Computer Aided Process Engineering CL303

Module-2

Microscopic view: Mass, momentum and energy conservation equations for different Unit Operations & Unit Processes

Unsteady state model formulation and Numerical methodology

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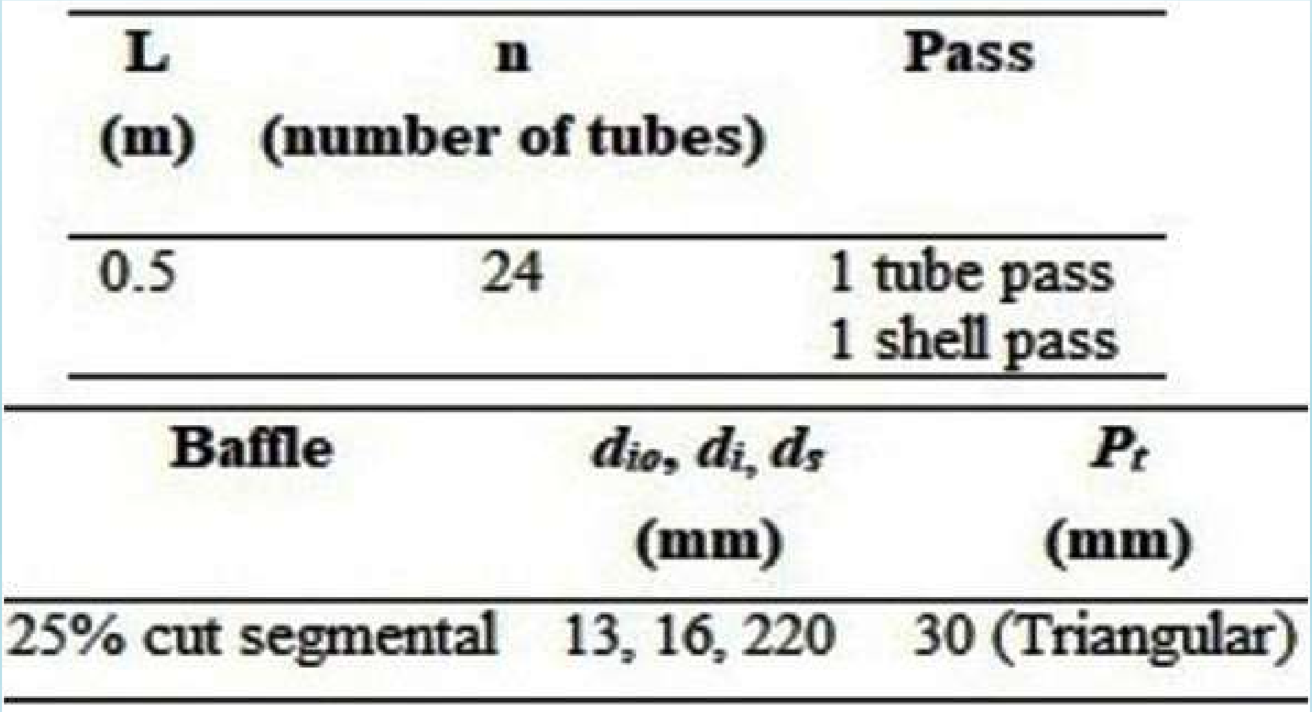
INTRODUCTION

- In chemical process industry, study of dynamic behavior of individual unit is essential in regard to operation and control of the overall process.
- To provide a safe operation of a plant during transients like, fluctuation of set point, load and plant start-up or shut-down, transient analysis of a unit is required.
- Transient analysis can be simulated and experimented in the prototype simulator and experimental facility, respectively before implementation of the units in a plant.
- The shell and tube heat exchangers are employed in various processes such as, in between two stripping column and preheat train of a crude distillation unit of a oil refinery, reactor feed heating, reactor product cooling, processing of food and milk pasteurization etc.

PROTOYPE SHELL AND TUBE HEAT EXCHNGER

- **A counter-flow shell and tube heat exchanger is chosen for simulated transient analysis**
- **Hot fluid is heated water in the tube side and cold fluid is water at room temperature in the shell side are circulated.**

Table. Specifications of shell and tube heat exchanger



L (m)	n (number of tubes)	Pass
0.5	24	1 tube pass 1 shell pass

Baffle	d_{io}, d_i, d_s (mm)	P_t (mm)
25% cut segmental	13, 16, 220	30 (Triangular)

Cont.

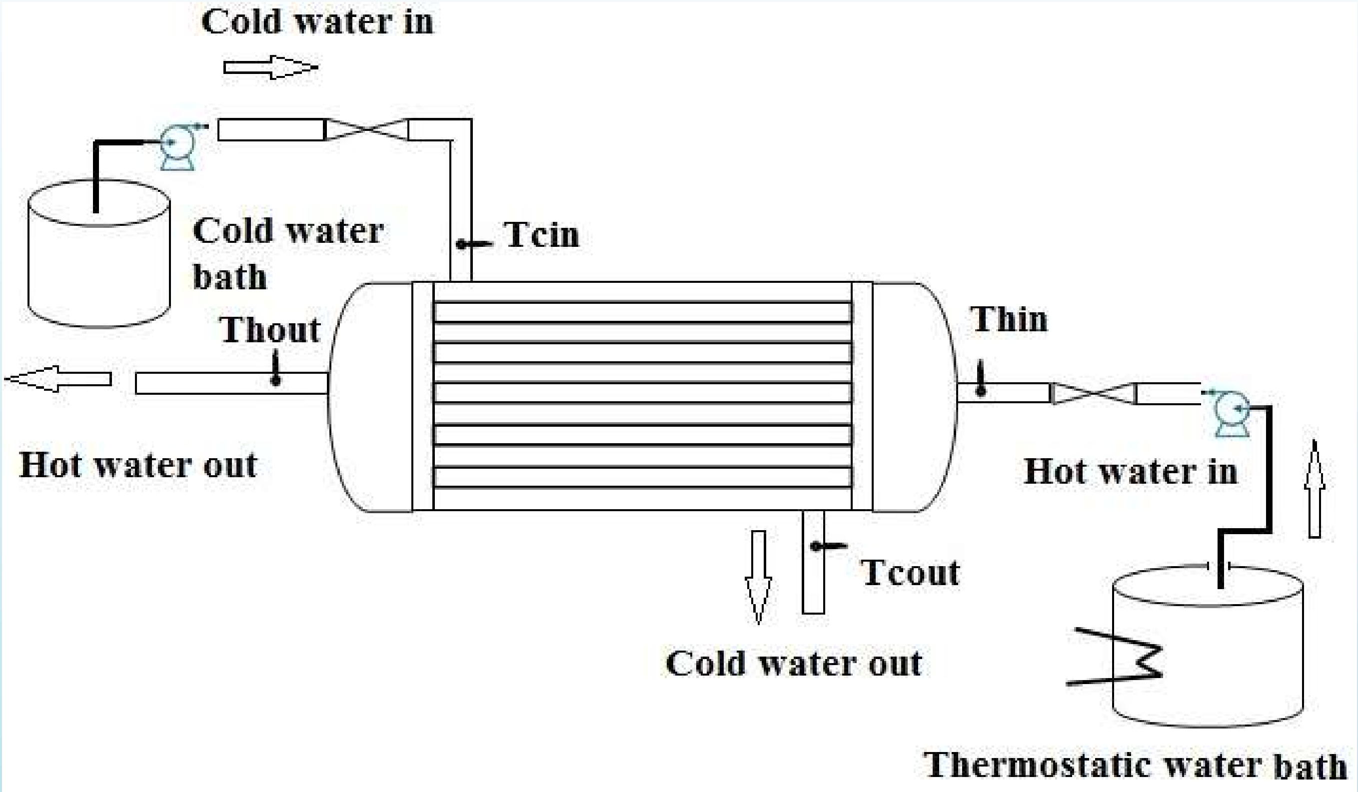
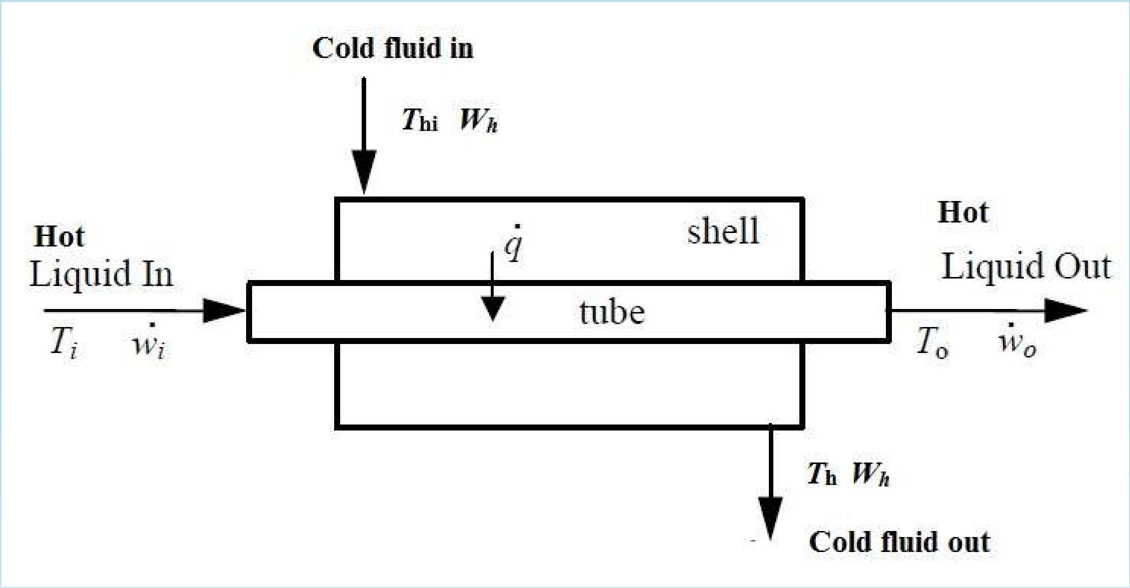


Fig. Schematic diagram of the prototype



Classifications

- It is based on conservation of mass, momentum and energy.
  Accumulation of property= In – Out – Generation
- Lumped parameter model (Macroscopic view)
- Distributed parameter model (Microscopic view)

Shell and Tube Heat Exchanger

- Governing equations are based on energy balance equation. The assumptions are following:

  a) Viscous energy dissipation terms are neglected

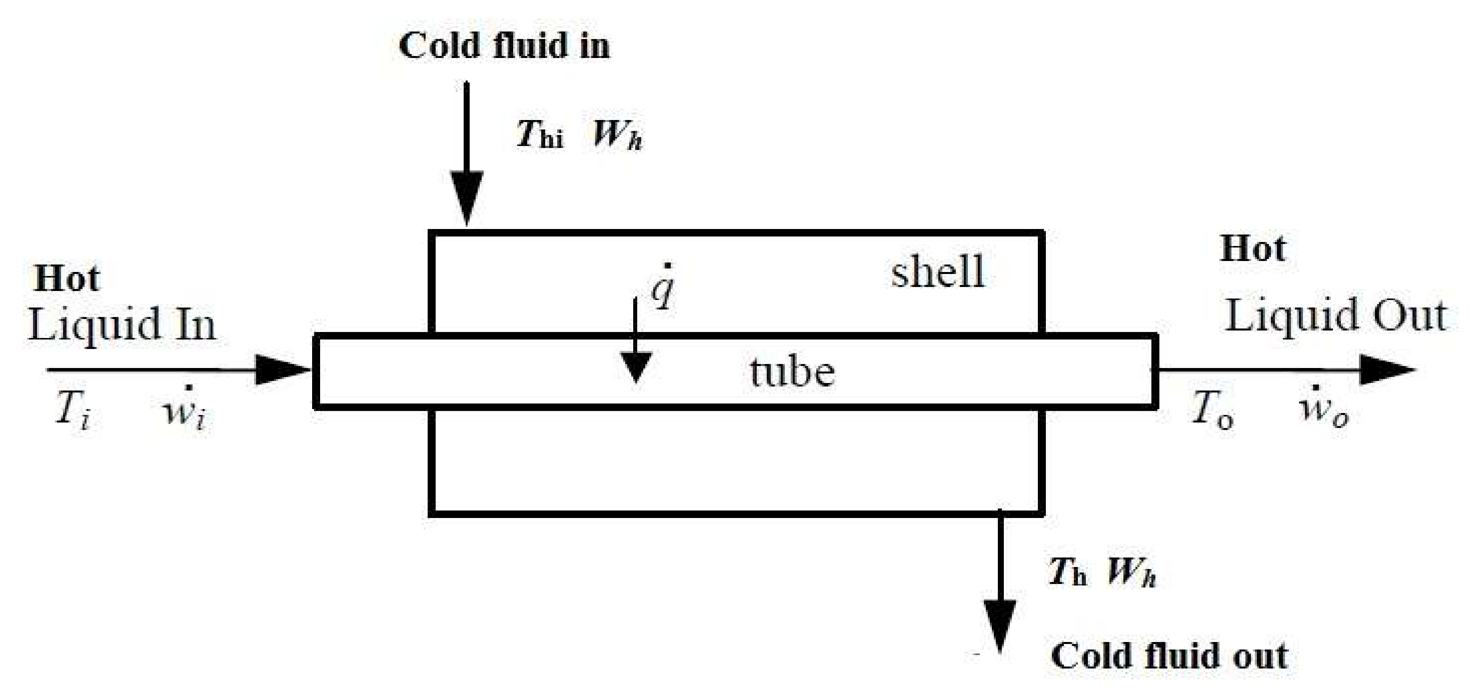
  b) pressure changing term, i.e., accumulation of mechanical energy is neglected for negligible coefficient of thermal expansion of fluid,

  c) velocity distribution along the length of the heat exchanger is neglected, i.e., the uniform velocity along the length is assumed,

  d) temperature change over the radial distance of the shell and tube is neglected for small equivalent diameter of the both side, i.e., one dimensional governing equation is assumed.

Lumped parameter model

- In the lumped parameter model, the spatial variation of a property is neglected or lumped. Here the independent variable is function of time only.
- The length of the heat exchanger, reactor, etc., is small enough that outlet temperature of heat exchanger in the both side is assumed to be same as the temperature inside those side (shell and tube).
- In other ward, small length gives efficient longitudinal mixing in the flow that the outlet temperature of any side is same as the temperature inside that side.



- The energy balance equation are based on the same assumptions as earlier model, except spatial distribution of independent variable is not considered here.

$$\rho_h V_h c_{ph} \frac{dT_h}{dt} = W_h c_{ph}(T_{hi} - T_h) + h_h A_h (T_w - T_h)$$

Hot fluid in tube side

$$\rho_c V_c c_{pc} \frac{dT_c}{dt} = W_c c_{pc}(T_{ci} - T_c) + h_c A_c (T_w - T_c)$$

Cold fluid in shell side

$$\frac{dT_w}{dt} = \frac{h_c A_c}{\rho_w V_w c_{pw}}(T_c - T_w) + \frac{h_h A_h}{\rho_w V_w c_{pw}}(T_h - T_w)$$

Wall material

SIMULATED TRANSIENT ANALYSIS

- Steady state solution of the governing equations (energy equation) is estimated.

$$0 = W_c c_{pc}(T_{ci} - T_c) + h_c A_c (T_w - T_c)$$

Cold fluid in shell side

$$0 = W_h c_{ph}(T_{hi} - T_h) + h_h A_h (T_w - T_h)$$

Hot fluid in tube side

$$0 = h_c A_c (T_c - T_w) + h_h A_h (T_h - T_w)$$

Wall material

- The matrix solution gives the solution $\begin{bmatrix} T_{hs} & T_{cs} & T_{ws} \end{bmatrix}'$
- Considering the steady state temperatures as initial condition, perturbations (step change) of inlet temperature and flow rate is given to obtain transient temperature response of the other side of the shell and tube heat exchanger using the Runge-Kutta numerical scheme.

Matlab-Simulink demonstration

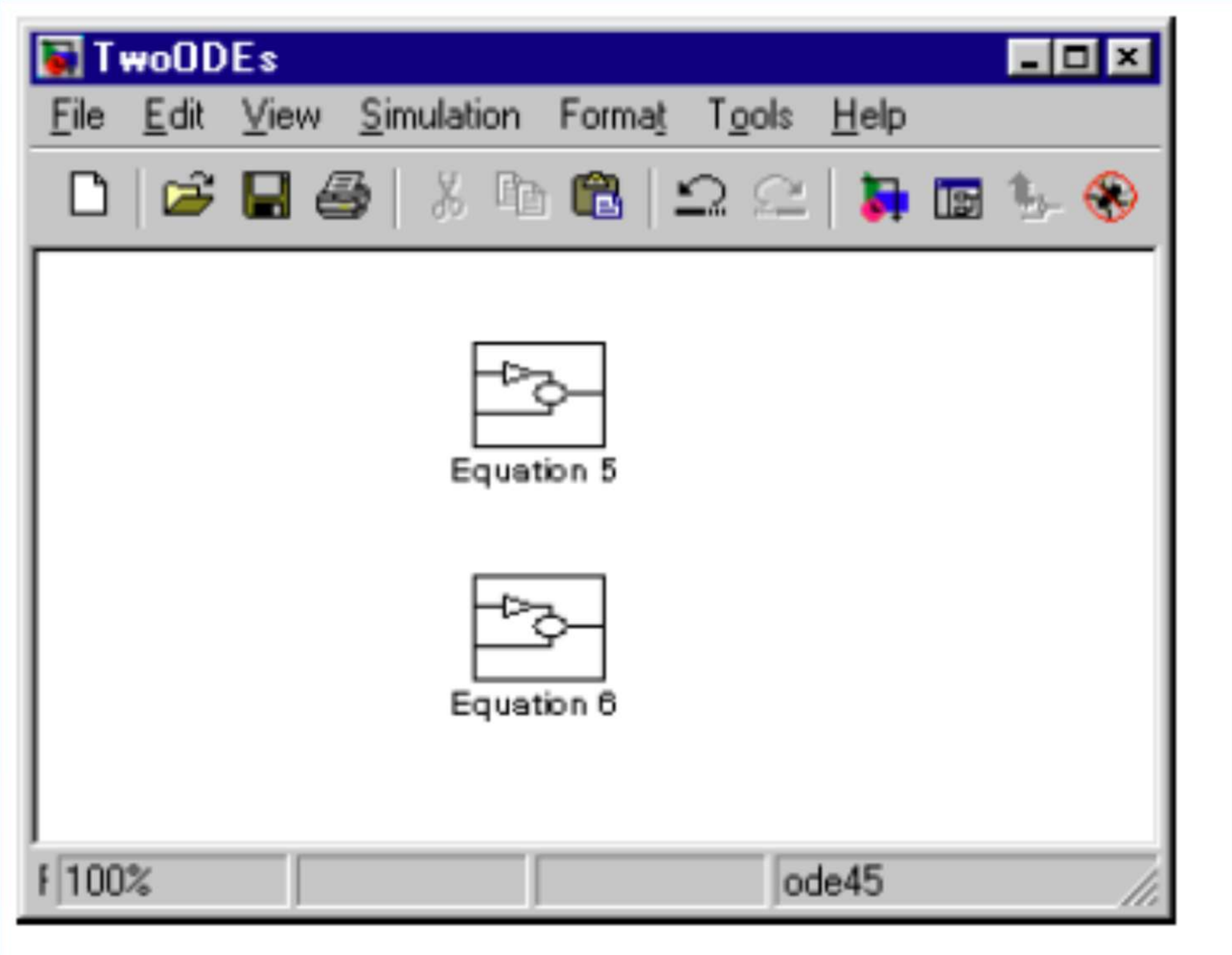
- Problem definition: A double pipe heat exchanger has been utilized to cool benzene flowing in the inner tube by cooling water flowing in the outer tube. Initial condition are as follows: Benzene hot side- W_h=0.804 lb/s; T_{hi} = 141 ^oF; c_{ph}=0.435 BTU/lb-^oF; h_hA_h=0.907845458 BTU/s- ^oF; $\rho_hV_hc_{ph}$= 14.07617 BTU/^oF.
- Water cold side- W_c= 2.168 lb/s; T_{ci} = 65 ^oF; c_{pc}=1 BTU/lb-^oF; h_cA_c= 2.249877874 BTU/s- ^oF; $\rho_cV_cc_{pc}$= 31.2454 BTU/^oF.
- Find steady state temperature of hot side, cold side and wall.
- Show transient analysis for step change of flowrate and temperature of hot side.

