Runaway Industrial Chemical Reactions

The March 2006 issue of the PEAC Newsletter was devoted to industrial accidents involving chemical reactors and looked at some examples. We will look at two more examples, both of which are or have been investigated by the U.S. Chemical Safety and Hazard Investigation Board (CSB). The results of the investigations have been or are being made public by CSB with the objective of "emphasizing the importance of implementing comprehensive safety management practices to control reactive hazards", borrowing words from one of their reports. The PEAC tool can help industry identify risks and possible consequences during the manufacture and storage of chemicals.

U.S. Chemical Safety and Hazard Investigation Board

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent federal agency charged with investigating industrial chemical accidents at fixed facilities. The agency does not issue fines or citations but does make recommendations to the industry involved and to regulatory agencies and labor groups. It is designed to conduct scientific investigations as to the root cause of chemical accidents and is not an enforcement or regulatory body. Most of the Board members and staff have degrees in chemical or mechanical or other engineering disciplines, have PE licenses, have chemical process industry experience, or are health or safety professionals. Congress in establishing CSB specifically stated (see 42 U.S.C. section 7412(r)(6)(G)): "No part of the conclusions, findings, or recommendations of CSB relating to any chemical incident may be admitted as evidence or used in any action or suit for damages arising out of any matter mentioned in an investigation report".

CSB was authorized by the Clean Air Act Amendments of 1990, but did not become operational until 1998. A thorough CSB investigation of an industrial accident can take several months, even sometimes over a year because of the complexity of the situation. First responders coming on scene of an accident only have limited information as to what is happening.

CSB Report "Improving Reactive Hazard Management"

In 2002, CSB issued a report titled *Improving Reactive Hazard Management.* This 150-page report can be downloaded by going to the CSB website, http://www.csb.gov, and entering the report name. The report documented 167 serious reactive chemical incidents in the United States between January 1980 and June 2001 that resulted in 108 deaths, hundreds of injuries, and significant public impacts. About 35% of the incidents resulted from runaway chemical reactions. Of the 167 incidents, 42% resulted in fire and or explosion, 37% resulted in toxic gas releases, 16% resulted in both toxic gas and fire/explosion, and the remainder (5%) involved a hazardous liquid spill only. Many of the runaway chemical reactions occurred in reaction tanks that failed or even exploded because of thermal runaway. The temperature of the reaction increased rapidly resulting in increased pressure as liquids evaporated, and the tank failed because of the increased pressure. Other incidents occurred because of inadvertent mixing of incompatible materials, or chemicals exploded because of instability. More than half of the 167 incidents involved chemicals not covered by OSHA regulations (20 CFR part 1910.119) or the EPA Risk Management Program regulations (40 CFR Part 68) at the time the CSB report was issued in 2002.

<u>Example Incident: T2 Laboratories, Inc., Jacksonville FL, 19 December 2007</u>

Coast Guard surveillance video watching Jacksonville harbor freezes the time of the blast. Stack at left and two cooling towers at center right are incidental. From CSB website.

Coast Guard surveillance video watching Jacksonville harbor freezes the moment the blast is first seen from a distance, one second later, at left.

Coast Guard surveillance video captures the scene five seconds later when the explosion is the most brilliant. (a vapor cloud explosion)

Arial view of site after blast from CSB bulletin

On 19 December 2007, at about 1:30 PM an explosion occurred at T2 Laboratories in Jacksonville, Florida. The explosion killed four T2 workers and resulted in hospitalizing 14 other people. Injuries requiring medical attention occurred as far away as 750 feet from the site. The blast was felt several miles away. Over 100 firefighters fought the ensuing blaze, which was described as a hellish inferno.

