### **Reaction Engineering and Design**

**Safety Module 3:** Exxon Mobil Torrance Refinery Explosion Involving a Straight Through Transport Reactor (STTR)

Reference: Example 10-6 in both

[1] H. S. Fogler, *Elements of Chemical Reaction Engineering*, 6<sup>th</sup> ed. Pearson, 2020.

[2] H. S. Fogler, *Essentials of Chemical Reaction Engineering*, 2<sup>nd</sup> ed. Prentice Hall, 2017.

**Problem Statement:** On Monday February 8, 2015, an explosion occurred at the Torrance California refinery's electrostatic precipitate unit, a pollution control device associated with the fluid catalytic cracking (FCC) unit. While the explosion occurred in the precipitator, the initiating events took place in the catalyst regeneration unit attached to a STTR. The spent catalyst from the STTR is covered with carbon compounds (coke) which are burned off in the regenerator. On a routine maintenance shut down, catalyst particles got lodged in the door that was supposed to prevent flammable vapor from flowing out of the regeneration unit and proceeding downstream. The flammable vapor escaped through the opening and proceeded downstream to the electrostatic precipitation where it found a spark and exploded.



Watch the Video: (<u>https://www.youtube.com/watch?v=JplAKJrgyew</u>)

### Incident Report Available At:

(https://www.csb.gov/assets/1/20/exxonmobil\_report\_for\_public\_release.pdf?15813)

CSB Incident Report No. 2015-02-I CA ExxonMobil Torrance Refinery, February 18, 2015. If you need more detailed information than can be found in the video, review pages 1-22 of this report.

**Coke Regeneration** (<u>http://www.umich.edu/~elements/6e/14chap/expanded\_ch14\_A.pdf</u>). This website describes the shrinking core model for coke being removed from catalyst pellets.

(a) It is important that chemical engineers understand 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 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: Hazard: Incident: Incident: Initiating Event: Preventative Actions and Safeguards: Contingency Plan/Mitigating Actions: Lessons Learned:

(b) Assume that all the coke produced in the reaction gets deposited on the catalyst. Find the volume fraction of carbon in the catalyst. <sup>[1], [2]</sup>

Use:  $\phi_c = \frac{C_{0_oil} X_{exit}}{\rho_c}$ 

Where,  $X_{exit}$  = conversion of gas oil at reactor exit

 $\phi_c$  is volume fraction of carbon in the porous catalyst

 $C_{0 oil}$  = inlet concentration of gas oil

Molar density of solid carbon (in/on catalyst pellet),  $\rho_{C}$ = 18.83 x 10<sup>4</sup> mol/m<sup>3</sup>

(c) The following equation gives the time required for the carbon interface to recede from a radius  $R_0$  to a radius R during the catalyst regeneration process.

$$t = \frac{\rho_{\rm C} R_0^2 \phi_{\rm C}}{6 D_e C_{\rm A0}} \left[ 1 - 3 \left( \frac{R}{R_0} \right)^2 + 2 \left( \frac{R}{R_0} \right)^3 \right]$$

Use this equation to estimate the time that the catalyst must spend in the catalyst regeneration unit for the entire coke deposit to be burned off.

Use: Effective diffusivity  $(D_e) = 2 \times 10^{-2} \text{ cm}^2/\text{s}$ Catalyst pellet Radius  $(R_0) = 0.5 \text{ cm}$  $C_{A0} \sim 3.8 \frac{\text{mol}}{\text{m}^3}$ 

 $\rho_{C}$  and  $\phi_{C}$  can be used from part (b) above

(d) Review the information in the <u>NFPA Diamond tutorial</u>. After reviewing the information, visit the <u>CAMEO</u> <u>Chemicals website</u> and fill out the blank NFPA Diamond to the right for butane, one of the components of 'light' hydrocarbons.



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 <u>here</u>. *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 <u>here</u>. After reviewing the information, create a BowTie diagram for the Exxon Mobil Torrance Refinery incident.
- (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 <u>here</u> 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: Fluidized Catalytic Cracking (FCC) Uni



The Spent Catalyst Slide Valve (SCSV) is used to regulate the catalyst flow from the reactor to the regenerator and the Regenerated Catalyst Slide Valve (RCSV) regulates the catalyst flow from the regenerator to the reactor. Consider the scenario of the unit operating under **both** normal conditions and safe park mode.

Level sensors are installed to measure the catalyst level in the reactor. If the catalyst level falls below the level sensor detection limit, then differential pressure measurement (PDC\_Tag4) is used to identify the catalyst level above the SCSV.



*Process parameters to consider under Normal Operating Conditions:* Flow of catalyst particles along with flue gas, Potential leak of hydrocarbons into regenerator

*Process parameters to consider in Safe Park Mode:* Flow of hydrocarbons, Flow of steam, Potential leak of hydrocarbons into regenerator