Trial solution

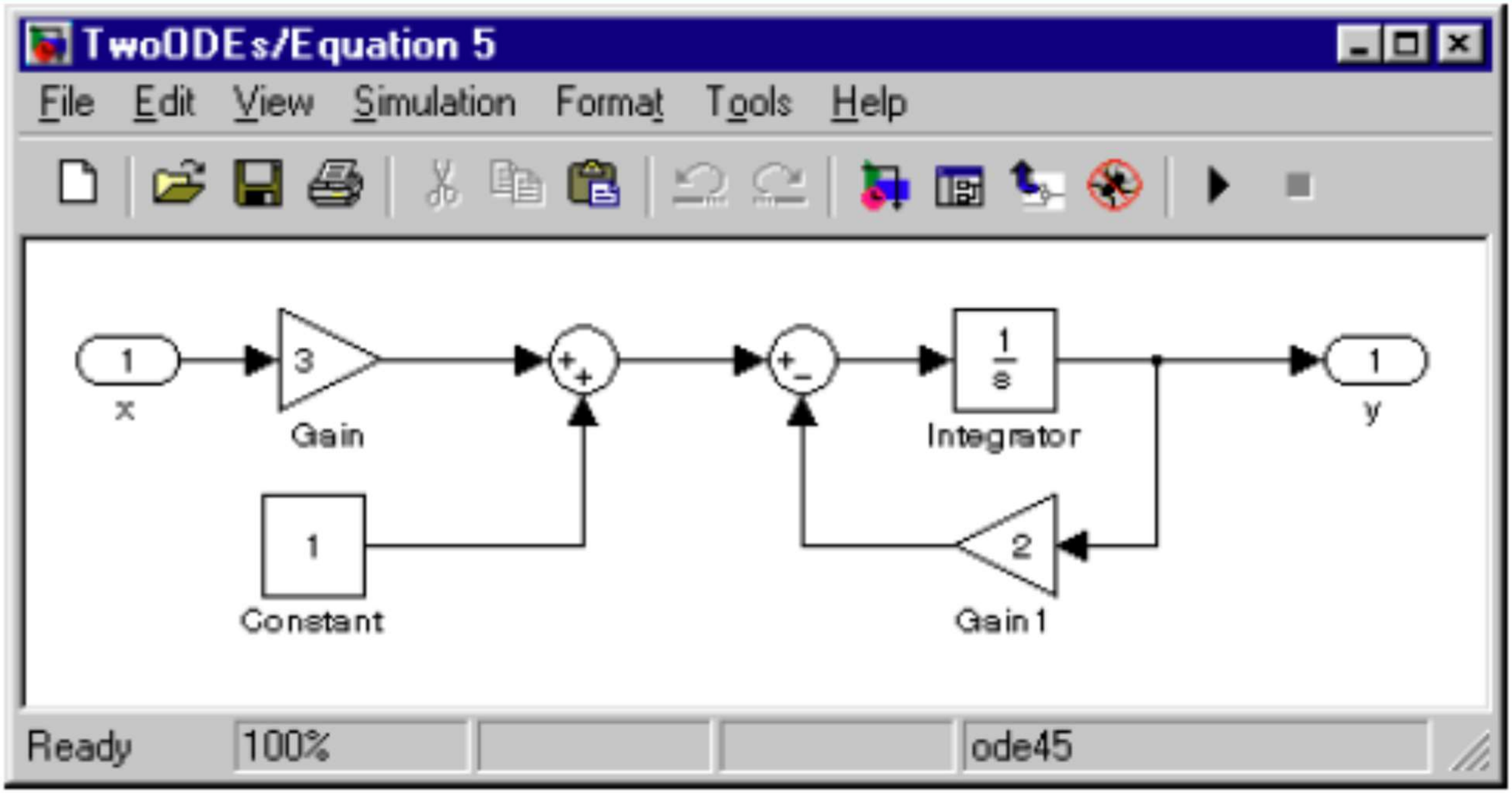
- Modeling of first order differential equation
- $\frac{dy}{dt} = 3x - 2y + 1$ Eq. (1);
- $\frac{dz}{dt} = 2x - y - 3z$ Eq. (2);

Simulink tutorial given by
N.L Ricker, Professor
Emeritus, Chemical
Engineering
University of Washington

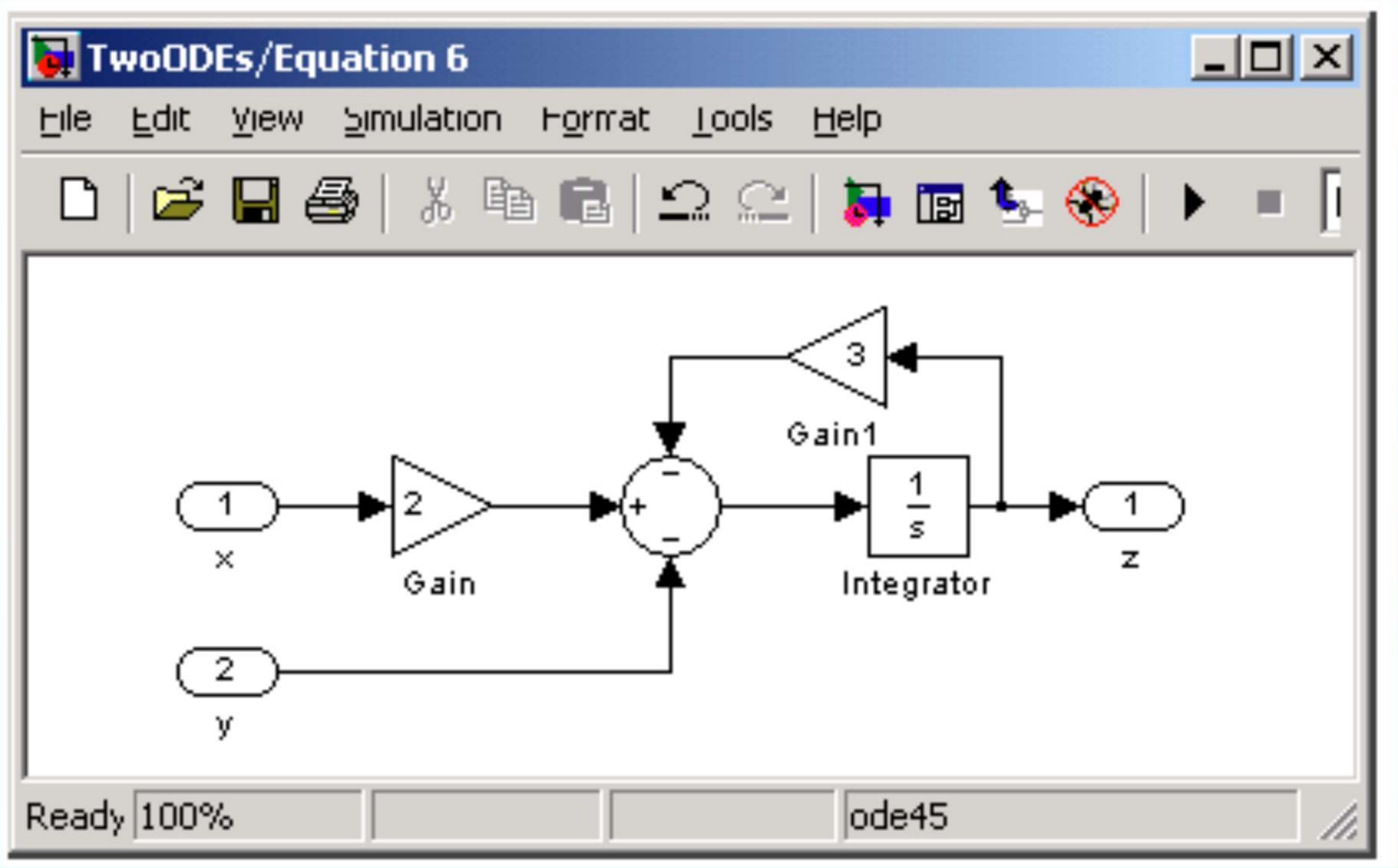
Selecting two subsystems



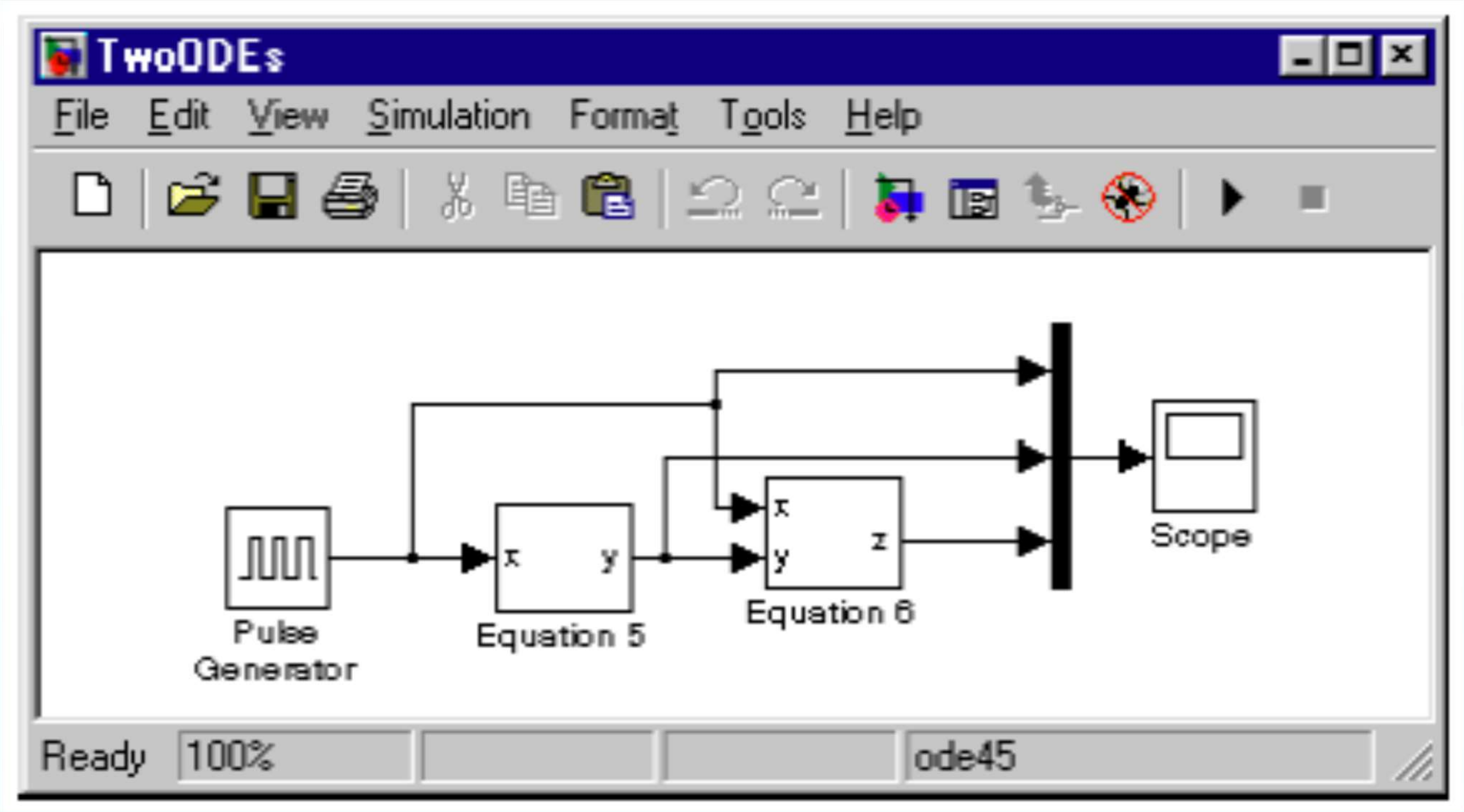
Generation of subsystem-I replicating Eq. 1



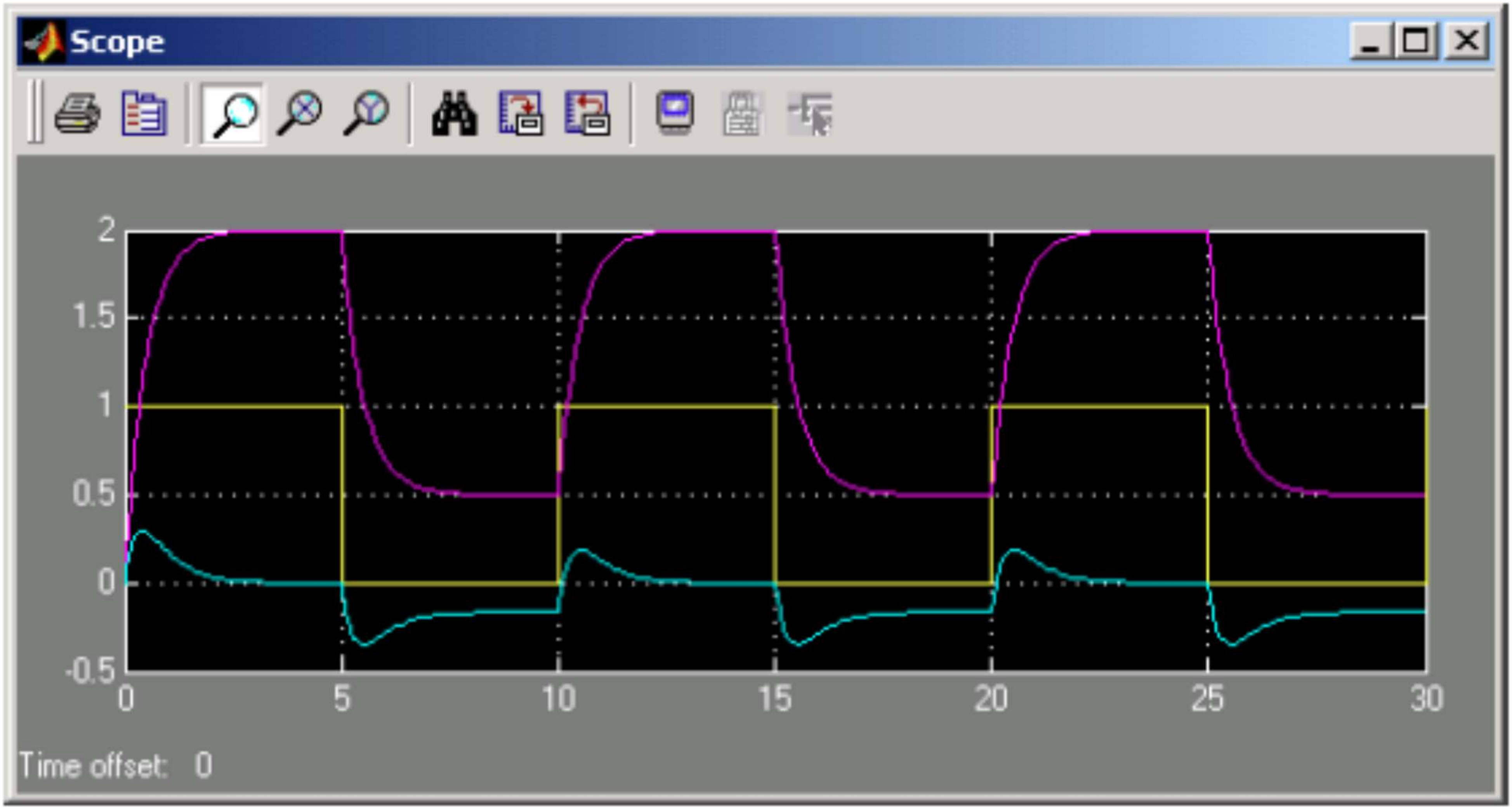
Generation of subsystem-II replicating Eq. 2



Overall system and transient analysis

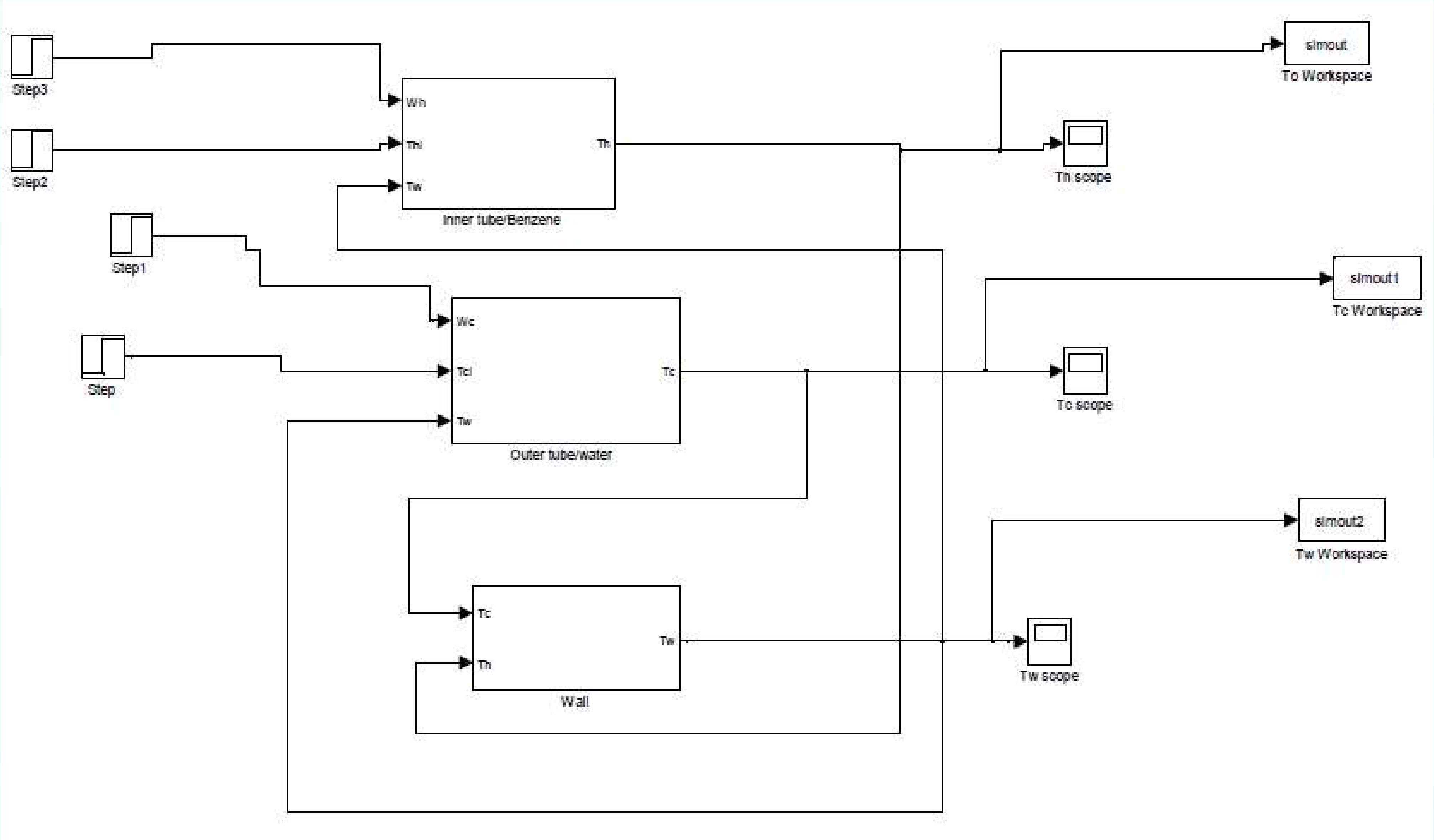


Displayed result in the scope

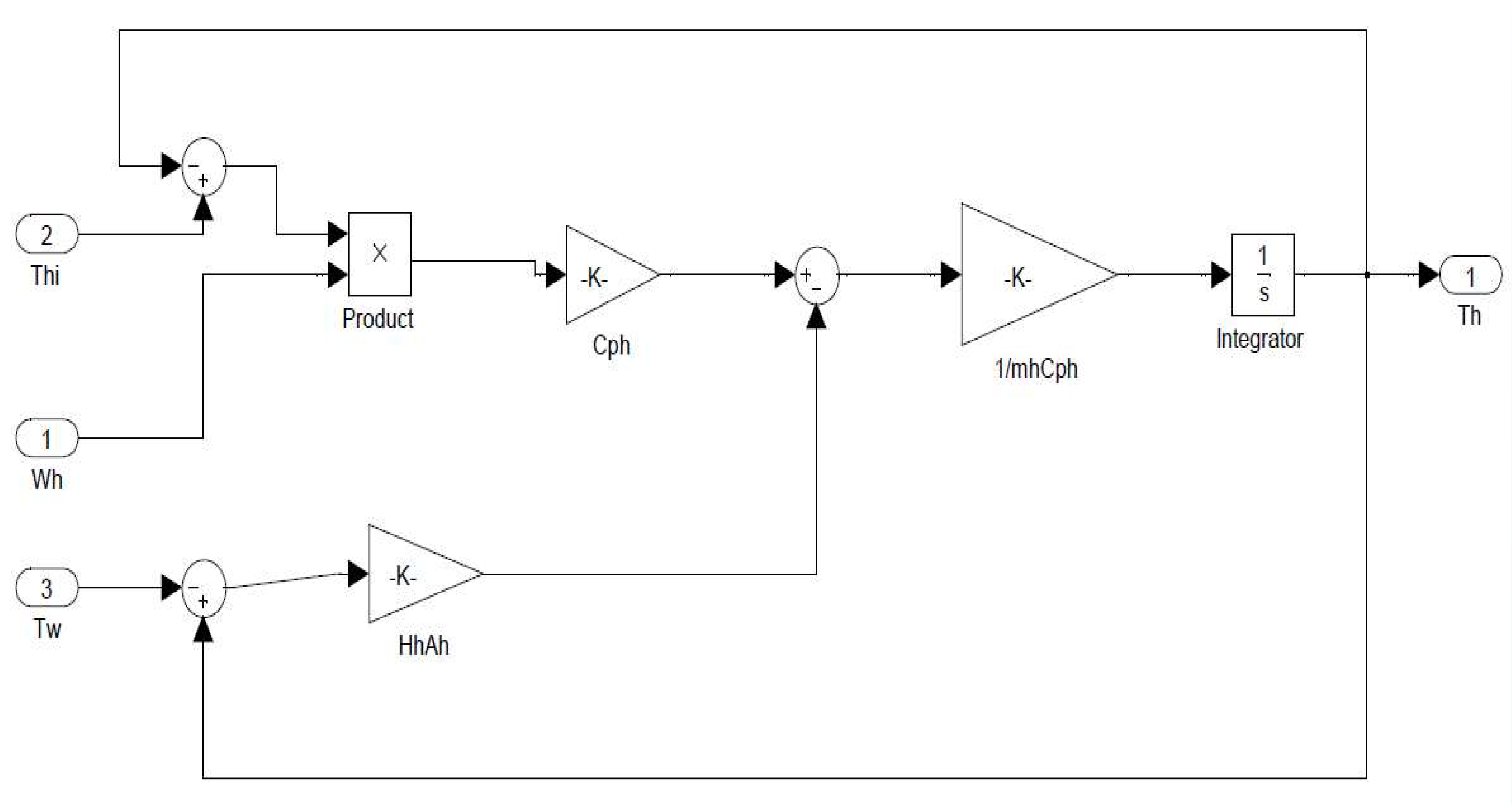


- Steady sate solution gives

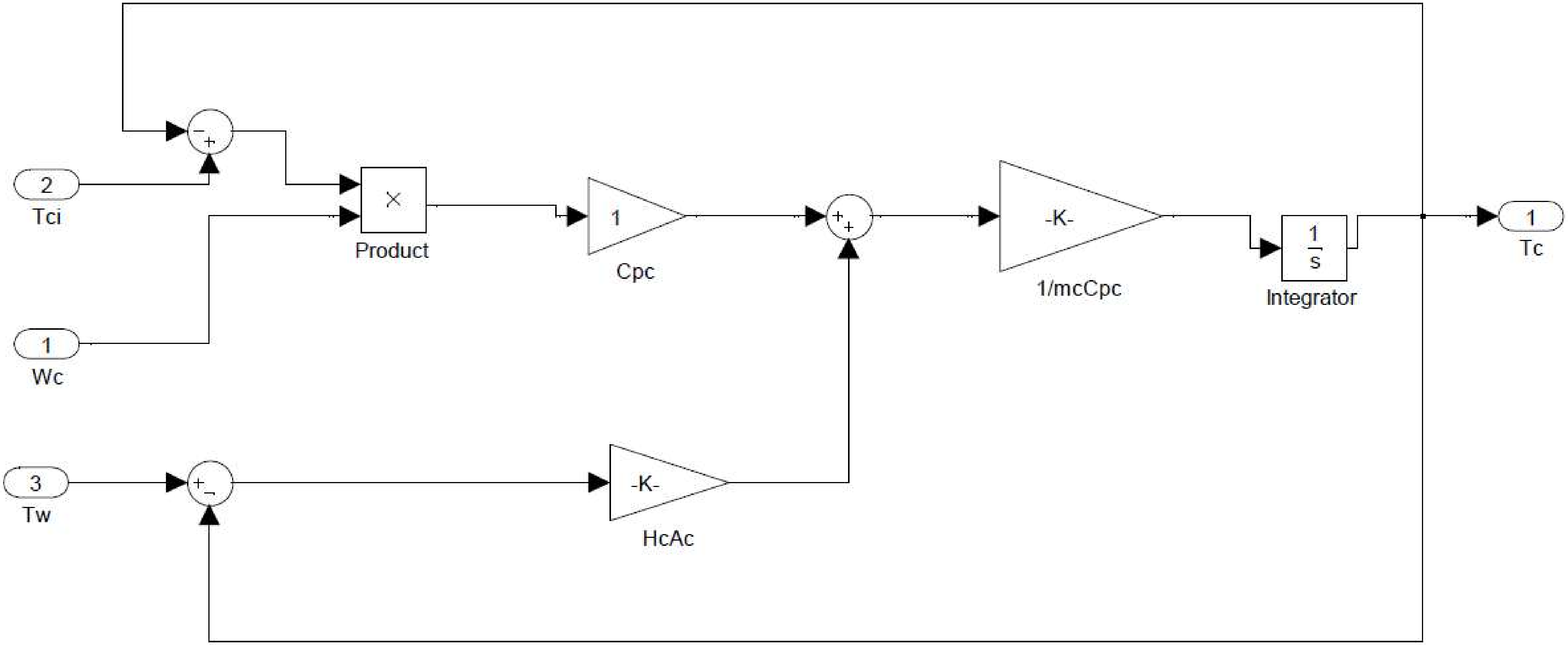
$$\left[T_{hs} \quad T_{cs} \quad T_{ws}\right]' = \left[96.34747144 \quad 72.20369 \quad 79.14505\right]'$$



