Process Dynamics and Control

†**Safety Module 1:** *T2 Laboratories Explosion, December 2007*

Problem Statement: In December 2007, an explosion at T2 Laboratories led to the death of four people in Florida, USA and injured 28 others. T2 Laboratories manufactured a chemical Methyl-Cyclopentadienyl Manganese Tri-carbonyl (MCMT) that is used as an additive for gasoline and other fuels. They used a batch reactor that involved a multi-step production process. Most of the reactions involved were exothermic in nature and some generated hydrogen gas. On the incident day, the loss of cooling water supply resulted in an uncontrolled temperature increase and eventually led to reactor rupture due to over pressurization. Subsequently, hydrogen and other flammable chemicals released ignited causing a severe explosion.

Courtesy of CSB investigation report

Watch the Video: (*https://www.youtube.com/watch?v=C561PCq5E1g/*)

Incident Report Available At: (*https://www.csb.gov/file.aspx?DocumentId=5661*)
(Relevant pages: 1-4, 26-27, 39-40)

T2 Process description:

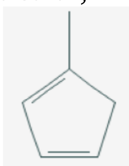
T2 produced Methyl-Cyclopentadienyl Manganese Tri-carbonyl (MCMT) in a batch reactor, in a three step process. We will restrict our analysis and description only to the first step, as the explosion took place while this was in progress.

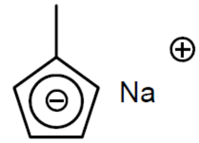
The first step involved the following two reactions:

Reaction 1: $$A + B \xrightarrow{k_1} C + \tfrac{1}{2} D$$

Reaction 2: $$S \xrightarrow{k_2} 3D + byproducts$$

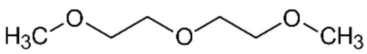
In particular,





Methylcyclopentadiene + Sodium —(Diglyme)→ Sodium Methylcyclopentadiene + Hydrogen

A **B** **S** **C** **D**

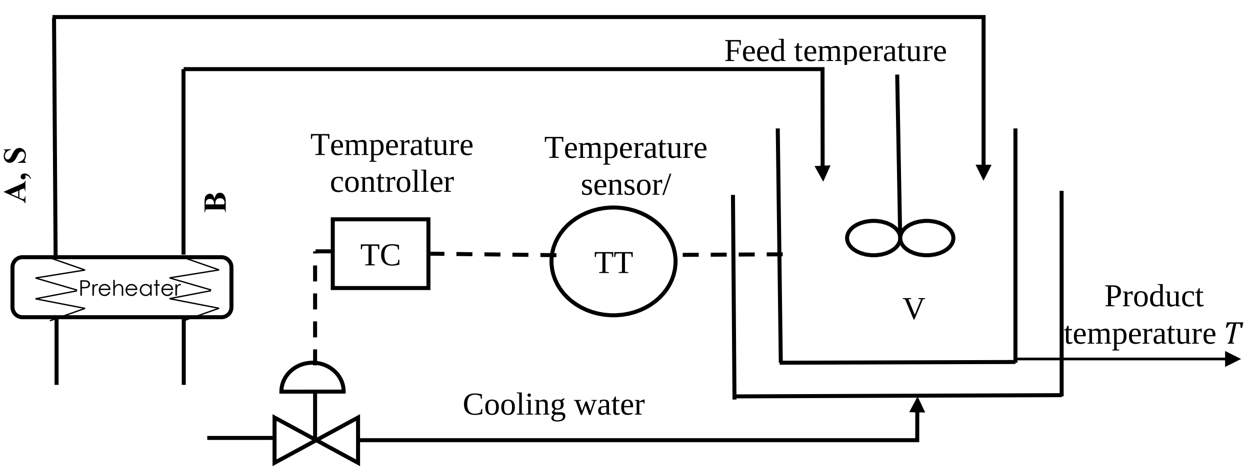


Diglyme —(Sodium)→ Hydrogen + byproducts

S **D**

The reactant methylcyclopentadiene (A) in solution in diglyme (S) was loaded to the reactor, along with sodium pellets. The reactor was then heated to the necessary temperature of 422 K for the sodium to melt and the reaction to initiate. In the first reaction, methylcyclopentadiene (A) and molten sodium (B) reacted in the presence of the solvent diglyme (S) to produce **desired intermediate product sodium methylcyclopentadiene (C)** and hydrogen gas (D). In the second (side) reaction, the solvent (S) decomposes in the presence of sodium (B) producing hydrogen (D) gas and other byproducts. **The second (side) reaction becomes significant only at elevated temperatures.** The hydrogen gas generated in the reactor was vented out through a pressure relief system. Both of these reactions are exothermic in nature and require cooling to keep the reactor temperature under control. An evaporating water jacket was used to provide the necessary cooling.

