



## **Progress in the Development of E-Series Catalyst Technologies for the Selective Hydrogenation of Acetylene in Various Hydrocarbon Streams**

Presented at the Thai Olefins Ethylene Technology Forum (October 2001)

Darin B. Tiedtke, Ph. D.  
Chevron Phillips Chemical Company LP  
Houston, TX, USA

Joe J. Bergmeister, Ph. D.  
Chevron Phillips Chemical Company LP  
Kingwood Technical Center, Kingwood, TX, USA

T. T. Peter Cheung, Ph. D.  
Chevron Phillips Chemical Company LP  
Kingwood Technical Center, Kingwood, TX, USA

Robert A. Rhoades  
Chevron Phillips Chemical Company LP  
Arvada, CO, USA

## Introduction

The effective removal of acetylene via selective catalytic hydrogenation is of particular challenge to ethylene producers. With over 20 years of experience in acetylene hydrogenation catalyst development and nameplate capacity of greater than 3,700 metric tons per year,<sup>1</sup> Chevron Phillips Chemical Company LP possesses the unique position to share our expertise in catalyst development as well as commercial experience with the E-Series catalyst technology.

As a consequence of operating three world-class ethylene units with a front-end de-ethanizer design, initial catalyst pursuits focused on the improvement of technologies for the selective hydrogenation of acetylene in  $\alpha$ -C<sub>2</sub> and lighter applications. Efforts in this area produced the first silver-promoted palladium catalysts, which are still widely used in a variety of acetylene hydrogenation applications today.<sup>2</sup> Chevron Phillips licensed this silver-promoted, palladium catalyst technology to Süd Chemie for use worldwide in all configurations of ethylene facilities under their trade names of G-83C, G-58D, G-58I, G-58F, etc. Due to limitations of this silver-promoted catalyst technology, Chevron Phillips developed the E-Series catalyst technology and made the business decision to market this new technology directly rather than license it to Süd Chemie or any other catalyst manufacturer. The initial formulations of E-Series catalyst were developed for the hydrogenation of acetylene in C<sub>2</sub> and lighter feed streams.

Building on the tremendous success in catalyst development for the front-end de-ethanizer application, our research efforts have expanded in focus to include the commercialization of technologies in areas of C<sub>3</sub> and lighter, raw gas and back-end applications. This paper will provide a brief summary of Chevron Phillips' endeavors in the development and commercialization of these technologies.

## Methods of Acetylene Hydrogenation

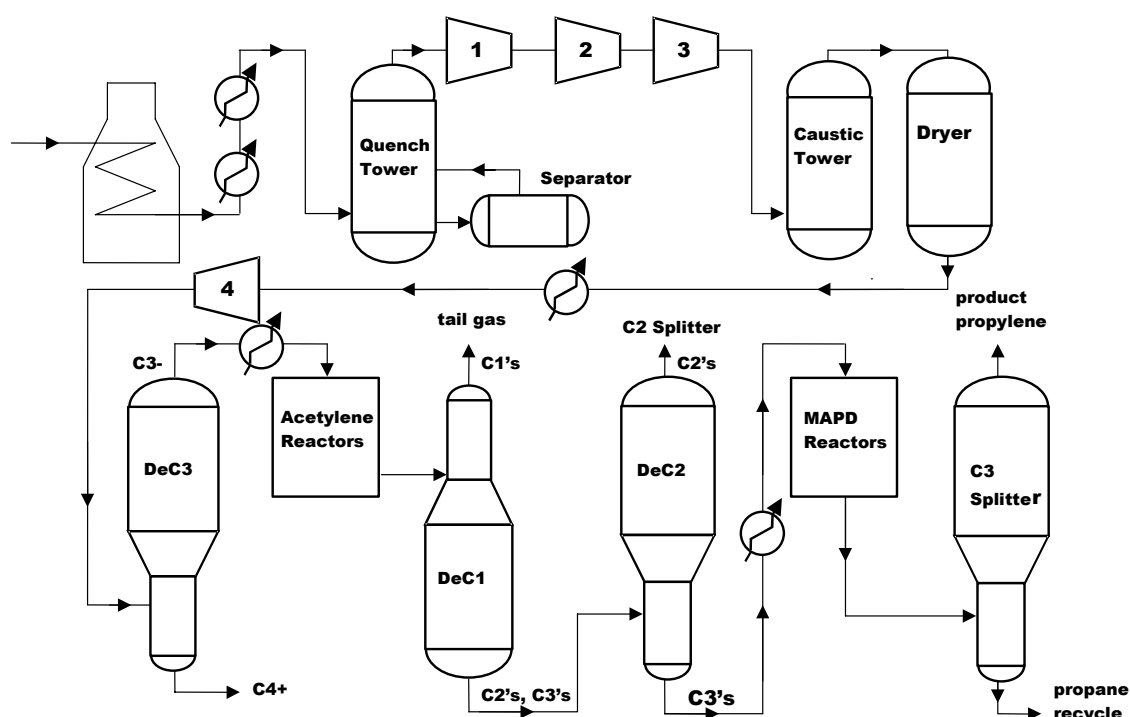
In the purification of the product ethylene, acetylene is hydrogenated in varying hydrocarbon feeds as the result of different types of plant configurations. Listed below are these types of plant configurations, followed by a brief description of the position of the acetylene removal units in these configurations.

1. Front-End Selective Catalytic Hydrogenation Reactors
2. Back-End Catalytic Hydrogenation Reactors
3. Cracked Gas Train or Raw Gas Catalytic Hydrogenation Reactors

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 40 mol percent. In a front-end de-ethanizer design, the de-ethanizer is the first distillation column and

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.

In back-end 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.



