



**CHEMICALS INFLUENCING THE ACTIVITY OF PALLADIUM-BASED
CATALYSTS FOR THE SELECTIVE HYDROGENATION OF ACETYLENE TO
ETHYLENE IN ACETYLENE CONVERTERS**

Presented at the 13th Ethylene Producers' Conference, Volume 10 (March 2001)

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ABSTRACT

Operation of acetylene converters can provide particular challenges to ethylene producers. Reactor optimization efforts may be maximized through understanding the chemicals influencing the performance of the catalyst specific to their plant and reactor configuration. In this session, chemicals that influence the short-term and long-term activity of palladium-based acetylene reactor catalysts will be discussed. The fundamental chemistry involved in the selective hydrogenation of acetylene in the presence of ethylene will also be addressed.

Introduction

The effective removal of acetylene via selective hydrogenation, using supported, palladium-based catalysts, is of particular challenge in ethylene production. Many factors can influence the success of this task. The selection of catalyst technology and the type of poisons to which this catalyst is exposed are two factors that can strongly impact the successful operation of the acetylene converters. The purpose of this paper is to improve ethylene producers' understanding of the nature and actions of these poisons and their impact on the operation and lifetime of palladium-based acetylene converter catalysts.

Method of Acetylene Removal

Many different techniques are utilized in the removal of acetylene in the purification of product ethylene. This technology has progressed through distinct stages that have emerged in the order listed below¹:

1. Solvent Extraction
2. Cracked Gas Train or Raw Gas Catalytic Hydrogenation Reactors
3. Backend Catalytic Hydrogenation Reactors
4. Front-End Selective Catalytic Hydrogenation Reactors

In the solvent extraction method, the acetylene is selectively adsorbed into a solvent, normally dimethyl formamide (DMF), followed by derivatization or sale of the resulting acetylene product.

In raw gas catalytic hydrogenation, the effluent of the cracked gas compressor, after minimal treatment, enters the acetylene converters for catalytic hydrogenation of the acetylene contained in the feed. Although the use of nickel catalysts has endured in this type of application, a progression to the use of the higher selective palladium technologies is occurring. In raw gas applications where the reactors precede the caustic tower, effective utilization of palladium catalyst is not possible without process modification. The feed in this case contains copious amounts of sulfur, which necessitate the use of supported, nickel-based catalysts.

In backend catalytic hydrogenation reactors, the acetylene is, typically, contained in a C₂-rich stream (see Table 1) to which stoichiometric amounts of hydrogen, and in some cases small amounts of carbon monoxide, are added to control the extent of acetylene and ethylene hydrogenation. In this type of application, the reactors are located at the overhead of the de-ethanizer, which is downstream of the demethanizer.

In front-end selective catalytic hydrogenation reactors, the acetylene reactors precede the demethanizer in the process. As a result, these reactor feeds contain a large excess of hydrogen—typically 10 to 35 mol percent. In a front-end de-ethanizer design, the de-ethanizer is the first distillation column and

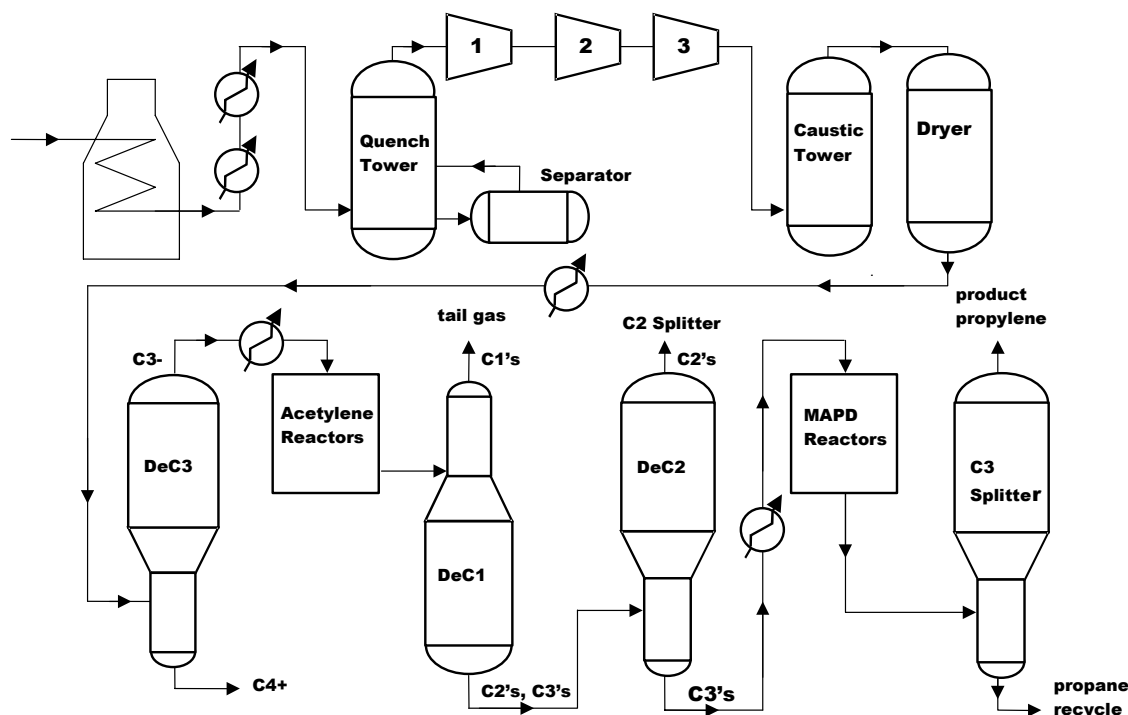


Figure 1. Location of acetylene reactors in a qualitative depiction of a front-end depropanizer configuration.

the reactors are on the overhead stream. Thus, the feed contains a C2 and lighter stream. Similarly, in a front-end depropanizer unit, the initial distillation column is the depropanizer (see Figure 1). As the acetylene reactors are on the overhead of this column, the feed to the reactors is composed of C3 and lighter hydrocarbons.

Chevron Phillips Chemical Company LP has operated front-end hydrogenation reactors for over 40 years. During this time, the company has conducted extensive research and development in the selective hydrogenation of acetylene in front-end reactors. As a result, the E-Series catalyst was developed to improve the operations and economics of these front-end units. Thus, the perspective of this paper will strongly lean toward front-end hydrogenation units. However, as the feed composition for backend and front-end de-ethanizer units contain similar hydrocarbons (see Table 1), the poisons that are contained in the feeds to these reactors are also comparable.

Table 1. Feed composition as a function of reactor location.