In this computer module, we will study the foregoing T2 chemical reactions **<u>in a CSTR</u>**, under similar conditions as the batch reactor of T2 Laboratories. Methylcyclopentadiene (A) in solution in diglyme (S) and molten sodium (B) are preheated and fed to the CSTR at the proper temperature so that the first reaction can proceed. Cooling is performed through an evaporating water jacket, where the heat transfer coefficient U can be manipulated by adjusting the cooling water flow rate (m_c). The reactor temperature T needs to be regulated at set point despite possible fluctuations in the feed temperature T_0.



Temperature control of the exothermic CSTR.

The control problem is therefore defined as follows:

- the **controlled output** is the **temperature in the reactor (T)**,
- the **manipulated input** is the **cooling water flow rate (m_c)** in the jacket.
- the **disturbance** is unanticipated **changes in the temperature of the feed streams (T_0)**.

The following key assumptions will be made:

-- the reactor is a *perfectly mixed CSTR*,
-- the *reactor volume is constant*,
-- the *feed to the reactor is the two reactants and the solvent* (not containing any of the products).
-- both the *temperature sensor and the cooling system are very fast*; their time constants are negligible.

Under ***normal operating steady state conditions***,
The flow rate of cooling water is $\overline{m_c}$ = 330 kg/h, the feed temperature is $\overline{T_0}$ = 410 K, and the corresponding steady state reactor temperature is $\overline{T}$ = 460.3 K.
This value of reactor temperature is the set point for the controller.

Numerical values of the process parameters for the CSTR are given at the end of this module.

(a) It is important that chemical engineers have an understanding of what the accident was, why it happened and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video on the T2 Laboratories explosion and fill out the following algorithm. See definitions on the last page. If necessary, view the incident report.

Safety Analysis of the Incident

Activity: ______________________________

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Hazard: ______________________________

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Incident: ______________________________

Initiating Event: ______________________________

Preventative Actions and Safeguards: ______________________________

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Contingency Plan/ Mitigating Actions: ______________________________

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Lessons Learned: ______________________________

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Click here *to download the Simulink and Matlab files, and go through the* Simulink tutorial *to solve the questions below.*

All the Simulink models are compatible with Simulink version 8.9 and above.

Note: In all the graphs obtained via simulink, the x axis denotes time with units of hours even though the simulink may show it as seconds.

(b) Open-loop Analysis *(use Open_loop.slx)*:

Changes in the feed temperature T_0 will disturb the operation of the reactor. It is expected that a small step change in T_0 will result in a small change in the reactor temperature steady state, but a large positive step change could represent a threat, as it might initiate the side reaction. You are asked to study the **effect of disturbance step size** on the operation of the reactor, when there is no control system available and the coolant water flow rate assumes its normal steady state value:

i. For up to what size of positive step change in the feed temperature, T_0, will the reactor temperature remain within 7 K of the normal steady state temperature, $\overline{T} = 460.3\ K$, as when the reactor temperature reaches around 472 K, the second side reaction starts becoming significant?

ii. What happens under a large step increase in T_0? Interpret the simulation results and explain what happens on physical grounds.
(Hint: Observe the values for Concentration of diglyme solvent, CS and reactor temperature, T with step increase of +10 K, +15 K and +20 K in T_0)

(c) Closed-Loop Analysis - Controller Tuning:

Process disturbances – Controller design specifications

The temperature controller must protect the reactor from unanticipated changes in the inlet temperature T_0. Step-like changes in T_0 within +5K are not uncommon. In the event of severe malfunction of the preheater, there might be a step-like increase in T_0 of magnitude up to 20K, and this could be dangerous, as it might initiate the side reaction. The controller should protect the reactor all the time, even under abnormal situations. The following controller design specifications must be met *for all possible step sizes* within the range $+5\text{K} < \Delta\text{T}_0 < +20\text{K}$.