**Figure 1. Acetylene reactors' location in a qualitative depiction of a front-end depropanizer plant configuration.**

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 more selective palladium technologies is occurring. In raw gas applications where the reactors precede the caustic tower, effective utilization of palladium catalysts 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.

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

Feed Component	Back-end (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	75.0	34.0	32.5
Ethane	24.0	22.0	5.5
Methyl Acetylene			0.3
Propadiene			0.3
Propylene		0.08	19.0
Propane			0.8

the operations and economics of these front-end units. Thus, the perspective of this paper will begin with front-end hydrogenation catalyst technology and progress to our back-end catalyst development efforts.

### Hydrogenation in Front-End Acetylene Reactors

It is generally accepted that reactants like acetylene first adsorb on the palladium metal sites on the catalyst.<sup>3</sup> The adsorption process activates the reactants, which subsequently react with hydrogen to form the hydrogenation products. The 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 is ethylene, even though the intrinsic rate of hydrogenation of ethylene is two orders of magnitude faster than that of acetylene.<sup>4</sup> So long as there are sufficient acetylene molecules available to cover 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.<sup>5,6</sup>

CO > acetylene >> conjugated diolefins ≥ 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.

Chevron Phillips Chemical Company LP has operated front-end hydrogenation reactors for over 30 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

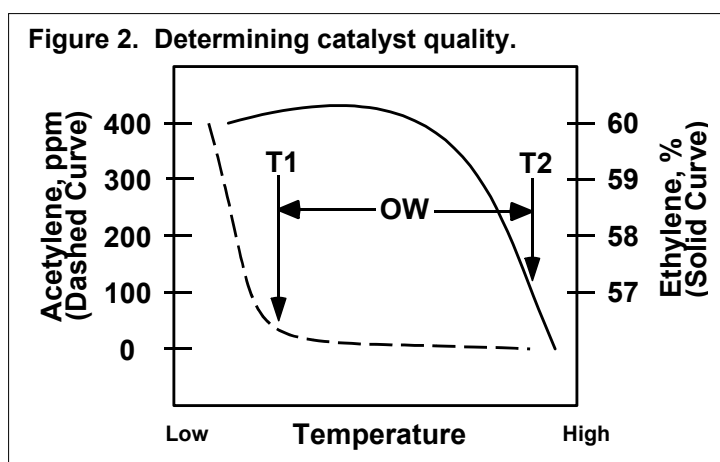
The adsorption mechanism also explains the tempering effect of methyl acetylene and propadiene (MAPD) in front-end depropanizer acetylene converters. In particular, methyl acetylene replaces the acetylene at the reaction sites as the acetylene is hydrogenated. So long as there is methyl acetylene (or 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. E-Series 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 preserved with the E-Series catalyst versus traditional Ag/Pd catalysts. Again, this is attributed to the catalyst's efficiency in adsorbing these types of species on the catalyst surface.

### Analysis of a Catalyst's Performance

One of the most useful tools in the development of new catalyst technology is the ability to evaluate the activity and selectivity of a 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 2. 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. (Typical feed compositions for the laboratory experiments are shown in Table 2.) The effluent of the reactor is analyzed using gas chromatography. The reactor is slowly warmed while monitoring the effluent gas composition. When the feed typically contains less than 20 parts per million weight (ppmw) acetylene in the gas, this temperature is described as the "clean-up" temperature and assigned the value of T1. While 20 ppmw 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. Further, the reactor is heated and loss of ethylene continues to occur. When this loss totals three weight percent of the ethylene in the feed gas 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, which is reflected in the OW

**Table 2. Feed composition as a function of laboratory test.**

Feed Component	C2 and lighter (mol %)	C3 and lighter (mol %)
Hydrogen	26	22
Carbon Monoxide	0.030	0.020
Methane	39	44
Acetylene	0.35	0.27
Ethylene	35	27
Ethane	0	0
Methyl Acetylene		0.10
Propadiene		0.10
Propylene		7

value. A lower T1 temperature correlates with a catalyst that is more active, while a larger operating window denotes a catalyst that is more selective in the hydrogenation of the acetylene in the feed.

The feed compositions for the laboratory testing are listed in Table 2. Notice that the ethane that is typically present in the plant feeds is replaced with methane in the laboratory. This

allows the ethylene hydrogenation reaction to be more easily monitored by gas chromatographic methods.

## Laboratory Results

Table 3 displays the results for commercial catalyst samples 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

**Table 3. Front-End De-Ethanizer Catalyst Comparison.**

<u>Catalyst</u>	<u>T1 (°C)</u>	<u>OW (°C)</u>
<b>E-Series</b>	<b>46.1</b>	<b>38.9</b>
<b>Ag/Pd</b>	<b>44.4</b>	<b>22.2</b>
<b>Pd only</b>	<b>40.6</b>	<b>16.1</b>

