Integrating Risk Assessment in the Unit Operations Laboratory

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Integrating Risk Assessment
in the Unit Operations Laboratory and Design Courses
Abstract

In light of the practical needs of the chemical engineering discipline and the new AIChE/ABET program criteria requiring knowledge of process hazards, we are developing strategies for making process safety a student mindset by integrating risk assessment in our unit operations laboratory and design courses. We believe that with the early, practical, and direct exposure to risk assessment in the laboratory, students can later approach process design with increased appreciation for the value of considering process hazards and will be knowledgeable and experienced in the evaluation of hazards and risk in their work.

In our approach, each group in the unit operations course is asked to perform a simplified Process Hazard Analysis (PHA) of a laboratory process before working on the experimental stand. Our units include small-scale and pilot-scale distillation columns for the separation of alcohol mixtures, an absorption column involving sodium hydroxide solutions, and an extraction column for the removal of propionic acid from kerosene. Students are required to construct an accurate flow diagram of each stand, consider general precautionary measures and operating limits for the process, perform “what if” analyses, take note of materials of construction and chemical compatibility for equipment components, identify physical properties of materials and their key safety data, and provide recommendations and a list of action items for future consideration. Compilation of a simple PHA in the succeeding process design course provides additional experience to the practice and reiterates its relevance in the planning and design stages. This is an approach that we expect to successfully address the new requirements of the AIChE Program Criteria; moreover, we expect that our students will graduate with abilities in process hazards analysis that will be of benefit in the workplace.

Background

In response to the updated ABET Program Criteria for chemical engineering that now require consideration of hazards associated with the processes that our students design, analyze, and control, we have acknowledged the need to provide additional exposure to risk assessment and more rigorous safety considerations in our baccalaureate chemical engineering curriculum. Therefore, we are adding simplified Process Hazard Analyses to both Unit Operations and Process Design courses to give students direct exposure to the basics of the practice.

Our approach aligns closely with the AIChE/SACHe guidelines for teaching safety and design, allowing students to gain appreciation for the importance and rigor of the process, providing simple guidelines to help students identify and characterize potential hazards, and exposing undergraduates to What-If analyses to reinforce the idea that hazards can be controlled or mitigated with appropriate design.

Methodology

Process Hazard Analyses are being integrated in two successive courses, Unit Operations (Laboratory Practice and Statistical Analysis) and Process Design and Optimization. In both courses, after an introductory presentation defining Process Hazard Analyses, students are asked to compile simple PHA's to put the process to practice. To guide and facilitate compilation of
the information and clarify our expectations, we are providing tables outlining the needed information. A simple and uniform format is expected to make the procedure less cumbersome and help establish a methodical approach that can be applied across systems for both experimental and design course tasks, or in future applications beyond the classroom. The template is based on the industrial experience of one of the authors (M.F.), who contributed to and compiled PHA’s while performing research and development work in the fields of microchannel technology (Velocys, Inc.) and biotechnology (Draths Corporation).

Unit Operations

In the Unit Operations course, students have direct, hands-on experience with representative chemical engineering processes of varying complexity, putting to practice the theoretical learning of the first two academic years. The course is particularly well suited to demonstrating the importance of safe operating conditions, since students find themselves on the front line in case of an accident. Although the laboratory experiments have been designed to minimize extreme hazards associated with toxic chemicals, high temperatures and pressures, students do need to deal with steam and flammable species and chemicals (ethanol, propanol, kerosene, hydrogen peroxide, acetone, etc.). Proper attention to these risks is required.

Experimental units in our teaching laboratory include small-scale and pilot-scale distillation columns for the separation of alcohol mixtures, an absorption column involving sodium hydroxide solutions, and an extraction column for the removal of propionic acid from kerosene. Before turning on equipment, students need to prepare a prereport, outlining the objectives of their experiments and their intended approach to performing the testing and analysis of the data, and describing the test stand and safety considerations. To date, the discussion of safety considerations has included identifying safety and operational hazards, with special attention given to precautions and emergency shutdown procedures in case the laboratory needs to be evacuated. Starting this year, in the spring semester of 2013, we are implementing a more rigorous safety review, requiring compilation of specific tables and lists to help students give the safety component of the experiments particular consideration. Whereas past emphasis has been on personal safety, we are expanding the view to include process safety.

