 2-octanol [kg/m3]
30	MwOctan = 130.23	Molar mass of 2-octanol [kg/kmol]
31	Nn = CnAq * Vr0	Number of moles of HNO3 [kmol]
32	Mw = 63	Molar mass of HNO3 [kg/kmol]
33	RhoAcid = 1500	Density of pure nitric acid [kg/m3]
34	CnAq = (NnO - Y * NaF - Np - 2 * Nx) / Vr0	Concentr. of HNO3 in the aq. phase [kmol/m3]
35	NnO = Vr0 * Percent * RhoAcid / Mw	Initial number of mole of HNO3 [kmole]
36	Percent = 0.6	Initial mass concentr of nitr. acid sol. [%]
37	d(Tr)/d(t) = (Qr + Qdos + Qcool) / Gamma	Reactor energy balance (Tr in K)
38	Tr(0) = 260	Temp. in the reactor at t = t0 (K)
39	Qr = Qnol + Qnone	Sum of the heat of reaction the reactions [W]
40	Qdos = Phi * RhoCPdos * (Tdos - Tr)	Heat input due to reactant addition [W]
41	Qcool = UAcool * (Tcool - Tr)	Heat removed by the cooling jacket [W]
42	Gamma = Gamma0 + RhoCPdos * Phi * t	Total heat capacity of the system [J/K]
43	Qnol = r1 * Vr0 * Hnol / (1 - Epsd)	Heat of reaction, 1 [W]
44	Qnone = r2 * Vr0 * Hnone / (1 - Epsd)	Heat of reaction, 2 [W]
45	Phi = Vdos1 / tdos	Volumetric flow rate of the feed [m3/s]
46	RhoCPdos = 2 * 10 ^ 6	Heat capacity of dose [J/m3/K]
47	Tdos = 293.15	Temperature of feed dose [K]
48	UAcool = UA0 + (UA1 - UA0) * Theta	Cooling surface heat transfer coefficient [W/K]

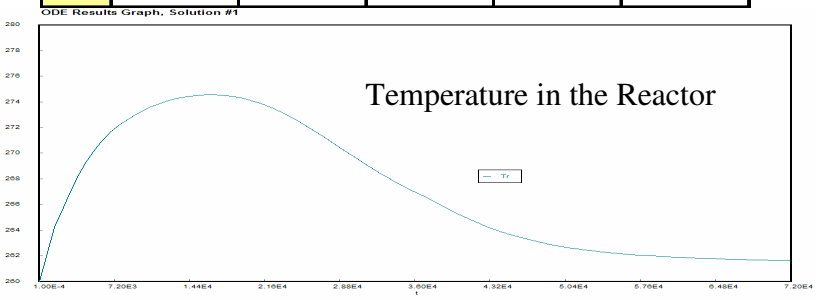
Semi-batch Reactor Model Representation in Polymath Format (3)

No.	Equation	Explanation
49	Gamma0 = 5.4 * 10 ^ 6	Initial heat capacity of the system [J/K]
50	Hnol = 160 * 10 ^ 6	Specific heat of reaction 1 [J/kmol]
51	Hnone = 520 * 10 ^ 6	Specific heat of reaction 2 [J/kmole]
52	UA0 = 1500	Initial cool. surface heat trans. coeff.[W/K]
53	UA1 = 2100	Final cool. surface heat trans. coeff. [W/K]
54	d(Tcool)/d(t) = (Fw * (Tcool_IN - Tcool) - Qcool / (Rl	Jacket energy balance (T in K)
55	Tcool(0) = 273.15	Coolant exit temp. at t = t0 (K)
56	Fw = 100 / 60 * 10 ^ (-3)	Flow rate of coolant [m3/s]
57	Tcool_IN = 260	Initial coolant temperature [K]
58	RhoCoolant = 1000	The density of coolant [kg/m3]
59	CpCoolant = 418	Heat capacity of coolant [J/kg/K]
60	Vj = 1.5	Volume of the jacket [m3]

Critical Parameters

Semi-Batch Reactor Operation – Normal Operating Cond.