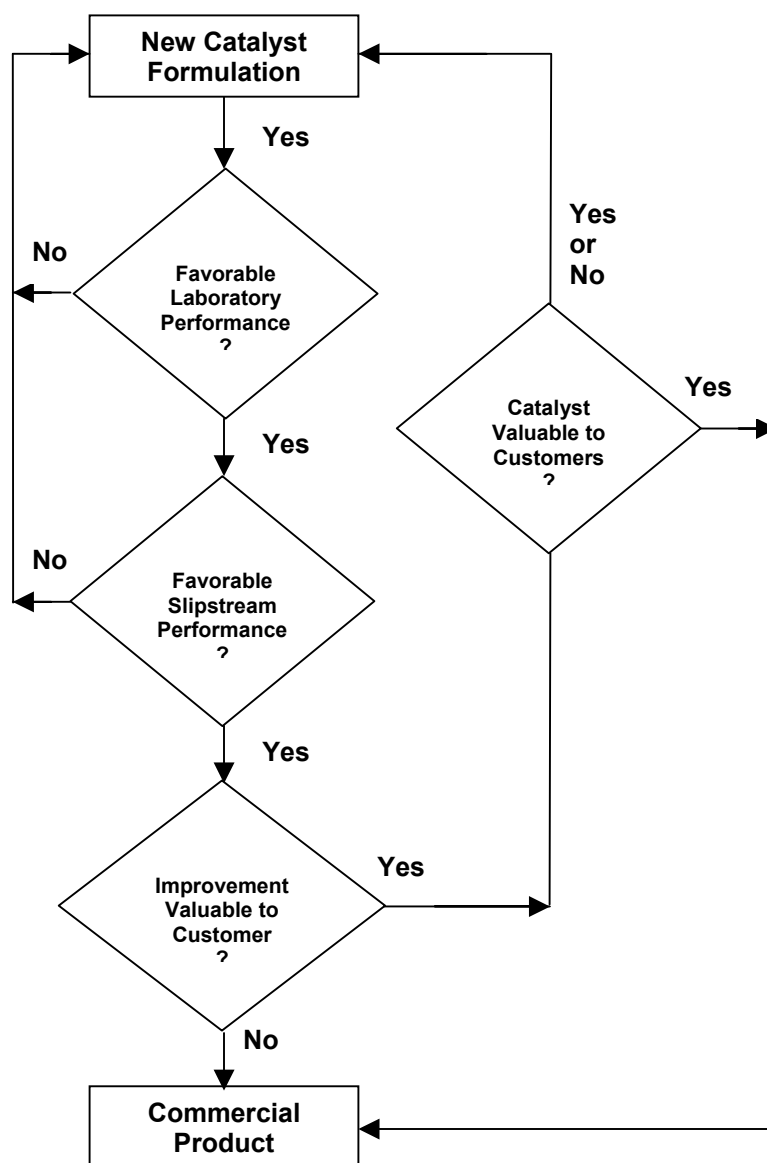
**Table 4. Front-End Depropanizer Catalyst Comparison.**

<u>Catalyst</u>	<u>T1 (°C)</u>	<u>OW (°C)</u>
<b>E-Series</b>	<b>53.3</b>	<b>32.4</b>
<b>Ag/Pd</b>	<b>56.1</b>	<b>21.1</b>
<b>Pd only</b>	<b>51.1</b>	<b>17.8</b>

the E-Series catalyst is almost two-and-a-half times that of the monometallic palladium catalyst and nearly twice that of the typical silver-promoted technology.

Similar results have been observed for laboratory testing of front-end depropanizer formulations of the E-Series catalyst. The data are displayed in Table 4. Again, the E-Series catalyst possesses a significantly larger operating window than competitive catalyst technologies. Further, the values for the operating window of this catalyst technology have continued to rise in our laboratories as improved and optimized formulations are being produced.

**Figure 3. Catalyst development flowchart.**



### **From Laboratory Catalyst to Commercial Formulation**

While the method of catalyst analysis described above assists in the development of laboratory catalysts, commercial success is more easily achieved with support from other experiments. One of the most valuable tools in the

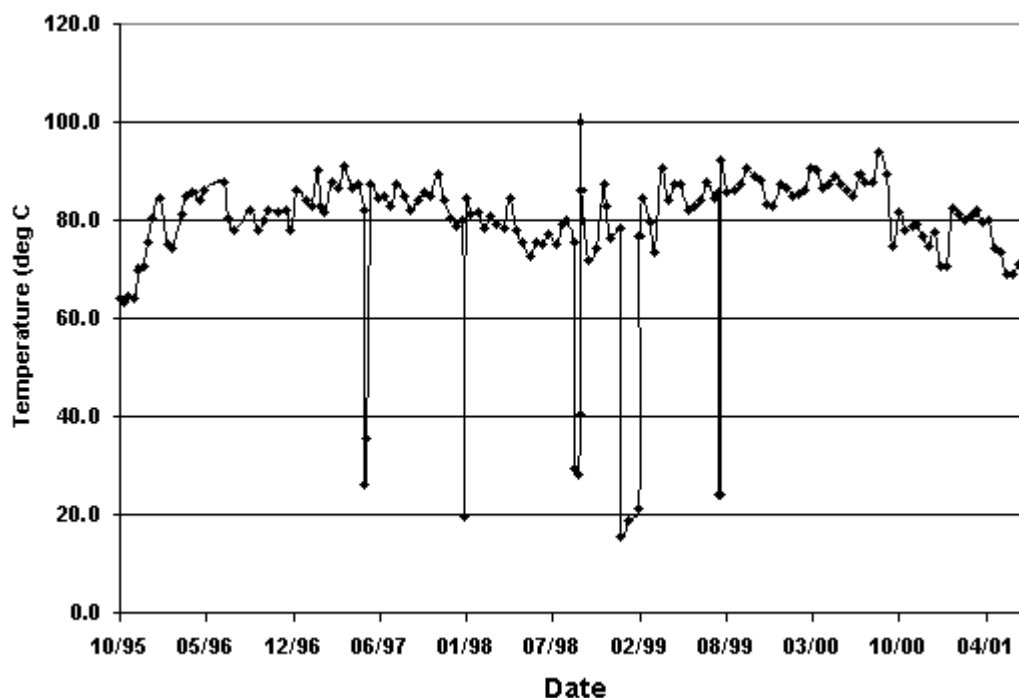
catalyst development arsenal is the examination of the laboratory catalyst formulations in slipstream reactors throughout the industry. The feeds used in the laboratory experiments are relatively poison-free. While experiments have been performed in Chevron Phillips' laboratories that mimic poisons that exist in various type of commercial feeds,<sup>7</sup> studies of the long-term effects of the feed components on the catalyst are best suited for small, slipstream reactor units.

