Chemical Hazard Engineering Fundamentals (CHEF)
Case Study – BP Texas City

REFINERY EXPLOSION AND FIRE
Texas City, Texas
March 23, 2005
Chemical Hazards Engineering Fundamentals (CHEF)

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We begin the study by **Identifying the Equipment or Activity** for which we intend to perform an analysis. We will often use the operation of a specific equipment item containing a specific chemical or chemical mixture to define the activity. For example, the operation of a storage tank, a reactor, a piping network, etc. Inputs are chemical data, equipment design information, operating conditions, and plant layout.
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Process Description

The ISOM unit provides higher octane components for unleaded gasoline, consists of four sections: an Ultrafiner14 desulfurizer, a Penex15 reactor, a vapor recovery / liquid recycle unit, and a raffinate splitter. At the BP Texas City refinery, the ISOM unit converted straight-chain normal pentane and hexane into branched-chain isopentane and isohexane for gasoline blending and chemical feedstocks.

We will start with the raffinate splitter section where a hydrocarbon mixture is separated into light and heavy components. About 40 percent of the raffinate feed was recovered as light raffinate (primarily pentane/hexane). The remaining raffinate feed was recovered as heavy raffinate. The raffinate splitter section could process up to 45,000 barrels per day (approximately 1300 gallons/minute) of raffinate feed.

This is an illustrative example and does not reflect a thorough or complete study.
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Process Description

The process equipment in the raffinate splitter section consisted of a feed surge drum; a distillation tower; a furnace with two heating sections, one used as a reboiler for heating the bottoms of the tower and the other preheating the feed; air-cooled fin fan condensers and an overhead reflux drum; various pumps; and heat exchangers.

Figure 1: Raffinate Splitter Tower System of the ISOM Unit
Liquid raffinate feed was pumped into the raffinate splitter tower near the tower’s midpoint. An automatic flow control valve adjusted the feed rate. The feed was pre-heated by a heat exchanger using heavy raffinate product and again in the preheat section of the reboiler furnace, which used refinery fuel gas. Heavy raffinate was pumped from the bottom of the raffinate splitter tower and circulated through the reboiler furnace, where it was heated and then returned below the bottom tray. Heavy raffinate product was also taken off as a side stream at the discharge of the circulation pump and sent to storage. The flow of this side stream was controlled by a level control.

Light raffinate vapors flows overhead, is condensed by air-cooled fin fan condensers, and then deposited into a reflux drum. Liquid from the reflux drum, was then pumped back into the raffinate splitter tower above the top tray.
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Hazard Identification and Risk Analysis (HIRA) Study

The scope of this presentation is focused on the Raffinate Column. As this evaluation is related to an incident investigation, little emphasis will be placed on Frequency Evaluation (the incident has already occurred) or Risk Analysis (evaluation of protection layers). However, a “worst case” consequence such as might be evaluated during risk analysis will be addressed.
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Raffinate Composition

Table G-1. Raffinate splitter column simplified composition model (Fisher, 2006)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>0.0383</td>
</tr>
<tr>
<td>2-methyl butane</td>
<td>0.0263</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.1519</td>
</tr>
<tr>
<td>2-methyl pentane</td>
<td>0.2950</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.3072</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.1300</td>
</tr>
<tr>
<td>n-nonane</td>
<td>0.0409</td>
</tr>
<tr>
<td>Heavies as n-decane</td>
<td>0.0104</td>
</tr>
<tr>
<td>Total</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

For entry into CHEF, the mixture is simplified to:
0.06 n-pentane (including isopentane)
0.45 n-hexane
0.31 n-heptane
0.18 n-octane

A composition (weight fraction):
- 0.06 n-pentane
- 0.45 n-hexane
- 0.31 n-heptane
- 0.18 n-octane

was used as representative. The operating pressure was 25 psig (172 kPa gauge) and the operating temperature of 112°C was estimated as the saturation temperature or temperature such that the estimated vapor pressure matches the operating pressure for a boiling liquid.

The chemical property inputs for the various worksheets will then be estimated from this composition at the appropriate temperature.
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Chemical Hazards

✓ An estimated mixture flashpoint of -48 °C (the minimum of any component) and estimated lower flammable limit of 1.15 volume % indicates a potentially high flammability hazard.

✓ An estimated ERPG-2 of >2000 ppm would indicate a low to moderate toxicity hazard. The NFPA Health Ratings for these materials range from 1 to 2 also indicating a low to moderate hazard.

