March 28, 2016

To: Dean Leo Kempel

From: Jeff Curtiss, Chair, Safety Advisory Committee


The College of Engineering Safety Committee met Thursday, March 10, 2016 to discuss safety questions, incidents and processes in various departments. Along with six of the departments, Genevieve Cottrell from EHS was on hand for a presentation.

Department technicians, familiar with lab contents and lab processes, are empowered to identify and correct most safety issues within their departments. Subsequent safety responses by DPPS indicate that this process is working.

2015-2016 Fire Safety Inspection results conducted October 30-31, 2015:

- Engineering Building
  1) Several fire doors were noted for adjustment by IPF
  2) Corridor egress obstructions were identified.
  3) Missing ceiling tiles in stairwells were referred to IPF for action.

- Jolly Road Facility
  2) R. Balliff will continue working with student groups to improve housekeeping.

- Engineering Research Complex –
  1) No violations noted.
  2) Housekeeping is very good

- ERC – E Wing
  1) No violations noted

-Concrete Preservation Lab
  1) No violations noted.

Presentation by Committee Chair
Emergency Action Team update – several positions remain unfilled and committee members were asked to encourage their staff and faculty to consider volunteering for this important role. Requests are made in April and the new list of EAT members is generated by mid-May. This shortage increased from 9 volunteers to 13. All but one are in backup positions.
Per Fire Marshall inspection, all combustible materials and non-anchored items must be removed from the egress corridors. A memo from Tom Voice to the buildings was issued. Compliance is not complete at this stage.

Major Safety Initiatives
- Delivered Safety presentation to Engineering Graduate Students during orientation.

**Presentation by Genevieve Cottrel – EHS**

Presentation on a spill incident at MBI concerning a recirculating loop system in the reactive distillation facility that is made up of a high pressure side and a low pressure side. Both the incident and the follow-up regime are included in an additional submittal.

**Action Items for Safety Committee Members**

- No Action items at this meeting. However the proposal was submitted and approved to investigate bi-annual committee meetings.
- Annual Unit Safety Reports were submitted from:
  - Chemical Engineering and Material Science
  - Composite Materials and Structures Center
  - Computer Science and Engineering
  - Electrical and Computer Engineering

**Additional Submittals**

- Copy of Fire Marshall Inspections
- Copy of the spill report at the MBI

The College of Engineering Safety Committee has continued its role with success in identifying and resolving college safety issues in the past through awareness, communication and cooperation.

Respectfully submitted,

Jeff Curtiss
Facility Coordinator
College of Engineering
Chair, Safety Advisory Committee
October 30, 2015

Leo Kempe, Ph.D., Dean
College of Engineering
3410 Engineering Building

Dear Dr. Kempel:

On Thursday, October 29, 2015, a fire safety inspection of the Engineering Building was conducted. I was accompanied by Fire Marshal Tom Miller and Mr. Jeff Curtiss.

The following fire safety issues were noted during the building tour and are listed below. The following items #1-9 were noted during the 2014 inspection and need to be repaired or corrected. Please note that these items were Fire Door issues that somehow did not receive attention by IPF. I believe IPF might have been waiting for a work order (that was not submitted in 2014). Jeff Curtiss will submit a work order this year. This should allow IPF to correct the issues. Some of the issues might be due to ventilation pressure which does not allow the doors to latch.

Fire Doors (IPF for repair) (Work order will be submitted by Jeff Curtiss)

1. Double doors next to Room 3249. The coordinator does not allow the doors to close properly.
2. Door next to Room 3530. The latching mechanism needs repair.
3. Double doors next to Room 3550. Both doors do not latch.
4. Double doors next to Room 3412. Coordinator is damaged.
5. Stairwell door next to Room 2153. The door catches on the floor not allowing it to close properly.
6. Three (3) stairwell doors next to Room 2266, 3266 and 1274. The door closures need to be adjusted to limit the doors swinging into each other. Current condition hinders emergency egress.
7. Double doors outside Room 2250. The coordinator needs repair and one closure is missing.
8. Double doors outside Room 2452. The coordinator does not allow the doors to latch.
9. Double doors next to Room 1420. The coordinator does not allow the doors to latch.

Other

10. Stairwell next to Room 4160. Replace the missing ceiling tiles. Missing tiles can adversely affect the operation of the sprinkler system.
11. The racing car needs to be removed from the corridor outside Room 1242.
Housekeeping throughout the facility continues to be excellent.

If you have any questions or concerns, please contact me at 432-1587.

Sincerely,

Denis Zielioy
Fire Marshal
MSU Police

CC:  Mr. Jeff Curtiss, Engineering Research Complex
     Fire Marshal Tom Miller
     Mr. Ken Crowell
     File
October 30, 2015

Leo Kempel, Ph.D., Director
Engineering Research
3410 Research Complex-Engineering

Dear Dr. Kempel:

On Friday, October 30, 2015 a fire safety inspection was conducted of the Engineering Research Complex facilities. The inspection included the facility at 2857 West Jolly Road. Mr. Jeff Curtiss accompanied me on the inspections.