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0.0001	0.0001	7.20E+04	7.20E+04
2	Np	0	0	3.122345	3.122345
3	Nx	0	0	0.252069	0.252069
4	Tr	260	260	274.571	261.6412
5	Tcool	273.15	260.3828	273.15	260.3828



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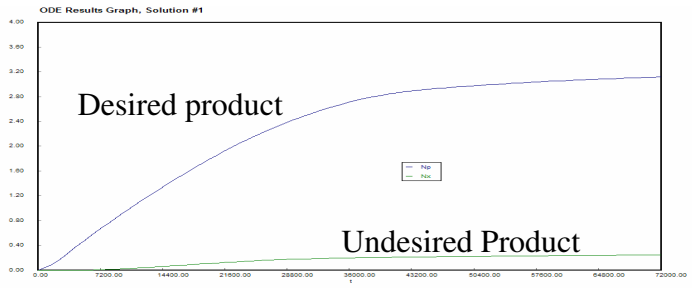

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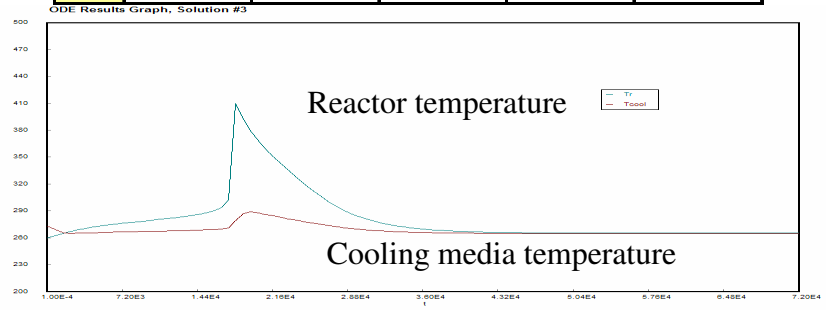
4	Tr	260	260	274.571	261.6412
5	Tcool	273.15	260.3828	273.15	260.3828

Tcool_IN = 265 K (instead of 260 K)

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0.0001	0.0001	7.20E+04	7.20E+04
2	Np	0	0	1.368575	0.335306
3	Nx	0	0	2.404981	2.404981
4	Tr	260	260	410.1594	265.6675
5	Tcool	273.15	265.1546	289.1191	265.1546

Semi-Batch Reactor Operation – Tcool_IN = 265

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0.0001	0.0001	7.20E+04	7.20E+04
2	Np	0	0	1.368575	0.335306
3	Nx	0	0	2.404981	2.404981
4	Tr	260	260	410.1594	265.6675
5	Tcool	273.15	265.1546	289.1191	265.1546



	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0.0001	0.0001	7.20E+04	7.20E+04
2	Np	0	0	1.368575	0.335306
3	Nx	0	0	2.404981	2.404981
4	Tr	260	260	410.1594	265.6675
5	Tcool	273.15	265.1546	289.1191	265.1546

Reduction of the Effective Heat Transfer Rate

effective heat transfer rate	100%	90%	81%	80%	70%	60%
n_P [kmol]	3.16	3.08	0.05	0.14	0.3	0.38
n_X [kmol]	0.26	0.33	3.71	3.3	2.63	2.64
$T_{cool,max}$ [°C]	-10.4	-10.2	8.88	6.42	0.3	2.37
$T_{reactor,,max}$ [°C]	1.31	3.9	195	177	147	128

Reduction of the Flow Rate of the Cooling Media

$F_w[l/\min]$	600	300	200	100	70
$n_P[kmol]$	3.18	3.17	3.16	3.07	0.01
$n_X[kmol]$	0.21	0.23	0.26	0.36	3.78
$T_{cool,max}[^\circ C]$	-11.5	-11.0	-10.4	-8.40	39.0
$T_{r,max}[^\circ C]$	-0.15	-0.55	1.31	4.38	196

Some Deviations that Cause Temperature Runaway in the Reactor

Guide Word	Deviation	Normal Value	Limit
None	No flow in the cooling jacket		
Less of	Lower cooling media flowrate	600 liter/m	less than 70 liter/m
Less of	Smaller heat transfer area	100%	less than 81%
More of	Higher Cooling Media Temp.	-15 ºC	more than -6 ºC
Less	Shorter dosing time	20 h	less than 7.5 h
More of	Larger dosing volume	0.6 m^3	more than 0.81 m^3
More of	Higher nitric acid concentration	59%	more than 64%