Figure 3 depicts the typical pathway that a catalyst formulation follows on its course to commercial production and sale. The flowchart may be oversimplified; however, it gives one a feel for the process. Also factored into this process is the performance of specific formulations in commercial units for our development direction.

### Commercial Performance of E-Series Catalyst

The impetus for the original E-Series catalyst development was to improve the reactors' performances at Chevron Phillips' ethylene facility in Sweeny, TX. Three units with front-end de-ethanizer reactors at this site use E-Series catalyst technology to selectively hydrogenate acetylene. The plot in Figure 4 shows the inlet temperature for the lead reactor at Unit 24. These data emphasize that the

Figure 4. Inlet temperature for lead reactor at Sweeny Unit 24.



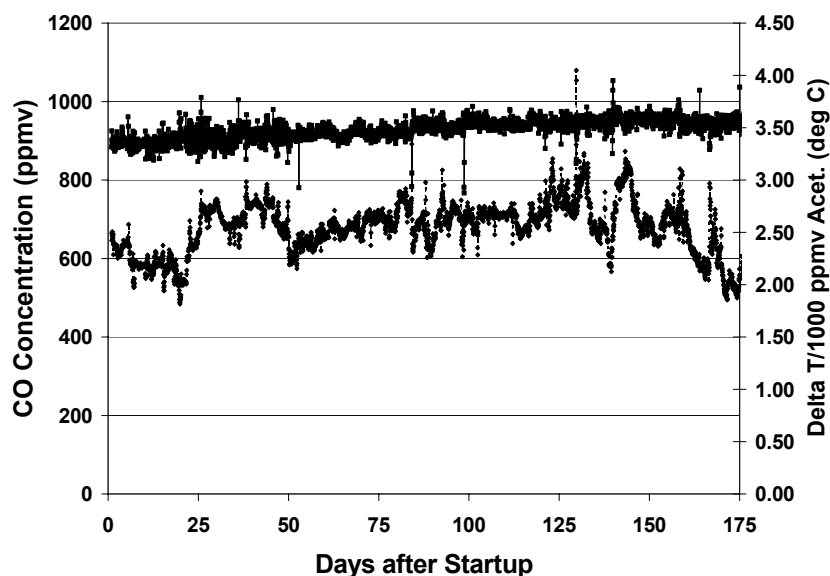
lifetime of the E-Series catalyst may exceed ten years. Unit 24 started up in October of 1995 and had a turnaround in October of 1998. The engineering group from this unit chose to continue with the same E-Series catalyst in place without regeneration, expecting to operate the reactor for five more years without

changing the catalyst. The inlet temperature of the catalyst in the lead bed has been steady for nearly six 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.

Using the E-Series catalyst for front-end de-ethanizer facility as a reference point, the technology has grown to include formulations providing superior performance for front-end depropanizer facilities, and soon to be in service in raw gas applications. Early experiments are also showing benefits of E-Series catalyst technology in back-end configurations as well.

Figure 5 shows the performance of an E-Series catalyst for a front-end depropanizer application. The data emphasize that the selectivity of the catalyst is constant over the catalyst lifetime, which is the case with the de-ethanizer

**Figure 5. Selectivity of E-Series catalyst in C3 and lighter application.**

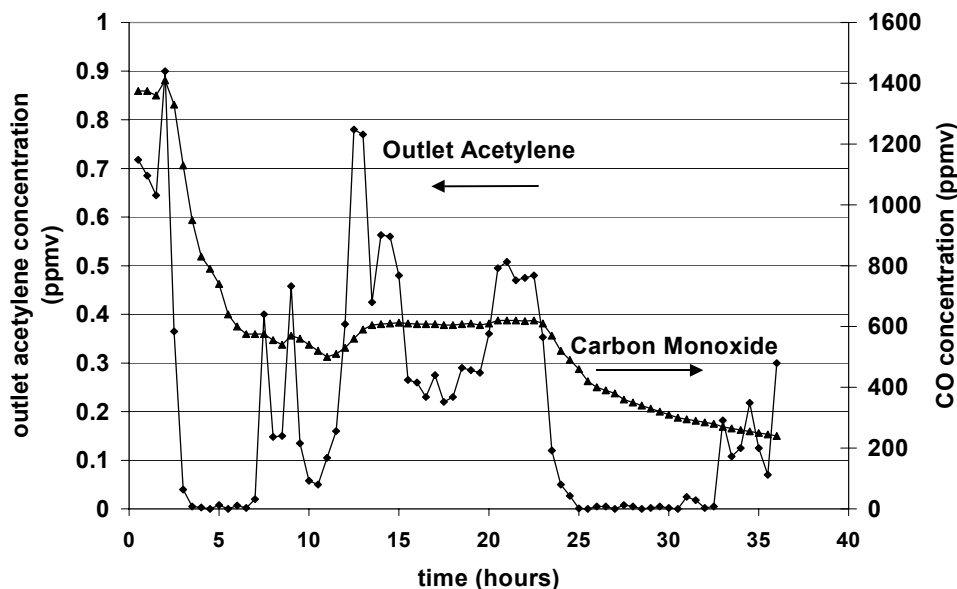


version. It is worthy of the note that as the CO level decreases to the right in this graph, the delta T per 1000 ppmv acetylene also rises slightly. This is attributable to the fact that as the CO concentration in the feed dropped, more methylacetylene and propadiene (MAPD) are adsorbed onto the catalyst surface and, subsequently, hydrogenated. The increased MAPD conversion is reflected in the slight rise in this delta T value. However, the selectivity was constant during this period.