To avoid making the process too time consuming, four of the five experiments students perform over the course of the semester require a basic safety review, and a compilation of general safety information and precautions. Only one of the experiments, involving the more complex stands, requires the thorough safety review intended to mimic the PHA methodology. The specific requirements for both basic and thorough safety reviews are listed below. Tables 1 through 4 specify the format and the required information for each item. Although MSDS’s do not need to be included with the reports, students need to refer to the MSDS of each chemical species to compile the tables.

For basic and thorough safety reviews, students are asked to include the following:

1. a list of the starting species, additives, products, and by-products (compilation of Table 1);
2. a list of physical and chemical properties of the species and their key safety data (compilation of Table 2);
3. a brief discussion of general safety and operational hazards and precautions;
4. an emergency shutdown procedure, in case the laboratory needs to be evacuated.

For the thorough safety review, students are asked to include the following additional information:
1. a flow diagram showing key valves, pumps, feed and product tanks;
2. material compatibility information and general operating limits for the stand and auxiliary equipment (as shown in Table 3);
3. a simple What If analysis including at least three possible failure modes (as shown in Table 4) and any recommendations and action items that require attention from the safety perspective.

Table 1. List of starting materials, additives, products, and by-products for the experiment.

<table>
<thead>
<tr>
<th>ID</th>
<th>Chemical Name(s)</th>
<th>Function in the Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
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<td>...</td>
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<td>n</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. List of physical and chemical properties of the chemicals used in the experiment.

<table>
<thead>
<tr>
<th>Chemical ID</th>
<th>1</th>
<th>2</th>
<th>...</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Name</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical Formula</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (ambient conditions) (g/cm3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decomposition Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auto-Ignition Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower Flammable Limit, LFL (%vol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Flammable Limit, UFL (%vol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Health Rating, NFPA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flammability Rating, NFPA</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Instability Rating, NFPA</td>
<td></td>
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<td></td>
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<tr>
<td>Special Hazards Rating, NFPA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odor Threshold</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TWA</td>
<td></td>
<td></td>
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<tr>
<td>STEL</td>
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<td></td>
</tr>
<tr>
<td>IDLH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hazards and Health Risks

| Required PPE |     |     |     |       |
| Spill or Leak Measures |     |     |     |       |
| Disposal method |     |     |     |       |
| Known Chemical Incompatibilities |     |     |     |       |
| Source(s) |     |     |     |       |
Table 3. Representative material compatibility information relevant to the experimental stand or auxiliary equipment. Compatibility notes should reference verified compatibility of the chemicals with the materials of construction with which they may come in contact at the intended operating conditions or potential questions about material compatibility.

<table>
<thead>
<tr>
<th>Equipment Component</th>
<th>Maximum Operating Temperature / Pressure</th>
<th>Materials of Construction</th>
<th>Stream Composition / Components</th>
<th>Compatibility Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed tank</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>feed pump</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>feed valves</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>feed lines</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>column / reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product lines</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product tanks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product drain valves</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sources for the compatibility information</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Representative, simplified What-If analysis for the experimental stand.

<table>
<thead>
<tr>
<th>What If ...</th>
<th>Causes</th>
<th>Consequences</th>
<th>Safeguards</th>
</tr>
</thead>
<tbody>
<tr>
<td>pump leaks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>column/reactor temperature spikes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product line leaks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examples of completed forms and their assessment and evaluation will be included in the presentation given at the ASEE meeting.

Process Design and Optimization

In the Process Design and Optimization course, students integrate fundamental chemical engineering processes, optimizing economics, process operation, and design. Having seen a practical application of the Process Hazard Analysis in the preceding Unit Operations course, additional exposure to PHA’s can help refine student understanding and appreciation for the insight PHA’s can provide, helping students determine appropriate materials of construction as well as the manner in which components are assembled and how the overall system may be designed to minimize safety hazards, with economic impact as a continuing consideration.