1) To be able to maintain proper conversion and product composition, tight temperature control is needed. Offsets, if any, must be less than half a degree K, to guarantee that the product is in specification.

2) Because of feasibility limits on the coolant flow rate, the feasible range for the flow rate of cooling water is $0 < m_c < 2100$ kg/h. This corresponds to the range for the overall heat transfer coefficient being $0 < U < 55$ $kJm^{-2}hr^{-1}K^{-1}$. The controller output must remain between these upper and lower limits *at all times*.

3) There are also limitations in the rate of change of the heat transfer coefficient (U), because of limitations in the pumping system for the coolant feed to the jacket (the numerical relationship between U and m_c is discussed in the **Numerical Values of Process Parameters** section). Since the operation of the CSTR is dependent on the overall heat transfer coefficient, the blocks associated with the closed loop including the P or PI controller should have U as a variable instead of m_c.
For feasible and smooth operation of the cooling jacket, the rate of change of heat transfer coefficient, dU/dt, requested by the controller should be less than $120\ \frac{\mathrm{kJ\ m^{-2}\ h^{-1}K^{-1}}}{\mathrm{h}}$ *at all times*.
Note: The red line in graph of U (obtained after running P_controller.slx and PI_controller.slx) is $U = \left|dU/dt\right|_{max} t + \bar{U}$*, where t is time,* $\left|dU/dt\right|_{max} = 120\ \frac{\mathrm{kJ\ m^{-2}\ h^{-1}K^{-1}}}{\mathrm{h}}$ *and* $\bar{U} = 12.42\ \mathrm{kJ\ m^{-2}\ h^{-1}K^{-1}}$. *The line represents maximum achievable rate of change of U, and hence, can be used to ensure that the third controller design specification is met.*

Specific tasks:

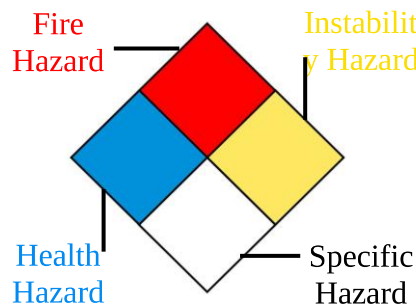
i. Determine whether the temperature controller should be direct acting or reverse acting.
(Hint: Think how U and m_c must be varied by the controller in order to control the reactor temperature T, when a step increase in T_0 is made as in part (b).)

ii. **Tune a P-controller** *(use P_controller.slx)*:
Find the "best-performing" P-controller, with the controller output satisfying the aforementioned feasibility constraints at all times.
(Hint: Controller gain (K_C) will be
- greater than zero if the temperature controller is reverse acting.
- less than zero if the temperature controller is direct acting.)

iii. **Tune a PI-controller** *(use PI_controller.slx)*:
Find the "best-performing" PI-controller, with the controller output satisfying the aforementioned feasibility constraints at all times.
(Hint: Controller gain (K_C) will be
- greater than zero if the temperature controller is reverse acting.
- less than zero if the temperature controller is direct acting.
Performance with varying parameters (of PI controller) can be compared w.r.t overshoot, number of oscillation and settling time to get T within 0.05 K.)

iv. Compare your "best" P- and PI-controllers. Discuss the effect of using integral action. If a better controller performance is desired, what could you do?

(d) Review the information in the NFPA Diamond tutorial. After reviewing the information, go through the Material Safety Data Sheet (MSDS) of MCMT and fill out the blank NFPA Diamond to the right for MCMT.