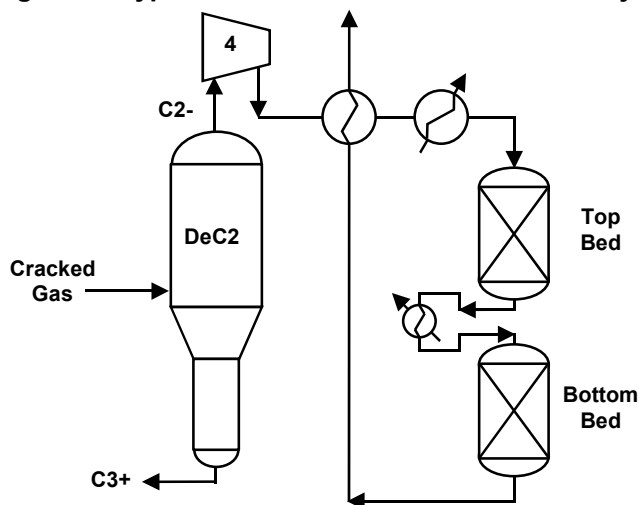
Feed Component	Backend (mol %)	C2 and lighter (mol %)	C3 and Lighter (mol %)
Hydrogen		30.0	12.0
Carbon Monoxide	0-5 ppmv	0.02	0.05
Methane		13.6	29.5
Acetylene	1.0	0.3	0.5
Ethylene	80.0	34.0	32.5
Ethane	19.0	22.0	5.5
Methyl Acetylene			0.3
Propadiene			0.3
Propylene		0.08	19.0
Propane			0.8
Cracking Feed	ethane	ethane	naphtha

Reactor System Design

A detailed description of reactor systems will not be undertaken in this paper as the focus of this discussion will be the poisons contained in the feed that affect the reactivity of the supported, palladium-based catalysts. However, a simplified description of the typical designs for each application follows.

Figure 2 depicts a commonly used, two-bed reactor system in a serial configuration. This is the predominant type of design for front-end de-ethanizer units. However, for

Figure 2. Typical front-end de-ethanizer reactor system.



depropanizer plants, the number of reactors varies from two to four, with three reactors being most prolific. Historically, the amount of acetylene present in the feed has dictated the number of reactors for these applications. In each of these cases, the reactors normally have a pre-heat capability on the inlet of the lead reactor and only inter-cooling capacity

between subsequent reactor beds. The shortcomings of this design will be addressed later in this discussion.

Typically, a backend hydrogenation unit consists of two parallel trains, each similar to that described in Figure 2, with only one train in service at any given time. The parallel trains impart to a producer the ability of on-line regeneration of the catalyst while the second reactor is performing the acetylene hydrogenation. The necessity of this type of arrangement is driven by the rapid formation of carbon oligomers, often referred to as "green oil", which impair the operation of the catalyst. Their effect is manifested in shortened cycle times for the catalyst compared to their front-end counterparts.

Hydrogenation in Front-End Acetylene Reactors

To understand how poisons affect the performance of a hydrogenation catalyst, one needs to examine the mechanisms of selective hydrogenation. It is generally accepted that reactants like acetylene first adsorb on the palladium metal sites on the catalyst.² The adsorption process activates the reactants, which subsequently react with hydrogen to form the hydrogenation products. The hydrogenation activity of the catalyst for a particular reactant is controlled by the availability of the palladium sites, and the selectivity depends on the preferential adsorption of the reactant. For instance, acetylene is more strongly adsorbed on palladium than ethylene, even though the intrinsic rate of hydrogenation of ethylene is two orders of magnitude faster than that of acetylene.³ So long as there are sufficient acetylene molecules available to cover, statistically, all the palladium sites, only acetylene is hydrogenated. Thus, the hydrogenation products will be mainly ethylene. As soon as the ethylene is formed, it desorbs from the reaction site and is replaced by another acetylene molecule.

It is known that the relative strength of adsorption on palladium, as reflected by the heat of adsorption, follows the order listed below.^{4,5}

CO > acetylene >> conjugated diolefins \geq alkyl acetylene > diolefins >> olefins

Carbon monoxide, at low concentrations, is a reaction modifier in front-end acetylene converters. Both CO and acetylene adsorb on the reaction sites. When the carbon monoxide concentration in the feed achieves a minimum level, it will prevent the adsorption of ethylene, even as the acetylene concentration is reduced to a very low level in the course of the hydrogenation reaction. Alternatively, CO competes with acetylene for the reaction sites, thus reducing the activity of the catalyst.

The adsorption mechanism also explains the tempering effect of methyl acetylene and propadiene (MAPD) in front-end depropanizer acetylene converters. In particular, methyl acetylene replaces the acetylene at the reaction sites as the acetylene is hydrogenated. So long as there is methyl acetylene (or propadiene) remaining, the hydrogenation of ethylene is suppressed.

One important feature of the E-Series catalyst is its ability to withstand sudden drops in the carbon monoxide level in the reactor without causing runaway reaction in front-end reactors. It is believed that the catalyst's proprietary promoter(s) minimize the impact of fluctuations in the CO concentration on the catalyst surface by maintaining the carbon monoxide level at a minimum level near the reaction sites. This minimum carbon monoxide concentration prevents the access of the ethylene to the reaction sites, even when the acetylene level is low.

The converse has also been observed in the laboratory and commercially. As the concentration of moderators like carbon monoxide increase in the feed to the reactors, the maintenance of the low level of acetylene exiting the reactors is more easily maintained with the E-Series catalyst versus traditional Ag/Pd catalysts. This is, again, attributed to the catalyst's efficiency in adsorbing these types of species on the catalyst surface.

Poisons reduce the activity of palladium catalysts in two major ways: first, by hindering or blocking the access of the reactants to palladium sites, and second, by changing the electronic properties of the palladium such that the adsorption strength of the reactant on the palladium is greatly reduced. Sulfur compounds represent the first class of poisons. Compounds like hydrogen sulfide (H_2S) or carbonyl sulfide (COS) adsorb strongly on the palladium. In this manner, these poisons block the acetylene from the reaction sites.

Poisons like the sp metals, such as arsenic and mercury, form "alloys" with the palladium. Electron transfer between the sp metals and the palladium drastically reduces the associated adsorption strength of acetylene. Since the reaction rate of acetylene is directly proportional to the rate of adsorption, which in turn depends exponentially on the heat of adsorption, a small reduction in the adsorption strength will translate to a significant drop in catalyst activity.