Google Earth image of T2 Laboratories site at 3043 Faye Rd before blast

T2 Laboratories is a small company employing about 12 people, and their facility in Jacksonville is their only production site. T2 Laboratories manufactured methylcyclopentadienyl manganese tricarbonyl (MMT) under the trade name Ecotane®. This chemical is used as a gasoline additive to boost octane rating of gasoline and to help lower tailpipe emissions of NO_x. It is also used in refinery processing to reduce emissions of nitrous oxide and increase the output of gasoline from crude oil. Over one million pounds per year are produced annually in the United States. More information on Ecotane® produced by T2 Laboratories is in a paper written by R.S. Gallagher and M.F. Wyatt available at http://www.t2labs.com/ecotane/e118-T2%20Labs%20Report%20R041000T%20Introduction%20to%20Ecotane%20MCMT.pdf. Robert Scott Gallagher was one of the people killed in the blast.

A description of a procedure for manufacture of MMT is in a December 2006 report prepared by the American Chemistry Council Petroleum Additives Panel as part of an Environmental Protection Agency program and is available from the EPA at http://www.epa.gov/HPV/pubs/summaries/mthmntri/c14889rt.pdf. The manufacturing process entails the following: Under a nitrogen atmosphere, methylcyclopentadienyl dimer is added to a dispersion of sodium metal in diethylene glycol dimethyl ether. A constant elevated reaction temperature is maintained to yield sodium-methylcyclopentadienyl, which is an intermediate in the reaction process. Manganese chloride is then added to the stirred mixture containing the sodium – methylcyclopendienyl intermediate. An elevated temperature is maintained during the addition. Upon completion, the reaction gives bis - (methylcyclopentadienyl)manganese, the second intermediate of the reaction process. The reaction vessel is then pressurized with carbon monoxide. The addition of carbon monoxide results in MMT which is separated from the reaction mixture via vacuum distillation.

The final product MMT is fairly safe to handle, but very energetic chemicals are used in its manufacture. We (AristaTek) were not able to confirm that the procedure summarized above was the one used at T2 Laboratories, but the CSB statement issued January 3 seemed to indicate that it was similar.

On 3 January 2008, the CSB investigator Robert Hall in charge of the investigation issued a public statement (available at the CSB website). The facility started producing MMT commercially several years ago using a batch reactor. The reactor blast occurred during the step involving heating and reacting methylcyclopentadienyl dimer with sodium metal. Prior to the rupture, eyewitnesses reported hearing loud hissing and seeing vapor venting, which indicated the development of excess temperature and pressure inside the reactor. The reactor with its flammable contents ruptured and the chemicals ignited releasing large amounts of thermal energy (see Coast Guard Video pictures shown above). The blast also ignited various solvents at the facility creating secondary fires and explosions. CBS estimated that the pressure inside the reactor vessel must have reached several thousand pounds per square inch. The reactor vessel steel walls were 3 inches thick. The vessel's head weighing several hundred pounds was located about one-quarter mile away after the blast. The explosion force was approximately equivalent to a ton of TNT. Debris was spread up to one mile from the plant. At the time of the CSB statement (3 Jan 07), the accident site still remained too hazardous for investigators to enter, and that a plan for safe entry needed to be developed.

A visit to the T2 Laboratories website reveals that the company was involved in producing a variety of flammable specialty solvents which accounted for the major fire and hazardous chemicals stored at the site.

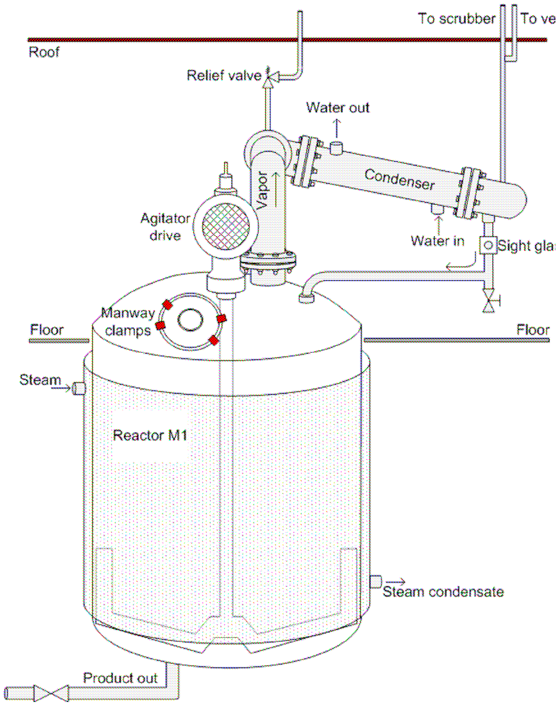
CSB indicated that they plan to conduct chemistry testing using T2's recipe to better understand exactly what went wrong inside the reactor on December 19. Their final report is expected this summer.