## Influence of Carbon Monoxide on E-Series Catalyst

An understanding of how carbon monoxide influences a palladium-based acetylene hydrogenation is crucial to the successful operation of these types of

**Figure 6. Outlet acetylene, as a function of CO concentration, for a commercial application using E-Series catalyst.**



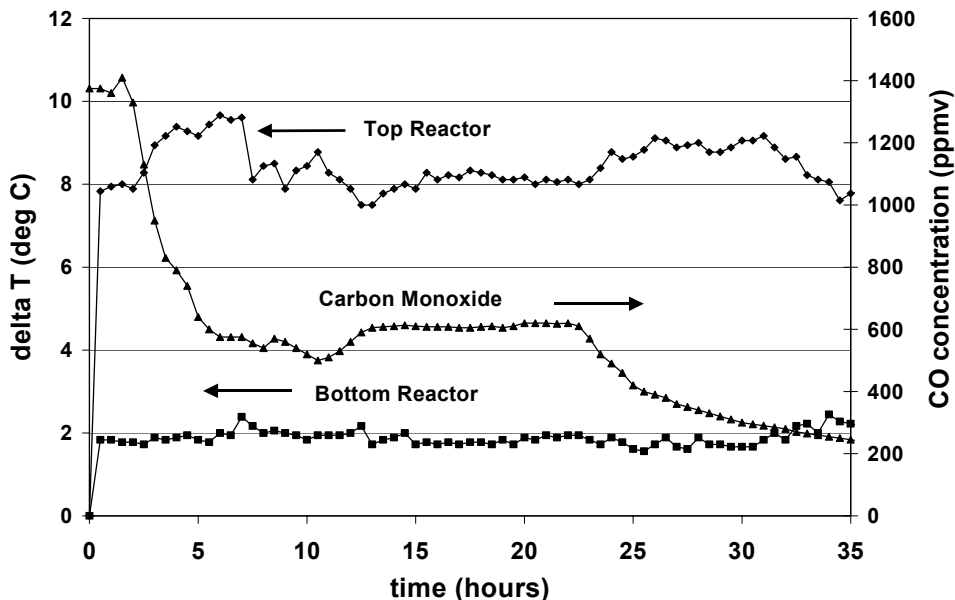
reactors. As CO adsorbs to palladium-based catalysts more strongly than acetylene, the influence that it exerts on the catalyst can be extremely strong. However, this influence is also technology dependent. The E-Series catalyst, with its proprietary promoter content, was designed to minimize the sensitivity to carbon monoxide concentration in the feed. The result is that E-Series catalyst exhibits a reduced dependence on catalyst activity as a function of the concentration of CO in the feed stream when compared to competitive technologies.

Figure 6 shows commercial reactor data from Chevron Phillips' Ethylene Unit 33 in Sweeny, TX. This plot displays the variation in the carbon monoxide concentration on the right axis while the outlet acetylene concentration is plotted on the left axis. During this 35-hour time period, the reactors maintained the acetylene specification in the product ethylene. One can also note from Figure 6 that during several time periods, the acetylene concentration at the outlet of the second reactor was less than 0.0 ppmv—a clear indication of a potential for over-hydrogenation of ethylene.

However, examination of Figure 7 indicates that this was not the case. This graph shows that even when the CO dropped from approximately 1400 ppmv to 500 ppmv (from hours 0 to 10) and the outlet acetylene dropped to less than 0.0 ppmv (from hours ~3 to ~7), very little hydrogenation of ethylene occurred. This is reflected in the less than two-degree jump in the lead reactor

delta T during this period, with very little variation in the delta T for the second bed. The steady delta T for the reactors indicates that the selectivity of the

Figure 7. Selectivity, as a function of CO concentration, for a commercial application using E-Series catalyst.

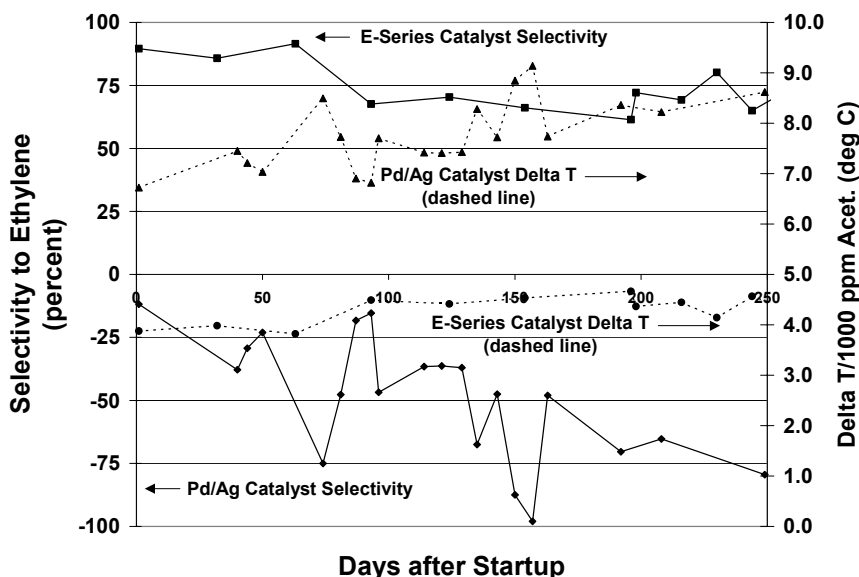


catalyst was remarkably constant during this event. (A similar event also occurred from hours ~24 to ~33 with the same results.)

