



Case Studies of Three Explosions and a Chemical Accident

An Online Continuing Education Course for Engineers

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Case Studies of Three Explosions and an Acid Accident

Case Study 1 – The Day the Slop Oil Tank Blew Up

Introduction

I would bet that there have been times when you heard about some big explosion at a refinery or chemical plant or whatever, and you wondered what the cause was. Or perhaps you have heard some TV announcer say something like, “Investigators at the scene are trying to determine the cause...” But have you ever considered the possibility that the explosion might have resulted from a chain of events, rather than as a result of a single event, and that if only one of those events had not occurred, the explosion would not have happened?

I have. I learned a long time ago that explosions sometimes happen exactly like that. The ones I’m going to tell you about occurred in the 1990’s at a refinery that shall remain unnamed. One of the refinery’s slop oil tanks blew up, releasing boiling hydrocarbon liquid and volatile gases. A huge, explosive, boiling-liquid-expanding-vapor cloud formed overhead and floated out over the refinery, where it found a source of ignition several minutes later, resulting in a tremendous explosion that killed four workers and caused millions in property damage.

In this course, you will see how human factors can come into play, in the sequence of events leading up to an explosion. You will see how greed, fear, ignorance, and defiance can all contribute.

Depending on your current state of knowledge, you may also learn a little about oil refineries. For example, I will tell you what a slop oil tank is for. I will describe the purpose of a catalytic cracking process and the purpose of an alkylation process. I will tell you what olefins are, and what an explosive envelope is, and what normally happens at the wastewater treatment plant. And you will see an excellent example of why the selection of the right material is vital in certain situations. Sometimes using duct tape is just not acceptable.

Discussion

Slop Oil Tanks

Refineries have slop oil from spills, off-test products, and other sources. Slop oil is captured in a wastewater treatment unit by a separator that operates on the simple principle that oil floats on water. The oil is decanted off from the separator and heated to 250-300 degrees Fahrenheit to lower its viscosity, making it easier to pump. The slop oil is then pumped to a slop oil tank, designated as such, and from there, recycled to oil back into the refining process.

Why would a slop oil tank explode? It is an uncommon thing to happen since slop oil is not usually very volatile. Why was boiling liquid involved in the explosion? If you suspect that something other than slop oil was in the tank, you would be correct. It turns out that the refinery was using the slop oil tanks temporarily to store highly volatile hydrocarbon liquids produced by the catalytic cracking unit.

Catalytic Cracking Unit

The catalytic cracking unit is a major processing plant in an oil refinery. It is commonly referred to as the cat cracker or just the cat unit. It operates at a high temperature and pressure. Using a fluidized catalyst, the unit breaks up long-chain petroleum molecules and converts them into propane, butane, and a variety of intermediate liquid products used to make gasoline, jet fuel, and heating oil.

Olefins

Propylene and butylene are cat cracker products. These compounds are called olefins, which is merely a generic label for unsaturated hydrocarbon compounds that contain one or more pairs of carbon atoms linked by a double bond. The olefins may be cyclic, like benzene, or non-cyclic, like propylene and butylene. Typically, propylenes and butylenes are used as feedstock for the alkylation unit. The alkylation unit, or the “alky” plant, as it is typically called, chemically combines the olefins with butane to make iso-octane, which is a key component of gasoline. These olefins are quite volatile.

Alkylation and Catalysts

Either hydrofluoric acid or sulfuric acid is used as a catalyst in the alkylation chemical reaction. The alkylation plant at this refinery used hydrofluoric acid as a catalyst. For a couple of days prior to the explosions, the acid pump seals kept failing. Every time the pump seal failed, the alkylation plant had to be shut down to replace the pump seals. The acid was disintegrating the pump seals and spewing out all over the place.

Imagine this in detail. The pump seals fail, and the plant is shut down. The seals are replaced with the same type of seals, and the plant is started up again. Once again, the

seals fail, causing the plant to shut down. This repeatedly happens, apparently with a different result expected each time. Does this make any sense?