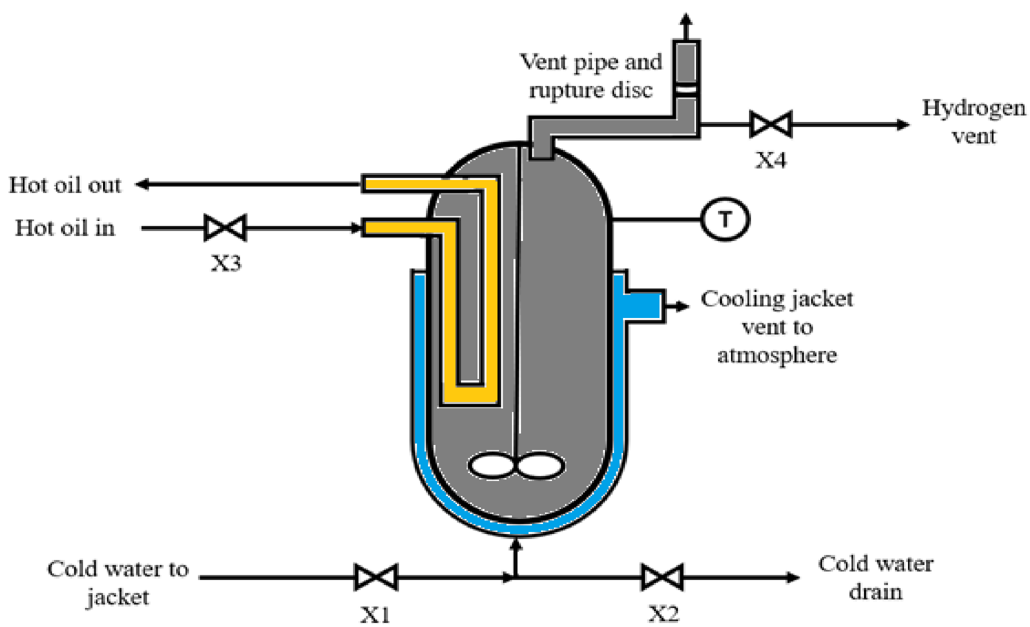


Parts (e)-(g) are based on industry practices used to assess process safety. For more information on process safety and its importance in chemical engineering, please visit the University of Michigan SafeChE website here. *It is recommended that professors only assign 1-2 of the following parts due to the similar nature of the questions.*

(e) Review the explanation of the components of a BowTie diagrams found here. After reviewing the information, create a BowTie diagram for the T2 Laboratories Explosion.

(f) A HAZOP study is structured analysis of process design to identify potential vulnerabilities in a facility. Review the background on how to conduct a HAZOP study here before completing one for the following system. It is important to note that not all guidewords and parameters will be relevant for different systems. Some information is given here for guidance:

System to consider: The batch reactor and its connected valves



The inlet of water to the cooling jacket is controlled by valve X1 and the drain from the cooling jacket is controlled by valve X2. The hot oil flow is controlled by valve X3, and the hydrogen vent is controlled by the pressure control valve X4. The temperature is measured using the temperature sensor T.

Process parameters to consider: Level, Flow Rate of Cooling Water, Temperature, Pressure, Closing of Oil Input Valve X3, Composition

(i) Fill out the HAZOP chart as shown in the tutorial. Some other information has been filled out here for you.

Guideword + Parameter = Deviation	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
More Level	Charging more feed in the batch reactor			
Less/No Flow Rate of cooling water to the jacket				
More (Higher) Temperature	Failure of cooling system			
	High amount of reactants which increases the heat release			
More (Higher) Pressure				
Later closing of hot oil input valve	Failure of control system leading to late closure of valve X3			
Other composition				

(ii) When conducting a HAZOP, you will often find combinations of guidewords and parameters that describe a possible situation for the system that is not hazardous. For the given process parameters, give an example, explain why the situation is not hazardous, and describe another consequence that could occur. *HINT: Consider process efficiency*

(iii) Write a short conclusion on some takeaways from completing a HAZOP for this system and recommendations you would make.

(g) A Layers of Protection Analysis (LOPA) is a semi-quantitative study to identify available safeguards and determine if the safeguards sufficiently protect against a given risk. Review the background on how to conduct a LOPA study here before filling the table out for the system described in this module. Some information is given for guidance:

- Assume that the plant can only accept a moderate risk
- The explosion at T2 Labratories resulted in 4 fatalities and significant damage to the plant

LOPA Study for T2 Labs Explosion		
Initiating Event	Cause:	Cooling water failure
	Consequence:	High temperature and pressure inside the reactor that can lead to rupture and explosion
	FOIE:	
IPL(s)	Description of IPL_1, IPL_2, ...	Rupture Disk
	$PFD = PFD_1 \times PFD_2 \times ...$	
MCF	MCF = FOIE x PFD	
	Category of MCF:	
Severity	Impact:	Multiple fatalities and extensive plant damage
	Category:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	
If risk evaluated above is unacceptable, please continue below:		
Proposed IPL(s) (P-IPL(s))	Description of $P\text{-}IPL_1$, $P\text{-}IPL_2$, ...	
	$P\text{-}PFD = P\text{-}PFD_1 \times P\text{-}PFD_2 \times ...$	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

(h) Describe what was the most unsettling to you about the incident.