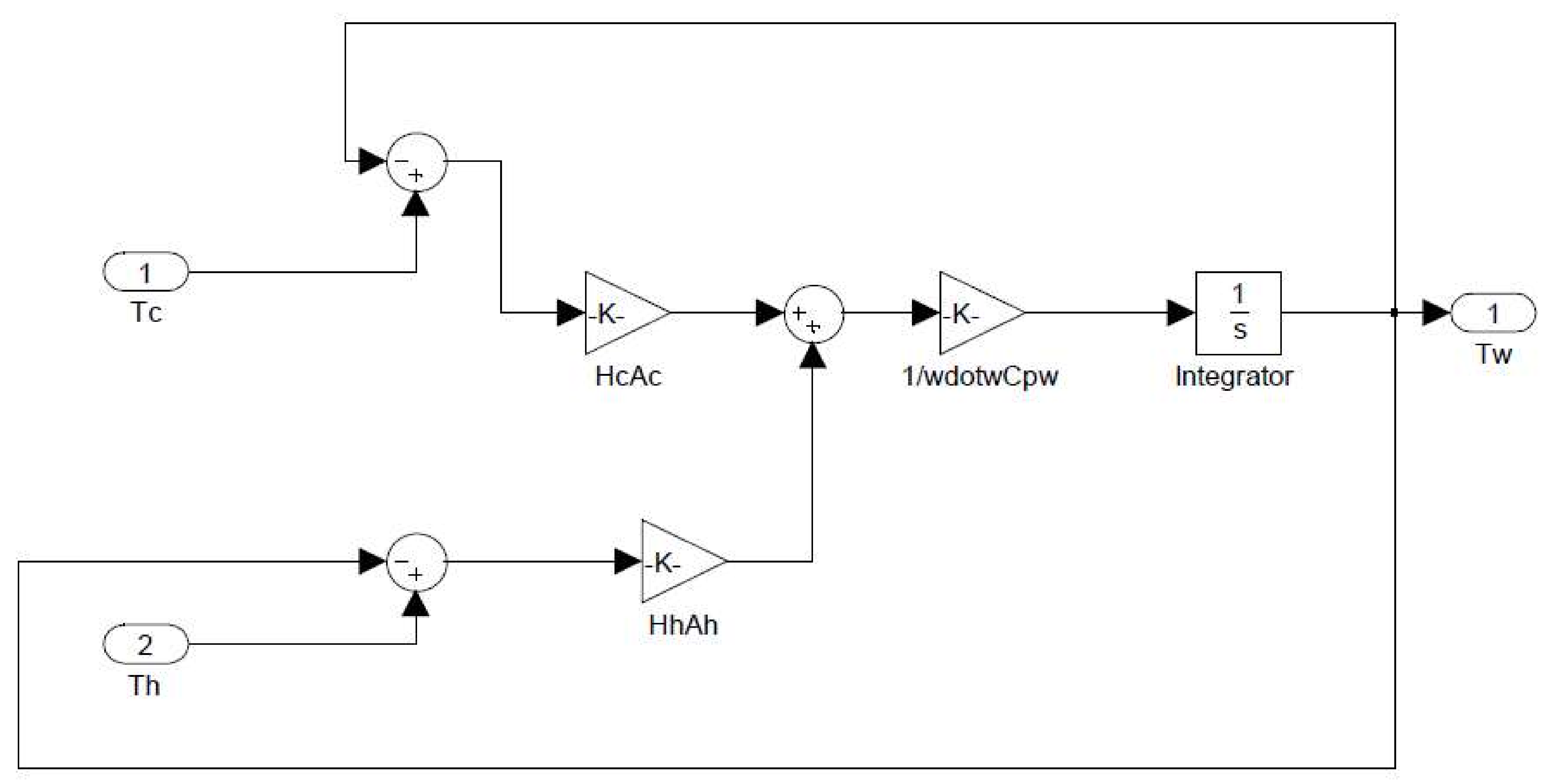
Subsystem for hot side



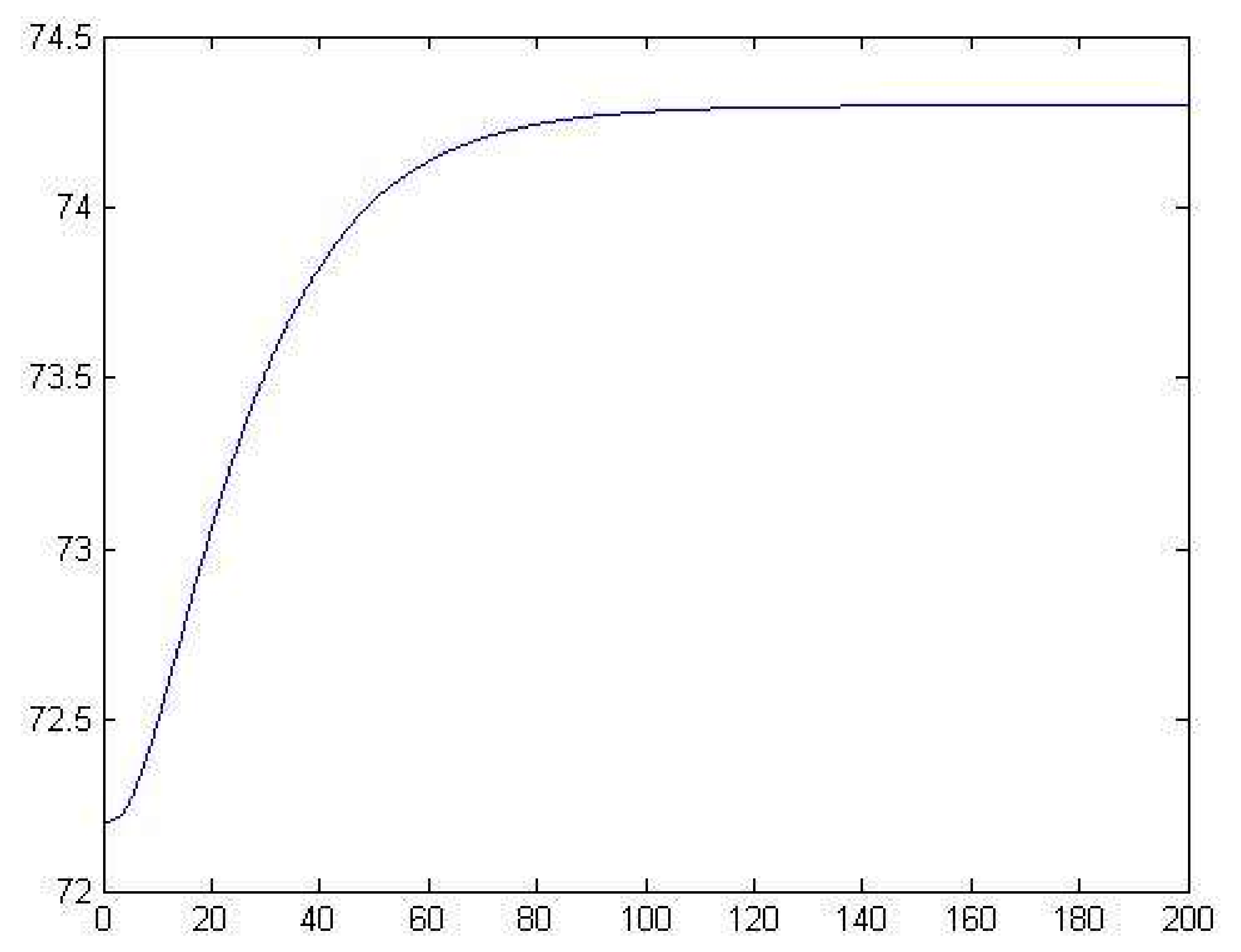
Subsystem for cold side



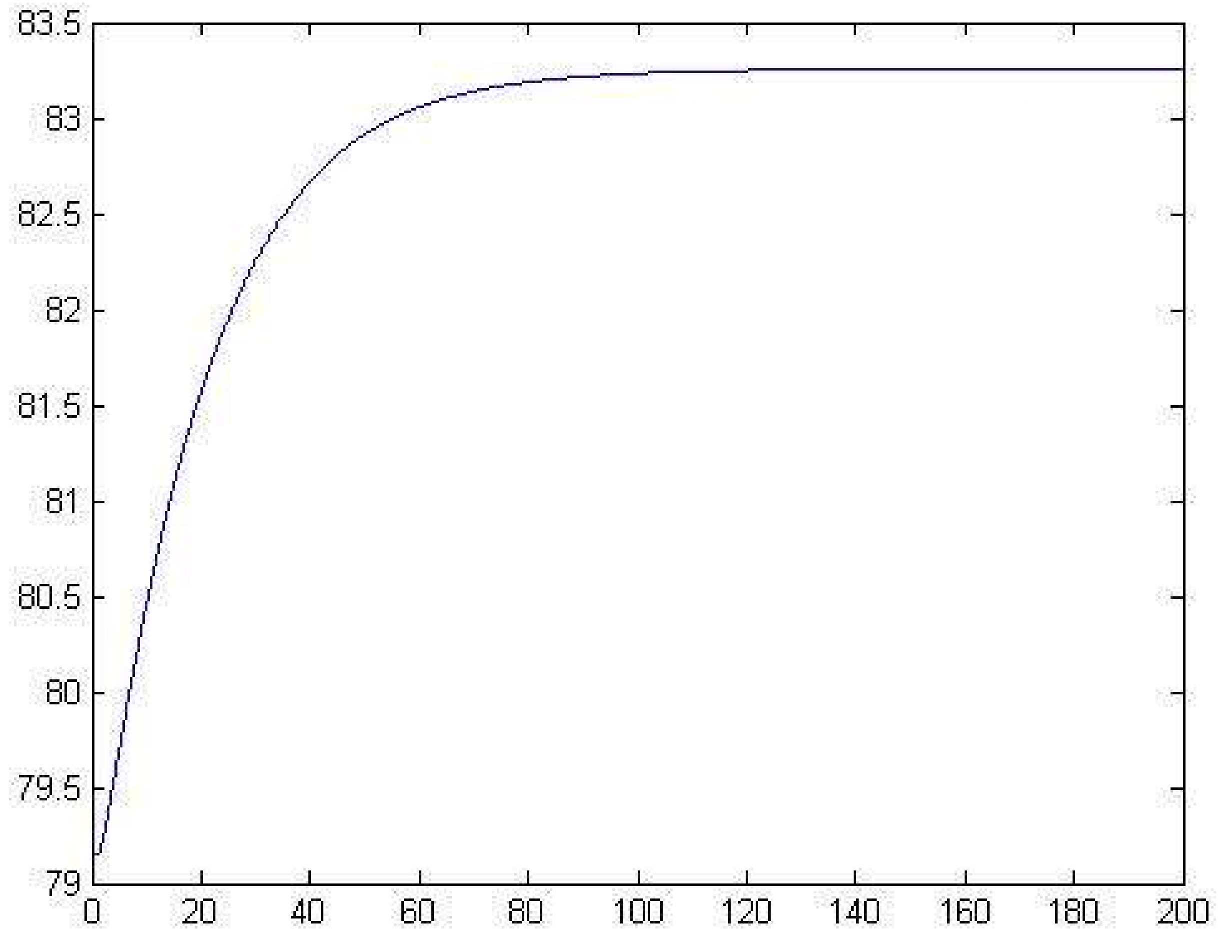
Subsystem for wall material



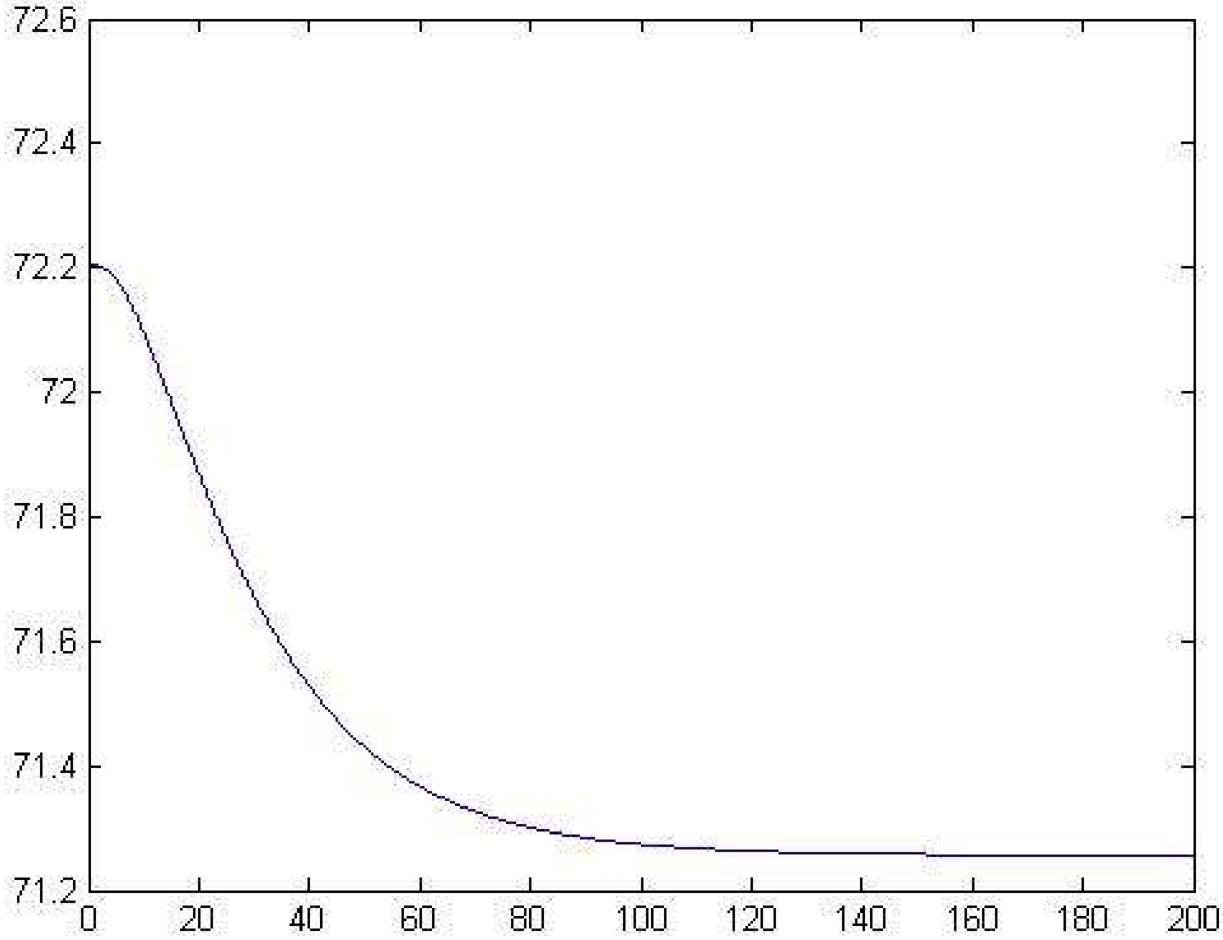
Results



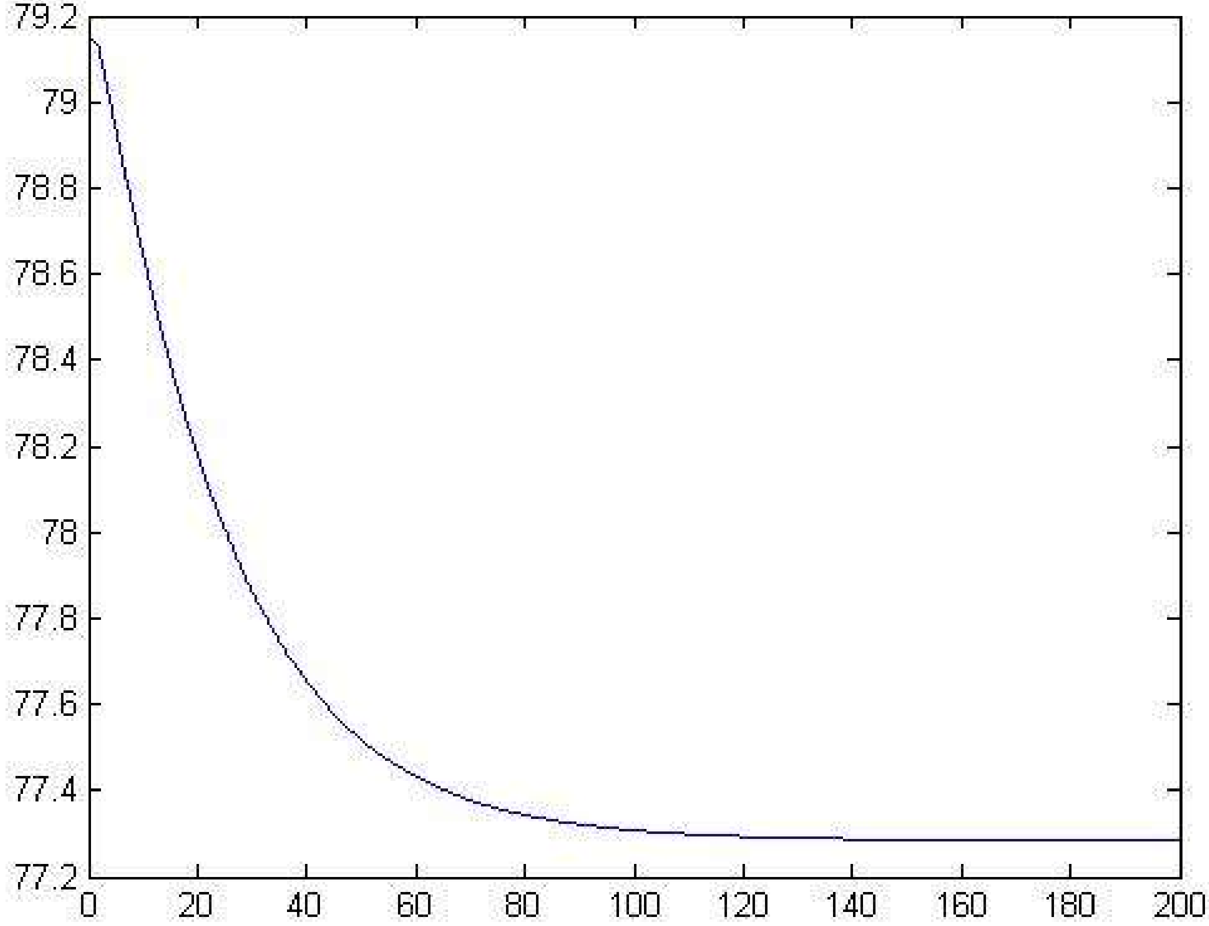
Cold side temperature change for step change of hot water flowrate (0.805+0.5) lb/s



Cold side wall temperature change for step change of hot water flowrate (0.805+0.5) lb/s



Cold side temperature change for step change of hot water temperature (141–10) ^{o}F



Cold side wall temperature change for step change of hot water temperature (141–10) °F

The distributed parameter model

Independent variables is the function of time and space, that can be represented by partial differential equation.