<u>Example Incident: Synthron, LLC, Morganton NC, 31 January 2006</u>

Illustration of Synthron site after the blast from CSB Report 2006-04-1. Morganton Dept. of Public Safety.

Google Earth image of the Synthron facility before the blast

On 31 January 2006, a runaway chemical reaction and subsequent vapor cloud explosion killed one worker and injured 14 people at the Synthron, LLC facility in Morganton, NC. The explosion destroyed the facility and damaged structures in the nearby community. CSB investigated the accident and issued a final report (No. 2006-04-I-NC) on 31 July 2007, which is available from the CSB website, http://www.csb.gov.



Reactor M1 (from CSB final report)

The runaway chemical reaction at Synthron occurred in their reactor M1 sketch at left. The reactor had a capacity of 1500 gallons and was rated at 75 psig (pounds per square inch gage) maximum. The reactor is used to produce acrylic polymers. In a typical operation, an acrylic monomer (purchased from a chemical supplier) is mixed with various flammable solvents in the reactor, and then steam is injected to heat the reaction mixture to a specified temperature (usually near the mixture boiling point). Then the steam is turned off, and a polymer initiating solution metered into the reactor. The heat given off by the reaction boils off the solvent which is condensed in the overhead water-cooled condenser. Liquid solvent from the condenser is drained back to the reactor. The system operates near atmospheric pressure controlled by a vent on the condenser.

The acrylic polymer products produced by Synthron is used for various coatings and paints. According to CSB, the company had received an order for their product, Modarez MFP-BH, which is a liquid acrylic polymer, and the order was for a slightly greater amount of product than what the reactor was designed to produce in a single batch. Operators began preparing for the 6080 pound acrylic polymer batch the previous day which was 12 percent greater than normal. The chemical ingredients were scaled up to take care of the increased polymer product, but because there was insufficient aliphatic solvent on hand in storage the operator actually scaled back on the on the aliphatic solvent.

On the day of the explosion, operations appeared normal until after the steam was turned off and the polymer initiating solution was pumped into the reactor. The operator in charge noted that initially the reaction did not proceed as vigorously as expected, but later the solvent evaporated and the condensed solvent flow returning to the reactor appeared within normal range. A few minutes later, the operator heard a loud hissing and saw vapor venting from the reactor manway. The irritating vapor forced him out of the building. Three other employees also left the building because of the vapors. The operator then reentered the building wearing a respirator and was able to start emergency cooling water flow to the reactor. The building exploded less than 30 seconds after he exited the second time. The blast injured the operator and five employees who had exited the building including two seriously. The maintenance supervisor who was on a lower level by the laboratory near the manufacturing area was killed. The other injuries occurred to employees in a nearby trailer and to two citizens driving by the site.

The blast damaged buildings nearby. Two church buildings and one house was condemned. Glass was broken up to one-third a mile distant from the site. The Morganton Department of Public Safety responded rapidly calling mutual aid from the county and surrounding municipalities, to assist injured employees and extinguish the resulting fire. Local residents were asked to shelter-in-place for several hours.