Starting last year, in the fall semester of 2012, we asked that students perform a simplified PHA as a part of one of their small design projects. This systematic review of their process designs helped clarify the need for appropriately placed pressure relief valves and rupture discs, flow diversion options, good temperature control systems, etc., with an emphasis on safety. Similarly
to the requirements of the Unit Operations course, students were asked to address specific points as described below:

1. a list of the starting species, additives, products, and by-products (as in Table 1);
2. a list of physical and chemical properties of the species and their key safety data (as in Table 2);
3. a brief discussion of general safety and operational hazards and precautions;
4. a process and instrumentation diagram showing key valves, pumps, feed and product tanks;
5. a simple What If analysis of three units in their process, including at least three possible failure modes for each unit (as in Table 4) and any recommendations and action items that require attention from the safety perspective.

Initial feedback was varied, with some students performing a very thorough review, others providing very little information. Process and instrumentation diagrams were included in separate sections of the student reports. Appendices A and B include two of the best reports provided by the students. Not all students followed the tabulated formats to collect the information. In some cases this led to lack of clarity; in others, the chosen format was clear and concise, nonetheless. We expect greater consistency in the PHA responses in the fall 2013 course, and will evaluate and compare results as the first full cycle comes to a close.

Concluding Remarks

Our goal is to give our students experience and appreciation for the PHA process. Therefore, we are beginning to integrate PHA's in two sequential courses, the Unit Operations laboratory and the capstone Process Design. Repeated exposure to the practice and its principles is expected to enhance student understanding and develop a ‘habit’ of integrating safety and risk considerations in their work as standard practice. By adopting a methodical and simple approach, allowing students to fill in tables rather than write extended prose, we expect the process to be less cumbersome without compromising student learning.

The first implementation of our approach in the Unit Operations lab is occurring in the spring 2013 semester. Our first Process Design PHA assignment was given in the fall 2012 semester to students who had not been first exposed to the practice in the Unit Operations course. We look forward to gauging the response and performance of this first set of students, comparing their approach to the response of the students who first adopted the practice in Process Design this past fall.

As implementation continues and we potentially expand the PHA approach to include other key courses in our curriculum, we will refer to available SACHE documents for additional insight and to enhance our preliminary approach. We expect that students will benefit from this practice both in the short term, as they work in the lab, and in the long term, as they assume responsibilities in the workplace. We also expect that this method can be easily adapted by other chemical engineering programs in the appropriate courses in their curricula.
Bibliography


Appendix A – Exemplary Student Report 1

Process Chemistry

A plug flow reactor thermally hydrodealkylates 2,000 barrels per day of toluene in the fresh feed to benzene. Toluene and hydrogen react at high temperatures by splitting the methyl group away from the toluene to produce benzene and methane (see Figure 1 below). However, due to the elevated temperatures, undesirable reactions occur: benzene and toluene can react to form methyl diphenyl; 2 moles of toluene can form dimethyl diphenyl; methyl diphenyl and dimethyl diphenyl will dealkylate to form diphenyl (see Figure 2 below). Only trace amounts of methyl and dimethyl diphenyl are present in a reactor effluent at high conversion. Accordingly, the kinetics and selectivity versus conversion relationships must be determined to optimize the operating conditions for the plug flow reactor.

Figure 1: Reaction 1- Toluene and hydrogen react to produce benzene and methane

Figure 2: Reaction 2- Main undesirable side reaction that occurs to form diphenyl
Process Description

The process has a stream for fresh toluene and a stream for fresh hydrogen to be fed into the system, which both independently enter a fired heater. The streams are then reacted together in a plug flow reactor. Afterward, the stream is cooled by a quench stream and enters three heat exchangers in series. The components are separated in a flash drum 1 where methane and hydrogen are vaporized and split into a purge and recycle stream. The recycle stream enters two compressors in parallel and mixed with the fresh hydrogen stream. The benzene, toluene, and diphenyl from the flash drum 1 are liquefied and split. Part of the stream is quenched to cool the products from the heat exchanger and the remaining of the stream is throttled. After the throttle, the stream enters flash drum 2 to remove any extra methane. The bottoms of flash drum 2 enter distillation column 1, where the distillate is benzene which is sold and the bottoms is sent to distillation column 2. In distillation column 2, the bottoms is diphenyl which is purged and the distillate is recycled into the toluene fresh free after the pressure is increased by a pump (see Appendix A; Figure A1).