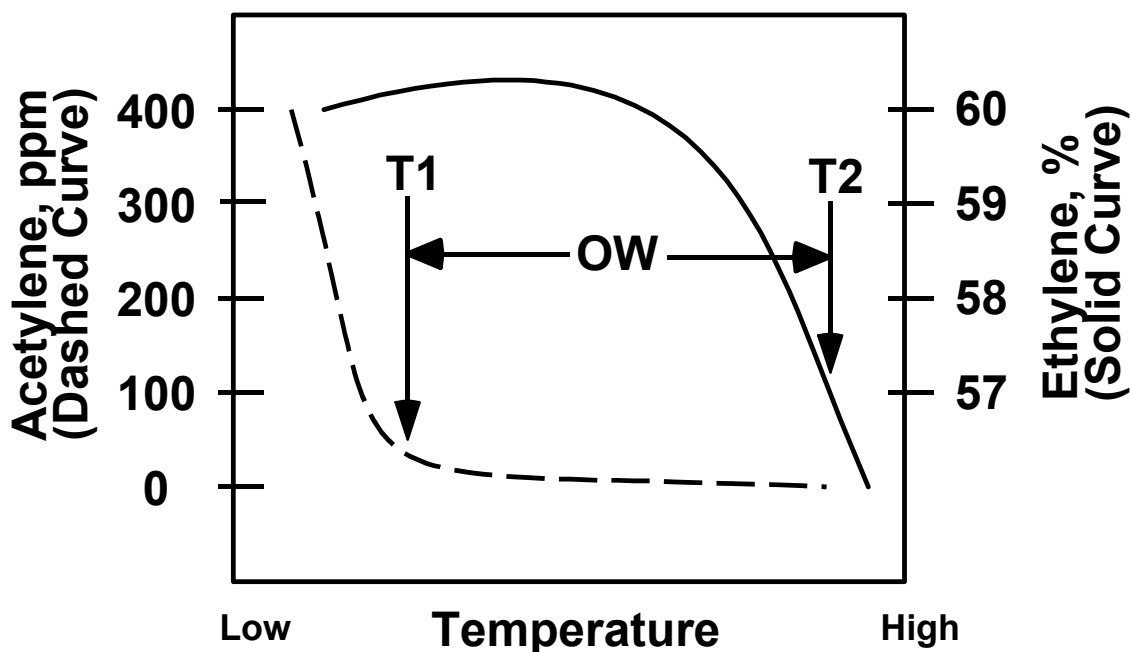
Although to a limited extent, silver behaves like a sp metal, however, its impact on palladium is less drastic in comparison to arsenic or mercury. Palladium catalysts with a silver promoter are not as active as catalysts containing only palladium. The beneficial effect of the silver is its modification of the relative adsorption strength of acetylene and ethylene on the palladium. The result is a catalyst with a small reduction in activity but an improvement in selectivity.

Analysis of a Catalyst

One of the most useful tools in the development of new catalyst technology is the ability to evaluate the activity and selectivity of a supported, palladium-based catalyst. One method of evaluation that is used in the screening of a catalyst for front-end applications is depicted in the plot in Figure 3. In the laboratory, a micro reactor is charged with catalyst, and feed, similar to

those outlined for front-end converters in Table 1, is passed over the catalyst at constant (and consistent) space velocity for the comparative studies. The effluent of the reactor is analyzed using gas chromatography. The reactor is slowly warmed while monitoring the effluent gas composition. When the feed

Figure 3. Determining catalyst quality.



typically contains less than 20 ppm acetylene in the gas, this temperature is referred to as the “clean-up” temperature and assigned the value of T1. While 20 ppm is certainly not appropriate for commercial reactors, the slope of the curve in this range is quite steep, and the limitations of the analytical method make this an acceptable value for this type of study. Similarly, the reactor is heated and further loss of ethylene occurs. When this loss totals three weight percent of the ethylene in the feed to the reactors, the “runaway” temperature, T2, is assigned. The selectivity and ease of operability of a catalyst depend on the differential between the T1 and T2. This value is referred to as the operating window, OW, of the catalyst. Catalysts with larger operating windows are more stable, even at this level of ethylene hydrogenation (T2), while catalysts possessing reduced operating windows can exhibit thermal instability at this temperature.

This method of analysis is an excellent tool for the examination of catalyst activity, as indicated by T1, and the selectivity, as indicated by the difference between the temperature the acetylene is removed and that at which ethylene hydrogenation becomes prevalent, or the operating window. A lower T1 temperature correlates with a catalyst that is more active, while a larger operating window reflects a catalyst that is more selective in the hydrogenation of the acetylene in the feed. This method will also be incorporated in later discussions, in the examination of the effects of transient poisons in the laboratory.

Table 2. Catalyst Comparison.

<u>Catalyst</u>	<u>T1 (°F)</u>	<u>OW (°F)</u>
E-Series	115	70
Ag/Pd	112	42
Pd only	105	29

Table 2 displays the results for some catalysts that were examined in Chevron Phillips' research laboratories. The E-Series catalyst noted in this case was that for a front-end de-ethanizer application. The data emphasize that, while the activities of the catalysts studied were similar, the

selectivities of the catalysts were quite different. In fact, the operating window of the E-Series catalyst is almost two-and-a-half times that of the mono-metallic palladium catalyst and nearly twice that of the typical silver-promoted technology.

Poisons Definitions

For the purpose of this paper, a poison will be considered any chemical, other than ethylene that inhibits the adsorption and/or hydrogenation of acetylene in the acetylene converter reactors. Further, the poisons will be categorized among three types as defined below.

Transient--those poisons whose effects subside when the concentration of the species diminishes.

Semi-transient--those poisons whose effects subside only after the catalyst undergoes proper steam/air regeneration.

Permanent--those poisons whose effects cannot be alleviated, even after the catalyst undergoes proper steam/air regeneration.

While the purpose of this discussion is to identify poisons and their inherent effects on palladium-based hydrogenation catalysts, for simplicity, the classification of the poisons should be viewed as general and not comprehensive.

Transient poisons are the contaminants that will challenge the day-to-day operation of the converters while semi-transient and permanent poisons will have longer-term impacts. Depending on the catalyst technology, these poisons can have a dramatic influence on the activity and selectivity that are achieved in either the front-end or backend catalytic hydrogenation of acetylene using a supported palladium catalyst.

Table 3. Classification of specific poisons.

Type of Poison	Classification	Examples
oxides	Transient	CO, O ₂ , H ₂ O
MA/PD	Transient	CH ₃ C≡CH, H ₂ C=C=CH ₂
amines/nitrogen	Transient	NH ₃ , NH ₂ R
sulfides	Transient	COS, H ₂ S, MeSH
phosphines	Semi-Transient	PH ₃ , PH ₂ R
carbon oligomers	Semi-Transient	Precursors: BD, acetylene
chlorides	Semi-Transient/Permanent	Cl ⁻
"mercury"	Permanent	Hg
"arsenic"	Permanent	AsH ₃
"heavy metals"	Permanent	Fe, Mn, Pb, Ti
"main group metals"	Permanent	Na, Ca, Mg

Description and Classification of Poisons

Table 3 contains a list and classification of poisons that are commonly present in feeds to acetylene converters. A description of these poisons is undertaken below, beginning with the transient poisons and concluding with the permanent species.