### Front-End Technology Comparisons

The unique position as operator and developer of this catalyst technology has also allowed Chevron Phillips the opportunity to compare various types of

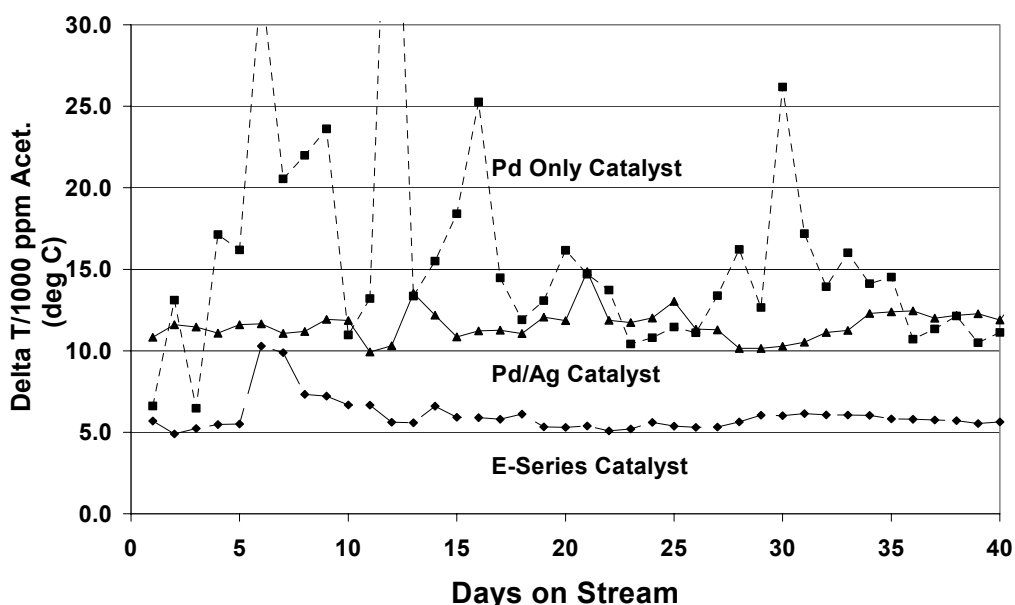
Figure 8. Comparison of Catalyst performances at Sweeny Unit 33.



E-Series Catalyst

catalyst technologies. The plot in Figure 8 shows a comparison of the E-Series catalyst for Sweeny Unit 33 accompanied by a similar run using a Pd/Ag catalyst. This application is one in which a C2 and lighter gas is fed to the reactors. The plot displays the selectivity, calculated using a thermodynamic model, and the delta T per 1000 ppmv acetylene hydrogenated for both technologies. It is evident from the graph that the delta T's are considerably lower for the E-Series catalyst when compared to the Pd/Ag version, which is also reflected in the higher selectivity to ethylene for the E-Series catalyst. This is one of many pieces of data that support the laboratory methods for analysis of these types of catalysts that were discussed in an earlier section of this paper. It is also apparent from this plot that the Pd/Ag catalyst shows a rather rapid decline in the selectivity over time; however, this is not the case with the E-Series catalyst. This catalyst has shown constant selectivity throughout the more than five-year cycle on Sweeny Unit 24, and the same has been seen at the other units at this facility.

Figure 9. Catalyst technology comparison in a C3 and lighter application.



In May of 2000, Chevron Phillips executed the first sale of E-Series catalyst for use on a C3 and lighter feed to Equistar Chemical Company for use at its Lake Charles, Louisiana plant. This culminated years of extensive research into the understanding of the different properties that this catalyst would need in comparison to the E-Series catalyst in C2 and lighter feeds. Since that time our list of customers for this application has grown to include The Dow Chemical facility in Freeport, TX, The Dow Chemical Company in Terneuzen, Holland, and Titan Petrochemical Company in Malaysia. While the two versions (“front-end de-ethanizer” and “front-end depropanizer”) of E-Series catalyst are very similar, the subtle differences are significant for success in this type of application.

E-Series Catalyst

In Figure 9 a plot of the performance of three different types of catalyst technologies are shown for one our “depropanizer” customers. This graph once again emphasizes the improved selectivity in the progression from a Pd only catalyst to a Pd/Ag catalyst and further to an E-Series catalyst. Notably, the delta T per 1000 ppmv acetylene decreases in that order, which translates to less hydrogenation of ethylene in the feed to the reactors. It is also noteworthy in this graph that the difference in the delta T’s for the Pd only and Pd/Ag catalyst is unexpectedly small. As has been detailed previously, this type of behavior has been observed in the laboratory with silver-promoted catalysts in the presence of carbonyl sulfide (COS). These experiments are also described in reference 7. This paper also details how Chevron Phillips has developed catalyst formulations in which the effects of COS on the catalyst performance are minimized.

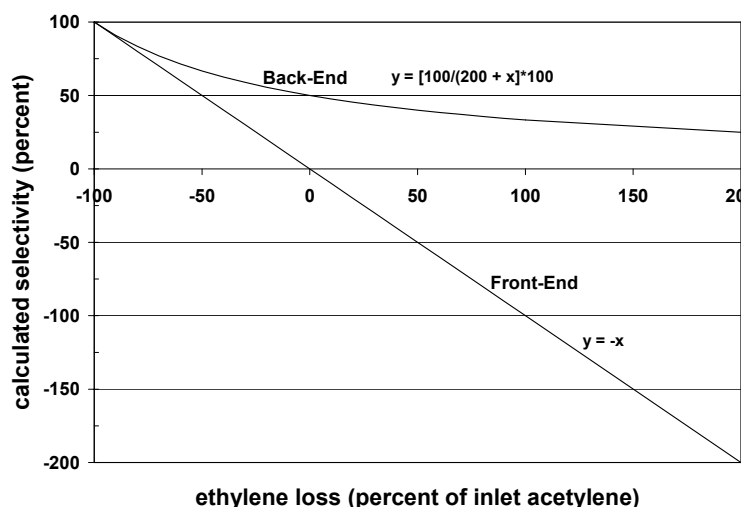
## Raw Gas Catalyst Developments

Chevron Phillips has also developed palladium-based catalysts for use in raw gas applications and has tested formulations in slipstream reactors at three commercial ethylene facilities worldwide. The product of this work was the recent agreement for sale of E-Series catalyst to Eastman Chemical Company. The startup for the reactors at this facility is scheduled for the fourth quarter of 2001 or the first quarter of 2002.