General Simulink Questions:

Refer to part (b) Open-loop Analysis and answer the following questions:

(i) Increase the steady-state value of the coolant flow rate (m_c). Does this help to maintain the reactor temperature in the desired range even for a relatively larger disturbance?

(ii) Vary m_c. Do you find *Reactor Temperature* profile unusual? Explain.

<u>Numerical Values of Process Parameters</u>

Reaction rate expressions and rate constants:
From the literature (H. S. Fogler, "Elements of Chemical Reaction Engineering", 5th Ed., 2016),

$r_1 = -k_1 * C_A * C_B$

$k_1 = k_{10}\exp(-\frac{E_1}{RT})$, where $k_{10} = 4 * 10^{14}\ l\ mol^{-1}h^{-1}$ and $E_1 = 1.28 * 10^5\ J\ mol^{-1}K^{-1}$

$r_2 = -k_2 * C_S$

$k_2 = k_{20}\exp(-\frac{E_2}{RT})$, where $k_{20} = 1 * 10^{84}\ h^{-1}$ and $E_2 = 8 * 10^5\ J\ mol^{-1}K^{-1}$

Heats of reactions: From the literature (ibid),

$\Delta H_1 = -45400 \frac{J}{mol\ of\ Sodium}$, $\Delta H_2 = -3.2 * 10^5 \frac{J}{mol\ of\ diglyme}$

Molar Flowrates of reactants and solvent fed to the reactor (assumed to be constant):
$F_{A0} = 1050\ mol\ h^{-1}$, $F_{S0} = 525\ mol\ h^{-1}$ and $F_{B0} = 1250\ mol\ h^{-1}$

Average molar density of feed containing A and S: $\rho_{AS} = 7.33\ mol\ l^{-1}$
Molar density of feed of B: $\rho_B = 36\ mol\ l^{-1}$

Reactor Volume: $V = 4000\ L$

Average molar density for the mixture in the reactor (assumed to be constant, independent of composition and temperature): $\rho = 7.31\ mol\ l^{-1}$

Average Specific Heat (assumed to be constant, independent of composition and temperature):
C_p = 430.91 $J\ mol^{-1}\ K^{-1}$

Coolant Temperature (assumed to be constant): $T_c = 373$ K

Heat Transfer Area: $A_x = 5.3\ m^2$

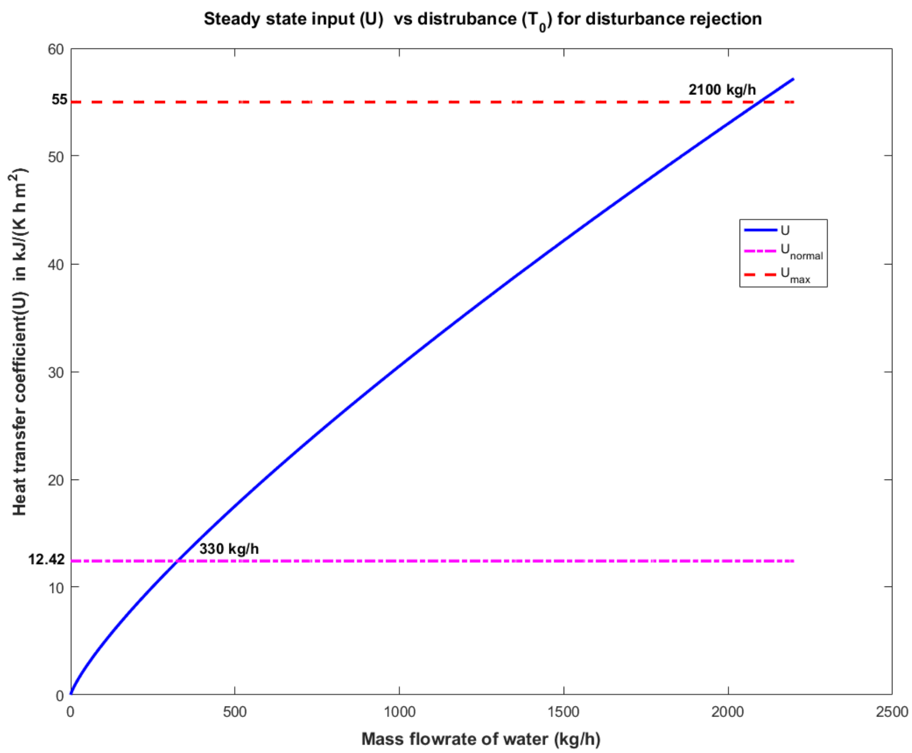
Overall heat transfer coefficient U as a function of the coolant flow rate (m_c):
The heat transfer coefficient can be calculated as a function of the water flow rate, using Lehrer's