$$\frac{\partial T_c}{\partial t} = -v_c \frac{\partial T_c}{\partial x} + \frac{h_c A_c}{\rho_c V_c c_{pc}}(T_w - T_c)$$

$$\frac{\partial T_c}{\partial t} = -v_c \frac{\partial T_c}{\partial x} + \frac{1}{\tau_c}(T_w - T_c)$$

Cold fluid in shell side

$$\frac{\partial T_h}{\partial t} = v_h \frac{\partial T_h}{\partial x} + \frac{h_h A_h}{\rho_h V_h c_{ph}}(T_w - T_h)$$

$$\frac{\partial T_h}{\partial t} = v_h \frac{\partial T_h}{\partial x} + \frac{1}{\tau_h}(T_w - T_h)$$

Hot fluid in tube side

$$\frac{\partial T_w}{\partial t} = \frac{h_c A_c}{\rho_w V_w c_{pw}}(T_c - T_w) + \frac{h_h A_h}{\rho_w V_w c_{pw}}(T_h - T_w)$$

$$\frac{\partial T_w}{\partial t} = \frac{1}{\tau_{cw}}(T_c - T_w) + \frac{1}{\tau_{hw}}(T_h - T_w)$$

Wall material

$$\frac{1}{\tau_c} = \frac{\pi n h_c d_{io} L}{\rho_c c_{pc} A_s L}$$

τ_c is time constant of cold side

$$\frac{1}{\tau_h} = \frac{4 h_h}{\rho_h c_{ph} d_i}$$

τ_h is time constant of hot side

Het transfer area

$A_c = \pi d_{io} n L \quad A_h = \pi d_i n L$

Fluid volume

$V_c = A_s L \quad V_h = n\pi d_i^2/4$

$$\frac{1}{\tau_{cw}} = \frac{h_c A_c}{\rho_w V_w c_{pw}}$$

$$\frac{1}{\tau_{hw}} = \frac{h_h A_h}{\rho_w V_w c_{pw}}$$

NUMERICAL SIMULATION

IMPLICIT FINITE DIFFERENCE SCHEME

- Discretized energy equation of cold side fluid at inlet node based on central difference scheme

$$T_{h_i}^{m+1}\left(1+\frac{\Delta t}{\tau_h}\right)+T_{c_{i-1}}^{m+1}\frac{\Delta t v_h}{\Delta x}=T_{hin}\frac{\Delta t v_h}{\Delta x}+T_{h_i}^{m}+\frac{\Delta t}{\tau_h}T_{w_i}^{m}$$

$$T_{c_i}^{m+1}\left(1+\frac{\Delta t}{\tau_c}\right)+T_{c_{i+1}}^{m+1}\frac{\Delta t v_c}{\Delta x}=T_{cin}\frac{\Delta t v_c}{\Delta x}+T_{c_i}^{m}+\frac{\Delta t}{\tau_c}T_{w_i}^{m}$$

- Discretized energy equation of hot side and cold side fluid at middle node based on backward difference scheme

$$T_{h_i}^{m+1}\left(1+\frac{\Delta t}{\tau_h}+\frac{\Delta t v_h}{\Delta x}\right)-T_{c_{i+1}}^{m+1}\frac{\Delta t v_h}{\Delta x}=T_{h_i}^{m}+\frac{\Delta t}{\tau_h}T_{w_i}^{m}$$

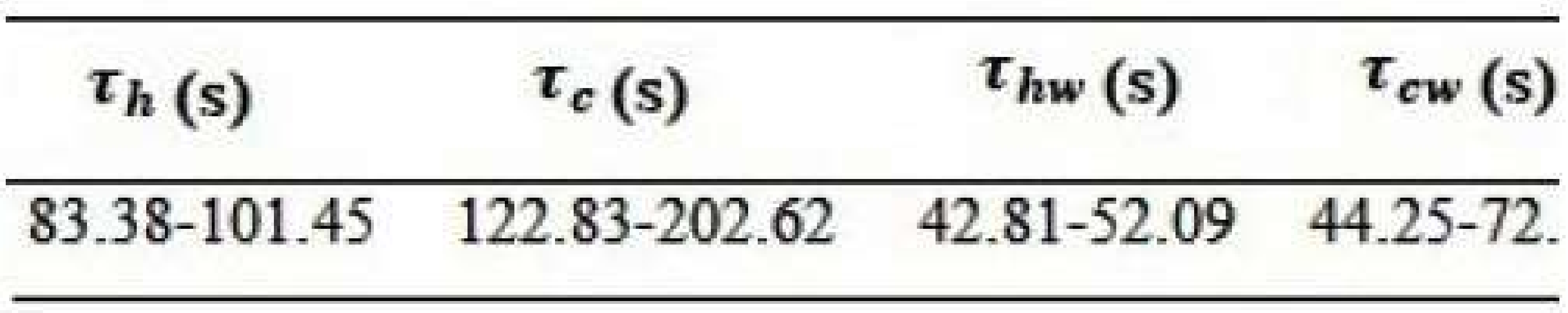
$$T_{c_i}^{m+1}\left(1+\frac{\Delta t}{\tau_c}+\frac{\Delta t v_c}{\Delta x}\right)+T_{c_{i-1}}^{m+1}\frac{\Delta t v_c}{\Delta x}=T_{c_i}^{m}+\frac{\Delta t}{\tau_c}T_{w_i}^{m}$$

- Discretized energy equation of wall material

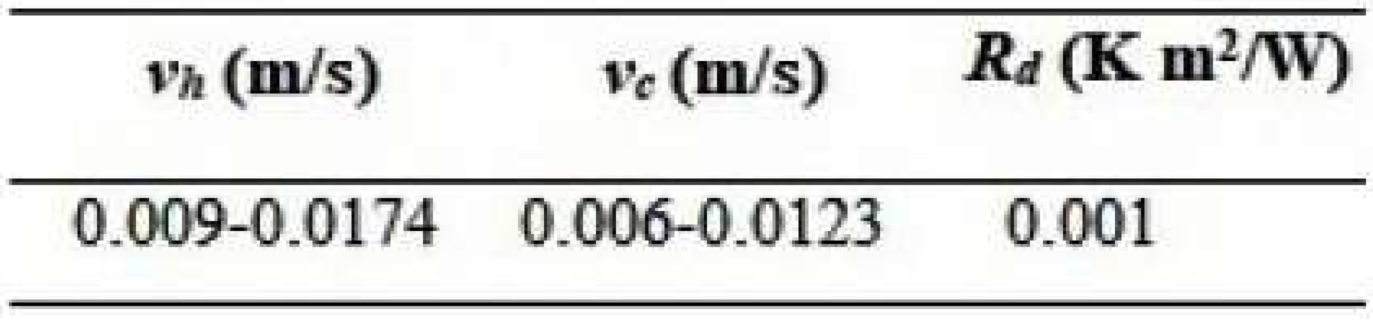
$$T_{w_i}^{m+1}\left(1+\frac{\Delta t}{\tau_{cw}}+\frac{\Delta t}{\tau_{hw}}\right)=T_{w_i}^{m}+\frac{\Delta t}{\tau_{cw}}T_{c_i}^{m}+\frac{\Delta t}{\tau_{hw}}T_{h_i}^{m}$$

- The generated tridiagonal matrix is solved using matrix inversion technique using a ***Matlab*** code.

Table. Range of model parameters, operating velocity and dirt factor



τ_h (s)	τ_c (s)	τ_{hw} (s)	τ_{cw} (s)
83.38-101.45	122.83-202.62	42.81-52.09	44.25-72.



v_h (m/s)	v_c (m/s)	R_d (K m^2/W)
0.009-0.0174	0.006-0.0123	0.001

SIMULATED TRANSIENT ANALYSIS

- Steady state solution of the governing equations (energy equation) is estimated.
- Based on the steady state solution, temperature distributions in the shell and tube side heat exchanger is obtained using the finite difference scheme.
- Considering the steady state temperature distributions as initial condition, perturbations (step change) of inlet temperature and flow rate is given to obtain transient temperature response of the other side of the shell and tube heat exchanger using the code.

ANALYTICAL SIMULATION AND TRANSIENT ANALYSIS

- The temperature deviations were derived from energy balance equations and presented in terms of Laplace domain model equation

$$\frac{d\bar{T}'_c}{dx} + \frac{p(s)}{v_{cs}}\bar{T}'_c = \frac{q(s)}{v_{cs}}\bar{T}'_h$$

$$p(s) = s + \frac{1}{\tau_c} - \frac{\tau_{hw}}{\tau_c(\tau_{hw}\tau_{cw}s + \tau_{cw} + \tau_{hw})} \text{ and } q(s) = \frac{\tau_{cw}}{\tau_c(\tau_{hw}\tau_{cw}s + \tau_{cw} + \tau_{hw})}$$

- The exact solution of the equation is

$$\bar{T}'_c = \bar{T}'_h \frac{q(s)}{p(s)}\left(1 - e^{-\frac{p(s)}{v_{cs}}x}\right)$$

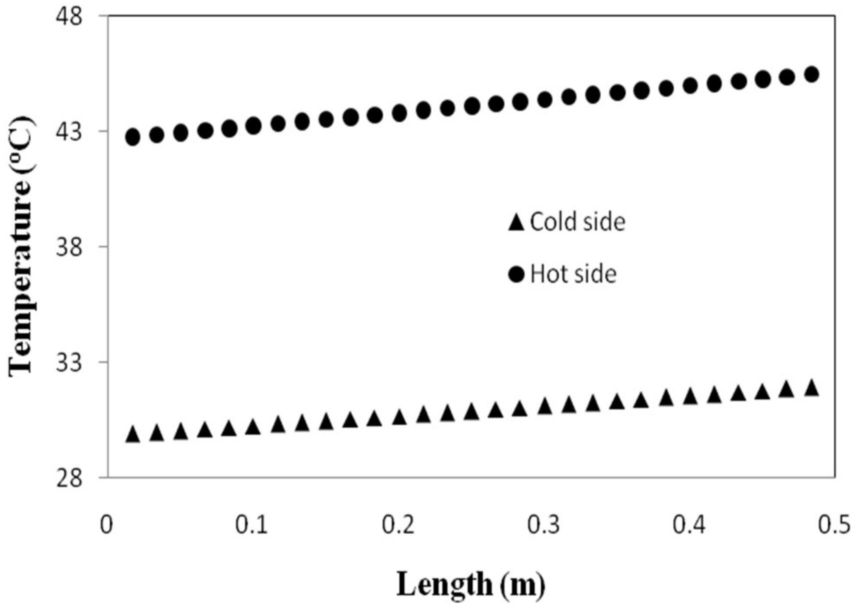
$$\bar{T}'_c = \frac{A}{s}\frac{q(s)}{p(s)}\left(1 - e^{-\frac{p(s)}{v_{cs}}L}\right)$$

For a step change of hot fluid temperature of amplitude, A^{o}C, the response of cold fluid temperature at x=L.

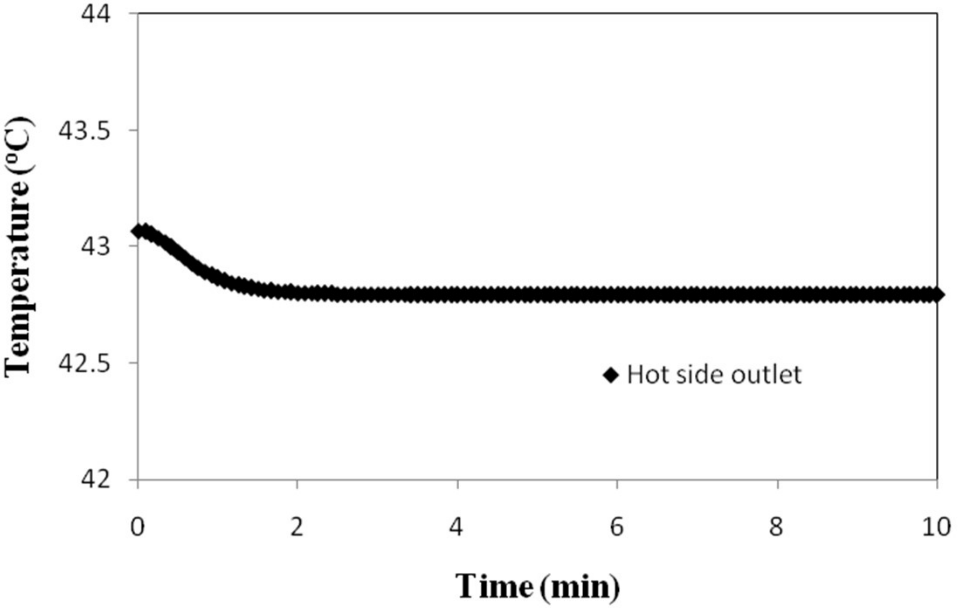
RESULTS AND DISCUSSIONS

NUMERICAL SIMULATION

Hot fluid velocity (0.0132 ±0) m/s and cold fluid velocity (0.009+0.003) m/s

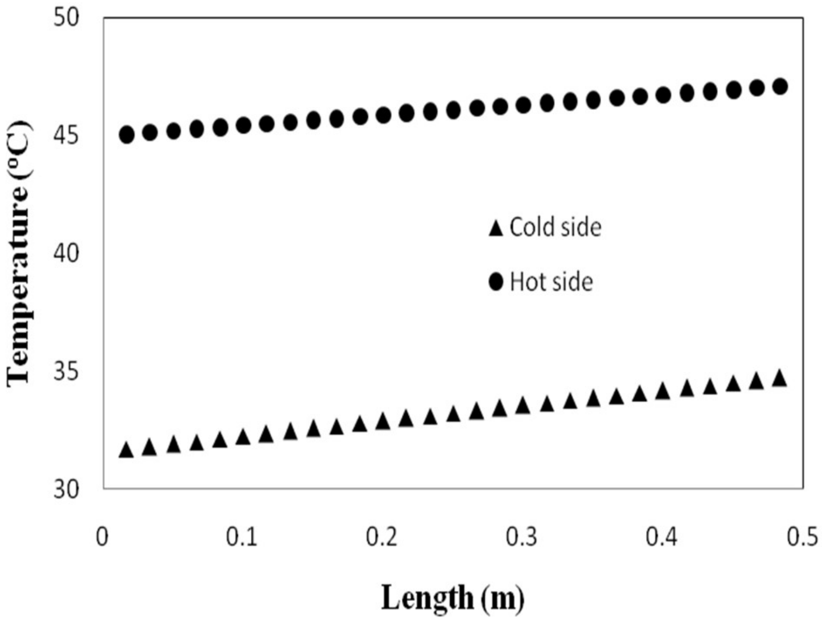


Computed steady state temperature distribution

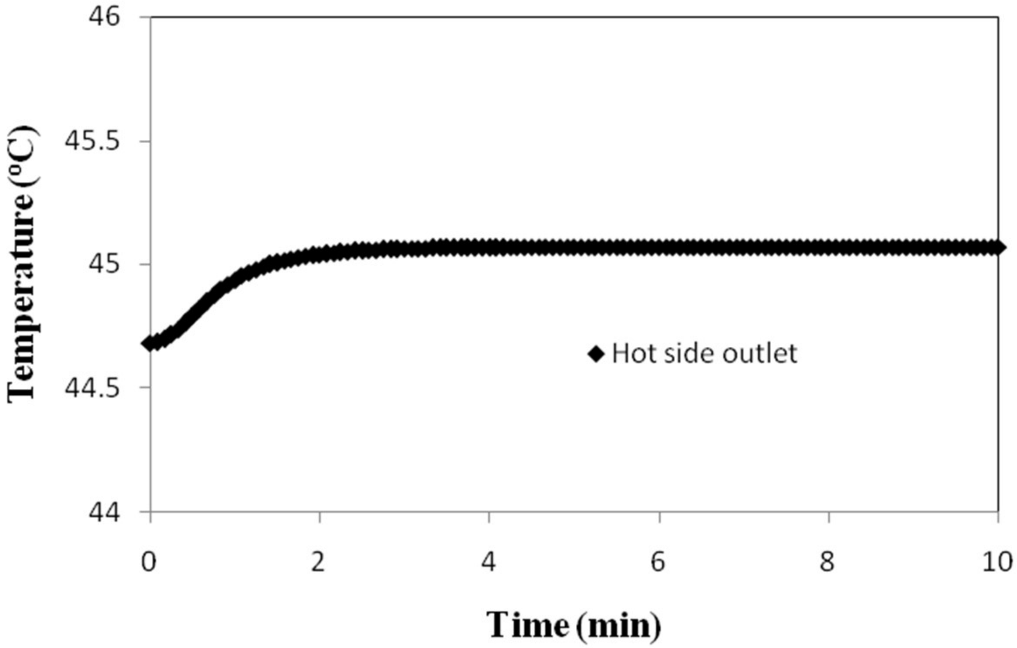


Transient response of hot side outlet temperature of water for step change of cold side water velocity by +0.003 m/s.

Hot fluid velocity (0.0132 ±0) m/s and cold fluid velocity (0.009- 0.003) m/s

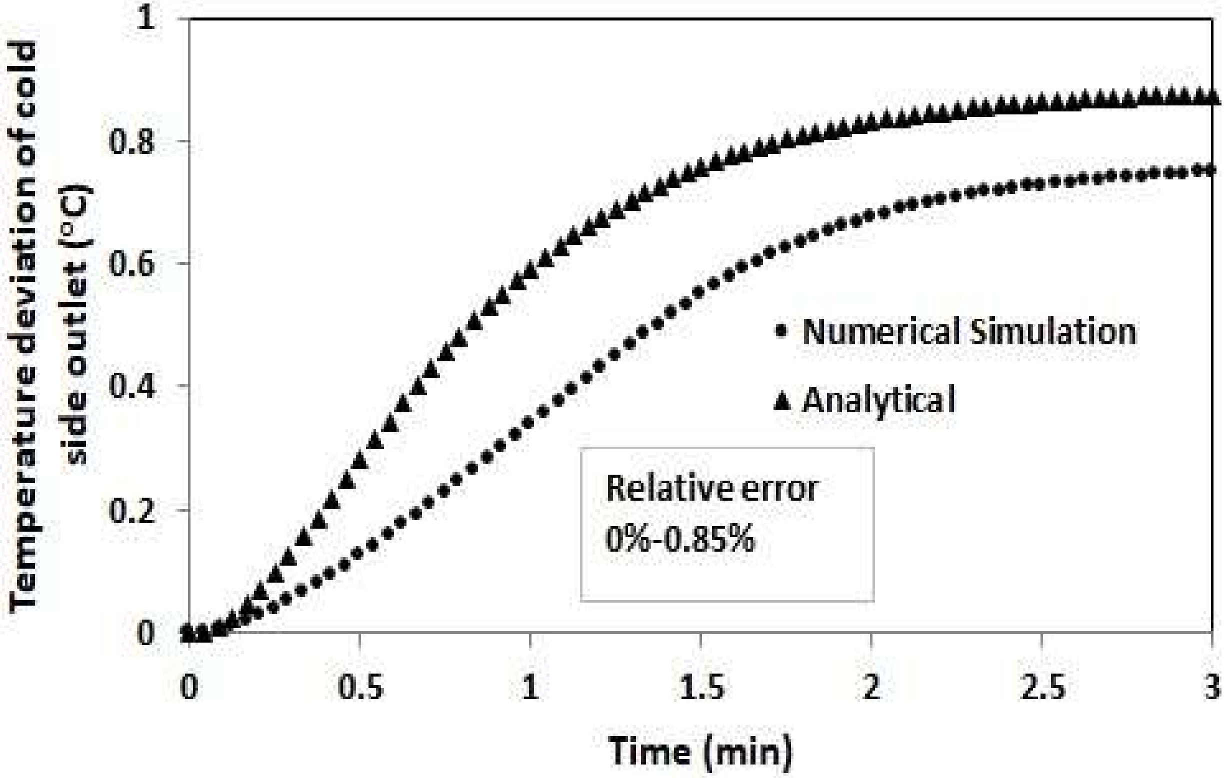


Computed steady state temperature distribution



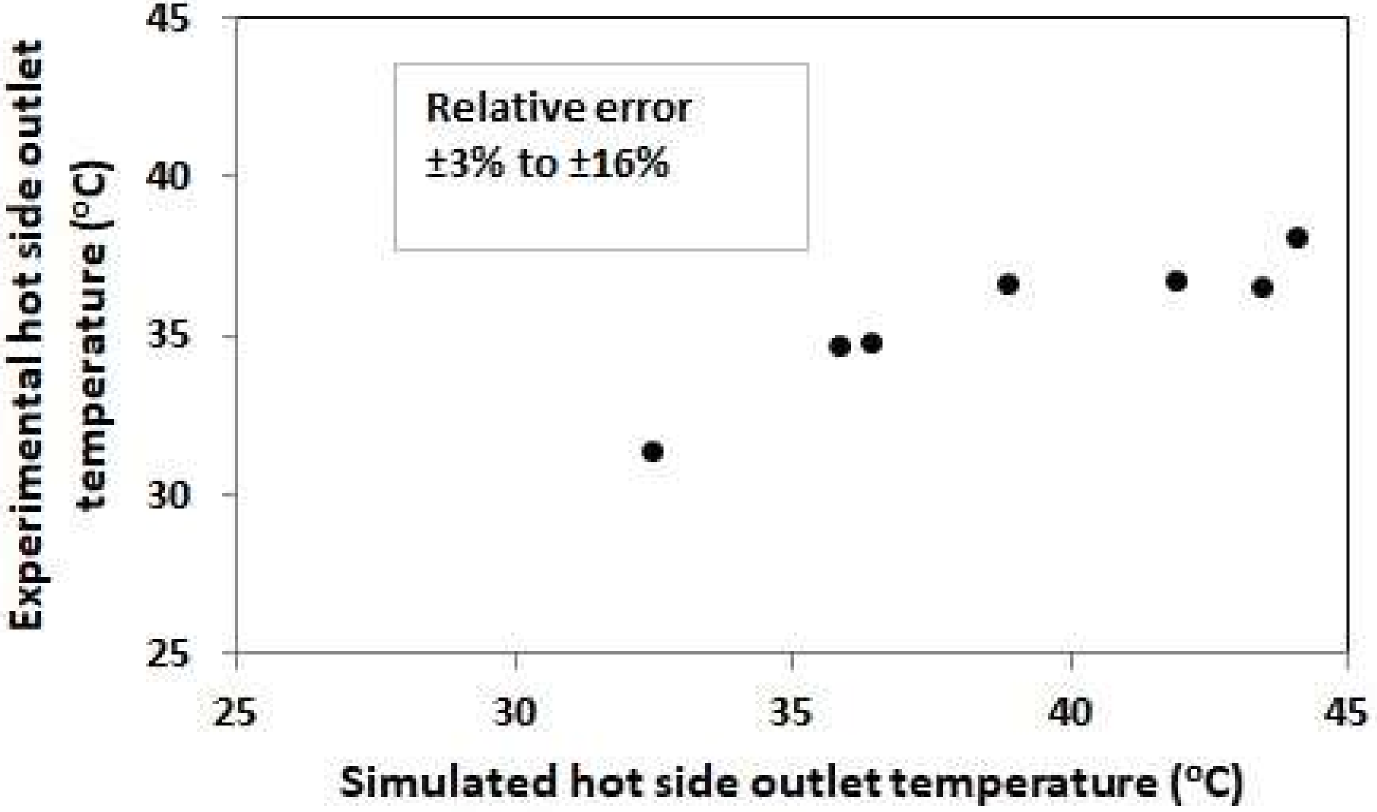
Transient response of hot side outlet temperature of water for step change of cold side water velocity by -0.003 m/s.