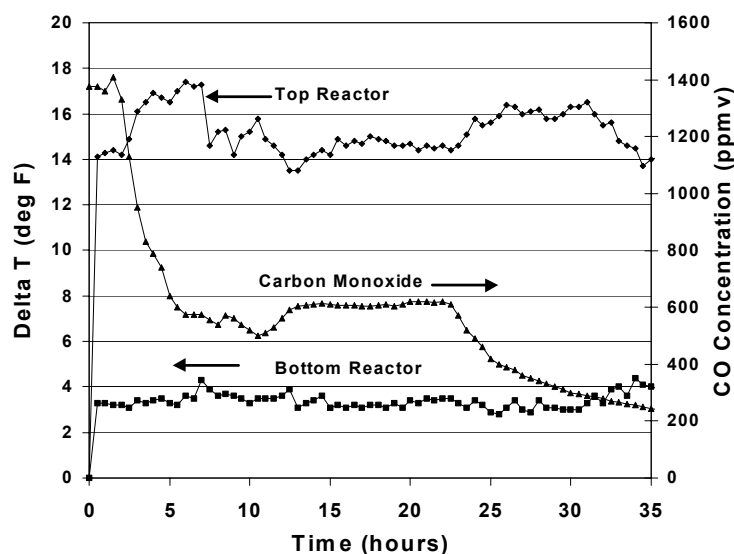


Figure 4. Selectivity, as a function of CO concentration, for a commercial application using E-Series catalyst.

According to the definition outlined previously, front-end hydrogenation reaction modifiers, such as carbon monoxide, methyl acetylene and propadiene, are categorized as transient poisons. An understanding of how carbon monoxide influences a palladium-based acetylene hydrogenation is crucial to the successful operation of these types of reactors.

As with all poisons, the influence that it exerts on the catalyst is very technology dependent. The E-Series catalyst, with its proprietary promoter content, was designed to minimize the influence of these reaction modifiers. This catalyst exhibits a reduced dependence on carbon monoxide adsorbed on the catalyst as

a function of the concentration of CO in the feed stream. The result is a diminished influence of this transient poison on the activity and selectivity of the E-Series catalyst.

Figure 4 shows commercial reactor data from Chevron Phillips' Ethylene Unit 33 in Sweeny, TX. During this 35-hour time period, the reactors maintained the acetylene specification in the product ethylene. This plot displays the variation in the carbon monoxide concentration on the right axis while the individual reactor delta T's are plotted on the left axis. With the acetylene concentration at the outlet of the reactors on-specification at all times during this period, the steady delta T for the reactors indicates that the selectivity of the catalyst was remarkably constant during this event.

Oxygen is also noted as an oxide poison that may be present in the feed to the reactors. As palladium-based catalysts also serve as excellent oxidation catalysts, the presence of oxygen in the feed results in the oxidation of various feed components such as carbon monoxide. This results in an increased delta T across the beds due to the exothermic nature of oxidation reactions and can produce a temperature excursion in the reactors. The presence of oxygen may also result in the ethylene going off specification on CO₂ in a front-end system. Another consequence of oxygen exposure is that the inlet temperature needed to accomplish the same extent of hydrogenation after this type of contamination is diminished. Oxygen partially "regenerates" the catalyst, oxidizing carbon that has been deposited on the catalyst, similar to what would be accomplished during normal steam/air regeneration.

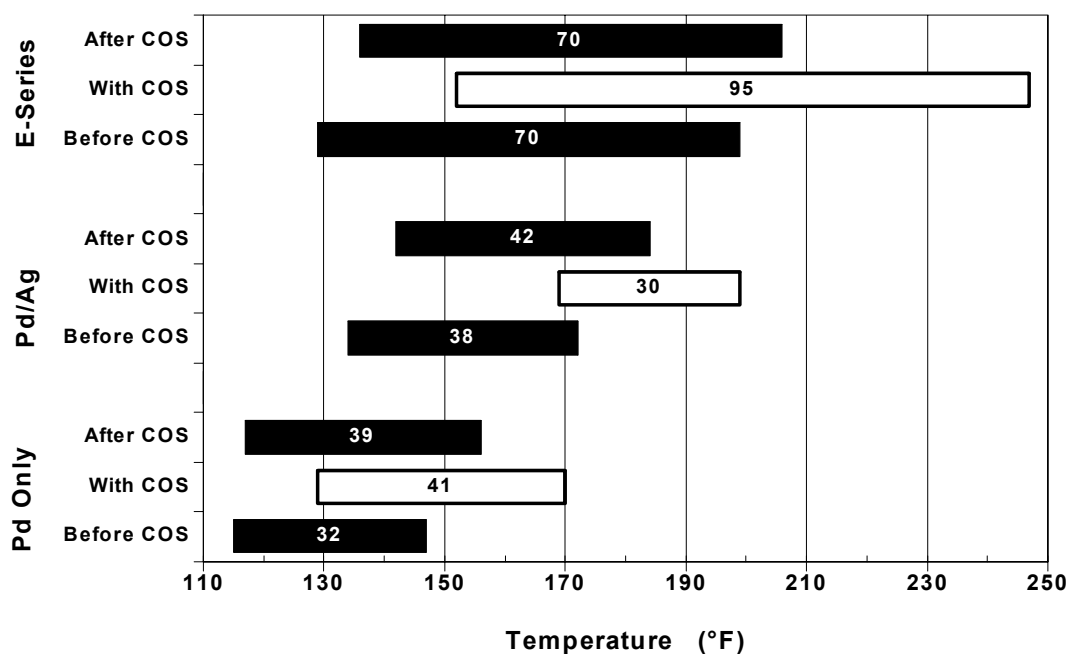
Water may also be produced from the catalytic hydrogenation of oxygen, or may be present as a contaminant in the feed. In either case, the presence of water will result in the slow deactivation of the catalyst over time. It will function similar to hydrogen sulfide (H₂S), which will be discussed subsequently; however, the interaction of water with palladium will be somewhat weaker.