## Selectivity Calculation Conventions

The selectivity of a catalyst is often used to gauge the performance of catalyst technologies in the hydrogenation of acetylene. It is common to express this value in terms of “selectivity to ethylene” in front-end plants, where 100%

Figure 10. Selectivity values as a function of ethylene loss.



selectivity represents production of only ethylene from the acetylene while 0% represents the point at which ethane gain begins in the effluent stream. However, it is common, particularly in back-end plants (and by some front-end users as well), to use a different convention for selectivity calculation. In this convention, conversion of the feed

components to ethane begins below 50%. This type of calculation is represented by equation 2 below. In this convention, there is a reciprocal relationship

between ethylene loss and the calculated selectivity, which results in diminished sensitivity to the loss of ethylene at low selectivity. With the front-end convention, a differential in calculated selectivity will always represent the same amount of ethylene loss/gain. This is evident from the plot in Figure 10.

The clarity of the front-end type calculation and its linearity with respect to ethylene loss make this convention appealing. The section below describes the manner in which the “back-end selectivity” may be converted to “front-end” values for selectivity (equation 6). Also included are a description of the individual selectivity equations and the derivation of this equation.

$$F = \text{“front-end selectivity”} = \{[1 - (B - A)/A]\} * 100\% \quad (1)$$

$$T = \text{“back-end selectivity”} = A/B * 100\% \quad (2)$$

where A = molar acetylene conversion

B = molar hydrogen consumed, or

B = molar acetylene conversion + molar ethylene loss, or

B = molar acetylene conversion + molar ethane production

Thus,

$$B - A = \text{molar ethylene loss} = \text{molar ethane gain}, \quad (3)$$

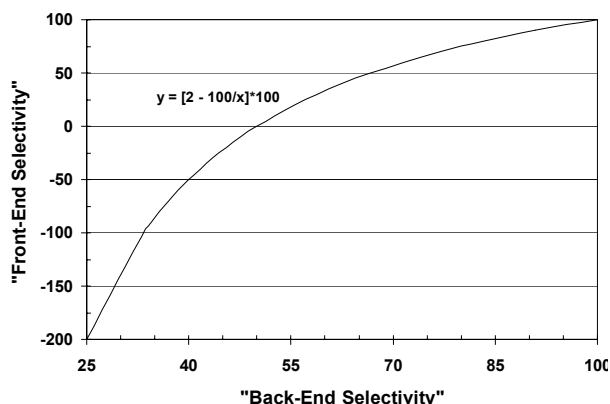
Rearranging equation one yields,

$$F = [1 - (B/A - 1)] * 100\% \quad (4)$$

Expressing B/A in terms of T in equation 2 gives,

$$B/A = 100\%/T \quad (5)$$

**Figure 11. Comparison of “back-end” versus “front-end” selectivity values.**



Substituting the value for the B/A term into equation 4 produces,

$$F = [2 - (100\%/T)] * 100\% \quad (6)$$

A direct comparison of the two types of selectivity calculations is shown in Figure 11. In practice, both of the selectivity values are normally derived from thermodynamic calculations of ethylene loss using the

temperature differential across the reactors. This method has proven to be the most reliable for accurate assessment of catalyst and reactor performance.

### Economic Impact of Catalyst Performance

The economic impact of acetylene reactors on unit operation is often underestimated. Table 6 shows how the difference in catalyst selectivity impacts

**Table 6. Economic impact of catalyst selectivity.**

<b>Input Parameters</b>	<b>Basis</b>
Flow Across Reactor (kg/hr)	240,000
Inlet Acetylene (ppmv)	6000
Ethylene Margin (\$/kg)	0.15
Feed Average Molecular Weight (g/mol)	22.00
Ultimate Ethylene Yield (percent)	75
<b>Differential Selectivity (acetylene to ethylene)</b>	<b>75</b>
<b>Results</b>	<b>Differential</b>
Ethylene Make (ppmv)	4500
Ethane Make (ppmv)	1500
Ethylene Make (kg/hr)	1377
Ethane Make (kg/hr)	492
Yearly Additional Production of Ethylene From Selectivity (kg)	12,062,520
Yearly Amount of Ethane Recycle (kg)	4,307,531
<b>Benefit From Enhanced Production of Ethylene (\$/yr)</b>	<b>\$1,809,378</b>
<b>Benefit From Reduced Ethane Recycle (\$/yr)</b>	<b>\$1,453,792</b>
<b>Increased Ethylene Production (kg/yr)</b>	<b>21,754,465</b>
<b>Total Potential Savings (\$/yr)</b>	<b>\$3,263,170</b>

the amount of ethylene that is produced by the reactors, along with ethylene produced 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 21.8 kilotons per year 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 reduced utility costs for reduced ethane

recycle or a reduction in the flaring of off-specification ethylene product. For a plant of this magnitude (90,000-kg/hr ethylene production) with an ethylene price of \$0.55/kg, the reduction of flaring by only ten hours per year will result in savings of \$500,000 for the year. Faster startups using E-Series catalyst and also a reduction of unplanned plant shutdowns due to temperature excursions will also add to the catalyst's impact.

