

CAUTION IS NOT SAFETY

by

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Introduction

Preventing dangerous actions is something we equate with being safe. Yet taking proper action is a more important aspect of safety. If you did absolutely nothing you might be quite safe - until hunger struck. Once you decide to take action to feed yourself simply not doing dangerous things is not enough. Traveling to get food and even food itself are inherently dangerous. You must choose safe transportation and even properly stored and cooked food. You must ACT to be safe. Caution alone is not safety.

This case study reviews a C4 Selective Hydrotreater Unit catalyst change and examines how seemingly cautious choices can increase risk.

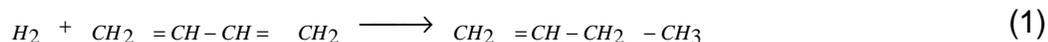
The Unit

The C4 Selective Hydrotreater treats Cat Cracked C4's before they are sent to the Alkylation Unit. As an olefinic mixture of C4 hydrocarbons, Cat Cracked C4's are an excellent Alkylation Unit feed. The Unit is termed a Selective Hydrotreater because only a portion of the convertible feed is reacted. Figure 1 Illustrates the Hydrotreater.

The Unit is fairly simple. The cracked feedstock is produced by the Fluidized Catalytic Cracker (FCC) and separated into the C4 stream through fractionation. The feed is caustic washed to remove Sulfur compounds before being sent to the C4 Hydrotreater. At the Hydrotreater, the C4's are mixed with Hydrogen and heated to complete vaporization. Hydrogen is supplied at only a slight excess. This helps minimize mono-olefin (1- and 2-Butene) saturation. Mono-olefins are key reactants in C4 Alkylation. Two fixed bed reactors in parallel are available with only one on-line at a time. The reactor effluent is cooled and flashed to vent light ends and residual Hydrogen.

Hydrotreating and Hydroisomerizing olefinic Alkylation plant feed has the following benefits:

- Reduced 1,3-Butadiene content. While 1- and 2-Butene are desirable C4 olefins, 1,3-Butadiene is undesirable in Alky Plant feed. It reacts to consume acid and produce acid soluble oils along with high end point low octane polymers in Alkylation reactors. Partially Hydrogenating 1,3-Butadiene produces 1-Butene as depicted in equation 1.



- Increased 2-Butene content. 2-Butene Alkylate is higher octane than 1-Butene Alkylate. Conditions necessary to partially hydrogenate 1,3-Butadiene are sufficient to allow 1-Butene and 2-Butene mixtures to reach equilibrium concentrations. Typically this favors higher relative 2-Butene concentrations than are produced in short residence time conversion processes such as cat cracking. The equilibrium shift favoring 2-Butene diminishes as the reactor temperature increases. 2-Butene reaction octane benefits are higher for HF acid plants versus Sulfuric Acid plants.

Note that 2-Butene exists in *cis* and *trans* isomers.

Catalyst Change

Hydrotreaters typically require routine catalyst change-outs. Catalyst bed fouling, plugging, and deactivation necessitate catalyst regeneration or replacement to maintain catalyst activity sufficient to meet process requirements. In some services catalyst lasts only months. In other services catalyst lasts many years between replacements.

Catalyst changes occur in varying degrees.

- Skim the top of the bed. Many processes are prone to develop a trash, particulate, or fouling build-up on the top or inlet of the bed. Usually this condition manifests itself as high bed pressure drop. Removal of the top few feet of the bed and topping off with new catalyst can alleviate this problem.
- Dump and screen the bed. Bed pressure drop, flow maldistribution, and poor performance can increase as catalyst ages due to catalyst crushing, attrition, the migration of smaller catalyst particles, and the formation of large catalyst clumps or 'clinkers' due to temperature excursions. Dumping and screening the bed to retain properly sized catalyst particles can mitigate this problem.
- Dump and replace. Complete catalyst replacement can be effected to return to Start of Run conditions. This is often the only option if the catalyst is poisoned or severely fouled.