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

| Guideword + Parameter =         | Causes                    | Consequences | Safeguards | Recommendations |
|---------------------------------|---------------------------|--------------|------------|-----------------|
| Deviation                       |                           |              |            |                 |
| More Flow of catalyst particles | Inadequate                |              |            |                 |
| along with flue gas under       | performance of gas        |              |            |                 |
| Normal Operating                | catalyst separator        |              |            |                 |
| Conditions                      |                           |              |            |                 |
|                                 |                           |              |            |                 |
| Other (Leak of hydrocarbon      | Accumulation of           |              |            |                 |
| into the regenerator) under     | catalyst particles in the |              |            |                 |
| Normal Operating                | regenerator standpipe     |              |            |                 |
| Conditions                      | due to closure of the     |              |            |                 |
|                                 | RCSV (The reactor         |              |            |                 |

|   | would not contain<br>sufficient catalyst<br>particles to block the<br>flow of gas into the<br>regenerator)                 |  |  |
|---|--|--|--|
| <i>Less/No</i> Flow of steam into the reactor when in <b>Safe Park mode</b>   | Human error in<br>estimating the<br>minimum steam flow<br>rate required  |  |  |
| <i>Reverse</i> Flow of hydrocarbons<br>into the reactor from main<br>column when in <b>Safe Park</b><br><b>mode</b> | <ol> <li>Lower Flow rate of<br/>steam</li> <li>Leaking heat<br/>exchanger in the<br/>pump-around</li> </ol>                |  |  |
| Other (Leak of hydrocarbon<br>into the regenerator) when in<br>Safe Park Mode                                       | Erosion of the SCSV<br>→ catalyst particles do<br>not accumulate above<br>the SCSV thus<br>allowing gas to pass<br>through |  |  |

(ii) 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 <u>here</u> 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 injured 4, and business losses were estimated to be more than \$2.4 Billion

| LOPA Study for ExxonMobil Refinery Explosion |  |   |  |  |
|--|--|---|--|--|
| Initiating Event                             | Cause:   | Operator Error (Lowering of steam pressure)             |  |  |
|  | Consequence:   | Flow of hydrocarbons to the ESP leading to an explosion |  |  |
|  | FOIE:  |   |  |  |
| IPL(s)                                       | Description of IPL <sub>1</sub> , IPL <sub>2</sub> , |   |  |  |
|  | $PFD = PFD_1 \times PFD_2 \times \dots$              |   |  |  |
| MCF  | MCF = FOIE x PFD                                     |   |  |  |
|  | Category of MCF:                                     |   |  |  |

| Gamarita  | Impact:  | Minor injuries and business impact of \$2.4 billio |  |  |
|---|--|--|--|--|
| Severity  | Category:  |  |  |  |
| Risk  | Type of risk:  |  |  |  |
|   | Acceptable / Unacceptable?                               |  |  |  |
| If risk evaluated above is unacceptable, please continue below: |  |  |  |  |
| Proposed IPL(s)<br>(P-IPL(s))                                   | Description of P-IPL <sub>1</sub> , P-IPL <sub>2</sub> , |  |  |  |
|   | $P-PFD = P-PFD_1 \times P-PFD_2 \times \dots$            |  |  |  |
| 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.

### Wolfram [1], [2]

Click <u>here</u> to download Wolfram CDF Player for free. Click <u>here</u> to view CDF installation tutorial. Click <u>here</u> to download Wolfram code for this module.

For more background on the equations used to create the graphs in this Wolfram section, please reference Example 10-6 in *Elements of Chemical Reaction Engineering*.



Figure 3.1 Wolfram sliders.







- (i) What happens to the activity (a), conversion (X), and rate  $(-r_a)$  when  $U_0$  is varied? Explain.
- (ii) Vary 'A' and describe how it affects conversion (X) and activity (a). (Note:  $a = \frac{1}{1+At^{1/2}}$ )
- (iii) Vary the temperature (T) and pressure  $(P_{A0})$  of the entering gas oil and describe what you find.
- (iv) Write a set of conclusions based on your experiments in parts (i)-(iii).

## **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.

# Module Specific for ExxonMobil Refinery Explosion

**Catalyst Activity:** The ratio of the rate of reaction on a catalyst that has been used for time 't' to the rate of reaction on a fresh catalyst

**STTR:** Straight Through Transport Reactor. The catalyst pellets and the reactant feed enter together and move rapidly through the reactor with the catalyst recycled after regeneration

**FCC:** Fluid Catalytic Cracking. An important conversion process in a petroleum refinery used to convert heavy hydrocarbons to shorter, light hydrocarbons.

**Deactivation due to fouling:** A mechanism of decay of catalyst that results due to deposition of coke on the surface of catalyst

| Symbol          | Description                                      | SI Unit  |
|-----------------|--|--|
| P <sub>A0</sub> | Pressure of entering gas oil in reactor          | Pa   |
| Т               | Temperature of entering gas oil in reactor       | K  |
| $U_0$           | Velocity of entering gas oil in reactor          | m.s <sup>-1</sup>                                      |
| Х               | Conversion of gas oil                            |  |
| a               | Catalyst activity                                |  |
| А               | Constant "A" in decay law                        | S <sup>-1/2</sup>                                      |
| $ ho_B$         | Bulk density of suspended catalyst               | kg.m <sup>-3</sup>                                     |
| $ ho_{C}$       | Molar density of the solid carbon                | mol.m <sup>-3</sup>                                    |
| Z               | Height of catalyst in the reactor                | m  |
| kprime          | Rate constant in catalytic rate law              | kmol.kg <sup>-1</sup> s <sup>-1</sup> Pa <sup>-1</sup> |
| φ <sub>c</sub>  | Volume fraction of carbon in the porous catalyst |  |
| De              | Effective diffusivity                            | m <sup>2</sup> .s <sup>-1</sup>                        |
| R <sub>0</sub>  | Catalyst pellet radius                           | m  |
| t               | time   | s  |

Table 3.1Nomenclature