Developing a Simulator for Operator Training and Educational Applications

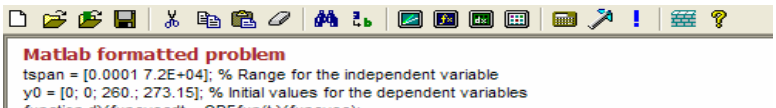
The development of the simulator is carried out in three stages:

Exporting the model to MATLAB as a *function* (carried out automatically by Polymath).

Testing the MATLAB function by comparing its results with the Polymath results (a *template* program, for this purpose is provided in Polymath's Help section).

Adding a *Graphical User Interface* (*GUI*) to the MATLAB function.

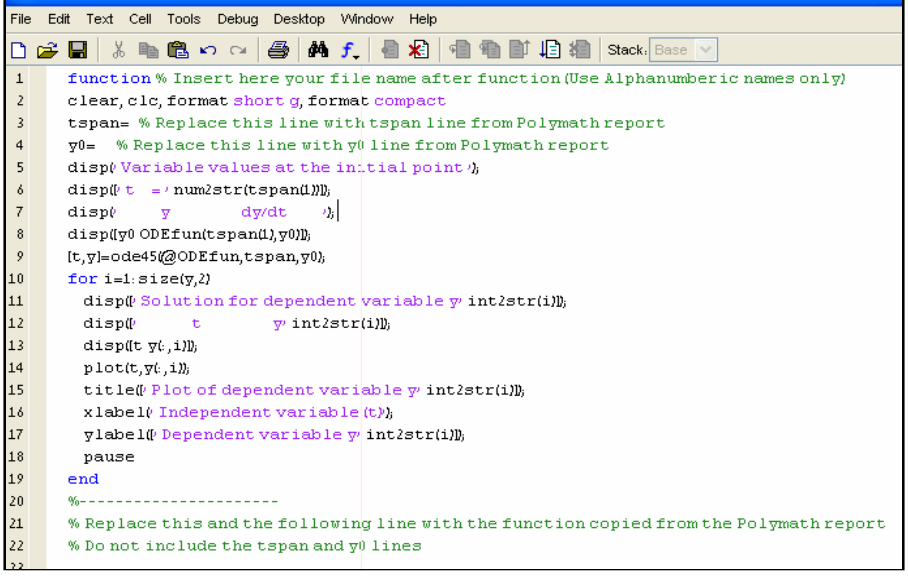
Exporting the Model to MATLAB
(part of the Polymath generated function)



Matlab formatted problem

```
tspan = [0.0001 7.2E+04]; % Range for the independent variable
y0 = [0; 0; 260.; 273.15]; % Initial values for the dependent variables
function dYfuncvecdt = ODEfun(t,Yfuncvec);
Np = Yfuncvec(1);
Nx = Yfuncvec(2);
Tr = Yfuncvec(3);
Tcool = Yfuncvec(4);
%Initial concentr. of nitrosonium ion Y=Nb0/NaF
Y = 0.035;
%Molar mass of HNO3 [kg/kmol]
Mw = 63;
%Initial volume in a reactor [m3]
Vr0 = 1.5;
%Final volume of the dose [m3]
Vdos1 = 0.6;
%Density of pure nitric acid [kg/m3]
RhoAcid = 1500;
%Initial mass concentr of nitr. acid sol. [%]
Percent = 0.6;
%Molar mass of 2-octanol [kg/kmol]
MwOctan = 130.23;
%dosing time [s], 10h
tdos = 36000;
%Density of 2-octanol [kg/m3]
RhoOctan = 820.7;
%Volume fraction of dispersed phase
Epsd = Vdos1 / (Vdos1 + Vr0);
```

Exporting the Model to MATLAB (a template for running the MATLAB function)