Key Hazards

Physical Data

Some of the key hazards and physical data for toluene, benzene, hydrogen, methane, and diphenyl are shown in Table 1 below.

Table 1: Key hazards and physical data

<table>
<thead>
<tr>
<th></th>
<th>Toluene</th>
<th>Benzene</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Diphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C(_7)H(_8)</td>
<td>C(_6)H(_6)</td>
<td>H(_2)</td>
<td>CH(_4)</td>
<td>(C(_6)H(_5))(_2)</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>92.14</td>
<td>78.11</td>
<td>2.016</td>
<td>16.04</td>
<td>154.21</td>
</tr>
<tr>
<td>Melting Point (deg C)</td>
<td>-95</td>
<td>5.5</td>
<td>-259.2</td>
<td>-182.5</td>
<td>68.9</td>
</tr>
<tr>
<td>Boiling Point (deg C)</td>
<td>110.6</td>
<td>80.1</td>
<td>-252.8</td>
<td>-161.5</td>
<td>254.5</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>3.1</td>
<td>2.8</td>
<td>0.0000835</td>
<td>0.000512</td>
<td>68.9</td>
</tr>
<tr>
<td>Flash Point (deg C)</td>
<td>4.44</td>
<td>-11.1</td>
<td>Flammable</td>
<td>-187.8</td>
<td>112.8</td>
</tr>
<tr>
<td>Auto-Ignition Temp (deg C)</td>
<td>480</td>
<td>497.78</td>
<td>565.5</td>
<td>537</td>
<td>540</td>
</tr>
<tr>
<td>LFL (% vol)</td>
<td>1.1</td>
<td>1.2</td>
<td>4</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>UFL (% vol)</td>
<td>7.1</td>
<td>7.8</td>
<td>74</td>
<td>15</td>
<td>5.8</td>
</tr>
<tr>
<td>Health</td>
<td>2</td>
<td>2</td>
<td>3 (liquid)</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Fire</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Reactivity</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TWA</td>
<td>200</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>STEL</td>
<td>500</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Toxicity and Exposure

Toluene
Toluene is absorbed through skin, dermal contact, eye contact, inhalation, and ingestion. Based on a four hour exposure, the acute oral toxicity is 639 mg/kg [Rat]. The acute dermal toxicity is less than 14,100 mg/kg [Rabbit]. The acute toxicity of vapor is 440 for 24 hours [Mouse]. The exposure limits in the United States are TWA: 200, STEL: 500, and CEIL: 300 ppm from OSHA. Repeated or prolonged exposure to toluene via inhalation may cause central nervous system and cardiovascular symptoms such as acute inhalation and ingestions. Additionally, exposure may also lead to liver damage/failure, kidney damage/failure, brain damage, weight loss, bone marrow changes, electrolyte imbalances, muscle weakness, and Rhabdomyolysis.

Benzene
Benzene is absorbed through skin, dermal contact, eye contact, and inhalation. Based on a four hour exposure, the acute oral toxicity is 930 mg/kg [Rat]. The acute dermal toxicity is less than 9,400 mg/kg [Rabbit]. The acute toxicity of vapor is 10,000 for 7 hours [Rat]. Repeated or prolonged exposure to benzene can lead to target organs damage. Therefore, exhaust ventilation must be provided or the use of other controls to maintain the airborne concentrations of vapors below their threshold limit value. The exposure limits in the United States are TWA: 0.5 and STEL: 2.5 ppm.