correlation that relates the Nusselt number to Prandtl (Pr) and Reynold's number (Re). For the specific reactor size and geometry, the relation is the following:

$$U = \left(0.03\,\mathrm{Re}^{0.75}\,\mathrm{Pr} \big/ 1 + 1.74\,\mathrm{Re}^{-0.125}(\mathrm{Pr}-1)\right) k/d_e$$

$$= \left(0.03\left(m_c d_e / A_{cx}\mu\right)^{0.75}\mathrm{Pr} \Big/ 1 + 1.74\left(m_c d_e / A_{cx}\mu\right)^{-0.125}(\mathrm{Pr}-1)\right) k/d_e$$

where d_e is the characteristic length (0.204 m) , μ is the dynamic viscosity ($0.281*10^{-3}$ Pa s), A_{cx} is the cross-sectional area of the jacket (0.6 m^2) and k is thermal conductivity of the fluid (0.683 W/ m K). Pr for the cooling water is 1.75 at 373 K.



The figure shows the relation between cooling water flowrate m_c and heat transfer coefficient U. For m_c varying between 0 and 2100 kg h^{-1}, the heat transfer coefficient varies within the range $0 < U < 55$ kJ $m^{-2}\,h^{-1}K^{-1}$. At normal operating steady state conditions, $\overline{m_c} = 330$ kg/h, which corresponds to heat transfer coefficient of $\overline{U} = 12.42$ kJ $m^{-2}\,h^{-1}K^{-1}$.
In this module, for simplicity, we are considering U as the manipulated input.

Definitions

Activity: The process, situation, or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to property, harm to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g., failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, (e.g., no flow from pump, valve closed, inadvertent human action, ignition). The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

BowTie Diagram: A qualitative hazard analysis tool through which potential problems and consequences associated with a hazard are studied through a pictorial representation. Necessary preventive and mitigating barriers are determined to reduce the process safety risk.

Hazard and Operability Study (HAZOP): A qualitative hazard analysis tool that uses a set of guide words to determine whether deviations from design or operating intent can lead to undesirable consequences. The existing safeguards are evaluated and if required, actions are recommended to mitigate the consequences.

Layer of Protection Analysis (LOPA): A semi-quantitative study that determines initiating event frequency, consequence severity, and likelihood of failure of independent protection layers (IPLs) to calculate the risk of a scenario. If the existing risk is intolerable, then additional IPLs are suggested to bring down risk to an acceptable level.

Table 1: Nomenclature

Symbol	Description	SI Unit
T_0	Feed streams temperature	K
$\overline{T_0}$	Feed streams temperature at steady state	K
T	Reactor temperature	K
$\overline{T}$ or T_s	Reactor temperature at steady state	K
U	Overall heat transfer coefficient	$J.s^{-1}K^{-1}m^{-2}$
$\overline{U}$ or U_s	Overall heat transfer coefficient at steady state	$J.s^{-1}K^{-1}m^{-2}$
t	Time	s
C_A or CA	Concentration of methylcyclopentadiene	$mol.m^{-3}$
C_B	Concentration of sodium	$mol.m^{-3}$
Cs or CS	Concentration of diglyme	$mol.m^{-3}$

Additional reading material (optional):
(i) Control of a CSTR

[†]In collaboration with Professor Costas Kravaris and Joshiba Ariamuthu Venkidasalapathy, Texas A&M University, Professor Xiaoxia (Nina) Lin, University of Michigan and Kshitiz Parihar, Indian Institute of Technology Bombay