While the economic 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 performance of the catalyst technology selected will have a tremendous economic impact on any ethylene unit in which the acetylene is hydrogenated. The various benefits are summarized below.

**Enhanced Selectivity**

- 1) increased production of ethylene
- 2) increased co-product production
- 3) less ethane recycle
- 4) constant selectivity throughout run

**Improved Operability**

- 1) ease in startup (faster on-specification time)
- 2) excellent response to CO swings
- 3) reduced off-specification production
- 4) fewer reactor shutdowns
- 5) minimal risk of thermal runaway
- 6) better resistance to poisons
- 7) longer run length

## Commercial Users of E-Series Catalyst

Table 7 lists the commercial user of E-Series catalyst technology—including customers who will be starting their acetylene hydrogenation reactors with E-Series catalyst in service in the near future. The success of the

**Table 7. Commercial users of E-Series catalyst technology.**

Company	Location	Start Date	Application	Comment
Chevron Phillips-Sweeny Unit 24	Texas (USA)	Oct-95	de-ethanizer	-
Chevron Phillips-Sweeny Unit 22	Texas (USA)	Sep-98	de-ethanizer	-
Dow Chemicals Canada Inc.	Canada	Sep-98	de-ethanizer	-
Equate-Kuwait	Kuwait	Apr-99	de-ethanizer	-
Chevron Phillips-Sweeny Unit 33	Texas (USA)	Oct-99	de-ethanizer	-
Nova Chemicals Ltd.	Alberta (Canada)	Aug-00	de-ethanizer	-
The Dow Chemical Company-PBB SAIC	Argentina	Mar-01	de-ethanizer	-
BP	Scotland	Aug-01	de-ethanizer	-
Chevron Phillips-Q-Chem	Qatar	Aug-02	de-ethanizer	-
Equistar	Louisiana (USA)	May-00	depropanizer	-
The Dow Chemical Company	Texas (USA)	Nov-00	depropanizer	lead bed only
Titan Petrochemical Company	Malaysia	Mar-01	depropanizer	lead bed only
The Dow Chemical Company	The Netherlands	Nov-01	depropanizer	-
The Dow Chemical Company	Texas (USA)	Dec-01	depropanizer	all beds
Eastman Chemical Company	Texas (USA)	Jan-02	raw gas	-

technologies is apparent from the extensive list of customers that has grown rapidly in the short time that the catalyst has been offered commercially.

## Summary

While many factors can influence the performance of the acetylene reactors (CO concentration, poison exposure, tightening acetylene specifications, etc.), the catalyst technology that a commercial producer selects will have the most dramatic impact—both operationally and economically. With over 30 years of acetylene hydrogenation catalyst operational experience, Chevron Phillips has a unique understanding of the operational needs of commercial ethylene producers. It is this perspective that has led us over the past 20 years, and will continue to lead us, to develop improved catalyst technologies. The product of these efforts is the E-Series line of acetylene hydrogenation catalysts. Laboratory and commercial reactor data comparisons show that the E-Series catalyst performs far superior to traditional Pd only or Pd/Ag catalyst technology.

---

## References

1. Oil and Gas Journal, April 23, 2001.
2. "The Effects of Silver Loading on Selective Hydrogenation Catalysts" prepared for the Süd Chemie Group, The 2<sup>nd</sup> Asian Ethylene Plant Catalyst Symposium, November 11-14, 1996, Fukuoka, Japan.
3. Lam, W. K., "Theory and Reaction Mechanisms for Commercial Selective Catalytic Hydrogenation Reactors," presented at the Petrochemical Session at PACHEC, October 19-21, 1988.
4. Bond, G. C. and Wells, P. B., *Advances in Catalysis*, vol 15, pp 9-226, Academic Press 1964.
5. Bond, G. C. and Sheridan, J., *Trans. Faraday Society*, **48**, 1952, p. 651.
6. Hall, J. B., Huggins, B. J., Kaminsky, M. P., and Meyers, B. L.; "Deactivation Mechanisms for Pd/Al<sub>2</sub>O<sub>3</sub> Acetylene Hydrogenation Catalysts," presented at the AIChE Spring National Meeting, 1994, Atlanta.
7. Tiedtke, D. B., Cheung, T. T. P., Leger, J., Zisman, S. A., Bergmeister, J. J., Delzer, G. A., "Chemicals Influencing the Activity of Palladium-Based Catalysts for the Selective Hydrogenation of Acetylene to Ethylene in Acetylene Converters," presented at the Petrochemical Session at the AIChE Spring National Meeting, April, 2001.
8. Experimental: Runs were made as follows. The catalyst was mixed with two times its volume of alundum and placed in a stainless steel jacketed reactor tube having an inner diameter of 1.9 cm. The catalyst was placed in the middle of the reactor, and the ends of the reactor were packed with approximately half the catalyst volume of alundum. Circulating ethylene glycol through the jacket of the reactor tube controlled the temperature. The catalyst was activated in a stream of hydrogen.

The catalyst was then contacted with the feed gas (approximately: ~15 wt% methane, ~85 wt% ethylene, ~1.1 wt% acetylene) at 13.8 barg. The reactor temperature was adjusted to yield 80% conversion of the acetylene. When the conversion of acetylene fell below 60%, the reactor temperature was increased to re-establish 80% conversion. Reactor effluent analyses were performed by gas chromatography.

Selectivity was calculated on a weight basis. Deactivation rates were calculated as the loss in conversion per unit time. Green oil makes were determined by the weight gain of the catalyst during the run.