The CSB final report blamed the explosion on the following combination of circumstances:

- Because there was a shortage of the aliphatic solvent in storage, the operator actually decreased the amount charged to the reactor by 12% compared with the standard recipe, and increased the acrylic monomer by 12%. With the adjustments made to the reactants to manufacture everything in one batch but with different proportions of chemicals, the heat release was at least 2.3 times that of the standard recipe.
- The waterside of the condenser had apparently never been cleaned and was fouled and could not remove the excess heat release as the solvents boiled. Once the heating rate exceeded the condenser cooling capacity, control of the reaction was lost resulting in a runaway reaction.
- Only 4 of the 18 clamps specified by the manufacturer were tightened for the manway cover. This was a labor-saving step as it was long-standing practice to open and clean reactor tank after every batch. The manway began to leak vapors (the hissing sound reported) when the pressure reached approximately 23 psig. The flammable vapors filled the room and ignited.

The CSB report also stated that Synthron had no chemical or other engineers on staff, and none had been contacted to evaluate the hazards associated with the reactive operations at the site. There was no comprehensive process hazard analysis review

Our Analysis

Both the T2 Laboratories and Synthron accidents involved vapor cloud explosions that were initiated when flammable chemicals escaped from batch reactors where runaway chemical reactions took place. In the T2 laboratory situation, a runaway reaction caused the temperature and pressure to increase inside the reactor, which resulted in reactor failure when a very high pressure was reached. The heated flammable contents gasified and exploded in a vapor cloud explosion equivalent (according to the CSB) to a ton of TNT. The root cause of the reaction runaway has not been determined as of January 2008, but several scenarios can be postulated including contact of sodium with accidental water in the system, or failure of a temperature control. In the Synthron accident, the flammable vapors vented into the room at the manhole cover of the reactor, and exploded in a vapor cloud explosion a few minutes later.

AristaTek does not have available the amounts of chemicals or the reactor arrangement for the T2 Laboratory situation, but the CSB indicated that the explosive power based on damage to the surroundings was approximately equivalent to a ton of TNT. Several chemicals were present which could have been under pressure at the time the reactor top blew off, including methylcyclopentadienyl, sodium, and diethylene glycol dimethyl ether (or a similar material). Diethylene glycol dimethyl ether has both oxygen and hydrocarbon fuel in the same molecule and would be expected to have a fairly high yield factor (the fraction of the energy in a chemical which participates in a vapor cloud explosion, the rest is released as heat in a fireball). This means that less chemical would be require to produce the same punch as one ton of TNT compared if say an aliphatic hydrocarbon such as heptane had been involved. Additionally, the reactor chemicals were under great pressure which was suddenly released, which means that the entire batch probably participated in the explosion and fireball.

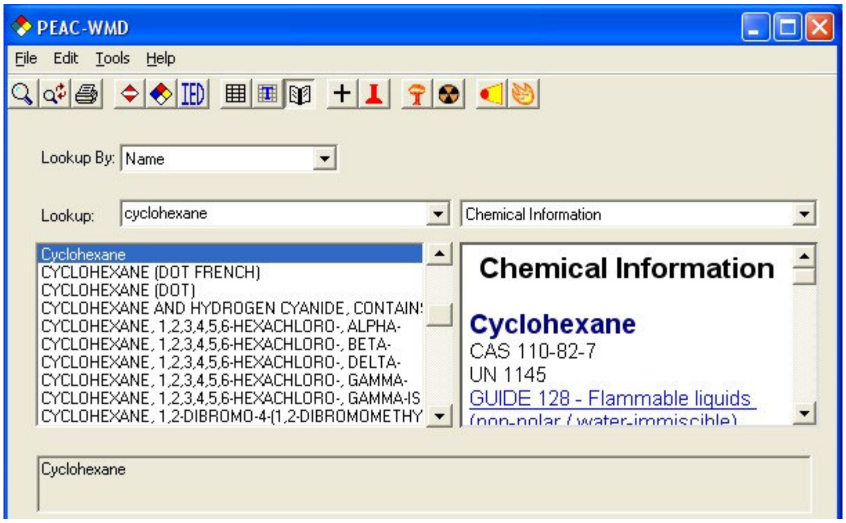
The CSB report did not identify the chemicals or the recipe used in the Synthron situation, only their boiling points. The chemicals consisted of (1) an acrylic monomer with a normal boiling point temperature of 297^{o}F, (2) an aliphatic solvent with a normal boiling point temperature of 178^{o}F, and (3) an aromatic solvent with a normal boiling point temperature of 234^{o}F. The monomer amount was increased 12% over the standard recipe. The recipe called for an equal amounts of aliphatic and aromatic solvents, but because there was insufficient aliphatic solvent in storage, the operator actually cut back on the aliphatic solvent and only increased the aromatic solvent by 6% according to the CSB report, which increased the maximum heat output.