Hydrogen
There is no significant effects regarding toxicity or critical hazards for hydrogen. Hydrogen is flammable in the presence of oxidizing materials. Hydrogen may cause burns or frostbite when contact with rapidly expanding gas or cryogenic liquid on the eyes or skin. Hydrogen acts as a simple asphyxiant.

Methane
Respiratory protection is required for methane concentrations above 1.0% (20% of the LEL). Therefore, proper ventilation is necessary to prevent accumulation of gas concentrations. No treatment is needed if methane is in contact with eyes or skin.

Diphenyl
Diphenyl is absorbed through dermal contact, eye contact, inhalations, and ingestion. The acute oral toxicity (LD50) is 2,400 mg/kg [Rat]. Diphenyl may cause damage to the nervous system and liver.

Reactivity and Stability Data

Toluene
Toluene is a stable product. Conditions of instability are heat, ignition sources (flames, sparks, static), and incompatible materials. Toluene is reactive with oxidizing agents. Toluene is incompatible with strong oxidizers, silver perchlorate, sodium difluoride, Tetranitromethane, and Uranium Hexafluoride. Bromine Trifluoride reacts violently with Toluene at -80 degrees Celsius. Toluene reacts chemically with nitrogen oxides, or halogens to form nitrotoluene.
Owing to nitrobenzene, and nitrophenol and halogenated products, respectively. Polymerization will not occur. Toluene is non-corrosive in presence of glass.

**Benzene**

Benzene is a stable product. Conditions of instability are heat, ignition sources, and incompatibles. Benzene is highly reactive with oxidizing agents and acids. Benzene vapors react with chlorine and light which causes explosion. Benzene also reacts explosively with bromine pentafluoride, chlorine, chlorine trifluoride, diborane, nitric acid, nitril perchlorate, liquid oxygen, ozone, and silver perchlorate. Uncontrolled contact with benzene may cause explosion. Polymerization will not occur. Benzene is non-corrosive in presence of glass.

**Hydrogen**

Hydrogen is a stable product and is extremely reactive with oxidizing materials. Hazardous decomposition products should not be produced and hazardous polymerization will not occur under normal conditions.

**Methane**

Methane is a stable product. A temperature of 52 degrees Celsius should be avoided for methane. Methane is incompatible with oxygen, halogens, and oxidizers. Hazardous decomposition products should not be produced and hazardous polymerization will not occur under normal conditions.

**Diphenyl**

Diphenyl is a stable product. Diphenyl is reactive with oxidizing agents and reducing agents. It is slightly reactive with acids and alkalis. Polymerization will not occur.

**Personal Safety Equipment**

Respiration protection is required. Safety glasses and/or face shield is required. Leather gloves are required and fire resistant suit in emergency situations. Safety shoes are required.

**Key What-If’s**

**Pump Failure**

**Causes**

A pump failure may occur because of a fitting failure, a crack in the pump head, or a crack in one of the containment vessels.

**Consequences/Hazards**

The consequences and hazards of a pump failure are un-reacted toluene leaks to the surrounding area, possible injuries by inhalation of fumes, and possible fire in case of a spark due to low liquid flash point.

**Safeguards**

There will be a feed valve shut down when the pump pressure falls below process conditions in case the pump fails. Additional there will be a detector and alarm with adequate ventilation for enclosed work area.

**Recommendations/Actions**

Oversee installation, operation, maintenance, and repair to ensure that machines and equipment
are installed and functioning according to specifications. The first action is shutting down the feed valve, and determines to call 911 or not based on the actual situation. Then let the technical repairman with the protective clothes check and fix the equipment. Also the fire-extinguishing installation must be prepared.

**Agitator Stops**

**Causes**
An agitator stop may occur because of an agitator motor failure, electrical utility loss, mechanical linkage failure, or operator failure to activate.

**Consequences/Hazards**
The consequence and hazards of an agitator stop are un-reacted hydrogen in the reactor is carried over to storage tank and released to the enclosed work area, and possible injuries or fatalities to workers due to hydrogen concentrations above LFL.