COMPARISON OF NUMERICAL AND ANALYTICAL RESULTS



Transient response of cold side outlet temperature of water for step change of hot side water temperature by +5°C

COMPARISON OF EXPERIMENTAL AND NUMERICAL RESULTS

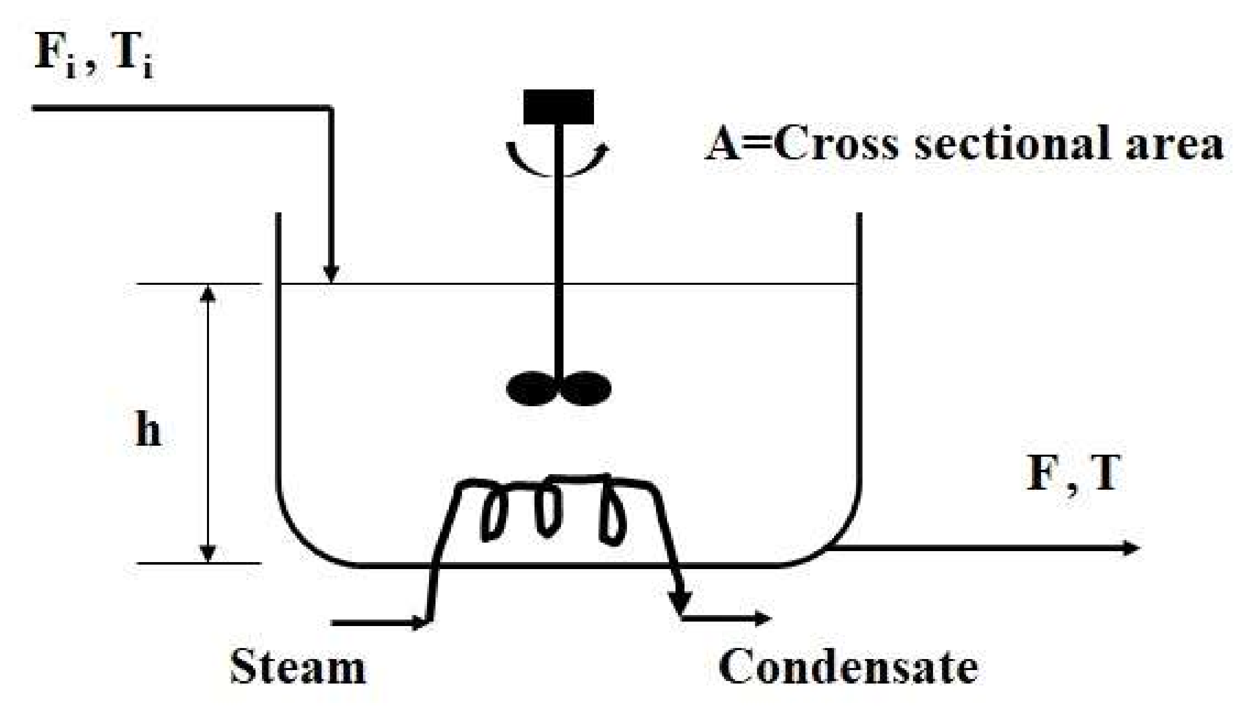


Comparison of experimental hot water outlet temperature with numerically simulated hot water outlet temperature at steady state

- Effectiveness relation as a function of number of transfer unit NTU is incorporated to model heat exchanger of more than one pass.

Stirred tank heater-A Nonlinear System

- Consider the stirred Tank Heater System (Figure): Total momentum of the system remains constant and will not be considered. **Write total mass balance**: Total mass in the tank at any time t =*r*V =*r*Ah where A represents cross sectional area, h represents height of liquid and *r* represents density of the liquid. Assuming that the density is independent of the temperature and remains constant. Take $F = 0.02236\sqrt{h}$. **Write energy balance** equation considering no change in kinetic energy and potential energy. For liquid system assume change of internal energy same as enthalpy change. Heat given through steam is *Q*=5 kW and it is remains unchanged. Draw *Simulink* model of the system - total mass balance and energy balance equations with state variables h (in material balance) and T (in energy balance). Find the steady state h and steady state T of the tank. Take inlet temperature of the tank T_i=30 ^oC, inlet flow rate of the tank F_i=0.01 m^3/min. A=1 m^2, *r*=800 kg/m^3, C_p=2000 J/kg-^oC. Show the response of h and T for a step change of F_i (0.01+0.012).



- Mass balance: $\frac{d(\rho A h)}{dt} = \rho F_i - \rho F; A\frac{dh}{dt} = F_i - 0.02236\sqrt{h}$
- Energy balance: $\frac{d(\rho A h c_p T)}{dt} = \rho F_i c_p T_i - \rho F c_p T + Q$

$$A\frac{d(hT)}{dt} = F_i T_i - FT + \frac{Q}{\rho c_p}$$

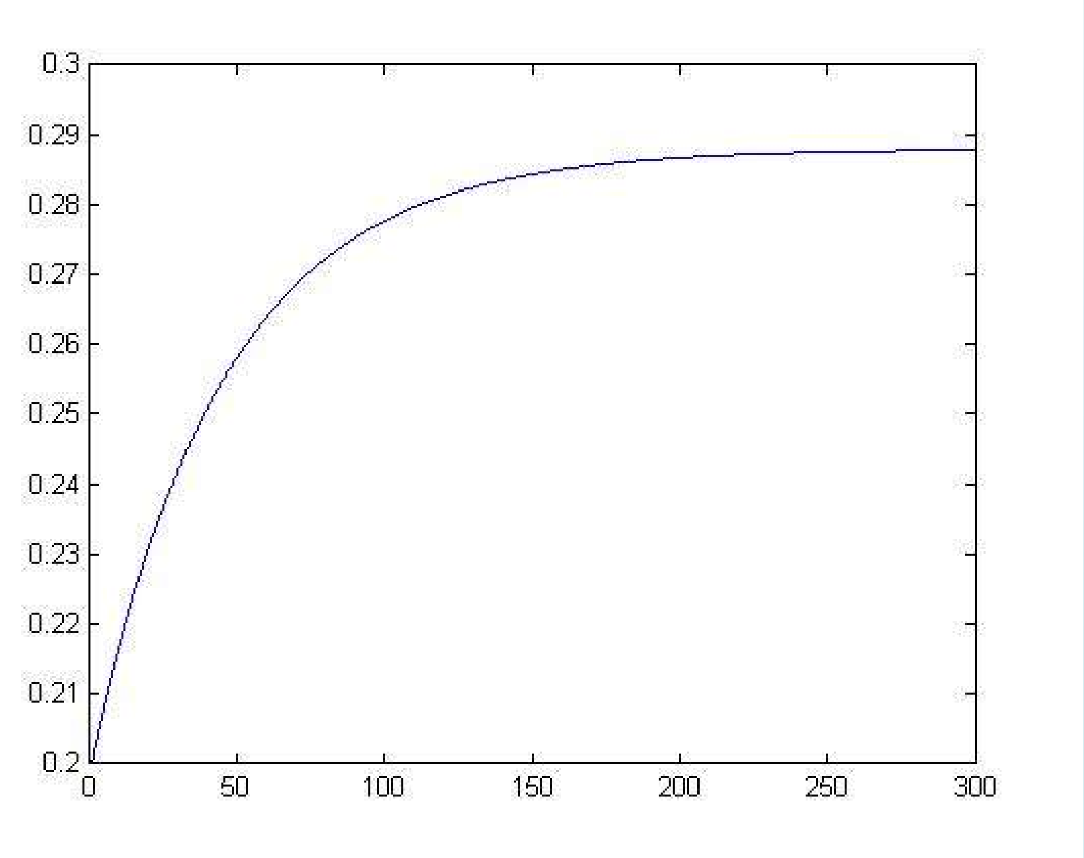
$$Ah\frac{dT}{dt} = F_i(T_i - T) + \frac{Q}{\rho c_p}$$

- Steady state solutions

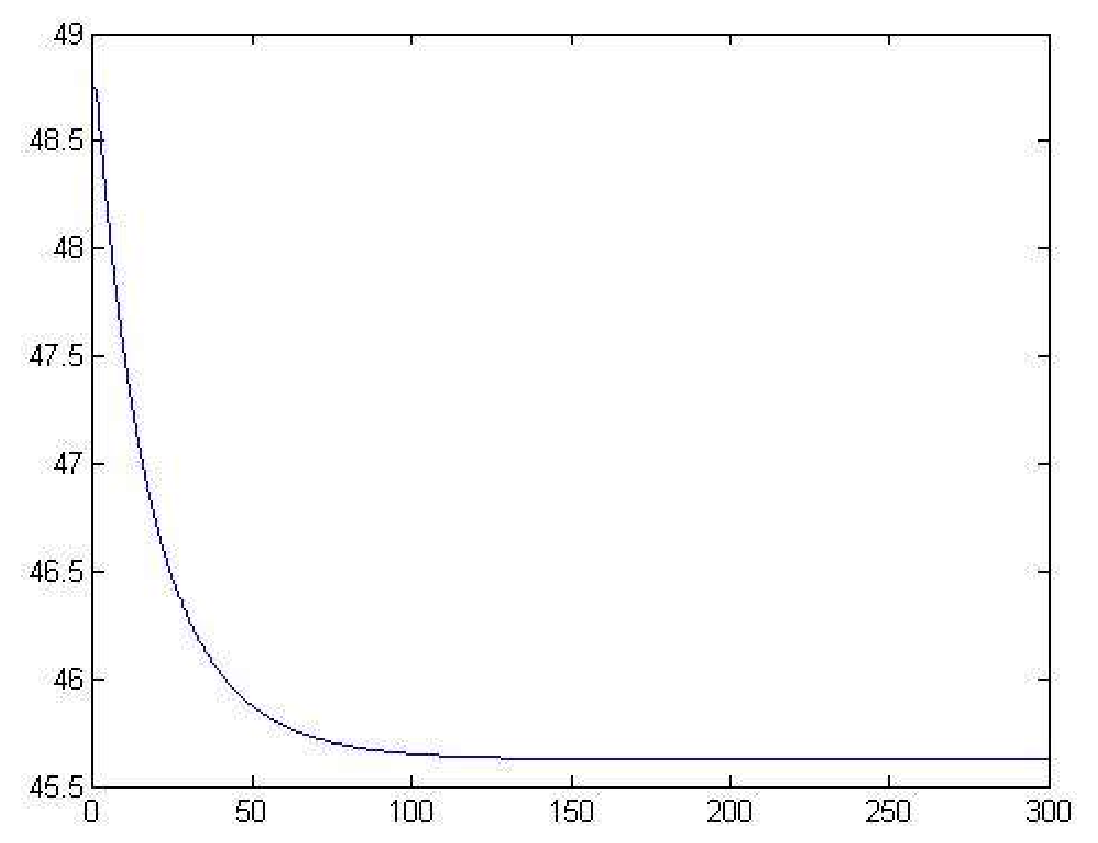
$$0 = F_i - 0.02236\sqrt{h}$$

$$0 = F_i(T_i - T) + \frac{Q}{\rho c_p}$$

$$[h_s\ T_s]' = [0.2\ 48.75]'$$

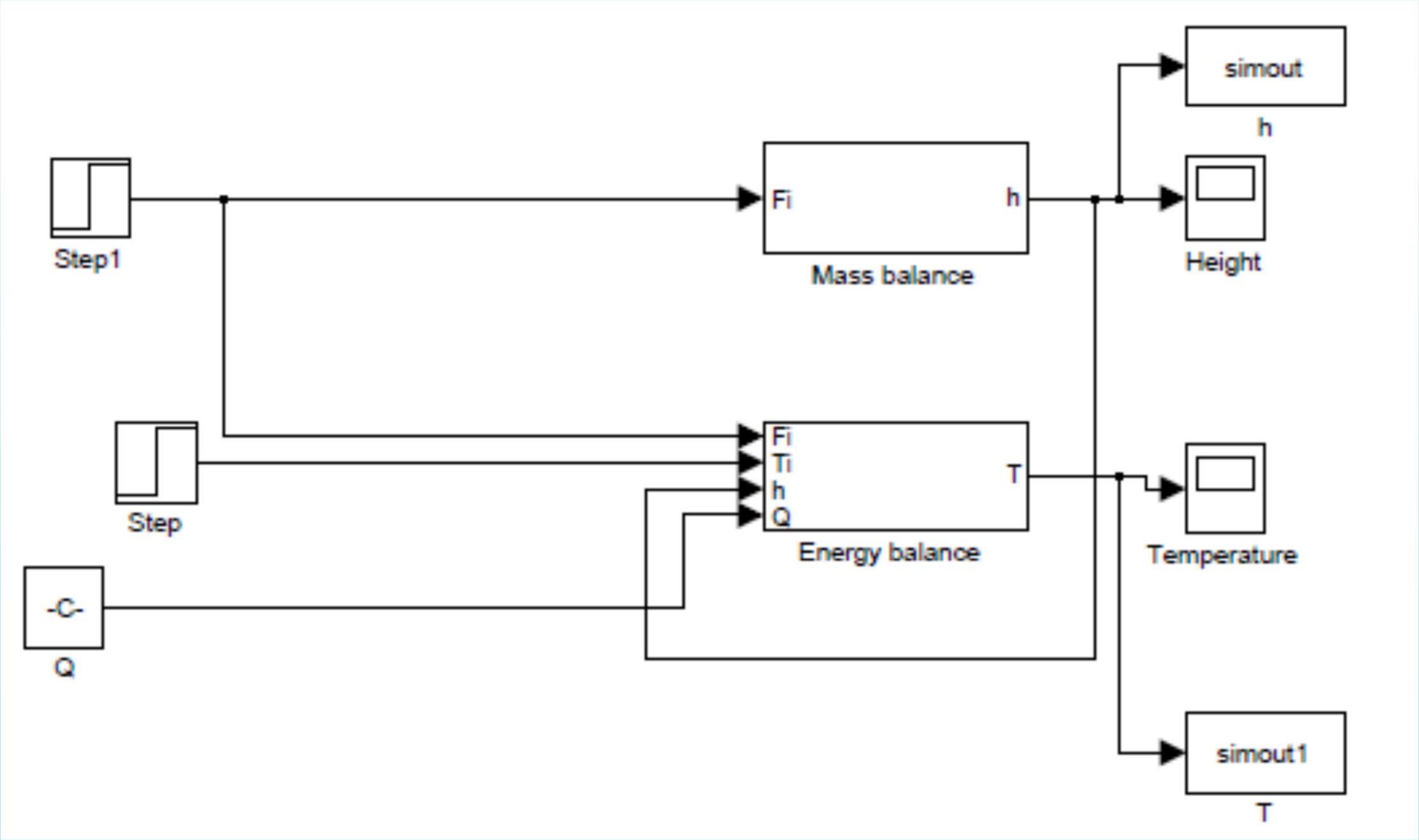


Response of tank level for the step change of inlet flowrate (0.01+0.002)

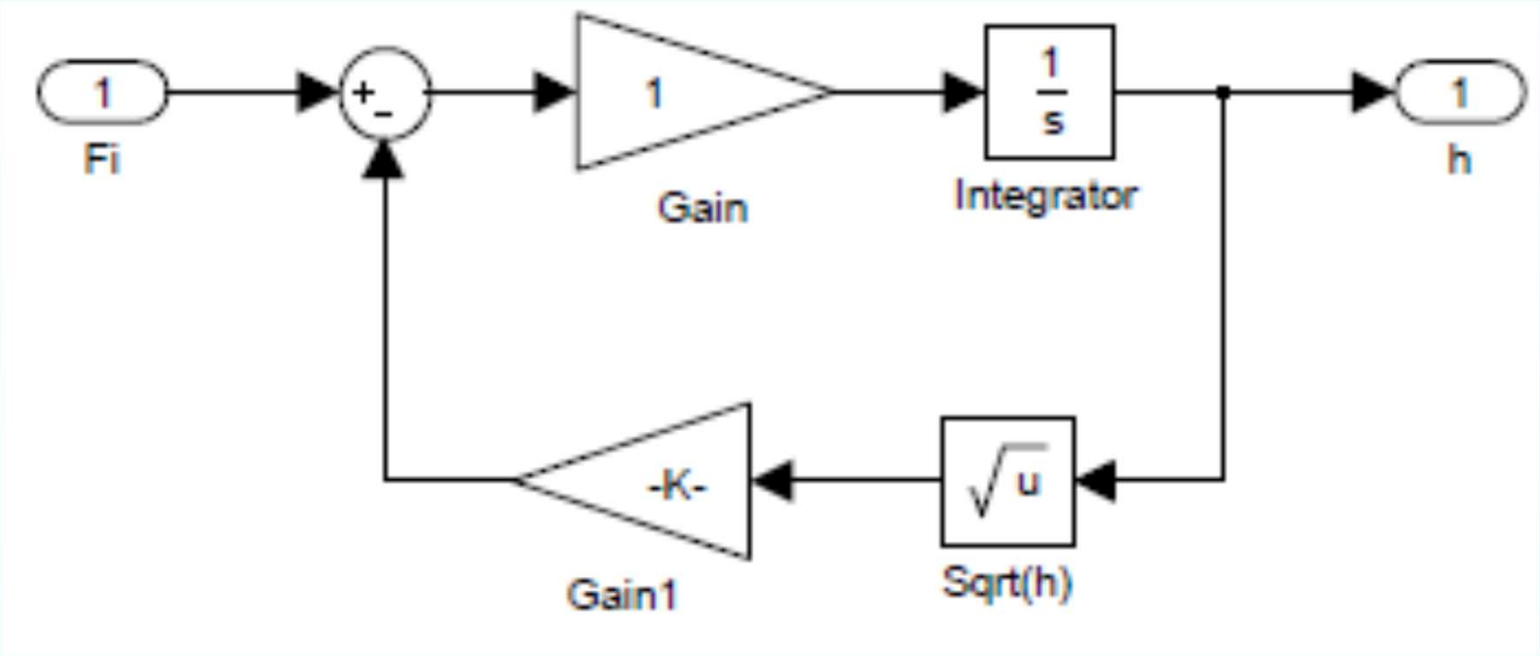


Response of tank temperature for the step change of inlet flowrate (0.01+0.002)