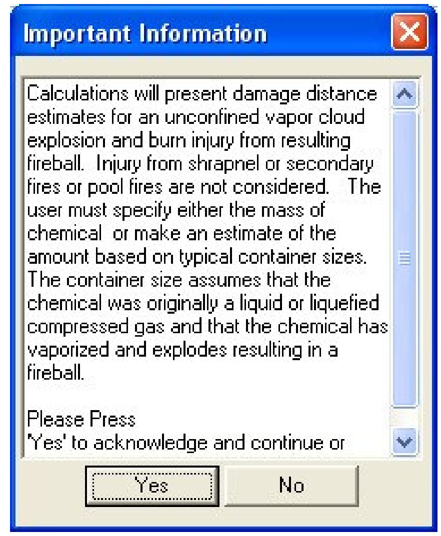
The CSB report did not state the TNT equivalent for the Synthron vapor cloud explosion, but the remark that glass was broken up to one-third mile away roughly is equivalent to several hundred pounds of TNT based on glass breakage.

<u>The PEAC Tool</u>

The PEAC tool is designed for use of a first responder or for use by industry for estimating the consequences of a potential dangerous situation. The user enters name of the chemical and amount or a tank or vessel size and the PEAC tool calculates the consequences if the chemical is released or participates in a vapor cloud explosion. The PEAC tool menu is set up for the user to enter information this way. The PEAC tool menu is not set up to do a “reverse engineering” analysis, where the user enters blast damage observations and different distances from the source and the PEAC tool calculates the amount of chemical or a container size which could potentially produce the damage observed. Additionally, because of uncertainties of the vapor cloud shape at the time of detonation, the PEAC tool incorporates a factor of two on the distance. The PEAC tool also assumes that the entire tank contents or amount specified participates in the explosion and fireball using the same yield factors as in the ARCHIE model. These assumptions are explained in the PEAC tool manual and on the PEAC tool disclaimer statement.

Let us look at a hypothetical example where 3000 lbs of cyclohexane is vaporized and participates in a vapor cloud explosion. We began by pulling up “cyclohexane” in the PEAC tool. Cyclohexane is an aliphatic solvent with a boiling point of 178^{o}F. We will make sure “mass” is selected under “options” so we don’t have to fuss with entering container sizes.





To initiate the calculation we select the explosion icon  which appears on the PEAC tool. A statement then appears on the screen, under "Important Information".

Several screens then appear. The user may select the coordinates of the accident if he/she wishes to have an overlay of the blast damage on a map. The user may select a container size or simply state the amount of chemical involved. We will dispense with these extra steps and simply enter 3000 lbs of cyclohexane and ask the PEAC tool to compute the damage distance to a 0.5 psig overpressure, and the distance to second degree burns for an unprotected human. The screen for the overpressure selection and fireball distance for the second degree burns appear at left. Because of uncertaintities on the vapor cloud shape, a factor of two is built in the distance display.