Well, no surprise: later it was discovered that the pump seals being used were not good for acid service, and that someone had purchased the wrong type. This could have been a purchasing error, or it could have been that these seals were just cheaper than the correct kind, and the decision to purchase them was a cost-based decision made without regard to the kind of service in which the seals would be employed. In any case, this was the first in a chain of events that would lead to the explosions. The second was when those who were installing the first set of replacement seals did not catch the error. The third and the fourth, and so on, were when the ineffective seals were repeatedly replaced.

No Place for the Cat Unit Olefins

With the alkylation plant out of commission, the plant feed tanks started filling up. Once they were full, there would be no place to put the olefins from the cat cracker. The refinery manager, being driven by corporate greed, was not about to shut down the cat unit, which was the main profit center in the refinery. Instead, he decided to put the olefins into railroad tank cars “for the time being.” Well, this plan worked out somewhat okay until the refinery ran out of tank cars. Then, the refinery manager decided to pump out the slop oil tanks, and put the olefins there “for the time being.” As a preventive measure, he had a written order entered into the wastewater treatment plant manager’s log, saying not to pump any slop oil to the slop oil tanks until further notice.

Slop oil tanks are vented to the atmosphere. At atmospheric pressure, propylene and butylene boil at temperatures well below zero degrees Fahrenheit. Consequently, the olefins in the slop oil tanks were boiling, and the explosive hydrocarbon vapors were being vented into the atmosphere. Moisture in the air froze on the outer surface of the tanks below the liquid level. Ice coated the exterior surface of the tank from the ground to the liquid level. You could see how full the tank was by where the ice line was.

Wastewater Treatment Plant

Meanwhile, down at the wastewater treatment plant, things were getting dicey. Slop oil that was piling up in the separator would soon start overflowing into the river. The plant manager was not about to get fired for letting that happen and get hit with huge cleanup costs and EPA fines for killing the fish, not to mention for losing product. He apparently experienced actual fear for his job. So, he ordered one of his men to drive over to the tank farm and look at the ice line on the slop oil tanks to see if there was any space left in either of them (there were two slop oil tanks).

Take note here that the wastewater treatment plant manager had no clue as to what might happen if he pumped 250-300 degree slop oil in with the olefins. He knew the ice formed on the tank because the olefins in it are boiling, but he could not equate that knowledge with anything other than how full the tanks were. He was thinking only in terms of how much room there might be left in the tanks. And the man whom he sent to look at the tank

had had no education about volatile hydrocarbons and their potential explosivity.

When the man directed to check the slop oil tanks got there, he looked at the ice line on the slop oil tanks, and then he radioed back to the alky plant manager that there were about four feet of room still left in the top of one of them. So, the wastewater treatment plant manager—with complete disregard for the refinery manager’s written order instructing him specifically to the contrary—started pumping the hot slop oil to the slop oil tanks at about 200 gallons per minute (this was clearly an act of defiance).

Boiling Liquid, Expanding Vapor Explosion (BLEVE)

Now, at atmospheric pressure, propylene liquid expands approximately 300 times when it boils into gas, and butylene liquid expands to about 200 times when it boils into gas. When the hot slop oil reached the tank, it instantaneously vaporized huge amounts of the olefins. The tank vents were woefully undersized to accommodate the enormous volume of gas suddenly being created inside the tank. The vents were designed to handle normal tank “breathing,” not something like this. The boiling liquid and expanding vapors blew the roof off, releasing an enormous volume of boiling hydrocarbon liquid and volatile gases.

Explosion Envelope

You may or may not know that the range of concentrations of hydrocarbon gases in air that forms an explosive mixture is typically fairly narrow. For example, gasoline vapor will not ignite unless there is at least about 1.4 % gasoline vapor in the air. This is known as the Lower Explosion Limit (LEL). On the high end, gasoline vapor will not ignite if there is more than about 7.6 % gasoline vapor in air, which is the Upper Explosion Limit (UEL). So, the “explosive envelope” for gasoline is between 1.4 % and 7.6 % in air. Corresponding values for propylene are 2.0 % and 11.1 % and for butylenes about 1.6 % and 10 %.