In the case under review, upsets in the caustic wash system treating the unit feed at the Cat Cracked Gas Fractionation Train resulted in caustic being sent to the C4 Hydrotreater. Sodium is a poison for many catalysts and caustic fed to a reactor can salt it causing increased pressure drop. Over time, the caustic wash excursions deactivated and plugged the C4 Hydrotreater catalyst leading to a reactor switch. Now the off-line reactor was to have its catalyst changed so that it would be prepared should the operational reactor become inadequate.

Figure 2 illustrates catalyst removal from the reactor. Under Nitrogen purge, the reactor catalyst dump nozzle is opened. Catalyst gravity flows into catalyst bins that also have been purged with Nitrogen. Dry ice (Frozen CO₂) is added to the filled containers to further air exclusion.

Some catalyst change procedures include a carbonate wash to cool and flush the catalyst before dumping. This wash reduces the potential for polythionic corrosion of Stainless Steel, and also lessens the likelihood of spent catalyst combustion. However, wet catalyst poses its own problems. Adding a Sodium solution to the catalyst likely will poison it. Wet catalyst is more difficult to process by the catalyst reclaiming who receives the spent catalyst and recovers its precious metals or, if possible, recycles the catalyst. Wet catalyst is substantially heavier than dry catalyst making handling more difficult and increasing shipping costs. And whatever solution is used to flush the catalyst must itself be processed – if only the amount that leaks from the dump shoot feeding the catalyst bin.

Excluding oxygen from spent catalyst is important to prevent combustion. Spent catalyst is often pyrophoric. Iron Sulfide or hydrocarbon polymers retained on the catalyst or reactor walls oxidize when exposed to air and may smolder or ignite. Additionally, steps taken to preclude spent catalyst oxygen exposure also minimize dust evolution during the catalyst change. Spent catalyst is a hazardous waste and inhalation of the high metals content spent catalyst particles is undesirable.

Because of the negatives associated with wet catalyst dumping, the C4 Hydrotreater was to have its catalyst dumped dry, under inert conditions. Since not all of the catalyst will gravity flow out of the vessel, someone must enter the reactor to shovel the remainder out of the bottom head. To prevent ignition of the catalyst, this entry was also to be under an inert atmosphere.

Inert Entry

Inert entry entails entering a confined space in which the atmosphere is inadequate to support life. It is similar to SCUBA diving. In industry the atmosphere is typically Nitrogen - an inert gas. Three independent air supplies usually support a person performing an inert entry. One of these is an egress bottle carried on their person. All three separate systems must fail simultaneously for the person to be at risk. Clearly an inert entry is more hazardous than a normally aspirated entry. But the risk is managed to the point that driving to the job site may expose you to more risk than encountered when a trained individual performs an inert entry. However, the risk must still be outweighed by the benefits of doing the work. It is an odd fact of everyday life that dangerous jobs are often less risky than routine tasks. A hazard is a sharp knife. Risk is how likely you are to get cut by the knife and how serious that cut will be. When we approach difficult, hazardous assignments we are more likely to include efforts to reduce risk. Thoughtful handling of a knife exposes you to nearly no risk at great benefit - cutting without a knife is slow work.

Inert entries are performed for various reasons. In a Hydroprocessing catalyst change they are used to clean out catalyst remnants that do not gravity flow out of the reactor. It is not unusual for spent catalyst to be pyrophoric. An inert entry allows complete catalyst removal without combustion inside the reactor. There can be many other hazards besides combustion that inert entry mitigates. Part of the justification for completing the catalyst dump using an inert entry was to preclude the formation of Nickel Carbonyl.

Nickel Carbonyl

Nickel Tetracarbonyl $Ni(CO)_4$ (Nickel Carbonyl) is a highly toxic compound readily absorbed through skin. 29 CFR 1910.1000 prescribes a personal exposure limit on an 8-hour time weighted average of 0.001 ppmv - a very, very low level. Nickel Carbonyl is considered a carcinogen and air concentrations of as little as 30 ppmv are considered lethal.

Nickel Carbonyl is formed by the reaction of elemental Nickel and Carbon Monoxide (CO) at low to moderate temperatures between 50 and 350 °F. Equation 2 describes the reaction.



Nickel Carbonyl decomposes in air fairly readily; once formed it may remain for an hour. Additionally, Nickel Carbonyl is a flammable, volatile, heavier than water pale yellow liquid at room temperature with a boiling point of ~109 °F. If Nickel Carbonyl is formed it may collect in low points or instrument tubing thereby reducing its exposure to air and its rate of evaporation.