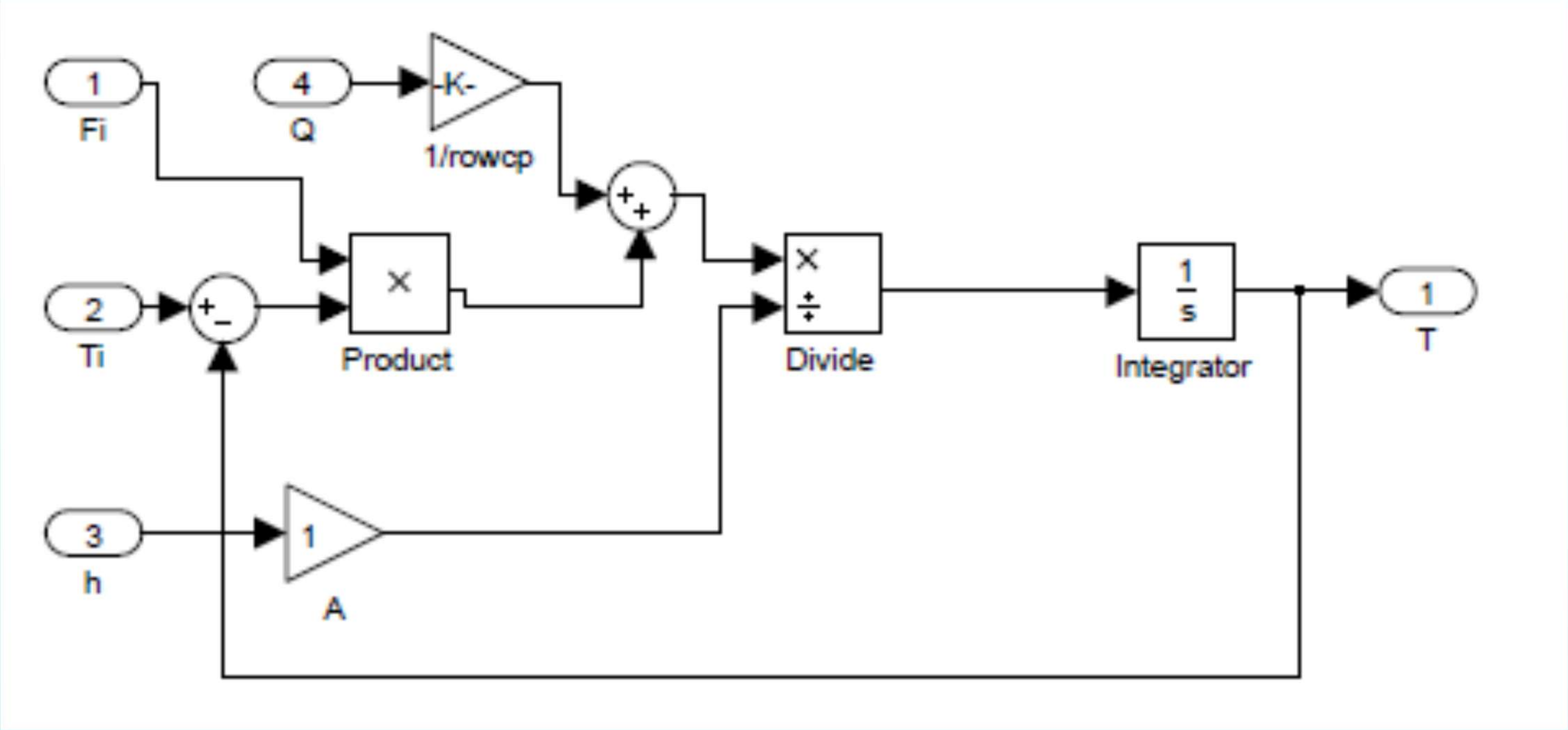
Simulink block diagram



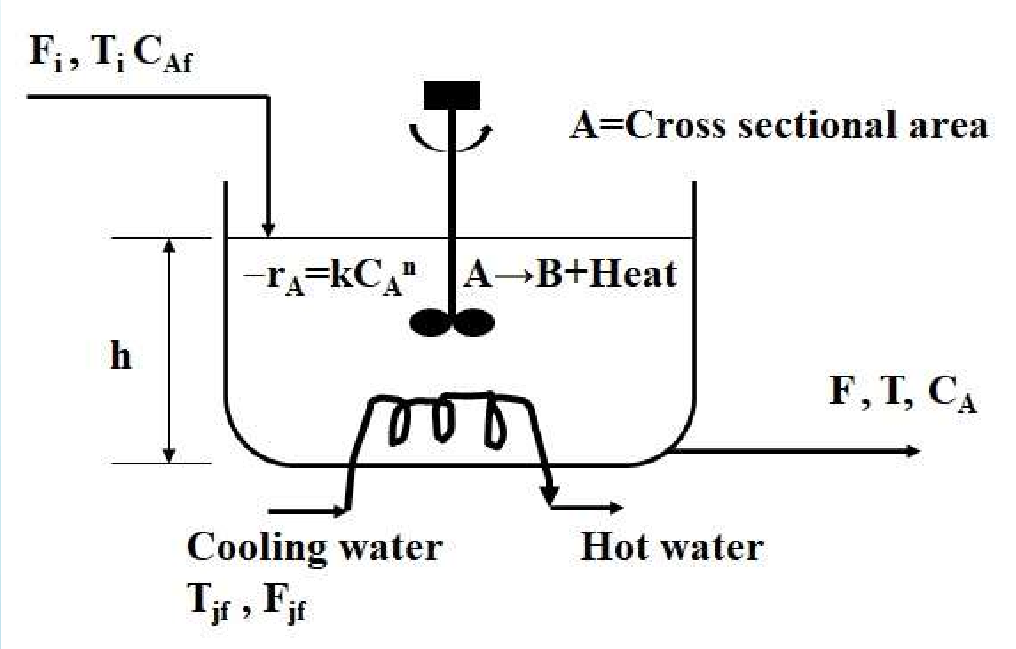
Mass balance subsystem



Energy balance subsystem



Exothermic CSTR with cooling system -A Nonlinear System with unstable dynamics



Mass balance of species A

$$\frac{dC_A}{dt}=\frac{F}{V}\left(C_{Af}-C_A\right)-k_0C_A\exp\left(\frac{-E_a}{RT}\right)$$

Energy balance balance of reactor

$$\frac{dT}{dt}=\frac{F}{V}\left(T_f-T\right)-\frac{\left(-\Delta H\right)}{\rho c_p}k_0C_A\exp\left(\frac{-E_a}{RT}\right)-\frac{UA}{V\rho c_p}\left(T-T_j\right)$$

Energy balance balance of jacket

$$\frac{dT_j}{dt}=\frac{F_{jf}}{V_j}\left(T_{jf}-T_j\right)+\frac{UA}{V_j\rho_j c_{pj}}\left(T-T_j\right)$$

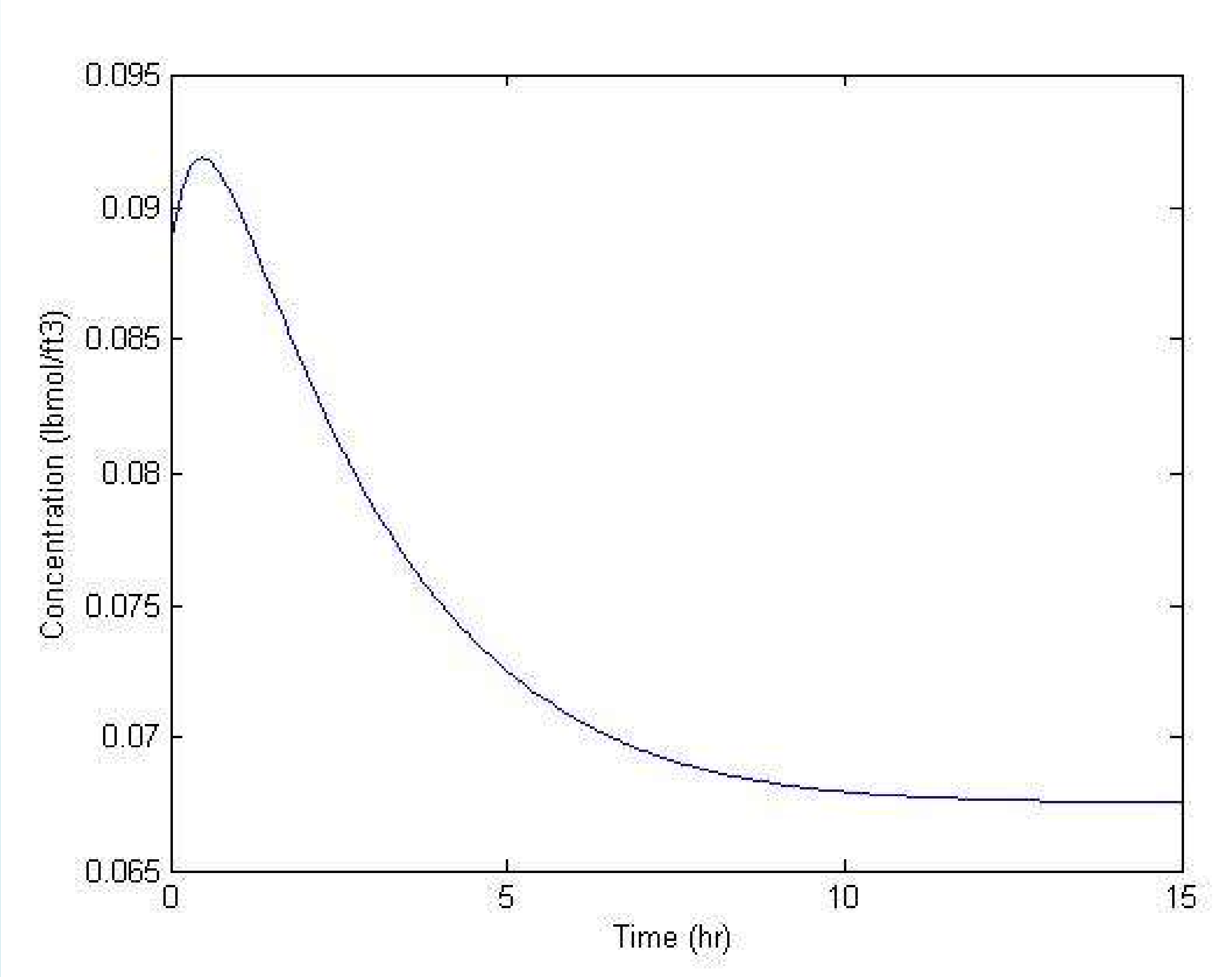
Transient using Matlab-function

```
function f=cstr(t,x)
global F Fjf V Vj rowcp rowjcpj U A Ea R k0 delH Tf Tjf Caf
C=x(1);
T=x(2);
Tj=x(3);
f(1)=(F/V)*(Caf-C)-k0*C*exp(-Ea/(R*(T+459.6)));
f(2)=(F/V)*(Tf-T)+(delH/(rowcp))*k0*C*exp(-Ea/(R*(T+459.6)))-(U*A/(V*rowcp))*(T-Tj);
f(3)=(Fjf/Vj)*(Tjf-Tj)+(U*A/(Vj*rowjcpj))*(T-Tj);
f=f';
```

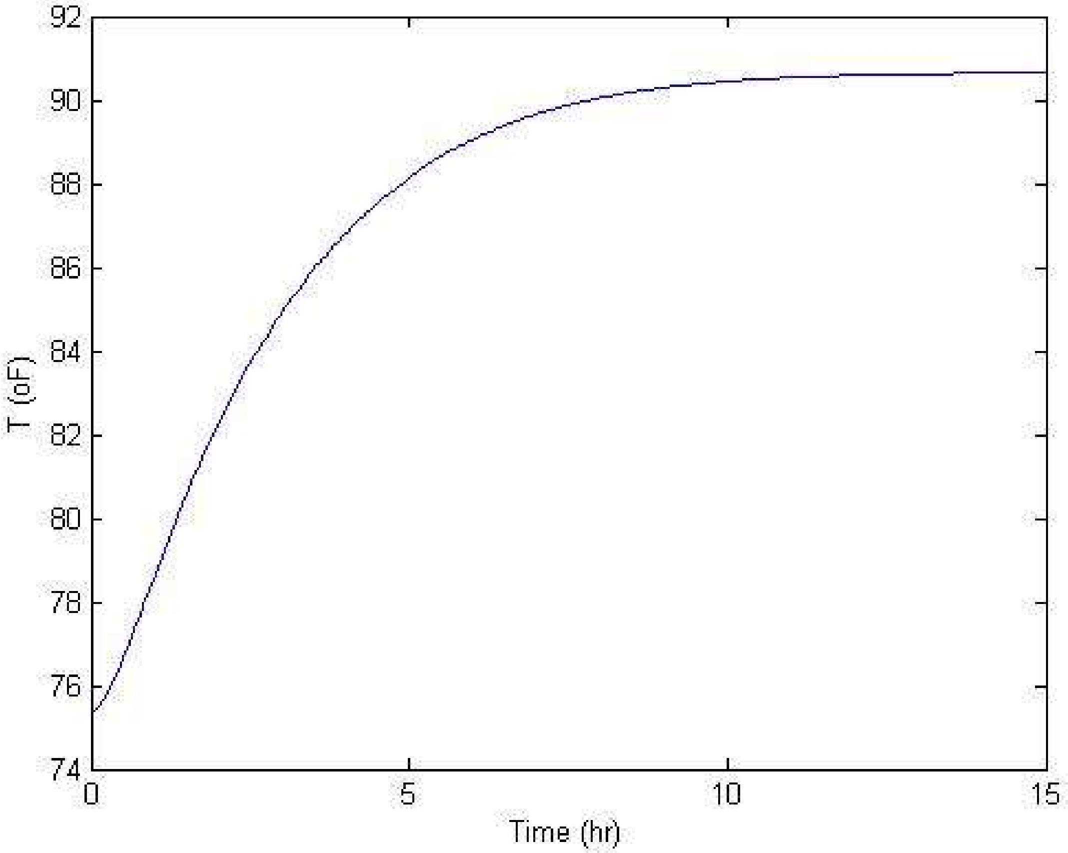
- Main program

```
    clc;
    clear all;
    global F Fjf V Vj rowcp rowjcpj U A Ea R k0 delH Tf Tjf Caf
    F=200+40; %F=(200+40)*0.0283168/3600 m3/s
    Fjf=300;   %F=300* 0.0283168/3600 m3/s
    V=100; %V=100*0.0283168 m3
    Vj=25; % Vj=25*0.0283168 m3;
    rowcp=53.25;%rowcp= 20699.53*53.25 J/m3/K
    rowjcpj=55.6; ;%rowcp= 20699.53*55.6 J/m3/K
    U=75;
%BTU/hr/ft2/oF to W/m2/oK
% U=425.86975;
    R=1.987;
    k0=16.96*10^(12);
% hr-1 to s-1
%k0=(16.96*10^(12))/3600;
% 1 lb-mol=0.45359237 kg mol
% 1 BTU= 1055.06 J
    delH=39000; % delH=39000*2326.021 J/kg mol
    Ea=32400;
%1 BTU/lb mol=2326.021 J/kg mol
%Ea=32400*2326.021;
    Caf=0.132; % Caf=0.132* 0.45359237/0.0283168 kg mol/m3;
    A=88; % A=88*0.092903 m2;
    Tjf=0;
    Tf=77;
    [t,x]=ode45(@cstr,[0 15],[0.08855 75.3563 21.36174]);
    plot(t,x(:,1))
```

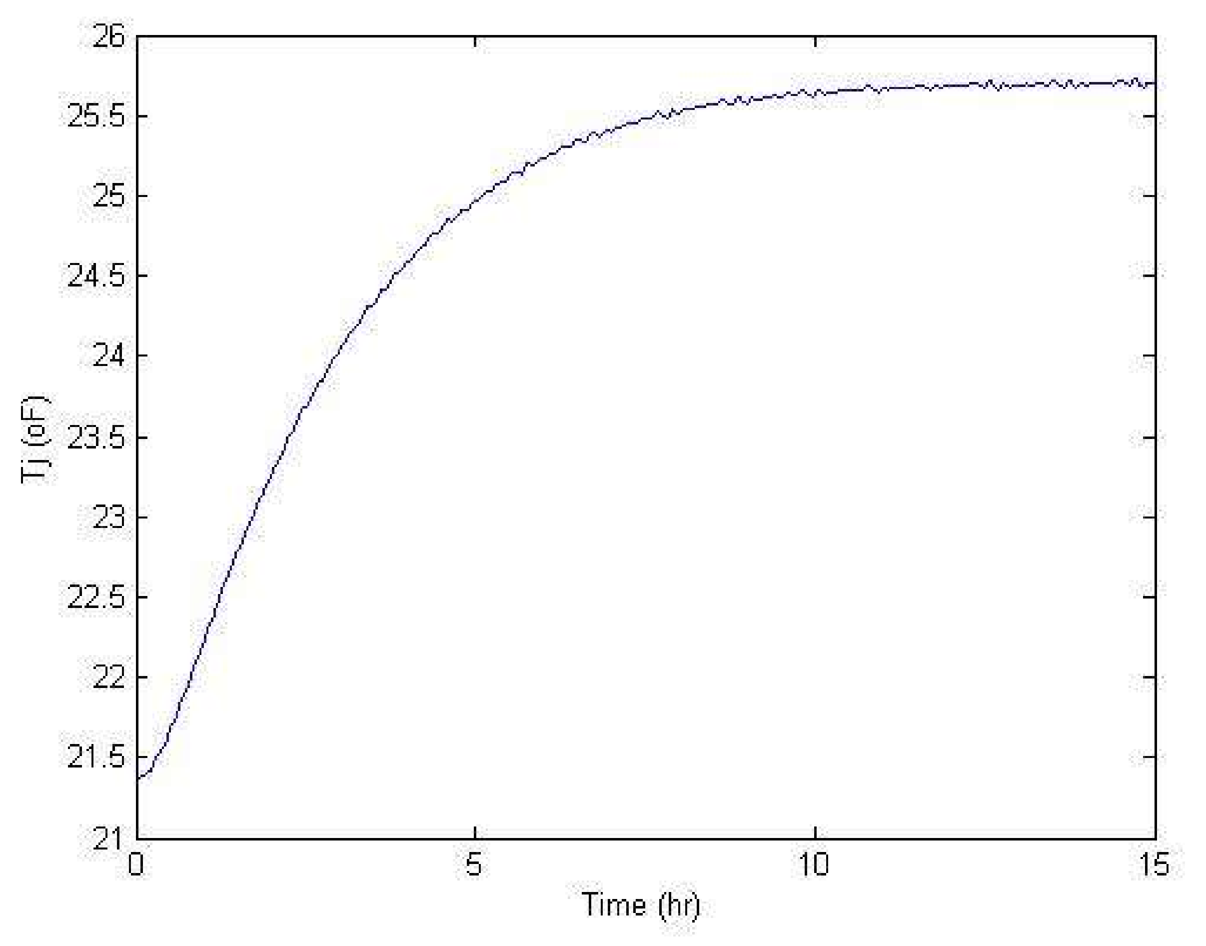
Result



Response of C_A for step change of feed flow rate (200+40) ft^3/hr



Response of T for step change of feed flow rate (200+40) ft^3/hr



Response of T_j for step change of feed flow rate (200+40) ft^3/hr

Linearization of process

- linearization of a nonlinear function is obtained using a Taylor series expansion. Considering first order truncation of the series,

Single variable

$$f(x) = f(x_s) + \left.\frac{df}{dx}\right|_{x_s} \left(x - x_s\right) + \text{higher order terms}$$

Double variable

$$f(x,y) = f(x_s, y_s) + \left.\frac{df}{dx}\right|_{(x_s, y_s)} \left(x - x_s\right) + \left.\frac{df}{dy}\right|_{(x_s, y_s)} \left(y - y_s\right) + \text{higher order terms}$$

x_s, y_s are the steady sate values of x and y respectively

Maas balance Equation in non-isothermal CSTR

$$\frac{dC_A}{dt} = \frac{F}{V}\left(C_{Af} - C_A\right) - k_0 C_A \exp\left(\frac{-E_a}{RT}\right)$$

Eq.(a)

$$\frac{dC_A}{dt} = \frac{F}{V}\left(C_{Af} - C_A\right) - k_0 C_{As} \exp\left(\frac{-E_a}{RT_s}\right) - k_0 C_{As} \exp\left(\frac{-E_a}{RT_s}\right)\left(C_A - C_{As}\right)$$

$$-k_0 C_{As}\left(\exp\left(\frac{-E_a}{RT_s}\right)\right)\left(\frac{E_a}{RT_s^2}\right)\left(T - T_s\right)$$

Eq.(b)

After linearization

$$\frac{dC_{As}}{dt} = 0 = \frac{F}{V}\left(C_{Af} - C_{As}\right) - k_0 C_{As} \exp\left(\frac{-E_a}{RT_s}\right)$$

Steady sate equation **Eq.(c)**

Maas balance Equation in terms of deviation variable

$$\frac{d\overline{C}_A}{dt} = -\frac{F}{V}\left(\overline{C}_A\right) - k_0 \exp\left(\frac{-E_a}{RT_s}\right)\left(\overline{C}_A\right) - k_0 C_{As}\left(\exp\left(\frac{-E_a}{RT_s}\right)\right)\left(\frac{E_a}{RT_s^2}\right)\left(\overline{T}\right)$$

Eq.(d)

The deviation variables are

$$\overline{C_A} = C_A - C_{As}$$

$$\overline{T} = T - T_s$$

$$\overline{T_j} = T_j - T_{js}$$

At steady state

$$\overline{C_A} = C_A - C_{As} = 0$$

$$\overline{T} = T - T_s = 0$$

$$\overline{T_j} = T_j - T_{js} = 0$$

Energy balance Equation of CSTR tank in terms of deviation variable

$$\frac{d\overline{T}}{dt} = -\frac{F}{V}\left(\overline{T}\right) - \frac{\left(-\Delta H\right)}{\rho C_p} k_0 \exp\left(\frac{-E_a}{RT_s}\right)\left(\overline{C}_A\right) - \frac{\left(-\Delta H\right)}{\rho C_p} k_0 C_{As}\left(\exp\left(\frac{-E_a}{RT_s}\right)\right)\left(\frac{E_a}{RT_s^2}\right)\left(\overline{T}\right)$$

$$-\frac{UA}{\rho C_p}\left(\overline{T} - \overline{T}_j\right)$$ **Eq.(e)**

Energy balance Equation of cooling jacket in terms of deviation variable

$$\frac{d\overline{T}_j}{dt} = -\frac{F_{jf}}{V_j}\left(\overline{T}_j\right) + \frac{UA}{V_j \rho_j C_{pj}}\left(\overline{T} - \overline{T}_j\right)$$ **Eq.(f)**

- State space model
- The Eqs.(d-f) can be represented to obtain state space model,
- $$\begin{bmatrix} \overset{\bullet}{\overline{C_A}} \\ \overset{\bullet}{\overline{T}} \\ \overset{\bullet}{\overline{T_j}} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} \overline{C_A} \\ \overline{T} \\ \overline{T_j} \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ b_{31} \end{bmatrix} F_{jf}$$

- Where,

$$\overline{C_A} = C_A - C_{As}$$
$$\overline{T} = T - T_s$$
$$\overline{T_j} = T_j - T_{js}$$

and

$$\begin{bmatrix} \overset{\bullet}{\overline{C_A}} \\ \overset{\bullet}{\overline{T}} \\ \overset{\bullet}{\overline{T_j}} \end{bmatrix} == \begin{bmatrix} \dfrac{d\overline{C}_A}{dt} \\ \dfrac{d\overline{T}}{dt} \\ \dfrac{d\overline{T}_j}{dt} \end{bmatrix}$$

$$a_{11} = -\frac{F}{V} - k_0 \exp\left(\frac{-E_a}{RT_s}\right) \quad a_{21} = -k_0 C_{As}\left(\exp\left(\frac{-E_a}{RT_s}\right)\right)\left(\frac{E_a}{RT_s^2}\right) \quad a_{31} = 0$$

$$a_{21} = -\frac{(-\Delta H)}{\rho C_p} k_0 \exp\left(\frac{-E_a}{RT_s}\right) \quad a_{22} = -\frac{F}{V} - \frac{(-\Delta H)}{\rho C_p} k_0 C_{As}\left(\exp\left(\frac{-E_a}{RT_s}\right)\right)\left(\frac{E_a}{RT_s^2}\right) - \frac{UA}{V\rho C_p}\bar{T}$$

$$a_{23} = \frac{UA}{V\rho C_p}$$

$$a_{31} = 0 \qquad a_{32} = \frac{UA}{V_j \rho_j C_{pj}} \qquad a_{33} = -\frac{F_{jf}}{V_j} - \frac{UA}{V_j \rho_j C_{pj}}$$

$$J_s = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

J_s is Jacobian matrix at steady state

$$\det(J_{ss} - \lambda I) = 0 \longrightarrow \det\begin{vmatrix} a_{11}-\lambda & a_{12} & a_{13} \\ a_{21} & a_{22}-\lambda & a_{23} \\ a_{31} & a_{32} & a_{33}-\lambda \end{vmatrix} = 0$$

Stability of nonlinear system

- Brusselator in terms of non-dimensional variables: It resembles dynamics of some typical reaction in CSTR.

$$\frac{dx}{dt} = a - bx + x^2 y - x$$
$$\frac{dy}{dt} = bx - x^2 y$$

Two coupled nonlinear ordinary differential equations- Brusselator dynamical system by Prigogine and Lefever in 1968 and dubbed the "Brusselator" by Tyson in 1973.