The final PEAC tool display (without an overlay on a map) is as follows:

Fireball Results

Cyclohexane

CAS 110-82-7
UN 1145
GUIDE 128 - Flammable liquids (non-polar / water-immiscible)

Initial Location and Time
Morganton NC
Latitude 81° 39' 24" N Longitude 35° 45' 32" W
1/15/2008 14:25:31

Source Strength
Mass: 3000 lb

Evacuation Thresholds
Overpressure: 0.5 psi (Some windows shattered; some minor blast damage to house structures.)
Thermal Heat: Second Degree Burns

Evacuation Distance to Thresholds

Overpressure: 1713 ft
Thermal Heat: 820 ft
(Safety factor of 2 applied to distances.)

The display is followed by distance estimates to varying blast damage for the 3000 lbs of cyclohexane.

Distance	Damage
Aircraft	
1017 ft	Control surface or other minor damage
628 ft	Major repair
402 ft	Complete destruction
Glass windows large and small	
1713 ft	Shattering, occasional frame failure[1]
763 ft	Severe frame failure [1]
Wood frame structures	
1713 ft	Roof rafters cracked
1017 ft	Studs and sheathing cracked
352 ft	Collapse
Metal (Butler type buildings)	
1713 ft	Corrugated aluminum/steel paneling moderately buckled/joints separated
1017 ft	Severe buckling/some panels torn off
482 ft	Complete destruction of siding/interior destroyed[2]
Concrete block or brick wall, 8-12inches (un-reinforced)	

1017 ft	size 1> severe damage shattering[3]
289 ft	Collapse
Corrugated asbestos siding	
1017 ft	Shattering
Reinforced concrete walls	
482 ft	Moderate cracking
316 ft	Severe spalling/wall displacement
237 ft	Concrete shatters, bare steal remains
199 ft	Complete destruction
Liquid storage tanks (un-pressurized)	
1713 ft	Slight damage
482 ft	Severe damage
268 ft	Collapse
Vehicles/trailers	
237 ft	Complete destruction
Heavy machinery (generators,compressors, etc)	
316 ft	Moderate damage
237 ft	Complete displacement
199 ft	Destruction

Liquid storage tanks (un-pressurized)	
1713 ft	Slight damage
482 ft	Severe damage
268 ft	Collapse
Vehicles/trailers	
237 ft	Complete destruction
Heavy machinery (generators,compressors, etc)	
316 ft	Moderate damage
237 ft	Complete displacement
199 ft	Destruction
Steel towers	
137 ft	Blown down[4]
Personal	
3616 ft	Temporary threshold ear damage[5]
Loaded rail cars	
1713 ft	Overturning
Corrugated steel or aluminum paneling	
1017 ft	Connection failure followed by buckling [2]
Brick wall panel 8-12 inches thick (un-reinforced)[2]	
289 ft	Shearing and flexure failure[3]
Wooden utility poles	
352 ft	Snapped failure

Liquid storage tank (un-pressurized)	
1713 ft	Slight damage
482 ft	Rupture
268 ft	Collapse
[1] Frame failure will not occur if glass is thin and breaks easily	
[2] Frame failure may occur if siding has been reinforced or strengthened	
[3] For reinforced walls or those built between rigid supports, pressures of 3.0-4.0 psi are needed for damage/shattering	
[4] Where Explosive quantities are large, lesser pressures may destroy towers	
[5] Temporary threshold ear damage may cause temporary loss of hearing depending on peak impulse pressure, speed and other factors	

Important Information
Calculations will present damage distance estimates for an unconfined Vapor cloud explosion and burn injury from resulting fireball. Injury from Shrapnel or secondary fires or Pool fires are not considered. The user must specify either the mass of chemical or make an estimate of the amount based on typical container sizes. The container size assumes that the chemical was originally a liquid or liquefied compressed gas and that the chemical has vaporized and explodes resulting in a fireball.

The PEAC tool is designed such that the user can enter different numbers rapidly. This makes the tool useful for doing a potential consequence analysis during a walk through of an industrial facility.