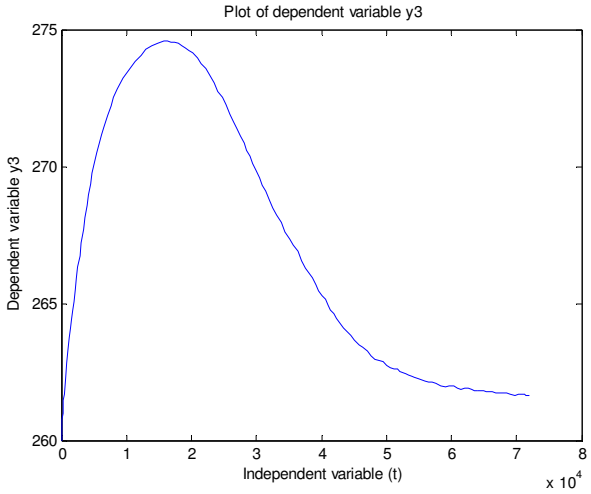


File Edit Text Cell Tools Debug Desktop Window Help

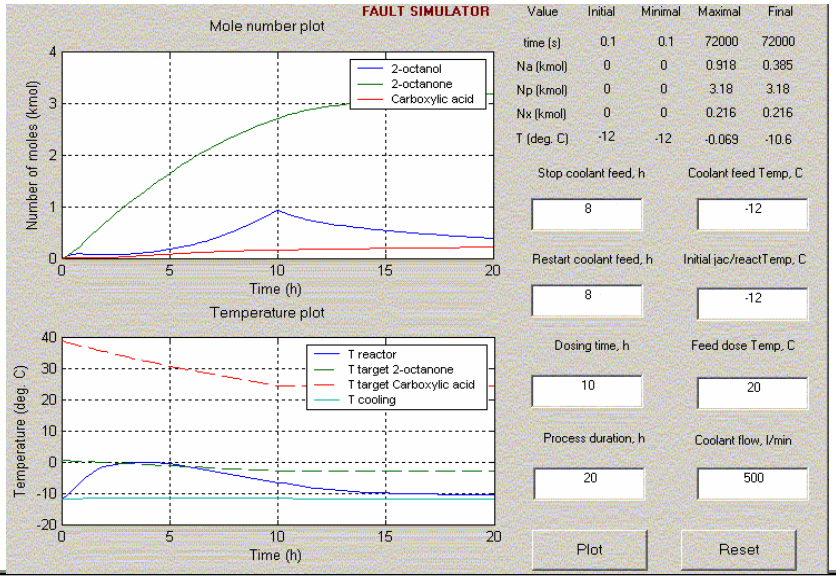
Stack: Base

```
1   function % Insert here your file name after function (Use Alphanumberic names only)
2   clear, clc, format short g, format compact
3   tspan= % Replace this line with tspan line from Polymath report
4   y0=  % Replace this line with y0 line from Polymath report
5   disp(' Variable values at the initial point ');
6   disp([' t  =' num2str(tspan(1))]);
7   disp('     y          dy/dt     ');
8   disp([y0 ODEfun(tspan(1),y0)]);
9   [t,y]=ode45(@ODEfun,tspan,y0);
10  for i=1:size(y,2)
11    disp([' Solution for dependent variable y' int2str(i)]);
12    disp('       t          y' int2str(i)]);
13    disp([t y(:,i)]);
14    plot(t,y(:,i));
15    title([' Plot of dependent variable y' int2str(i)]);
16    xlabel(' Independent variable (t)');
17    ylabel([' Dependent variable y' int2str(i)]);
18    pause
19  end
20  %----------------------
21  % Replace this and the following line with the function copied from the Polymath report
22  % Do not include the tspan and y0 lines
```

Reactor Temperature Plot Generated by MATLAB – Normal Operating Conditions



MATLAB Graphical User Interface for the Semi – Batch Reactor Simulator



Conclusions

- Quantitative aspects have been added to the HAZOP analysis by defining the *threshold value* for a deviation from normal operating conditions which may lead to catastrophic events.

- It was demonstrated that dividing the process into *smaller independent sections* reduces considerably the level of complexity associated with the dynamic simulation of a process in emergency conditions.

- The model of the process can be easily converted to a Simulator (for educational applications and operator training) by using the *Polymath – MATLAB conversion* utility and the *MATLAB GUI* utility