✓ There may be other hazards to consider such as thermal due to a maximum process temperature greater than 60 to 80 °C.
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Hazard Identification and Risk Analysis (HIRA) Study
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### Partial List of Hazard Scenarios per CHEF Example Scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Hazard Type</th>
<th>Initiation</th>
<th>Effect</th>
<th>Mitigation/Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drain or Vent Valve Open</td>
<td>Flow-Loss of Containment</td>
<td>All</td>
<td>Procedure Failure (Human Error)</td>
<td>Drain or Vent Leak</td>
</tr>
<tr>
<td>Excessive Heat Input - Pool Fire Exposure</td>
<td>Temperature-High Pressure-High Heat Input-High</td>
<td>All</td>
<td>Scenarios involving spill plus ignition in nearby liquid-containing equipment</td>
<td>Relief Venting Equipment Rupture Equipment Damage</td>
</tr>
<tr>
<td>Overfill, Overflow, or Backflow</td>
<td>Level-High Flow-Backflow</td>
<td>All Liquid Containing Equipment</td>
<td>Level Control Failure Procedure Failure (Human Error)</td>
<td>Overflow Release Equipment Damage</td>
</tr>
<tr>
<td>Overfill - Flooding or Plugging</td>
<td>Level-High</td>
<td>Adsorber/Scrubber Distillation Vapor Quench</td>
<td>Level Control Failure Pressure Control Failure Flow Control Failure</td>
<td>Overflow Release Equipment Damage</td>
</tr>
<tr>
<td>Relief Device Failure</td>
<td>Flow-Loss of Containment</td>
<td>All</td>
<td>Mechanical Failure</td>
<td>Relief Hole Size Leak</td>
</tr>
<tr>
<td>Vacuum Damage</td>
<td>Pressure-Low</td>
<td>All</td>
<td>Pressure Control Failure Mechanical Failure</td>
<td>Full-Bore Leak Equipment Damage</td>
</tr>
</tbody>
</table>
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Suggested Scenarios for Raffinate Column

**WORKING WITH YOUR EVALUATION TEAM:**

- Review the suggested list of scenarios. Do these represent what you would expect for a distillation column?
- Are there scenarios that have been “screened out” (shown in gray) that should be considered?
- Are there scenarios missing? (Possibly similar scenarios with different Initiating Events)
- Do you agree with the “worst” Consequence (Tolerable Frequency Factor) for the scenario listed?
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Suggested Scenarios for Raffinate Column

WORKING WITH YOUR EVALUATION TEAM:

- Utilize an Appropriate Hazard Evaluation Technique (HAZOP, What If, etc.) to capture additional scenarios.
- Capture existing Safeguards and Recommendations for each Scenario. Note the Dates and Names of participants in the Study.
- Select which Scenarios warrant more detailed Risk Evaluation (such as Layers of Protection Analysis).
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Hazard Identification and Risk Analysis (HIRA) Study

What are the Hazards?
What can go Wrong?
How Bad could it Be?
How Often might it Happen?
Is the Risk Tolerable?

Select Equipment or Activity to be Analyzed
Identify Chemical and Process Hazards
Develop Scenarios
Analyze Consequences
Estimate Frequency
Analyze Risk
Implement Additional Safeguards as Needed
Sustain Performance for Life Cycle of Facility

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Case Study – BP Texas City

Site Layout

Several wooden trailers are located approximately 200 m from the raffinate splitter housing 20 people. The trailers are “low strength” construction. In addition, the process area appears to be relatively “low” equipment congestion.

The blowdown tank which receives the discharge from the raffinate splitter relief devices is located 60 m from the wooden trailers and vents at an elevation of 36 m.
Use a Specified Release rate equal to feed rate of 55 kg/sec for Overfill at the Release Temperature of 112°C

Leave Elevation Blank for now as Discharge was to a Blowdown Tank which then Overflowed to the Atmosphere

Total Airborne Rate of 55 kg/sec with a liquid pool of 1310 m²
Use a Flashing Liquid Release with Averaging Time Correction for Flammable Evaluation

Chemical Properties at Blowdown Tank Release Temperature of 74.9 C (estimated normal boiling point)

Vapor Rate from Source Model of 55 kg/sec. Leave two-phase velocity and initial fraction vapor blank for now

Elevation of Blowdown stack is 36 but release will be assumes ground elevation for a flashing liquid

Distance to Concentration of Interest (lower flammable limit) is 235 m at the default wind speed of 3 m/sec and Class D Stability
Vapor Cloud Explosion

Simple Modeling Approach within CHEF and RAST

The entire vapor cloud is considered a single Potential Explosion Site with epicenter at the center of the flammable cloud (0.5 $X_{LFL}$).

An single overall level of congestion and confinement for the entire cloud is used.