Housekeeping throughout the research facilities is excellent.

ENGINEERING RESEARCH COMPLEX
No violations noted.

E-WING
No violations noted.

JOLLY ROAD FACILITY (Accompanied by Roy Bailiff)
Mr. Bailiff is working with the student groups to improve housekeeping and safety issues. The facility was in good condition at the time of this inspection. Exits were clear of stored items.

CONCRETE LAB (Accompanied by Mr. Ravanbakhsh)
No violations noted.

If you have any questions or concerns, please contact me at 432-1587.

Sincerely,

Denis Zietlow
Fire Marshal
MSU Police

Cc: Mr. Chuck Reid, Director Land Management
109 Agriculture Hall
Mr. Jeff Curtiss
Mr. Roy Bailiff
Analysis of Accident at MBI on February 12, 2016.

Environmental Health and Safety
Genevieve Cottrell, Senior Chemical Hygienist
March 14, 2016

Equipment description

The apparatus that the accident took place at was a recirculating loop system in the reactive distillation facility at MBI that is made up of a high pressure side and a low pressure side. The high pressure side begins at the recirculator pump, which provides the high pressure (200-300 psig) for the system, a fixed bed flow reactor where reaction takes place, and a back pressure regulator that regulates the high pressure at a set value. The low pressure side includes a heater just downstream of the back pressure regulator, a vessel serving as a flash pot to separate liquid and vapor formed, a second liquid level pot (where feed to the system enters) with a level indicator to control the liquid level in the pot, and tubing back to the recirculator pump. The liquid level control operates by sensing the liquid level in the level control pot and sending a signal to the system feed pump to control the feed rate to the system and thus maintain a constant level in the control pot. The system is interfaced with a computer to facilitate data collection of feed mass, product mass, several system temperatures, and level in the level control pot.

Reaction System

The reaction under study is urea + methanol to form methyl carbamate, and then reaction of methyl carbamate with methanol to form dimethyl carbonate. This project is sponsored by a corporate partner as part of a DOE Phase II SBIR award in which MSU is a subcontractor.

Description of the accident

On February 12, 2016, a significant release of urea, methyl carbamate (MC) and methanol (MeOH) occurred in the reactive distillation facility in the MBI pilot plant. The following is a summary of the events that took place over the course of the accident.

11:00 a.m.  The recirculating reactor system was up at temperature, and feed to the system was begun.
12:00 p.m.  The system was at steady state and a sample of the loop composition was taken for analysis.
12:55 p.m.  The operators, Dr. Lars Peereboom and Dr. Aspi Kolah left the apparatus for a short meal and restroom break.

12:58 p.m.  A tube breach occurred on the low-pressure side of the recirculating loop, between the level control pot and the recirculator pump. The tube breach below the level control pot led to the immediate emptying of the liquid level control pot, releasing approximately 200 ml of a
solution containing MeOH, urea, and a significant fraction (10-20 wt%) of MC. As the liquid level in the pot dropped, the level controller sent a signal to the feed pump to increase the feed rate to refill the pot. The feed pump soon reached its maximum feed rate of 60 ml/min of a solution of urea in MeOH, which continuously flowed through the level control pot and out the tube breach below the level pot. This continued for approximately 30 minutes (see below). Simultaneously, because material was no longer flowing through the tube to the recirculator pump, the flow to the high pressure side of the recirculating loop stopped. The heater downstream of the back pressure regulator emptied and then its temperature increased from its set point of 80°C to 240°C. This temperature increase occurred because there was no liquid flowing through the heater and because the heater was controlled by a Variac, which inputs constant power to the heater.

1:16 p.m. The operator (Kolah) returned to the equipment, noticed the high heater temperature, and immediately turned off the heater power and the power to the reactor heaters. Dr. Kolah inspected the fixed bed reactor and noticed a small leak at the top of the reactor.

1:27 p.m. Dr. Kolah noticed that the feed pump was operating at a high rate and turned off the feed pump.

1:45 p.m. Dr. Peereboom returned and together the two decided they needed to relieve the pressure in the high pressure side of the reactor.

1:49 p.m. Dr. Kolah was working at the fixed bed reactor, attempting to drain the contents of the reactor, when Dr. Peereboom lowered the set point of the back pressure regulator controlling the pressure on the high pressure side of the loop. When this happened, the regulator released contents from the reactor, which flowed through the flash pot, liquid level pot, and out the tube breach, spraying the equipment and Dr. Kolah with approximately 300 ml of a MeOH/urea/MC mixture. Dr. Kolah and Dr. Peereboom then took immediate action to remove Dr. Kolah’s contaminated clothing and PPE, and to wash his head and hands thoroughly.

Summary of quantities spilled

A total of approximately 500 ml of mixture of urea/MeOH/MC was released from the recirculating loop, approximately 200 ml immediately following the breach and 300 ml when the reactor pressure was released. Another approximately 1.8 kg of 10 wt% urea in MeOH was released because of the feed pump operating at high speed for 30 minutes following the tube breach.