Other transient contaminants include nitrogen-based species such as ammonia or low molecular weight amines. These chemicals are reversibly adsorbed onto the catalyst, effectively reducing the number of active sites available to the acetylene. The result is a decrease in the concentration of the acetylene adsorbed on the catalyst and the extent of hydrogenation of the acetylene in the feed. An increase in reactor temperature will be necessary to achieve the same outlet acetylene concentration while this poison is present. While this is similar to the functions carbon monoxide provides in front-end reactors, nitrogen containing compounds are also adsorbed onto the acid sites contained in the alumina support and have a much longer lifetime on the catalyst. Carbon monoxide does not show this propensity to interact with the catalyst support. Lastly, exposure of supported, palladium-based catalysts to copious amounts of amines or ammonia can result in semi-transient poisoning of the catalyst.

The effects of sulfur-based compounds are dependent on the species containing the sulfur. While compounds like methyl mercaptan (MeSH) and hydrogen sulfide (H₂S) will impact the catalyst in a manner similar to amines, the effects of carbonyl sulfide parallel those of carbon monoxide. The primary difference between amine species and the analogous sulfur compounds is that the sulfur compounds will bind to the palladium sites (and silver sites if present) on the catalyst more tightly. The result is a longer-lasting impact of the sulfur-based poisons relative to their nitrogen counterparts.

The influence of COS is quite similar to that of carbon monoxide. However, subtle differences do exist. The impact that sulfur compounds exert on the activity of palladium-based catalysts is strongly dependent on the silver content of the catalyst, as can be seen in the laboratory results outlined in Figure 5. In these sets of experiments, the T1 and operating window (as depicted previously in Figure 3) were measured for three types of catalysts—an E-Series

Figure 5. Examining the influence of carbonyl sulfide on the operating window of different types of catalysts.



catalyst, a Pd/Ag catalyst, and a mono-metallic palladium version. Three measurements were undertaken for each catalyst type. The T1 and operating window data were collected: 1.) prior to exposure to carbonyl sulfide, and 2.) while carbonyl sulfide was present 2.) after the carbonyl sulfide exposure, but with no COS in the feed. The bar in the plot represents the operating window measured for each test, with the T1 (“clean up”) temperature correlating to the left edge of the bar and the T2 (“runaway”) temperature represented by the

opposite end of the bar. The width of the operating window, for each case, is also displayed on the individual bars.

The plot in Figure 5 emphasizes the dramatic influence of the silver content of the catalyst on the chemistry occurring on the surface of the catalyst. While a mono-metallic catalyst exhibits a slight shift in the operating window, this ppmv level of COS contamination of the feed actually improves the selectivity of the catalyst. However, traditional supported Ag/Pd catalyst selectivity and activity are severely impaired by the presence of the carbonyl sulfide. However, the E-Series catalyst technology was developed not only to widen the operating window and selectivity of the catalyst in front-end applications, but to also diminish the influence of sulfur compounds on the operating window and activity of the catalyst. This is emphasized by the large overlap in the three operating windows measured for the E-Series catalyst, as displayed in Figure 5.

Carbonyl sulfide is of increased concern for front-end depropanizer units as the COS is concentrated in the C3 fraction. Further, as carbonyl sulfide is formed from the reaction of carbon monoxide with hydrogen sulfide in the pyrolysis furnaces, feeds with high H₂S concentrations, such as refinery propane, will contribute to the generation of higher concentrations of carbonyl sulfide. Hydrogen sulfide and methyl mercaptan are the primary sulfur contaminants seen in C2-rich reactor streams.

Among the semi-transient poisons that impact the hydrogenation of acetylene by supported palladium catalysts are oligomeric and polymeric forms of carbon. This type of poisoning is much more predominant in backend acetylene converters in which “green oil” impacts the catalyst selectivity and activity. “Green oil” is composed of unsaturated, even-numbered, long-chain hydrocarbon compounds that are formed as the result of oligomerization and/or polymerization of highly unsaturated hydrocarbons such as acetylene and butadiene. It is believed that the partial hydrogenation of acetylene results in the formation of acetylene radicals, also called ethylidyne radicals, which initiate the oligomerization of the unsaturated species. As the formation of the ethylidyne radicals is suppressed by the presence of hydrogen, its partial pressure will have a dramatic influence on the quantity of “green oil” that is formed. And in backend applications, where only stoichiometric amounts of hydrogen are added, “green oil” is most prevalent. These high molecular weight compounds coat the catalyst surface, diminishing the activity of the catalyst as a result of mass-transfer effects. To offset the loss in activity in this type of situation, heat is added to the reactors which, in turn, contributes to the loss in selectivity observed.

The formation of carbon oligomers in front-end applications during “normal” operations is of a reduced rate when compared to backend reactors. The formation of coke on palladium catalysts in front-end de-ethanizer plants is, normally, the lowest of all types of front-end applications. High coke content on the supported, and promoted, palladium catalysts is normally due to temperature

excursion in the beds in which copious amounts of carbon will be deposited on the catalyst in very short, “catastrophic” periods. The presence of carbon monoxide, and/or MAPD and these types of moderators inhibit the oligomerization reactions stemming from ethylene adsorption on the catalyst via desorption of lighter oligomers (such as C4’s and C6’s), making long chain formation less likely. Also, the high hydrogen partial pressure inhibits the formation of ethylidyne radicals as in the backend case. However, the presence of higher concentrations of butadiene in a C3 and lighter feed to palladium catalysts may contribute to more rapid “coke” formation on the catalyst. It is also worthy of note that, although we have seen very little difference in “heavies” formation when using an E-Series catalyst or a traditional Ag/Pd catalyst in the laboratory, mono-metallic palladium catalysts show a dramatically higher production of heavier hydrocarbons. The formation of coke on the catalyst will result in a diminished ability to selectively hydrogenate acetylene similar to its effect in backend units.

Empirically, we have observed that proper steam-air regeneration of catalysts with “coke” deposits normally leads to a slight loss in the activity while actually resulting in a slight increase in selectivity (< 5 °F increase in OW) of the same catalyst. This may be attributable to the fact that fresh supported palladium catalysts possess a small fraction of very active and unselective palladium sites. These sites are deactivated over a “seasoning” period. These sites would serve to decrease the T1 temperature measured in lab, and, as they are less selective, would also lessen the operating window of the catalyst. These highly active palladium sites are only present in the fresh catalyst, and the regenerated version will, consequently, have a higher T1 and operating window. However, experiments to validate such a theory have not been undertaken.

Another type of semi-transient poison that a palladium catalyst may be exposed to is phosphine, PH_3 . Phosphine will impact the catalyst very similar to amines and sulfur compounds. However, the interaction of the palladium with phosphorus-containing species is, generally, stronger than the interaction of nitrogen species or sulfur compounds. The ability of the phosphine to act also as a π -acid, like carbon monoxide, is attributable to this stronger interaction with the palladium. Although the table shows phosphine as a semi-transient poison, the possibility for desorption of the phosphine under the proper conditions also exists. Any phosphorus on the catalyst will be converted to phosphate ions upon regeneration and will be rather innocuous to the subsequent activity and selectivity of the catalyst.