Wind direction is assumed toward greatest population or building with highest occupancy.

Methodology is described in the CHEF Guide
Site Layout

Congestion or Obstacle Density Categories

The method described in CHEF is limited to consideration of the entire cloud volume as a single Potential Explosion Site (PES) at an overall or average category of process equipment congestion. This technique does not account for small localized areas of higher congestion where blast overpressure will be higher.

**Low** – Only 1-2 layers of obstacles. One can easily walk through the area relatively unimpeded.

**Medium** – 2-4 layers of obstacles. One can walk through an area, but it is cumbersome to do so. Medium Congestion is assumed in RAST if a category is not entered by the user.

**High** – Many layers of repeated obstacles. One could not possibly walk through the area and little light penetrates the congestion.
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Consequence Analysis – Explosions

Use Vapor Cloud Explosion and Distance of Interest as 60 m from Release Point to Project Trailers

Chemical Properties at Blowdown Tank Release Temperature of 74.9 C (estimated normal boiling point)

Enter Distance to LFL from Vapor Dispersion estimate, vapor rate and “low” degree of congestion

Estimated Distance to 1 psi Blast Overpressure is 308 m and Estimated Overpressure at 50 m Distance of Interest is 3.2 psi
A simplification in RAST is wind direction toward the highest population. This is quite reasonable in Risk Analysis where the wind direction is unknown.

In the actual incident, the wind direction was toward the southeast rather than west toward the wooden trailers.

Wind Direction represents a key difference between estimates for Risk Analysis versus Incident Investigation. Blast overpressure at the wooden trailers would likely have been higher if the wind direction was toward the trailers.
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**Consequence Analysis – Impact Estimation**

### Clear Inputs

**ONSITE IMPACT ASSESSMENT INPUT INFORMATION**

**STEP 1 - Select Location and Scenario Outcome**
- Release Location: Outdoor
- Scenario Outcome: Vapor Cloud Explosion

**Number of Personnel Routinely in the Immediate Vicinity?**
- Leave Input Value Blank to accept Chemical Data Table Values

**Personnel in the Immediate Vicinity include those associated with procedures requiring operator attendance such as unloading a tank truck, sampling, in addition to personnel using nearby walkways, etc.**

**STEP 2 - Enter Chemical Properties (or Select Chemical Name from Pic List)**

**Chemical Name**

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Cas No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Leave Input Value Blank to accept Chemical Data Table Values)</td>
<td></td>
</tr>
</tbody>
</table>

**Lower Flammable Limit, LFL**
- Input Value: 1.16
- Input Units: vol %
- Equation Input: Equation Units

**Fuel/Machinry, EPPG-3 Concentration**
- Input Value: 2
- Input Units: ppm
- Equation Input: Equation Units

**Explosion Overpressure at Center of Occupied Building**
- Impact Area (Equation 14-1), $A = 0.3 \times 26.67$ m
- Equation Units

**Step 3 - Enter Hazard Distances**

- Concentration at Distance to Fence Line or Public Exposure (Equation 14-1)
- Equation Units

- Distance to Multiple of Lower Flammable Limit, LFL
- Equation Units

- Distance to LFL Concentration - Daytime Conditions
- Equation Units

- Distance to LFL Concentration - Nighttime Conditions
- Equation Units

- Distance to Severe Blast Impact
- Equation Units

**Step 4 - Enter Low Strength Building with 20 Occupants**

**Enter Blast Overpressure at Distance to Center of Occupied Building from Explosion Worksheet**

**Enter Distance to Fraction of LFL concentration (0.5 in this example) for Flash Fire Impact from Vapor Dispersion Worksheet**

**Flash Fire**
- Impact Area (Equation 14-1), $A = 0.3 \times 26.67$ m
- Equation Units

**Flash Fire Personnel Seriously Impacted, $N = 0.918 \times 20 = 18.36$ People**

**Vapor Cloud Explosion (VCE)**
- Total Airborne Quantity, AQ
- Equation Units

**Number of Building Occupants Severely Impacted = Vulnerability times Total Building Occupants**
- Equation Units

**Total Personnel Severely Impacted = Flash Fire + Occupants Impacted**
- Equation Units

**Estimate of 18 fatalities within Occupied Building and addition 6 to 7 outdoors from Flash Fire at default population density**

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**June 28, 2021**
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Hazard Identification and Risk Analysis (HIRA) Study

What are the Hazards? What can go Wrong? How Bad could it Be? How Often might it Happen? Is the Risk Tolerable?

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To understand the Consequence Severity and Tolerable Frequency, the values for key Study Parameters and a Risk Matrix may be viewed on the Workbook Notes worksheet. These values may be updated on hidden worksheets and should reflect the company’s specific risk criteria.