- Steady state solution is $\begin{bmatrix} x_{ss} & y_{ss} \end{bmatrix} = \begin{bmatrix} a & b/a \end{bmatrix}$
- Jacobian matrix at steady state is $J_{ss} = \begin{bmatrix} \frac{\partial(dx/dt)}{\partial x} & \frac{\partial(dx/dt)}{\partial y} \\ \frac{\partial(dy/dt)}{\partial x} & \frac{\partial(dy/dt)}{\partial y} \end{bmatrix}_{ss}$
-
- After estimating derivatives $J_{ss} = \begin{bmatrix} b-1 & a^2 \\ -b & -a^2 \end{bmatrix}$

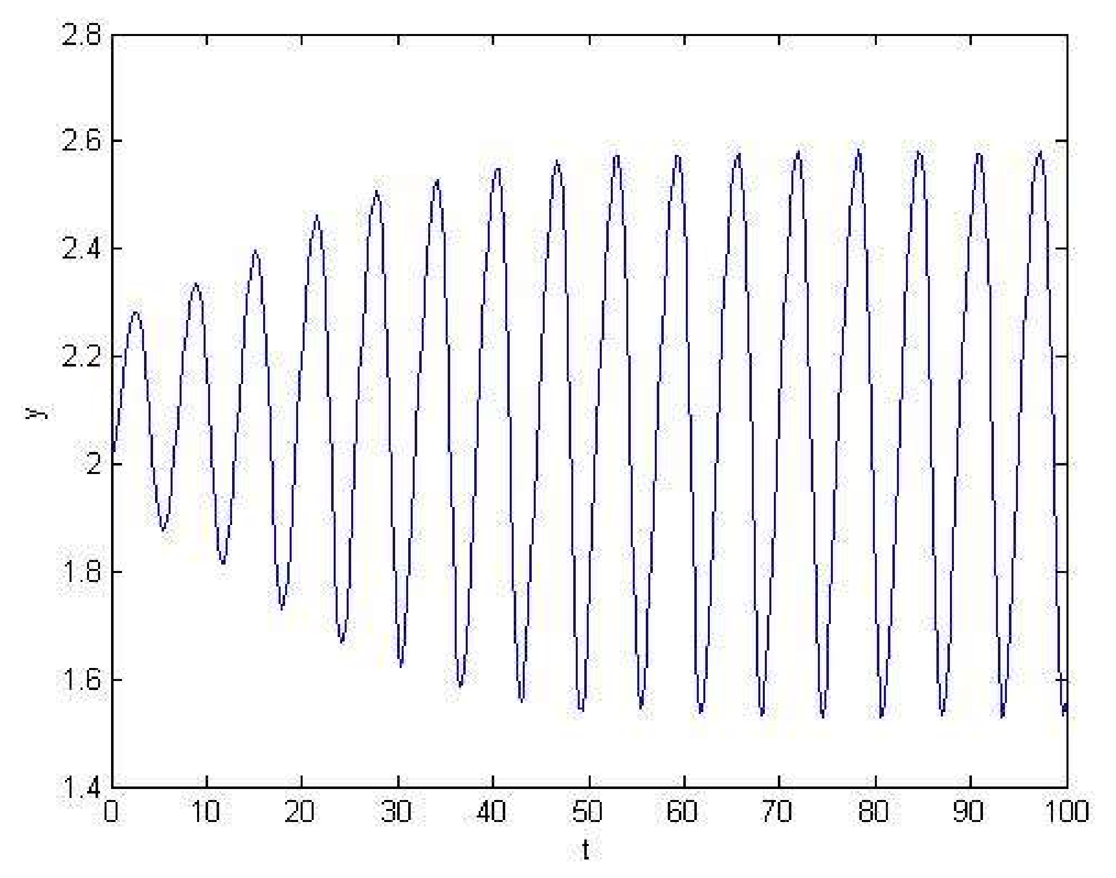
$$\begin{array}{rl}
A \rightarrow X & \qquad k_1 \\
B + Y \rightarrow Y + D & \qquad k_2 \\
2X + Y \rightarrow 3X & \qquad k_3 \\
X \rightarrow E & \qquad k_4
\end{array}$$

$$\det(J_{ss} - \lambda I) = 0 \longrightarrow \det\begin{vmatrix} b-1-\lambda & a^2 \\ -b & -a^2-\lambda \end{vmatrix} = 0$$

$$\lambda^2 + \lambda(a^2 + 1 - b) + a^2 = 0$$

- The is an eigenvalue.
- The stability of the steady state will depend on the sign of the eigenvalue or $(a^2 + 1 - b)$
- When any eigenvalus has positive real part it will be unstable.
- When all eigenvalus has negative real part it will be stable.

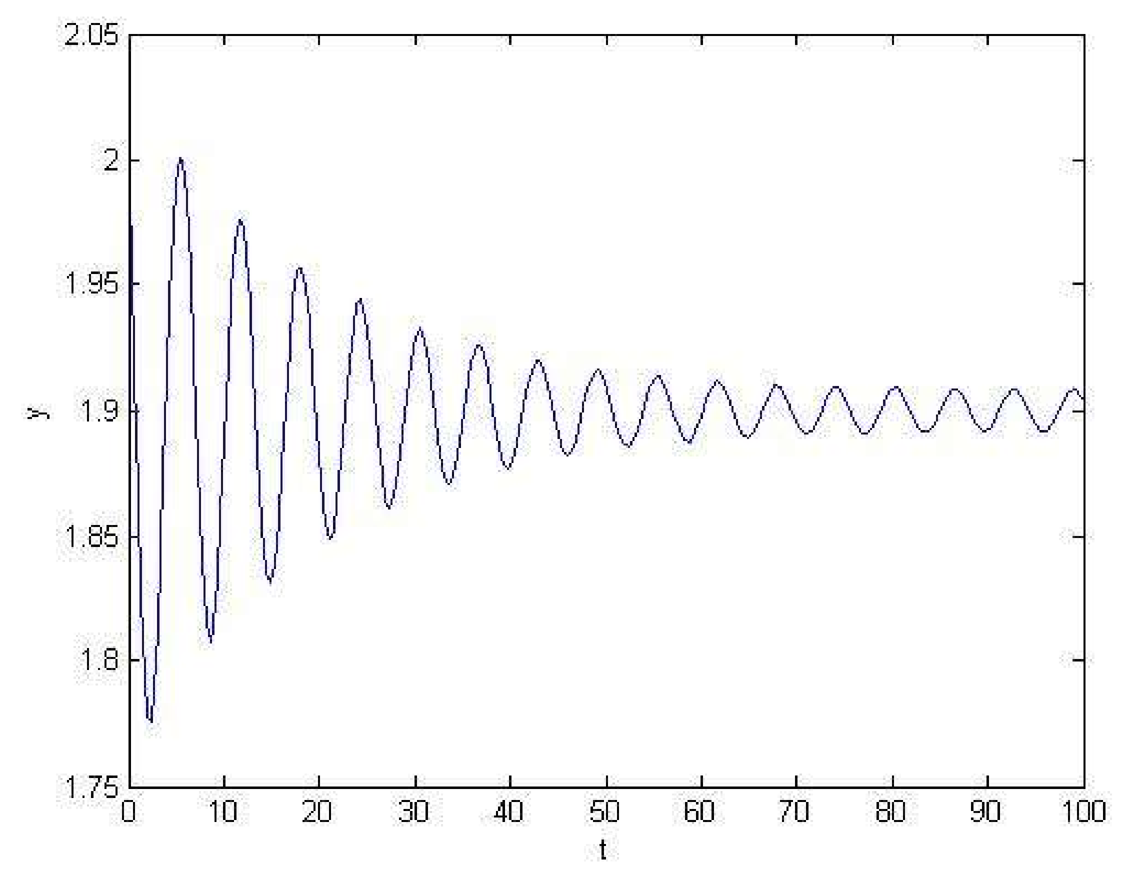
$$a = 1; b = 2.1 \qquad \lambda = \begin{bmatrix} 0.05 + 0.9987\mathrm{i} \\ 0.05 - 0.9987\mathrm{i} \end{bmatrix}$$



When any eigenvalus has positive real part with an imaginary part it will be unstable after attenuating.

$a = 1; b = 1.9$

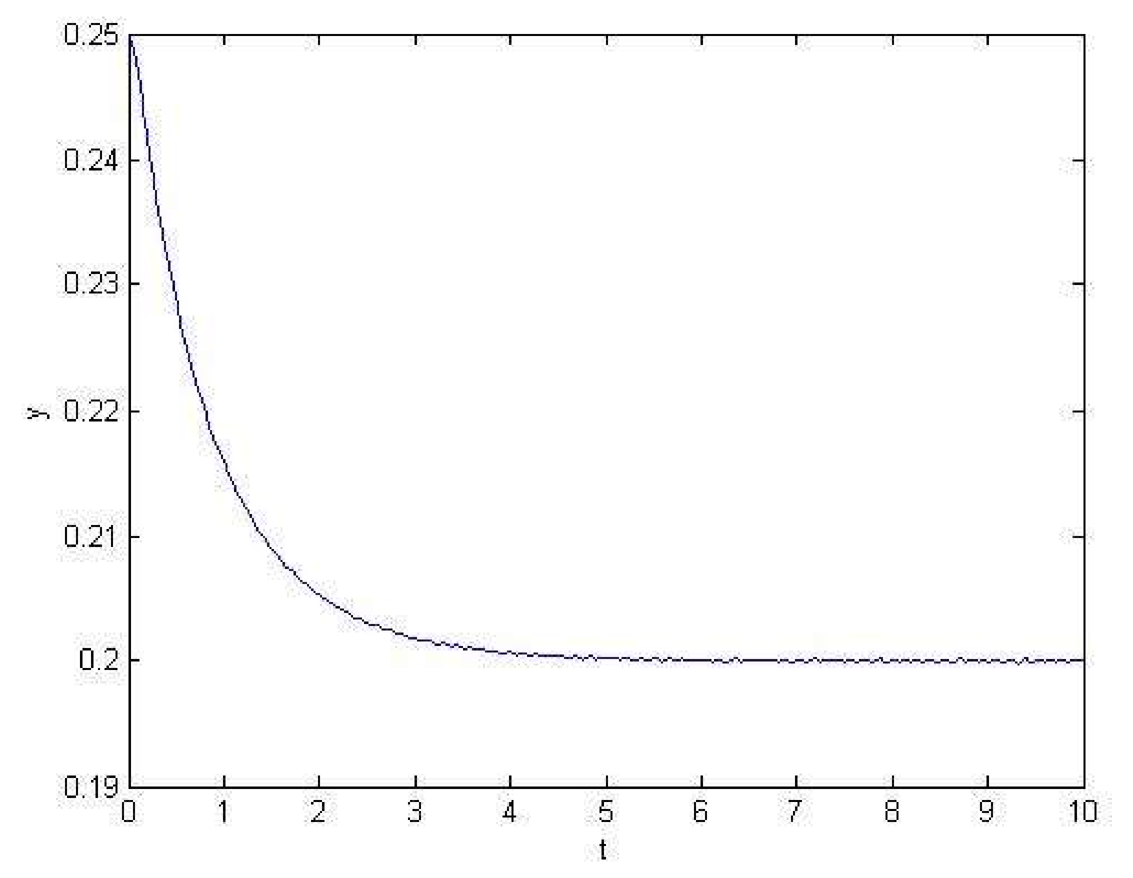
$$\lambda = \begin{bmatrix} -0.05 + 0.9987\mathrm{i} \\ -0.05 - 0.9987\mathrm{i} \end{bmatrix}$$



When all eigenvalus has negative negative real part and an imaginary part it will be stable after dumping.

$$a = 5; b = 1$$

$$\lambda = \begin{bmatrix} -1.0435 \\ -23.9564 \end{bmatrix}$$



When all eigenvalus has negative negative real part with no imaginary part it will be stable.

Bifurcation in CSTR

- Liquid-solid catalytic reaction is carried out in a CSTR.

Maas balance Equation in non-isothermal CSTR

$$V\frac{dC_A}{dt} = F\left(C_{Af} - C_A\right) - k_0 C_A V \exp\left(\frac{-E_a}{RT}\right)$$

Energy balance Equation in non-isothermal CSTR

$$\left[\phi\left(\rho c_p\right)_f + (1-\phi)\left(\rho c_p\right)_f\right]\frac{dT}{dt} = \left(\rho c_p\right)_f F\left(T_f - T\right) - (-\Delta H) k_0 C_A V \exp\left(\frac{-E_a}{RT}\right)$$

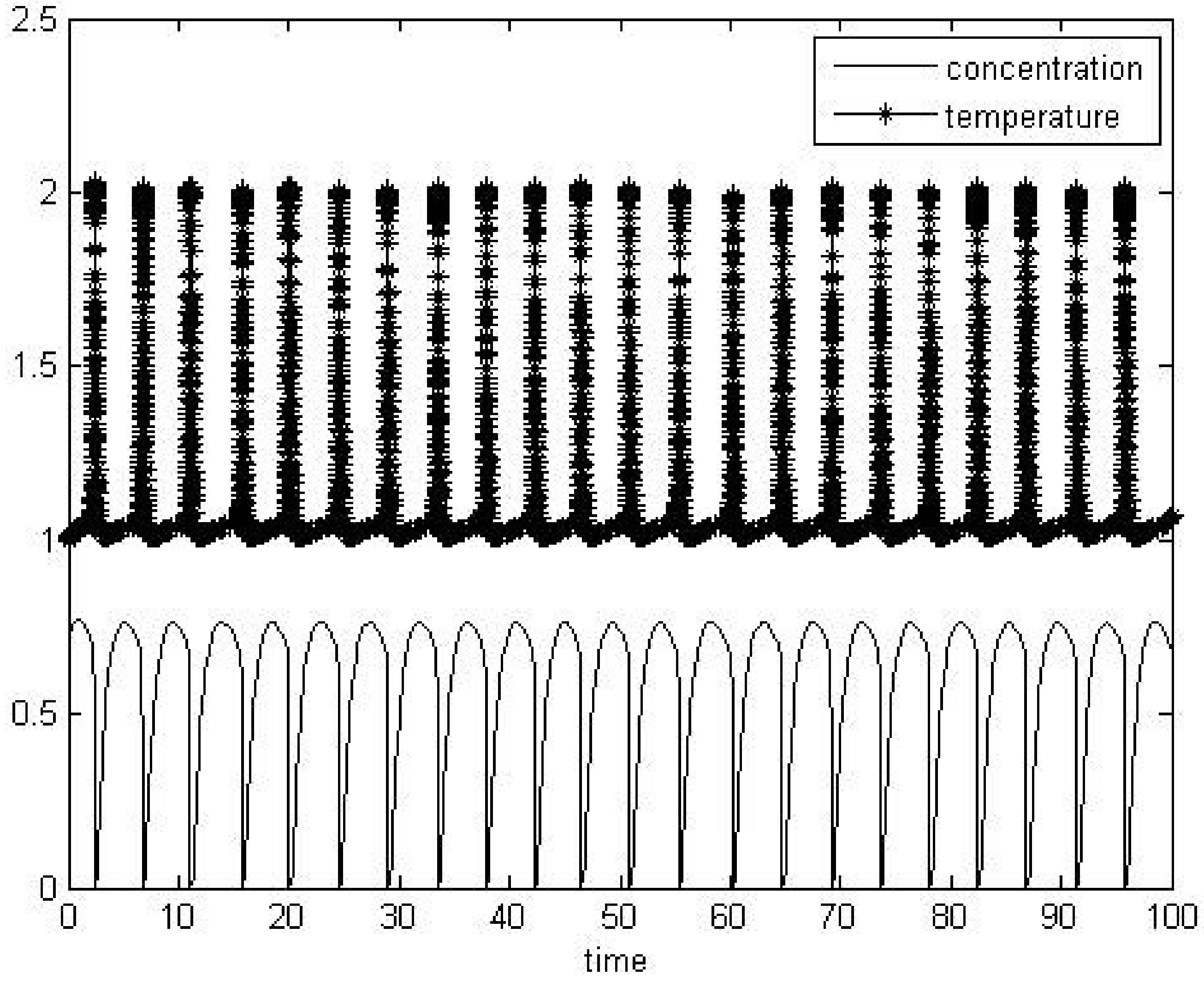
Dimensionless mass balance equation

$$\frac{dc'}{dt'} = (1 - c') - c' Da \exp\left[\gamma\left(1 - \frac{1}{T'}\right)\right]$$

Dimensionless mass balance equation

$$Le\frac{dT'}{dt'} = (1 - T') + \beta c' Da \exp\left[\gamma\left(1 - \frac{1}{T'}\right)\right]$$

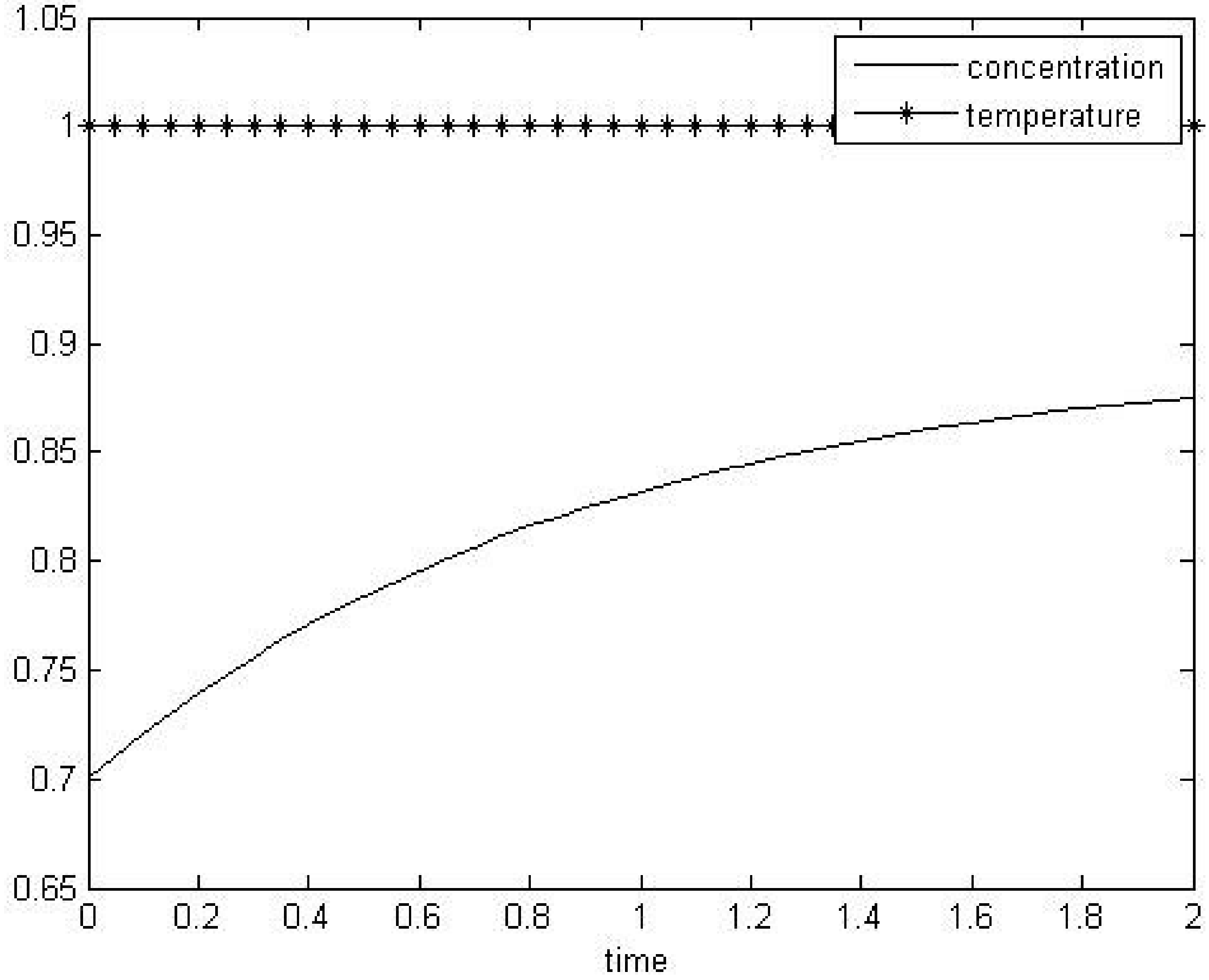
B.A. Finlayson, Introduction to Chemical Engineering Computing, WILEY



`beta=0.15;  gamma=30;` Le no=0.1; Da number=0.115;

Le=Lewis no=Thermal diffusivity / molecular diffusivity

Da=Damköhler number =Consumption of A by reaction/ Consumption of A by convection



beta=0.15; gamma=30; Le no=1080; Da=0.115

Tubular Plug Flow Reactors
Jörg Sauer, Nicolaus Dahmen, Edmund Henrich,
Ullmann's Encyclopedia of Industrial Chemistry