Halides comprise the last of the semi-transient poisons that will be addressed in this discussion. Chlorides in particular will be the focus as the presence of this species is most common among the halides. While the palladium halides are often incorporated in the production of acetylene hydrogenation catalysts, their presence in the feed to the reactors will impact the catalyst. Low-level, short-term exposure may result in similar consequences as

would be seen for exposure to hydrogen sulfide or amines. However, the chemistry, from the aspect of the palladium, is more like that which occurs with oxygen exposure. Palladium metal is oxidized to Pd^{2+} , which is much less active toward unsaturated hydrocarbon hydrogenation. Thus, there may be a transient reduction in the activity of the catalyst until the palladium chloride is reduced, again, to palladium metal. However, unlike the case where the catalyst is exposed to oxygen, and its selectivity is maintained and activity is improved after the exposure, with chlorides there is a risk of a reduction in catalyst selectivity. The loss in selectivity is a consequence of the increased mobility that the chloride imparts on the palladium upon conversion to palladium (II). The palladium, which is selective when it is deposited as a thin “skin” on its support, can penetrate, aided by halides, deeper into the support, resulting in the subsequent loss in selectivity. Once the palladium has migrated from the surface of the support, its return to this position cannot be facilitated by traditional steam/air regeneration methods, and, thus, the effects of these contaminants can be permanent.

The last of the main group poisons to be discussed is “arsenic”, which is typically seen in the form of arsine, AsH_3 . Unlike its lighter group V congeners, arsine has been shown to form alloys with supported palladium catalysts at the relatively moderate temperatures seen in acetylene converters. The electronic interaction of the arsine with the palladium was noted earlier in this paper. Arsine’s effects are more long-term as the result of the inability to remove it from the catalyst during steam/air regeneration. While the arsenic may be initially separated from the palladium during regeneration, if high temperatures are experienced (such as those seen during a thermal excursion), the arsenic oxides are reduced. This increases the mobility of the arsenic which, in turn, “finds” the palladium once again. Similar results have been attributed to palladium poisoning as a result of exposure to mercury.

Heavier metal poisoning and main group metal poisons, in general, have shown similar effects on palladium catalysts in acetylene hydrogenation applications. They serve to slowly reduce the activity of the catalyst. As these species produce low volatility species during steam/air regeneration, their removal is particularly difficult. Thus, the activity of the catalyst is not restored, and the effects are permanent. The method by which these metals impact the activity will vary with the type of metals. Some metals may serve, as silver does, to improve the selectivity of the catalyst, but in doing so, severely affect the activity of the catalyst. Others may inhibit the ability of the catalyst to adsorb the acetylene or hydrogen on the surface of the catalyst, reducing activity. Some metals may also bind reaction modifiers like carbon monoxide so tightly that acetylene adsorption is severely retarded. Though the precise mechanism of inhibition may not be the same for each metal, the outcome is analogous—permanent reduction in catalyst activity.

Poison Diagnosis

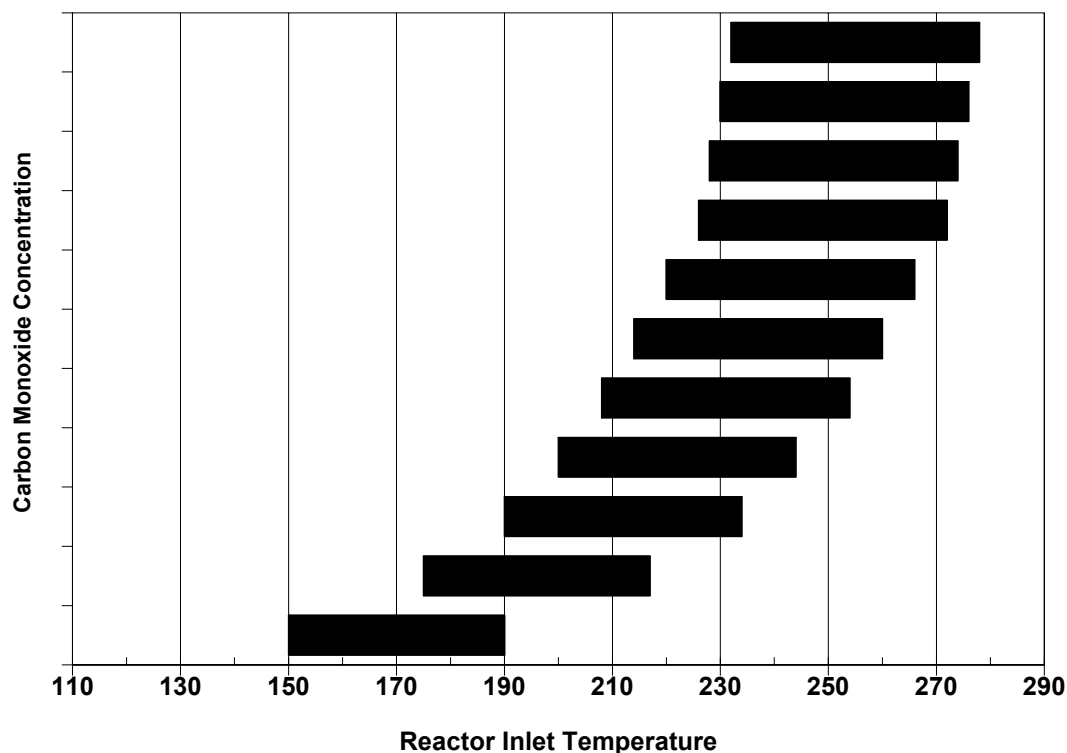
Table 5 outlines the short-term effects that various poisons will exhibit on the operation of acetylene hydrogenation reactors. In front-end reactors, carbon monoxide, methyl acetylene and propadiene commonly impact the operation of

Table 5. Short-term impact of poisons on acetylene converter operations.