**Safeguards**
There will be a detector and alarm, automatic system shutdown and cooling system if there is loss of agitation, and adequate ventilation for enclosed work area.

**Recommendations/Actions**
Oversee installation, operation, maintenance, and repair to ensure that machines and equipment are installed and functioning according to specifications. If the situation occurs, shut down the feed valve and turn on the cooling system. Then let the technical repairman with the protective clothes check and fix the equipment. If there is a fire, put out the fire with a carbon dioxide extinguisher or dry powder extinguisher after turning off the feed.

**Pressure Drops Below Set Value**

**Causes**
A pressure drop below set value may occur due to a leak in the lines or no flow from the pump.

**Consequences/Hazards**
If there is a leak in the lines, the un-reacted toluene spreads to the surrounding area, possible injuries by inhalation of fumes, and possible fire in case of a spark due to low liquid flash point. If no flow from the pump, the excessive feed may damage the equipment.

**Safeguards**
There will be a detector and alarm to record the pressure and warn if the pressure is close to the lower limit, also the automatic shutdown system and cooling system are required to shut down and cool the system when the pressure reaches the lower limit.

**Recommendations/Actions**
Check the tube flowing situations, the accuracy of the detector, the alarm, automatic shutdown system and cooling system periodically. If the case occurs, turn off the feed valve and cool the reactor. Then check the pump and pipes to determine the problem and fix it. If there is a fire, put out the fire with a carbon dioxide extinguisher or dry powder extinguisher after turning off the feed.

**Pressure Rises Above Set Value**

**Causes**
A pressure rise above the set value may occur due to a line plug to product precipitation, too high a temperature in the reactor, or too high a flow in the tubes and reactor.
Consequences/Hazards
The production precipitation will affect the reaction conversion. The high temperature may damage the equipment and cause the fire, even explosion. The high flow rate may also damage the equipment (deformation and leak) and affect the efficiency of the process.

Safeguards
There will be a detector and alarm to record the pressure and warn if the pressure is close to the upper limit, also the automatic shutdown system and cooling system are required to shut down and cool the system when the pressure reaches the upper limit.

Recommendations/Actions
Check the tube flowing situations, the accuracy of the detector, the alarm, automatic shutdown system and cooling system periodically. If the case occurs, turn off the feed valve and cool the reactor. Then check the pipes and the reactor to determine the problem and fix it. If there is a fire, put out the fire with a carbon dioxide extinguisher or dry powder extinguisher after turning off the feed.

Temperature Rises Above Set Value
Causes
A temperature rise above the set value may occur due to a heater malfunction, or thermocouple malfunction or misplacement.

Consequences/Hazards
The high temperature may affect the efficiency of the process, damage the equipment (deformation and leak) and cause the fire, even explosion.

Safeguards
There will be a thermocouple and alarm to record the temperature and warn if the temperature is close to the upper limit, also the automatic shutdown system and cooling system are required to shut down and cool the system when the temperature reaches the upper limit.

Recommendations/Actions
Adjust the temperature arrangement based on the different seasons. Check the accuracy of the detector, the alarm, automatic shutdown system and cooling system periodically. If the case occurs, turn off the feed valve and cool the reactor. Then check the heater and thermocouple to determine the problem and fix it. If there is a fire, put out the fire with a carbon dioxide extinguisher or dry powder extinguisher after turning off the feed.

Temperature Falls Below Set Value
Causes
A temperature fall below the set value may occur due to a heater malfunction, or thermocouple malfunction or misplacement.

Consequences/Hazards
The low temperature will affect the reaction so that too many un-reacted hydrogen in the reactor is carried over to storage tank and released to the enclosed work area, and possible injuries or fatalities to workers due to hydrogen concentrations above LFL.

Safeguards
There will be a thermocouple and alarm to record the temperature and warn if the temperature is close to the lower limit, also the automatic shutdown system and cooling system are required to shut down and cool the system when the temperature reaches the lower limit.
Recommendations/Actions
Adjust the temperature arrangement based on the different seasons. Check the accuracy of the detector, the alarm, automatic shutdown system and cooling system periodically. If the case occurs, turn off the feed valve and cool the reactor. Then check the heater and thermocouple to determine the problem and fix it. If there is a fire, put out the fire with a carbon dioxide extinguisher or dry powder extinguisher after turning off the feed.