Large Scale Commercial Applications	
3.2.1.	Olefins by Steam Cracking of Naphtha
3.2.2.	Gas Oil Cracking in the FCC Riser Reactor
3.2.3.	Vinyl Chloride Production by EDC Dehydrochlorination
3.2.4.	High Pressure Ethylene Polymerization for Low Density Polyethylene (LDPE) → Polyethylene
3.3.	Other Commercial Applications
3.3.1.	Gas Phase Halogenation of Methane and Light Alkanes
3.3.2.	HCN-Production in the Degussa BMA Process
3.3.3.	Ketene via Acetic Acid or Acetone Cracking
3.3.4.	Ethylene Glycol via Ethylene Oxide Hydrolysis
3.3.5.	Various Additional Applications
3.4.	Research and Development

THANK YOU

Unsteady state model of heat exchanger

Shell & Tube type

Macroscopic view / Lumped parameter model.

$$\frac{dT_h}{dt} = \frac{W_h C_{ph}}{(\rho V C_p)_h}(T_{hi} - T_h) + \frac{(hA)_h}{(\rho V C_p)_h}(T_w - T_h) \quad \text{— (i)}$$

$$\frac{dT_c}{dt} = \frac{W_c C_{pc}}{(\rho V C_p)_c}(T_{ci} - T_c) + \frac{(hA)_c}{(\rho V C_p)_c}(T_w - T_c) \quad \text{— (ii)}$$

$$\frac{dT_w}{dt} = \frac{(hA)_c}{(\rho V C_p)_w}(T_c - T_w) + \frac{(hA)_h}{(\rho V C_p)_w}(T_h - T_w)$$

$$\frac{dT_h}{dt} = F_1(T_h, T_c, T_w, t) \quad \text{— (i)}$$

$$\frac{dT_c}{dt} = F_2(T_h, T_c, T_w, t) \quad \text{— (ii)}$$

$$\frac{dT_e}{dt} = F_3(T_h, T_e, T_w, t) \quad \text{(iii)}$$

Fourth order Runge-Kutta method

Initial condition $T_{hi}, T_{ci}, T_{wi}, t_0$.

after time $t_1 = t_0 + \Delta t$ (1st iteratation)

$$T_h^{t_1} = T_{hi} + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad \text{— (iv)}$$

$$T_c^{t_1} = T_{ci} + \frac{1}{6}(l_1 + 2l_2 + 2l_3 + l_4) \quad \text{— (v)}$$

$$T_w^{t_1} = T_{wi} + \frac{1}{6}(m_1 + 2m_2 + 2m_3 + m_4) \quad \text{— (vi)}$$

↳ R.K fourth order formula

~~$k_1 = F_1(T_{h_i}, T_{c_i}, T_{w_i}, t_0)$~~

~~$k_2 = F_1(T_{h_i} + \frac{k_1}{2}, T_{c_i} +$~~

$k_1 = F_1(T_{hi}, T_{ci}, T_{wi}, t_0)$; $l_1 = F_2(T_{hi}, T_{ci}, T_{wi}, t_0)$

$m_1 = F_3(T_{hi}, T_{ci}, T_{wi}, t_0)$.

$$k_2 = F_1\left(T_{h_i} + \frac{k_1}{2}, T_{c_i} + \frac{l_1}{2}, T_{w_i} + \frac{m_1}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$l_2 = F_2\left(T_{h_i} + \frac{k_1}{2}, T_{c_i} + \frac{l_1}{2}, T_{w_i} + \frac{m_1}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$m_2 = F_3\left(T_{h_i} + \frac{k_1}{2}, T_{c_i} + \frac{l_1}{2}, T_{w_i} + \frac{m_1}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$k_3 = F_1\left(T_{h_i} + \frac{k_2}{2}, T_{c_i} + \frac{l_2}{2}, T_{w_i} + \frac{m_2}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$l_3 = F_2\left(T_{h_i} + \frac{k_2}{2}, T_{c_i} + \frac{l_2}{2}, T_{w_i} + \frac{m_2}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$m_3 = F_3\left(T_{h_i} + \frac{k_2}{2}, T_{c_i} + \frac{l_2}{2}, T_{w_i} + \frac{m_2}{2}, t_0 + \frac{\Delta t}{2}\right)$$

$$k_4 = F_1\left(T_{h_i} + k_3, T_{c_i} + l_3, T_{w_i} + m_3, t_0 + \Delta t\right)$$

$$l_4 = F_2\left(T_{h_i} + k_3, T_{c_i} + l_3, T_{w_i} + m_3, t_0 + \Delta t\right)$$

$$m_4 = F_3\left(T_{h_i} + k_3, T_{c_i} + l_3, T_{w_i} + m_3, t_0 + \Delta t\right)$$

in 2nd iteration $t_2 = t_0 + 2\Delta t = t_1 + \Delta t$

$T_{hi} = T_h^{t_1}$; $T_{ei} = T_e^{t_1}$, $T_{wi} = T_W^{t_1}$.

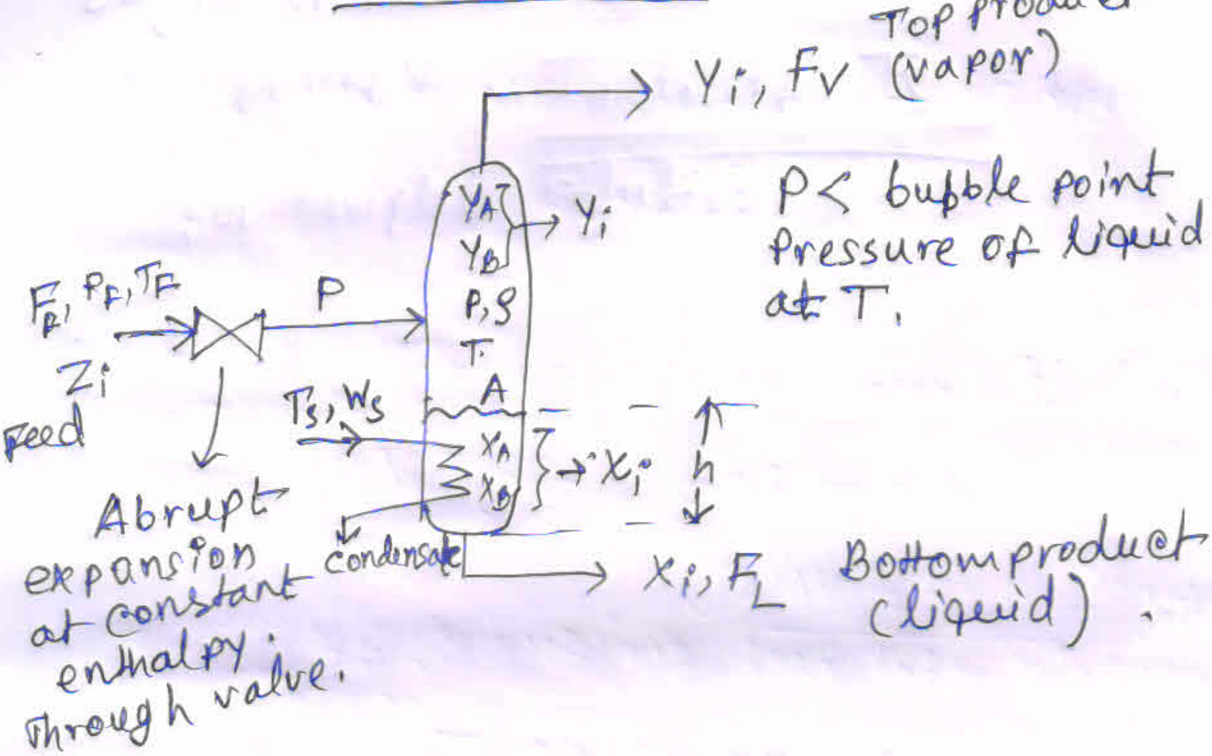
& $t_0 = t_0 + \Delta t$ $\quad$ $t_0 = t_1$.

and the previous steps are repeated.

to evaluate $T_h^{t_2}$, $T_e^{t_2}$, $T_W^{t_2}$,

using equation (iv), (v) & (vi).

Flash chamber



$P <$ bubble point pressure of liquid mixture at T.

Total mass balance

$$A\rho \frac{dh}{dt} = F_F - (F_V + F_L) \quad -①$$

Component balance

$$A\rho \frac{d(hx_i)}{dt} = F_F Z_i - (F_V Y_i + F_L x_i) \quad -(ii)$$

$$i = 1, 2, 3 \cdots N-1.$$

∴ N = number of component in ~~equad~~ liquid mixture.

∴ Total $N-1+N = N$ number of independent material balance equation

heat balance (Internal energy balance).

$$C_{P,L} A \rho_L \frac{d(hT_L)}{dt} = C_{P,F} F_F T_F \rho_F - (\rho_V C_{P,V} F_V T_V + \rho_L C_{P,L} F_L T_L) + UA_S(T_S - T_T)) \quad -(iii)$$

Assuming $T_V = T_L = T$ at equilibrium between vapor and liquid phases.

A = tank cross seectional area.

$$C_{p,L} A \rho_L \frac{d}{dt}(h \cdot T) = C_{p,F} F_F T_F \rho_F - (\rho_V C_{p,V} F_V T + \rho_L C_{p,L} F_L T) + UA_S(T_S - T) \quad \text{— (iv)}$$

Where T_S = Steam temperature for heating (K)

U = heat transfer coefficient (overall) (W/m²-K) between steam and Flash chamber.

A_S = surface area for heat transfer. (m²).

Equilibrium relation

$$y_i = K_i(T, P)x_i \quad [i = 1, 2, 3, \cdots, N]$$

$$y_i = K_i x_i \quad \text{— (v)}$$ [Number of equations]

$$\left.\begin{aligned} \Sigma x_i &= 1 \quad \text{— (vi)} \\ \Sigma y_i &= 1 \quad \text{(vii)} \end{aligned}\right\}$$ [2 equations]

∴ Total independent equations

$$\underbrace{N}_{\text{Material balance}} + \underbrace{1}_{\text{Energy balanee}} + \underbrace{N}_{\text{Equibirium relation}} + \underbrace{2}_{\text{sumof comosisions.}} = 2N+3.$$

∴ constants (must be specified).

$A, A_S, \rho, U, C_{p,F}, C_{p,V}, C_{p,L}, K_i \; (i = 1, 2, \cdots, 3, \cdots N)$.

$= N+7$

~~F_F, ρ, P~~

Externally specified T_F, z_i $(1, 2, \cdots N-1)$.

$1 + N-1 = N$

unspecified variable $F_F, F_V, F_L, P, T, h, T_S$

x_i, y_i (2N). $= 2N+7$

∴ Degree of freedom $= 2N+7-(2N+3) = $ ④

Degree of freedom ④

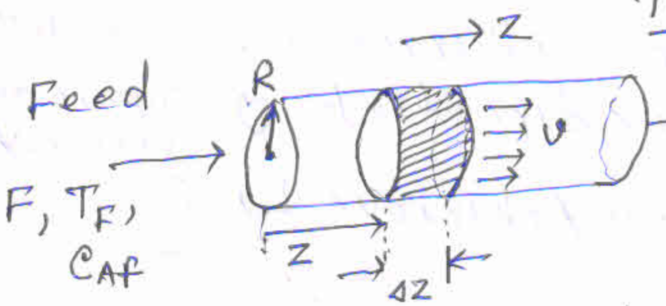
∴ specify , $\underline{\underline{T,\ P,\ F_f,\ T_s}}$ ~~to~~

for complete solution.

Unsteady state model of a tubular plug flow reactor.'

Microscopic view.

Tubular plug flow reactor



→ F, T_0, C_{Aout}.

$\boxed{A \rightarrow B + \text{heat}}$ (exothermic irreversible reaction)

Consider a elementary volume ΔV in the reactor of length ΔZ.

$\therefore \Delta V = \pi R^2 \Delta Z$. [R = Radius of the reactor]

Mole/Mass balance of species A in the control volume ΔV.

$\Rightarrow \Delta V \cdot \frac{\partial C_A}{\partial t}$ = rate of mass/mole in due to bulk transport + molecular transport − rate of mass/mole out due to bulk transport + molecular transport.

+ generation of species A in the ~~rea~~ volume (element).

$\frac{\Delta C_A}{\Delta t} \leftarrow \frac{\Delta C_A}{\Delta t}$ t = time

$\therefore$ rate of mass transport = bulk transport rate + Molecular transport rate.

$= FC_A - D\frac{\partial C_A}{\partial x}$. [where D = Diffusion coefficient]

D in m^2/s, C_A = mol/m³ $J_A = -D\frac{\partial C_A}{\partial x}$ Fick's Law of molecular transport

$\Delta C_A/\Delta t$

$$\frac{\partial C_A}{\partial Z}(\pi R^2 \Delta Z) = FC_A|_{\Delta Z} - FC_A|_{Z+\Delta Z} + \left(-D\frac{\partial C_A}{\partial Z}\right)\Big|_{Z}\pi R^2 - \left(-D\frac{\partial C_A}{\partial Z}\right)\Big|_{Z+\Delta Z}\pi R^2$$

$\cancel{+(r_A\Delta V)}$. $+ r_A \Delta V$

Where $r_A = -kC_A^n$ [rate of reaction]

Divide both side by $\Delta V = \pi R^2 \Delta Z$

$$\frac{\Delta C_A}{\Delta t} \leftarrow \frac{\partial C_A}{\partial Z} = -\frac{F}{\pi R^2}\left[\frac{C_A|_{Z+\Delta Z} - C_A|_Z}{\Delta Z}\right] + D\left[\frac{\frac{\partial C_A}{\partial Z}\Big|_{Z+\Delta Z} - \frac{\partial C_A}{\partial Z}\Big|_Z}{\Delta Z}\right] - KC_A^n$$

Now as $\Delta v \rightarrow$ and $\Delta z \rightarrow 0$ and $\Delta t \rightarrow 0$

The equation becomes:

$$\frac{\partial C_A}{\partial t} = -\upsilon \frac{\partial C_A}{\partial Z} + D \frac{\partial^2 C_A}{\partial Z^2} - K C_A^n \quad \text{—①}$$

→ Isothermal condition

If the reaction is non-isothermal.

Where $\frac{F}{\pi R^2} = \upsilon$

K is temperature dependent, υ = superficial velocity.

$K = K_0 e^{(-E/RT)}$ [From Arhinious Law]

$$\boxed{\therefore \frac{\partial C_A}{\partial t} = -\upsilon \frac{\partial C_A}{\partial Z} + D \frac{\partial^2 C_A}{\partial Z^2} - K_0 e^{-(E/RT)} C_A^n \quad \text{—②}}$$

Nonisothermal condition.

In case of negligive dispersion of species. compared to bulk transport. $D \frac{\partial^2 C_A}{\partial Z^2}$ term can be neglected.

$$\therefore \frac{\partial C_A}{\partial t} = -\upsilon \frac{\partial C_A}{\partial Z} - K_0 e^{(-E/RT)} C_A^n \quad \text{—③}$$

Where n = order of chemical reaction.

E = Activation energy of the reaction.

υ = Superficial linear velocity of ~~[illegible]~~ fluid.

Now energy balance equation can be derived. (non-adiabatic reactor)

Internal energy

$$\frac{\partial T}{\partial t} = -\upsilon \frac{\partial T}{\partial Z} + \frac{e^{(-\frac{E}{RT})}}{\rho C_p} K_0 C_A^n (-\Delta H_r) - \frac{UA}{\rho C_p} (T - T_j)$$

heat disappearance

$-\Delta H_r$ = heat of reaction.

T_j = Jacket fluid temperature.

U = overall heat transfer coefficient between reactor fluid and jacket fluid.

ρC_p = heat capacity of reactor fluid.

$$\frac{\partial T}{\partial t} = -\upsilon \frac{\partial T}{\partial Z} + \left(K \frac{\partial^2 T}{\partial Z^2}\right) + \frac{e^{(-E/RT)}}{\rho C_p} K_0 C_A^n (-\Delta H_r) - \frac{UA}{\rho C_p} (T - T_j)$$

→ heat transport due to conduction

molecular heat transport.

Mole balance in a tubular reactor

Mole balance of a reactant species A (**r_A=-kC_A^n, n=order of the reaction, k=reaction constant**) in a tubular reactor with dispersion coefficient D can be written with partial differential equation (PDE) as

$$\frac{\partial C}{\partial t}+\frac{\partial UC}{\partial x}=D\frac{\partial^2 C}{\partial x^2}+r_A \tag{1}$$

If the order of the reaction n=1 and axial velocity U is constant over the length of the reactor the eq. 1 can be written as

$$\frac{\partial C}{\partial t}+U\frac{\partial C}{\partial x}=D\frac{\partial^2 C}{\partial x^2}-kC_A \tag{2}$$

Finite difference discretization

This PDE can be discretized with finite difference method with time (Δt) and space (Δx) marching as

$$\frac{C_i^{t+\Delta t}-C_i^t}{\Delta t}+U\frac{C_{i+1}^{t+\Delta t}-C_{i-1}^{t+\Delta t}}{2\Delta x}=D\frac{C_{i+1}^{t+\Delta t}-C_i^{t+\Delta t}2+C_{i-1}^{t+\Delta t}}{\Delta x^2}-kC_i^{t+\Delta t} \tag{3}$$

Here *i* is denoted by elements of space marching or number of nodes.

Multiplying the eq. by Δt and can be rearranged as

$$\left(k\Delta t+1+\frac{2D\Delta t}{\Delta x^2}\right)C_i^{t+\Delta t}+\left(\frac{\Delta tU}{2\Delta x}-\frac{D\Delta t}{\Delta x^2}\right)C_{i+1}^{t+\Delta t}-\left(\frac{\Delta tU}{2\Delta x}+\frac{D\Delta t}{\Delta x^2}\right)C_{i-1}^{t+\Delta t}=C_i^t \tag{4}$$

$$pC_i^{t+\Delta t}+qC_{i+1}^{t+\Delta t}-rC_{i-1}^{t+\Delta t}=C_i^t \tag{5}$$

Where,

$$p=k\Delta t+1+\frac{2D\Delta t}{\Delta x^2} \tag{6}$$

$$q=\frac{\Delta tU}{2\Delta x}-\frac{D\Delta t}{\Delta x^2} \tag{7}$$

$$r=\frac{\Delta tU}{2\Delta x}+\frac{D\Delta t}{\Delta x^2} \tag{8}$$

Initial condition

Initial condition is at t=0, and i=1,…, 5, $C_i^t=0.8$

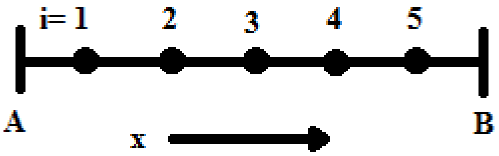
Boundary condition

Now Boundary condition (BC) for face A is C_A=0.8;

BC for face B is $\frac{\partial C}{\partial x} = 0\,;\, \frac{C_{i+1}^{t+\Delta t} - C_{i}^{t+\Delta t}}{\Delta x} = 0\,;\; C_{i+1}^{t+\Delta t} = C_{i}^{t+\Delta t}$

i.e., for i=5, $C_{5+1}^{t+\Delta t} = C_{5}^{t+\Delta t}$

Let divide the whole length of the reactor into 5 nods (distance between two consecutive nodes is Δx) between boundary face A and B in the Figure below. Now write equation 5 for five nodes (i=1,…, 5).



For i=1 (left boundary node),

$$pC_{1}^{t+\Delta t} + qC_{2}^{t+\Delta t} - rC_{A} = C_{1}^{t}$$

$$pC_{1}^{t+\Delta t} + qC_{2}^{t+\Delta t} = C_{1}^{t} + rC_{A} \tag{9}$$

For i=2,3.., 4 (middle nodes),

$$pC_{i}^{t+\Delta t} + qC_{i+1}^{t+\Delta t} - rC_{i-1}^{t+\Delta t} = C_{i}^{t} \tag{10}$$

For example, 2 node equation will be,

$$pC_{2}^{t+\Delta t} + qC_{3}^{t+\Delta t} - rC_{1}^{t+\Delta t} = C_{2}^{t} \tag{11}$$

For i=5 (right boundary node),

$$pC_{5}^{t+\Delta t} + qC_{5+1}^{t+\Delta t} - rC_{4}^{t+\Delta t} = C_{5}^{t}$$

Putting BC for right face, $C_{5+1}^{t+\Delta t} = C_{5}^{t+\Delta t}$

$$pC_{5}^{t+\Delta t} + qC_{5}^{t+\Delta t} - rC_{4}^{t+\Delta t} = C_{5}^{t}$$

$$pC_{5}^{t+\Delta t} + qC_{5}^{t+\Delta t} - rC_{4}^{t+\Delta t} = C_{5}^{t}$$

$$(p+q)C_{5}^{t+\Delta t} - rC_{4}^{t+\Delta t} = C_{5}^{t} \tag{12}$$

Now five equations for 5 no. of nodes can be written in the form of

$$AX = B \tag{13}$$

$$A = \begin{bmatrix} p & q & & & \\ -r & p & q & & \\ & -r & p & q & \\ & & -r & p & q \\ & & & -r & p+q \end{bmatrix} \tag{14}$$

Matrix A is called tri-diagonal matrix.

$$X = \begin{bmatrix} C_1^{t+\Delta t} \\ C_2^{t+\Delta t} \\ C_3^{t+\Delta t} \\ C_4^{t+\Delta t} \\ C_5^{t+\Delta t} \end{bmatrix} \tag{15}$$

$$B = \begin{bmatrix} C_1^t + rC_A \\ C_2^t \\ C_3^t \\ C_4^t \\ C_5^t \end{bmatrix} \tag{16}$$

$$\begin{bmatrix} p & q & & & \\ -r & p & q & & \\ & -r & p & q & \\ & & -r & p & q \\ & & & -r & p+q \end{bmatrix} \begin{bmatrix} C_1^{t+\Delta t} \\ C_2^{t+\Delta t} \\ C_3^{t+\Delta t} \\ C_4^{t+\Delta t} \\ C_5^{t+\Delta t} \end{bmatrix} = \begin{bmatrix} C_1^t + rC_A \\ C_2^t \\ C_3^t \\ C_4^t \\ C_5^t \end{bmatrix} \tag{17}$$

Equation 17 in implicit form has been solved using a suitable algorithm of linear algebra like Gauss elimination, Gauss-Seidel, or Cholesky decomposition methods.