Poison	Reactor ΔT	Outlet C2 \equiv	Response	Consequence
Steady CO, MAPD	stable	stable	none	life is good
Rising CO, COS	decreasing	increasing	increase inlet T	off-spec acetylene?
Falling CO, COS	increasing	decreasing	decrease inlet T	temp excursion?
H ₂ S, MeSH	decreasing	increasing	Increase inlet T	Off-spec acetylene?
O ₂	increasing	increasing	decrease inlet T	off-spec CO ₂ , lower inlet T after event
NH ₃ , NH ₂ R	decreasing	increasing	Increase inlet T	off-spec acetylene?
PH ₃ , PH ₂ R	decreasing	increasing	Increase inlet T	off-spec acetylene? decreased cycle time

the acetylene converters. These three chemicals are acetylene (and ethylene) adsorption inhibitors, and, as their concentration increases, the temperature needed to accomplish the same level of acetylene conversion will also increase. Figure 6 illustrates this point for carbon monoxide; however, the concept can be expanded to methyl acetylene and propadiene. This plot attempts to qualitatively outline the effects of changing carbon monoxide on a catalyst that has an

Figure 6. Effects of carbon monoxide on inlet temperature and operating window.



operating window of 40 °F at an inlet temperature of approximately 150 °F. As the CO concentration rises, the inlet temperature must rise to offset the reduced number of active sites available to the acetylene. Thus, the bars representing

the operating window appear as steps as the CO increases. A slight improvement on the operating window may be observed at low carbon monoxide levels; less impact will be observed at higher concentrations.

As the extent to which acetylene is hydrogenated is measured by the delta T, one will see this value diminish (in the short-term) if an increase in CO concentration is not compensated for by raising the inlet temperature to the reactors. However, as the inlet temperature is increased, and the extent of acetylene hydrogenation is equal, the reactor delta T should be similar. This may not be the case if the catalyst technology in place shows a dramatic dependence on carbon monoxide content of the feed.

The converse of this situation would be dropping carbon monoxide concentration in the feed. The consequences of this scenario can be far more serious. As the CO concentration drops, the activity of the catalyst increases. For example, assume that the reactor delta T is 25 °F on the “bottom step” in Figure 6. As the CO level increases, the same extent of hydrogenation is achieved on “step two” at the higher CO level. With the same delta T, but a 25 °F rise in the inlet temperature, the outlet temperature of the reactor would be 200 °F. If the carbon monoxide concentration returns to its previous level without removal of heat, one can see that the 200 °F lies far outside of the operating window of the bottom bar in Figure 6. This would produce a temperature excursion in the reactors. This type of situation can arise any time a sudden drop in carbon monoxide concentration occurs, and is highly dependent on the width of operating window of the catalyst.

Of course, this illustration is an oversimplification. The situation in this case would be exacerbated by the fact that more ethylene would be hydrogenated as the CO level drops, generating even more heat. The purpose of this discussion is to emphasize the importance of the catalyst’s operating window on safe and smooth acetylene converter operation.

The short-term influence of sulfur, nitrogen and phosphorus exposure will be similar. If the levels in the feed are low, one will see a diminishing of the delta T across the reactors, as fewer palladium sites on the catalyst are active toward acetylene adsorption and hydrogenation. This will be accompanied by a decrease in the acetylene converted in the reactors, ultimately requiring an increase in the inlet temperature to maintain the low acetylene concentration at the reactors’ outlet. For most of these poisons, the activity of the catalyst will be restored after the poison is removed from the feed stream.

Oxygen in the feed is one poison in which the palladium catalyst responds quite differently. Palladium will catalyze the oxidation of organic species in the reactors, generating more heat across the reactors as it does so. Palladium will oxidize carbon monoxide to produce CO₂, which may result in the feed containing an off-spec value for this species. Once the poison is removed,

assuming this has occurred prior to a temperature excursion, the catalyst performance may actually improve, with more activity and equivalent selectivity.

One semi-transient effect of carbon oligomerization on the catalyst will be a slow rise in the inlet temperature over time—or a rapid rise if a single, “catastrophic” event such as a temperature excursion has caused the formation. Accompanied with the decrease in the activity of the catalyst will be a rise in the delta T for the reactor beds. This results from the diminished selectivity that the catalyst will exhibit as coke is formed on its surface. As temperature excursions may also cause sintering of the supported palladium, this will also reduce the catalyst’s ability to selectively hydrogenate acetylene. Both of these effects may manifest as “hot spots” in the temperature profile of the reactor beds—a delta T of larger than 10 °F may be indicative of sintering of the palladium or copious amounts of coke formed in localized area of the beds. Highly localized coke formation may cause flow distribution problems that will manifest as these “hot spots.” In the palladium sintering case, the high delta T stems from excessive ethylene hydrogenation due to the loss in catalyst selectivity.

The short-term consequences of exposure to heavier metals, such as arsenic and mercury, would be similar to those detailed for sulfur, nitrogen and phosphorus above. However, the effects of these poisons will be permanent and the activity lost will not be completely recovered. As these poisons are heavier species, they are more likely to be present in reactors containing C3 streams. These poisons can present a particular challenge to ethylene producers who operate C3 and lighter types of reactors.

It is worthy to note that the ability only to cool the feed between beds can limit the operational flexibility in the three- and four-bed depropanizer units. The increased presence of poisons in this feed typically results in a more rapid deactivation of the catalyst in the lead bed. This produces a shortened lifetime for the catalyst in the lead bed compared to those in subsequent reactors in the same train. In some aspects, the lead bed serves as a guard bed for the other acetylene reactor beds. Replacement of only the catalyst in the lead reactor does not allow a similar operation of beds two and three after catalyst replacement. The “new” catalyst hydrogenates the acetylene at a much lower temperature, resulting in the existence of too little heat at the inlet of the second reactor to accomplish the conversion needed to meet acetylene specification. Without the ability to heat the feed between the beds, one must increase the conversion of the acetylene in the lead bed. With the limited operating window of some technologies, this can set up a very tenuous situation, prompting the question, “Will the catalyst have the operating window necessary to accomplish the conversion needed to drive the hydrogenation in subsequent reactors?” Thus, the selectivity of the catalyst one chooses for this type of reactor can be crucial to the success of the entire process.

Commercial Results

Table 6. Commercial palladium catalyst poisoned.

Poison Analysis	Sample A Poison Content (wt. %)	Sample B Poison Content (wt. %)
As	not observed	1.3 (ppm)
Hg	not observed	32.5 (ppm)
Ca	not observed	no analysis
Cl	not observed	no analysis
Fe	not observed	no analysis
K	not observed	no analysis
Mg	0.053	no analysis
Na	0.056	no analysis
Ni	not observed	no analysis
P	not observed	no analysis
S	not observed	no analysis
Si	not observed	no analysis
Ti	0.093	no analysis
carbon	no analysis	6.75

Table 6 outlines the poisons that were observed upon analysis of the catalyst samples at the end of their respective lifetimes from two different front-end depropanizer units. For analysis of metal contents greater than 500 ppm, X-ray fluorescence was employed, while lower level contaminants were quantified via ICP-MS.

The samples were selected to emphasize the more extreme nature of the depropanizer first application. In fact, we have seen carbon content in excess of ten percent

on a mono-metallic palladium catalyst in the acetylene converters in this type of ethylene plant.