Because the C4 Hydrotreater used a Nickel based catalyst, catalyst combustion or the oxidation of Iron Sulfide or C4 Polymers might generate Nickel Carbonyl. The inert entry was planned to obviate this possibility.

Caution is not Safety

A coordination meeting was held prior to the catalyst change. Besides ensuring effective execution, part of the meeting's purpose was to introduce and orient a new safety manager that had arrived at the plant. Things went smoothly at first: Good procedures, good support, proper testing, and catalyst in hand. Then a review of the contractor's qualifications to do the work directly commented on their inert entry capabilities. Trouble began.

Surely an inert entry was not contemplated for such routine work? Surely this was unnecessary! A discussion followed which laid out the risks and benefits that had been used to justify the inert entry. In the end there was only one person who would not agree that an inert entry was justified: The new Safety manager. In fact, this person stated that they would never approve an inert entry under any circumstances - it was just too dangerous. Perhaps the new manager was trying to make a point during one of their first official acts. Perhaps they didn't realize the point they were making.

At this facility a Safety Department reporting directly to the facility's general manager had final approval authority over all hot work and vessel entry permits. They had sets of rigid rules that they enforced and strictly followed. For routine tasks that was fine. But it is startling how many non-routine things happen at industrial complexes.

An inert entry occurred maybe once a year at this complex. Even though it was known which tasks required inert entry, each time one was contemplated it was scrutinized to ensure there was no better way. The contractors hired to perform the entry were thoroughly reviewed. There were special procedures and equipment. It was a good example of a hazardous situation that had been worked until its risk was very low. It was soon to be obvious that the risk of NOT performing an inert entry was much greater.

The Work

A mistake was made. Because an inert entry would not be permitted, it was removed from the catalyst dump procedures. However, no other change was made to account for the possibility of catalyst residue combustion. The confusion and frustration of the coordination meeting led to an approach of: eliminate the inert entry and let's get on with it. But the hazard still existed, and because management of the hazard had been forfeited, the risk increased.

Catalyst dumping began and went well. Bin after bin was purged with Nitrogen, filled with catalyst, topped off with Dry Ice and sealed. Soon only the dregs remained in the bottom head. Industrial Hygiene personnel tested the reactor atmosphere and found no Nickel Carbonyl. A steam driven air mover was installed on the reactor outlet piping using a large flanged nozzle built into the pipe expressly for that purpose. The Nitrogen filling the vessel

during the primary catalyst dump had to be displaced by air to allow a non-inert entry to complete catalyst removal. Soon air was being sucked through the reactor - and through the material remaining within.

Because the reactor is deinventoried by draining from the bottom, the residue that collects in the lower head of the vessel is largely catalyst from the bed top. Over the catalyst's life, part of the olefinic feed had reacted to form unsaturated polymers at the bed inlet. This rubber was now piled at the bottom of the reactor, oxidizing as air was pulled through the vessel. The rubber began to burn.

On top of the reactor a worker prepared to enter the vessel to clean out the catalyst vestiges. The feed inlet nozzle at the center of the upper head served as the entry man way. Donning fresh-air breathing equipment the worker prepared to descend the rope ladder dangling within the volume. Even though the atmosphere within the reactor was composed of air, it also contained catalyst particles. A positive-pressure, supplied-air, full-face mask was required for entry in addition to gloves, coveralls, etc.

As the worker peered down into the vessel garbed for the decent, they noticed a red glow. Allowing their eyes to adjust to the relative darkness of the reactor, flames were seen licking through the top of the catalyst residue in the bottom head. There was a fire in the reactor.

Gestures, and shouts muffled by an air mask to others on top of the reactor caused several people to look in. Quickly there was a radio call to those on the ground that there was a fire. Startled disbelief was replaced by action as first those on top of the reactor raced to get off, and then those on the ground scampered up to make sure. A large perimeter around the vessel was cordoned off inside of which everyone was to wear full-face supplied air breathing equipment. The air mover on the reactor outlet piping was shut down.