References

Appendix B – Exemplary Student Report 2

Safety and Health Considerations

Environmental, health, and safety concerns are becoming more important as the effects of certain materials are being seen in animals, plants, and humans. There is a huge movement to make work environments safer both because of governmental regulation and companies’ desires to have a good public image. This image is important for consumers, so they want to purchase the companies’ products and also so the companies can attract the best work force and keep them. This results in increased attention to the impact of processes and hazard analysis. One way to go about it is to do a what-if chart and tabulate the key hazards and properties of chemicals used in the process to organize and display all the information.

The first piece of equipment analyzed was the reactor. Several problems that could occur include exceeding the maximum temperature in the reactor that could be caused by incorrect set point of the heater prior to entering the reactor, broken heater, or a runaway reaction. Exceeding the maximum pressure is another possible issue that could be caused by incorrect settings, a pump failure prior to the reactor, or relief valve failure. This can result in the deformation of the outer steel shell or even a leak, which releases carcinogenic benzene and also hydrogen which if ignited, is an invisible flame (Table 1). Safe guards to be put in place include a separate detector and alarm in the reactor to warn the operator if the reactor temperature reaches above set temperature and pressure, as well as having an automatic system shut down should the reactor reach a higher predetermined temperature and pressure. Another option would be to buy a reactor shell that is strong enough to be more than satisfactory for withstand the amount of heat that might be applied to it or increasing the thickness of the refractory to reduce heat flow further; this would be the company’s decision, weighing between whether or not it was a degree of safety they would be able to afford.

Similar to the reactor, the phase separators and the compressors must have safety procedures for malfunctioning or leaking parts. The main concern for these pieces of equipment within this process would be the controlling of any leakage that may occur. It would be recommended to have no ignition sources near these to avoid igniting of any hydrogen or methane that may escape and mix with air.

The heat exchangers are another significant piece that could lead to serious safety issues. Exceeding the maximum volume in the exchangers as well as the maximum temperature and pressure caused from incorrect set points or a lack of cooling water flow. The result of this could be a leak causing the cooling water and product to mix which causes not only a loss in product but contaminates the water supply. There could be an external leak as well causing the hydrogen fire and un-reacted benzene to leak as well. Again there will be sensors and automatic shut offs. As for the water contamination having the steam or hot water leaving go through a sensor to detect for anything other than water and if a certain set concentration of another component is present having the stream be directed into a holding tank and shut down the system.

The fired heater is a big safety hazard in a process containing hydrogen as it is a source of ignition in case of a leak. A leak could be due to exceeding pressure, temperature, or erosion of
materials. This could lead to an explosion, so having the furnace in a separate area of the plant with ambient monitoring as well as temperature and pressure monitoring of the flows in order to check for leaks or malfunctions would reduce the chance of injury. This could be caused from leaks due to exceeding pressure, temperature, or erosion.

Adequate ventilation throughout the system process as well as evacuation plans will be put in place before the plant begins operation and will be tested and readdressed with the operators after operation has begun to ensure the plan will work. Exposure limits should be continually monitored in key areas of the process, as well as periodically monitored throughout the process. Proper personal protection equipment needs to be part of regular training procedures as well as being required and readily available for applicable procedures. Such personal equipment includes fire-resistant jackets in case of fuel gas ignition and gas masks in case any of the dangerous fumes leak out of the process without the operators’ knowing. Gloves should also be worn when handling any of the chemicals within the process.

Table 1: Key Hazards and Physical Data of components in the process.