For this case study, the Risk Matrix (right) has been used. The Human Harm criteria is based on an estimated number of people severely impacted (severe injury including fatality).
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Risk Analysis / Layers of Protection Analysis (LOPA)

**Initiating Event** – either Basic Level Control System failure (instrument was not indicating the correct level) or Human Performance Failure as “operators routinely deviated from written procedures maintaining a high liquid level during startup to minimize the potential for costly damage to the fired heaters”. From the CCPS Book, Layers of Protection Analysis, a frequency of 0.1 per year may be appropriate.

**Loss Event** – Overfill of the Raffinate Splitter Column to the Blowdown Tank with subsequent release of flammable material to the atmosphere.

**Incident Outcome and Consequence** – Vapor Cloud Explosion resulting in greater than 10 potential fatalities.
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Risk Analysis / Layers of Protection Analysis (LOPA)

Conditional Modifier – the probability of ignition for an unknown source assuming “good” ignition controls

~0.15

Cloud Area ~ 0.3 (235 m)² = 16568 m² = 1.66 hectares

A reasonable probability of ignition for this case may be 0.1 to 0.15 as the process area is likely electrically classified with “good controls”.

CCPS, Guidelines for Determining the Probability of Ignition of a Released Flammable Mass, (2014)
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### Risk Analysis / Layers of Protection Analysis (LOPA)

<table>
<thead>
<tr>
<th>Scenario Number</th>
<th>Equipment Identification</th>
<th>Scenario Title</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raffinate Column</td>
<td>Overfill Scenario during Startup</td>
</tr>
</tbody>
</table>

**Date:**

**Consequence Description/ Category:**

- Column Overfill resulting in flammable release to the atmosphere and vapor cloud explosion.

**Risk Tolerance Criteria (Category or Frequency):**

- Potential for greater than 10 fatalities, 1.E-06

**Initiating Event (typically a frequency):**

- Failure of Level Control Loop or Human Performance Failure for filling the column above level reading during startup, 1.E-01

**Enabling Condition or Event:**

**Conditional Modifiers (if applicable):**

- **Probability of Ignition:** 1.E-01
- **Probability of Personnel in Affected Area:**
- **Probability of Fatal Injury:**
- **Others:**

**Frequency of Unmitigated Consequence:** 1.E-02

### Independent Protection Layers (IPLs)

- **BPCS:**
  - High Column Pressure shut off of heat to the column reboiler, 1.E-01
- **Human Intervention:**
  - Blowdown Tank High Level with Procedure to close manual Feed valves, 1.E-01
- **SIF:**
  - Raffinate Column High Level Alarm with Automated shutoff of Heat and Feeds, 1.E-01
- **Pressure Relief Device:**
- **Other Protection Layers (must justify):**
  - Restricted Access near Isom Unit during Operation or Startup, 1.E-01

**Safeguards (Non-IPLs):**

- **Total PFD for all IPLs:** 1.E-04
- **Frequency of Mitigated Consequence:** 1.E-06
- **Risk Tolerance Criteria Met? (yes/no):**

**Actions Required to Meet Risk Tolerance Criteria:**

- Ensure all Protections are Inspected, Tested, and Maintained to company standards. Restrict placement of temporary occupied buildings beyond blast contour unless blast resistant buildings are used.

**Notes:**

- Meets Tolerable Criteria for Harm to On-Site Personnel

**References (link to originating hazard review, PFD, P&ID, etc.):**

- LOPA Analysis (and Team Members)
The existing safeguards were close to sufficient for managing this scenario to a tolerable risk level had they been adequately maintained and some actions automated rather rely only on operator response to an alarm. In addition to those listed in the LOPA worksheet, several other alarms existed (such as high pressure) that may have contributed to reducing the overall scenario frequency if the potential for column overfill would have been recognized.
Risk Analysis Screening Tools (RAST)

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Risk Analysis and Incident Investigation often use similar methods to better understand the scenario. Risk Analysis “anticipates” what could go wrong and what the potential consequences may be. For Incident Investigation, the Incident Outcome and Consequences are known in addition to the actual weather conditions and wind direction.

For the Raffinate Splitter, a column overfill would be one of many scenarios to consider. It would need to be recognized that a Vapor Cloud Explosion could be a feasible Incident Outcome for an Overfill loss event. CHEF was conservative in estimating blast damage as actual wind direction was not toward the wooden trailers and a simplified single Potential Explosion Site of “average” congestion and confinement was assumed. However, the “order of magnitude” estimate of consequences seems reasonable.
Questions?