As part of the entry permit requirements, a small fire hose had been run to the top of the reactor. This was now employed to douse the flames. As the reactor was filled with water, streams leaked from the dump nozzle and the nozzle to which the air mover was connected. Steam flashed from the hot catalyst and vented out the top head inlet nozzle through which the water was sprayed. Industrial Hygiene personnel collected air samples and reported that Nickel Carbonyl was detected – though only in trace amounts.

After the fire was extinguished, the water-catalyst slurry in the reactor had to be removed. The mixture was dumped from the vessel as had been done with the dry catalyst. Bins were filled with the catalyst bearing water. Because the entry permit had been voided, and the Safety Department would not approve another, every last bit of catalyst was washed out of the reactor from above using the fire hose. There were quite a few heavy, waterlogged bins at the end of the job.

The response of contractors, operators, and maintenance crews was excellent. Even with the advent of unexpected and hazardous conditions they made proper accommodations. It was another case of well-trained, highly skilled people doing their jobs well. A common but overlooked condition.

The remainder of the work was thankfully boring by comparison. The reactor was dried, inspected, recharged with catalyst and buttoned up. When later put into operation it performed as expected.

Summary

The work could have been done safely without an inert entry. It would have required wet dumping of the catalyst, but it could have been done. However, wet dumping carries its own set of risks and benefits. These had been evaluated and judged too onerous. As is common, last minute changes and managerial edicts coupled with time constraints led to a flawed course of action. Instead of minimizing risk, the approach was to minimize hazard. No one was injured, no equipment was damaged, and the added cost was small. In the end, it was a painless way to learn an important lesson.

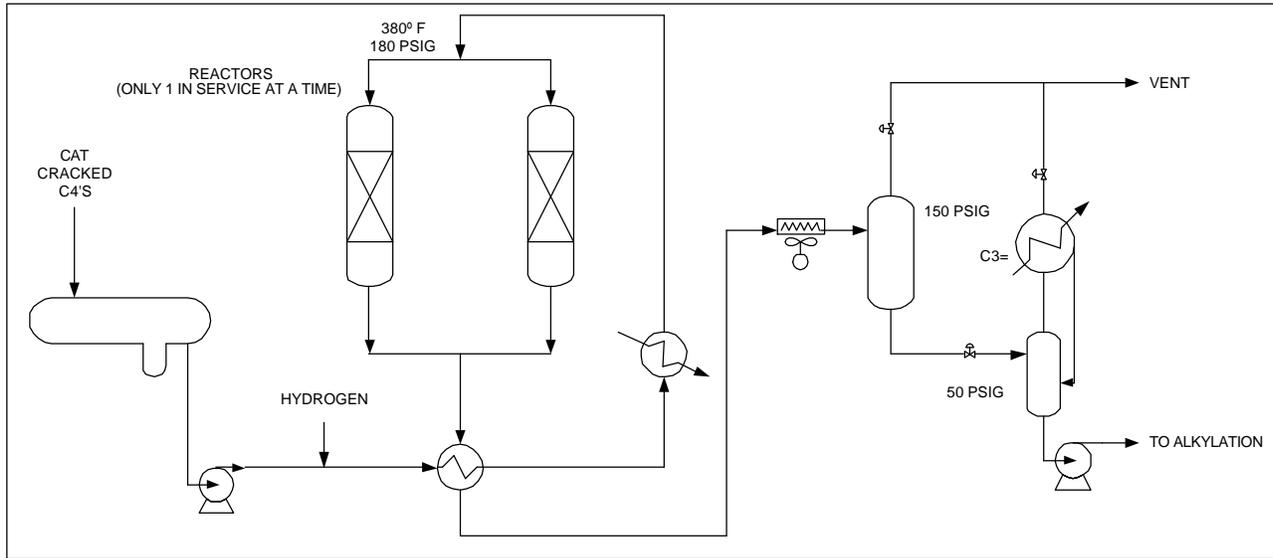


FIGURE 1: C4 Hydrotreater.