<table>
<thead>
<tr>
<th>Name</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>H2</td>
<td>CH4</td>
<td>C7H8</td>
<td>C6H6</td>
<td>C12H10</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>2.016</td>
<td>16.04</td>
<td>92.14</td>
<td>78.11</td>
<td>154.21</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-259.2°C</td>
<td>-183.0°C</td>
<td>-93.0°C</td>
<td>5.5°C</td>
<td>70°C</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>-252.8°C</td>
<td>-161.0°C</td>
<td>110.6°C</td>
<td>80.1°C</td>
<td>255°C</td>
</tr>
<tr>
<td>Density (ambient conditions) (g/cm3)</td>
<td>0.08342</td>
<td>0.00055</td>
<td>0.865</td>
<td>0.88</td>
<td>0.991</td>
</tr>
<tr>
<td>Decomposition Temperature (°C)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>N/A</td>
<td>N/A</td>
<td>4°C</td>
<td>-11.0°C</td>
<td>113°C</td>
</tr>
<tr>
<td>Auto-Ignition Temperature (°C)</td>
<td>570°C</td>
<td>537°C</td>
<td>535°C</td>
<td>562°C</td>
<td>540°C</td>
</tr>
<tr>
<td>Lower Flammable Limit, LFL (%vol)</td>
<td>4%</td>
<td>5%</td>
<td>1.20%</td>
<td>1.3%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Upper Flammable Limit, UFL (%vol)</td>
<td>74.5%</td>
<td>15%</td>
<td>7%</td>
<td>8%</td>
<td>5.8%</td>
</tr>
<tr>
<td>Health, NFPA</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Fire, NFPA</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Reactivity, NFPA</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TWA</td>
<td>N/A</td>
<td>N/A</td>
<td>50 ppm</td>
<td>0.5 ppm</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>STEL</td>
<td>N/A</td>
<td>N/A</td>
<td>150 ppm</td>
<td>2.5 ppm</td>
<td>N/A</td>
</tr>
</tbody>
</table>
### What-If’s

Table 2: What If Table. A table view of possible issues in the plant, what caused them, the effects of those issues, and the safeguards in place to maintain a safe process.

<table>
<thead>
<tr>
<th>WHAT IF …</th>
<th>CAUSES</th>
<th>CONSEQUENCES</th>
<th>SAFEGUARDS</th>
</tr>
</thead>
</table>
| Pump fails | A fitting failure  
A crack in the pump head  
A crack in one of the containment vessels | Un-reacted toluene leaks to the surrounding area.  
Possible injuries by inhalation of fumes.  
Possible fire in case of a spark due to low liquid flash point. | Feed valve shut down when pump pressure falls below  
…..  
….. |
| Agitator stops | Agitator motor failure  
Electrical utility loss  
Mechanical linkage failure  
Operator failure to activate | Un-reacted hydrogen in the reactor is carried over to storage tank and released to the enclosed work area.  
Possible injuries or fatalities to workers due to hydrogen concentrations above LFL. | Detector and alarm  
Automatic system shutdown if have loss of agitation  
Adequate ventilation for enclosed work area |
| Exceed maximum reactor temperature | Heater control failure  
Operator set level error  
Run away reaction | Leak – hydrogen fire – invisible  
-Benzene carcinogenic  
-Explosion - fuel gas ignition  
Deform outer steel shell | Separate detector & alarm  
Safety masks  
Automatic shutdown  
Adequate ventilation  
Evacuation Procedure |
| Exceed maximum pressure in reactor | Relief valves fail  
Previous pump failure  
Incorrect set point | Leak – hydrogen fire – invisible  
-Benzene carcinogenic  
-Explosion - fuel gas ignition | Separate detector & alarm  
Automatic shutdown  
Adequate ventilation  
Evacuation |
| Exceed maximum pressure in distillation column | Relief valve fails  
Previous pump failure  
Incorrect set point | Leak – Benzene carcinogenic | Safety masks  
Adequate ventilation  
Evacuation |
| Exceed maximum pressure in heat exchanger | Incorrect water flow set point | Tube rupture  
Get products into water supply | Emergency water return shut off with a holding tank before it is recycled |
| Exceed maximum volume of heat exchanger | Incorrect water flow set point | Not enough cooling  
Tube rupture  
Get products into water supply | Emergency water return shut off with a holding tank before it is recycled |

### References