Thus, for the gas to be explosive, it must be diluted tenfold or more with air. To put this into perspective, suppose that one cubic foot of liquid propylene forms 300 cubic feet of propylene gas. This is diluted with air to form between 2,700 and 15,000 cubic feet of explosive gas-air mixture, depending on the dilution factor ($300/0.111 = 2,727$, and $300/0.02 = 15,000$).

Unconfined Vapor Cloud Explosion

The olefin vapor cloud floated out over the refinery, with air diluting it as it went. By the time the cloud contained enough air to make it explosive, it was enormous, and it was searching for a competent source of ignition. It found one about 300 yards away from the slop oil tank that blew up. Three men were working with welding equipment, and a tremendous explosion occurred. For obvious reasons, this kind of explosion is typically referred to as an unconfined vapor cloud explosion.

All four men died—the man sent to the slop oil tank as well as the three men in the welding crew. His body was found near the slop oil tank that blew up. The unconfined vapor cloud explosion destroyed several million dollars worth of refinery equipment.

Summary

These explosions—the slop oil tank explosion and the subsequent vapor cloud explosion— illustrate that explosions may result from a chain of events instead of just one event. Neither one of these explosions would have occurred if any one of the following had taken place:

- The purchase of alkylation plant pump seals that were not appropriate for acid service
- The failure to catch the error when the seals were first installed
- Repeatedly installing the same type of seals while expecting different results
- The refinery manager's decision to store olefins in the slop oil tanks
- The wastewater treatment manager's decision to disregard a specific written order not to pump hot slop oil into the tanks while they contained olefins

When greed, fear, ignorance, and defiance come together, disaster cannot be far behind.

Case Study 2 – A Rotary Kiln Explosion

Introduction

A company produces Tungsten Carbide Cobalt Powder. Their manufacturing plant uses a batch production process that involves several steps, and the next to last step is known as the carburization process. This occurs in one or the other of two rotary kilns, which are known as Kiln A and Kiln B. Carburization involves heating a mixture of cobalt tungstate powder and tungsten oxide powder while adding carbon monoxide, hydrogen, and methane. Chemical reactions that occur amongst these reactants produce tungsten carbide-cobalt powder. The chemical reactions occur at high temperatures inside a rotating kiln tube. Natural gas burners located outside the tube supply heat, and the tube contains an internal auger that promotes loading and unloading the powder, as well as continuous mixing of the powder while the tube is rotating.

On a Monday night in September of 2000, the company intended to re-carburize the second half of a batch of previously made product, because it did not satisfy certain quality specifications. Kiln A was to be used for the re-carburization. The first half of the same batch of off-test product had already been re-carburized a couple of weeks before, also in Kiln A. An employee had already loaded Kiln A with the second half of the off-test batch of powder in the late afternoon on that Monday, and Kiln A was cold at the time. It had been cold since the previous Friday, and it had been open to the atmosphere for the entire weekend prior to this particular Monday. An employee was just beginning the re-carburization step when an explosion occurred in the Kiln hood. At the time, the natural gas burners were still off, and the hood was closed. Fortunately, no one was injured, but the kiln interior was damaged.

I was retained to assist in the investigation of the explosion. I traveled to the plant, and for the next several days, I interviewed employees, investigated the investigation and analysis of the explosion. I traveled to the plant and several plant employees about that

Discussion

Description of the Carburization Process

Cold powder from the previous batch is loaded into Kiln A or Kiln B. Next, air is purged from the kiln. Then, the natural gas burners are lit. The powder is heated while synthetic gas ("s gas") is added. The synthetic gas is a mixture of hydrogen (H₂) and carbon monoxide (CO) in a 1:1 ratio (by volume).

Then, carbon dioxide (CO₂) is added for 12 minutes. The period of 2 hours and 12 minutes constitutes one cycle. Eighteen (18) cycles are typically required to carburize a

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