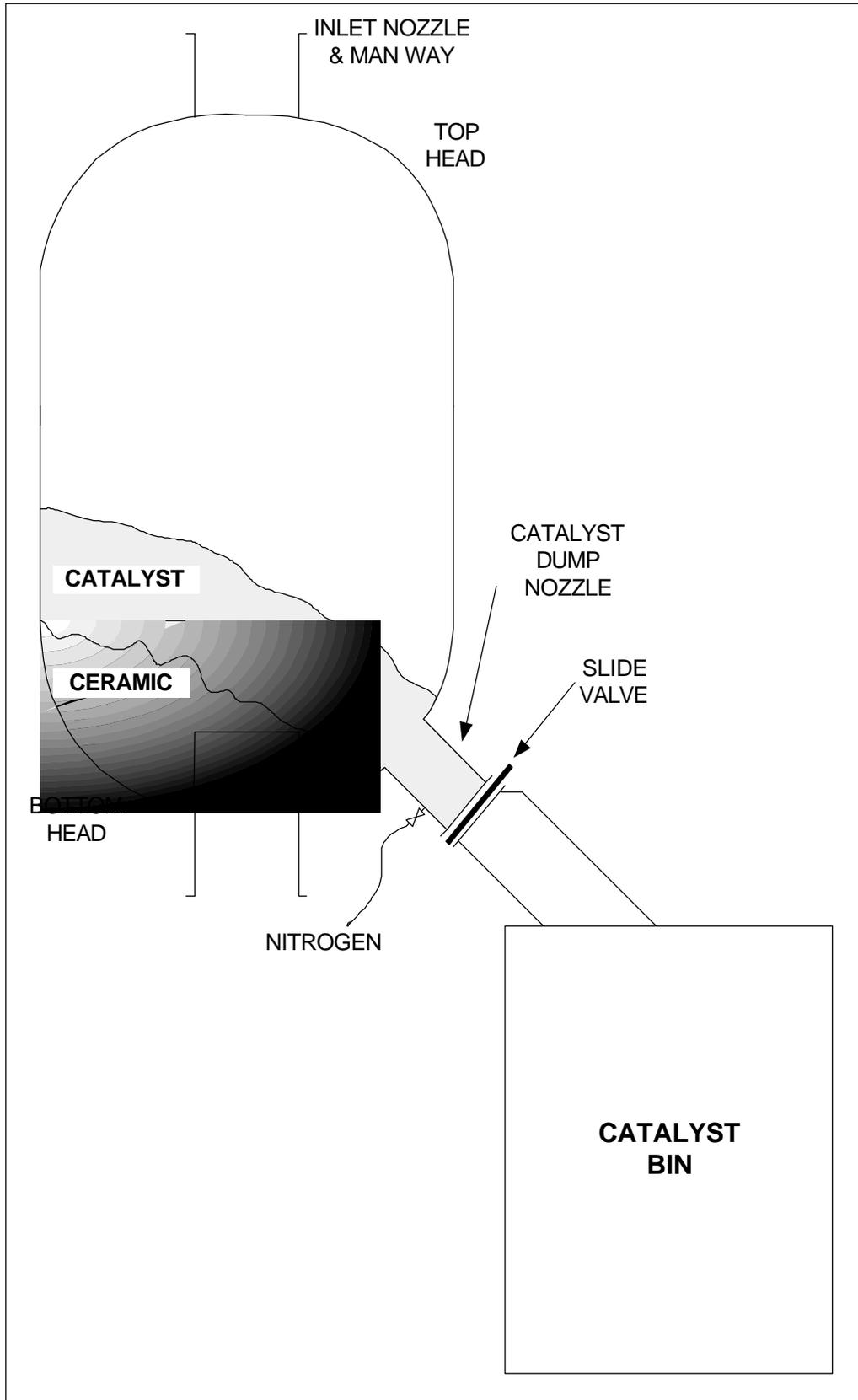


FIGURE 2. Catalyst unloading.

Author Biography

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Don Schneider is President of Stratus Engineering, Inc., Houston, Texas. Previously he worked as a senior engineer for Stone & Webster Engineering, and as an operating and project engineer for Shell Oil Co. He holds a B.S. from the University of Missouri-Rolla, and an M.S. from Texas A&M University, both in chemical engineering. Don has authored or co-authored over a dozen technical papers and articles and is a registered professional engineer in Texas.

Author's Previous Publications

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