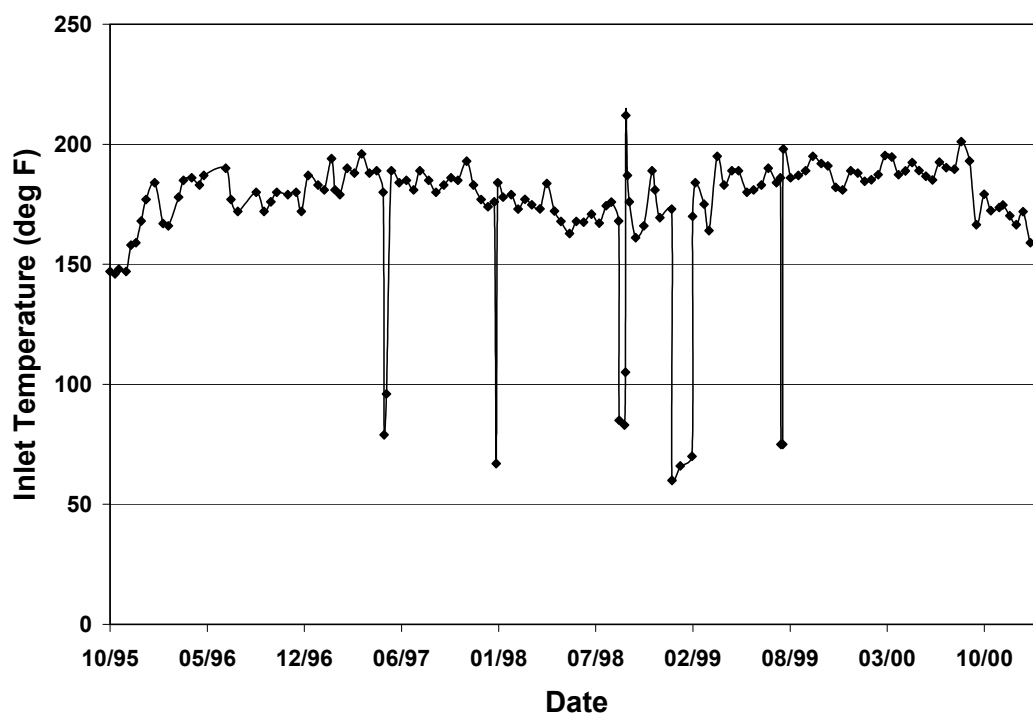


Figure 7. Inlet temperature versus date for the lead reactor in the acetylene converters at Sweeny Unit 24.

While these cases may be representative of the poisons that may be commercially experienced in the acetylene converters in a front-end depropanizer plant, exposure to metals poisoning of this type has not been evident at Chevron Phillips Chemical Company LP three front-end de-ethanizer plants in Sweeny, TX. These three units use our E-Series catalyst technology to selectively hydrogenate acetylene. The plot in Figure 7 emphasizes that, with the incorporation of proper poison mitigation techniques, coupled with the E-Series catalyst technology, the lifetime of a catalyst may exceed ten years. Unit 24 started up in October of 1995, had a turnaround in October of 1998, and its engineering group chose to continue with the same E-Series catalyst in place without regeneration, expecting to operate the reactor for five more years without changing the catalyst. The inlet temperature of the catalyst in the lead bed has been steady for over five years. Remarkably, the selectivity to ethylene has also remained steady over this period of time for the E-Series catalyst at Unit 24. Similar results have also been observed at the other acetylene converters at the Sweeny facility.

Table 7. Economic impact of catalyst selectivity on a 1.75 billion pound per year ethylene plant.

Input Parameters	Differential
Flow Across Reactor (lb/hr)	528,000
Inlet Acetylene (ppmv)	6000
Ethylene Margin (\$/lb)	0.07
Feed Average Molecular Weight (g/mol)	22.00
Ultimate Ethylene Yield (percent)	75
Selectivity (acetylene to ethylene)	75
Calculated Value	Results
Ethylene Make (lb/hr)	3029
Ethane Make (lb/hr)	3245
Yearly Production of Ethylene From Selectivity (lb)	26,537,544
Yearly Amount of Ethane Recycle (lb)	28,429,704
Yearly Additional Production of Ethylene From Reduced Recycle (lb)	21,322,278
Benefit From Enhanced Production of Ethylene (\$/yr)	\$1,857,628
Ethylene Benefit From Reduced Ethane Recycle (\$/yr)	\$1,492,559
Increased Ethylene Production (lb/yr)	47,859,822
Total Potential Savings (\$/yr)	\$3,350,188

Economic Impact of Catalyst Poisoning

The economic impact of acetylene reactors on unit operation is often underestimated. Table 7 shows how the difference in catalyst selectivity impacts the amount of ethylene that is produced by the reactors, along with ethylene

produce from diminished ethane recycle for a typical 1.75 billion pound per year (800 KTA) front-end depropanizer ethylene plant. The calculation shows that a differential in catalyst selectivity of 75 percent over its lifetime will result in an additional 48 million pounds per year (21.8 KTA) of ethylene—or over 2.7 percent of the plant's ethylene capacity.

It is worthy of note that these calculations do not take into account any additional benefits for the accompanied co-product formation (propylene, butadiene, BTX, hydrogen, etc.) as a result of increased ethane feed capability. Nor do the calculations account for reduction in the flaring of off-specification ethylene product. For a plant of this magnitude (200,000-lb/hr ethylene production) with an ethylene price of \$0.25/lb, the reduction of flaring by only ten hours per year will result in savings of \$500,000 for the year. The reduction of unplanned plant shutdowns due to temperature excursions will also add to the catalyst's impact.

While these numbers are dramatic, the greatest benefit that a plant may realize is the ease in operation of the reactors with a catalyst possessing increased selectivity and a larger operating window. Thus, the selectivity of the catalyst technology chosen and proper mitigation of poison exposure to the catalyst will have a tremendous economic impact on any ethylene unit in which the acetylene is hydrogenated.

Summary

While the configuration within which an ethylene producer's acetylene reactors are located may vary, the contaminants that affect the supported, palladium-based catalysts are quite similar. These poisons have been classified into three basic types, depending on the method of restoration of catalyst activity and selectivity. The types of poisons can be transient, semi-transient, or permanent. Common types of each of these poisons and their short- and long-term effects have been described.

The type of technology selected, as well as the methods employed for the mitigation of poison exposure, will affect the performance of acetylene converters. And, because of the economic impact that the selective hydrogenation of acetylene can have on the entire unit, careful consideration of the reactors' performance should be taken when selecting from the technologies available.

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