Cause of tube breach

The tube breach occurred on the low pressure side of the recirculating loop, where the pressure was no greater than a few psig. The breach occurred because of improper joining of the ¼” OD plastic tubing that makes up the low pressure connection between the level control pot and the recirculator pump. The improper joint had been made in a previous project and was hidden behind equipment in the enclosure, and thus it was not known that the joint was present.
Spill cleanup

Following notification and discussion with EHS personnel, Dr. Kolah cleaned up the spill material over the next three weeks. Walls of the enclosure and surfaces of affected equipment, including Unistrut and piping, were wiped multiple times with wiping cloths containing an ethanol-water mixture, until the wiping cloth appeared clean (no discoloration). Contaminated wiring was wiped individually with the same cloths containing ethanol-water and then separated from the contaminated equipment. In some cases, items and wiring were contaminated beyond cleaning and were simply disposed of as hazardous waste. Rack clamps were all discarded as they were more difficult to clean than to dispose. Contaminated insulation was removed from several pieces of equipment and disposed.

Several samples of contamination were taken early during the cleanup and analyzed by GC and HPLC. These samples showed that the major component of the contamination by far was urea, with MC making up less than 1% of the contaminated sample in all cases. This is consistent with the spill scenario described above. The distillation enclosure cleanup was finished, and samples were taken according to the method below.

It is noteworthy that Dr. Peereboom conducted an experiment in which he placed a few crystals of MC in an open container in the hood of 2535 EB and left them over the weekend. After the weekend, the MC crystals had lost approximately 15% of their mass. After leaving the MC crystals in the hood for two weeks, they completely sublimed. This suggests that any residual MC left in the column enclosure will likely sublime over time, thus leaving no hazardous residue from the spill.

Swipe Procedure

Following extensive cleanup of the column, several surfaces in the column interior were swiped with a 90/10 ethanol/water solution soaked into a square of sampling paper provided by EHS. The paper and deposited into sample vials and sealed. The approximate sampling area was 10 cm x 10 cm or similar dimension as was possible.

The locations that the swipes were taken are as follows:

1. Level 1 back plexiglass wall
2. Level 1 aluminum tray at bottom of column (where contamination was)
3. Level 2 Unistrut
4. Level 3 back wall
5. Level 3 Reactor head next to the PFR used for urea to DMC
6. Level 3 Unistrut
7. Level 3 back wall
8. Level 3 grating
9. Level 4 back wall and unistrut (not shown).
Swipe Analysis:

The swipes were extracted with 1g of acetonitrile and run on the GC with FID detection; MC was identified only by the retention time of the standard MC solutions. Standard solutions were prepared at 1, 10, 100, 1000, and 10000 ppm MC. Blank acetonitrile samples showed a peak at the location of MC but a 1 ppm sample showed a two fold increase in the area of this peak. This shows that the detection limit is ~1 ppm. The swiped samples show many peaks; no attempt was made to identify the other peaks. The worst case integration of the sample with the largest peak assumed to be MC gave concentrations <15ppm. It is possible that the peak that is at the MC location is not even MC.

Precautions and procedures to avoid repeated incident:

1. During extended operation of the equipment, two people will always be present, and one will always be on duty during operation.
2. All tubing joints, including low pressure lines, will be joined by proper sealed fittings such as Swagelok fittings. Flexible tube connections will be made only with hose barbs and metal screw clamps.
3. Reaction systems will be configured to avoid long tubing runs wherever possible, to avoid hidden or inaccessible joints and to keep all active equipment visible to operators during operation.
4. An emergency power shutoff system will be installed on the distillation apparatus, allowing instant shutdown of power to the distillation system and pumps with the push of a single button or a limited number of buttons (because of multiple voltage/phase requirements of the system).

Conclusions:

The cleanup of the spill has been successfully completed. There is no visible residue of the spill anywhere on the column or enclosure surfaces at the MBI distillation facility. Aided by the fact that MC sublimes relatively rapidly, we expect that any small quantities of MC remaining in areas difficult to access are gone by this time. No one appears to have been adversely affected or injured by the events that took place.
Figure 1: Blank acetone sample before and after standards and samples

MC (8.51 min)
Figure 2: Blank action titre (green) vs 1 ppm HCl standard (red).
A 10 ppm MC standard, 1 ppm MC standard, 0.1 ppm MC standard, 0.01 ppm MC standard. The MC peak is at 8.5 ppm. The lowest (red) curve is shown with 28 acetone samples extracted with 18 acetone samples.
Figure 5: Sample Identification

18. Level 4 back wall and unit tray (not shown).
17. Level 3 back wall
16. Level 3 back wall
15. Level 3 unit tray
14. Level 3 reactor head next to the PPR used for urea to DMC
13. Level 3 back wall
12. Level 2 unit tray
11. Level 2 aluminium tray at bottom of column (where contamination was)
10. Level 1 back plastic wall