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## Catalyst Selection – A Refiner's Perspective

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## Catalyst Selection – A Refiner’s Perspective

**George Hoekstra, Hoekstra Trading LLC**

The refining industry is fortunate to have the catalyst suppliers as our partners. They have been leaders in developing new technology for refining. Some of their innovations have been worth billions. Let’s look at one story of a billion dollar innovation.

This story begins in 1998. It was a time of oil industry layoffs, mergers, and restructurings. The refining business was starving for profits.

This was the environment in 1998, when Akzo Nobel introduced their STARS hydroprocessing catalysts.

### STARS catalysts

Figure 1 is an excerpt from a 1999 Akzo NPRA paper published shortly after the rollout of their STARS catalyst KF 757.

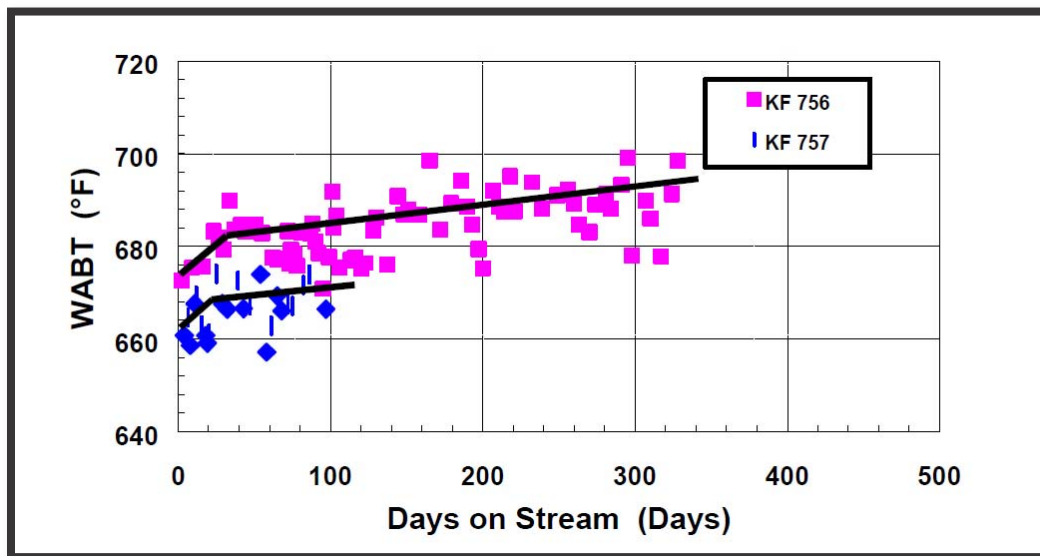


Figure 1 Excerpt from Akzo Nobel / Nippon Ketjen NPRA paper AM99-40 (ref 1) shows better performance of KF 757 compared to KF 756

The chart shows reactor temperature versus time for a commercial diesel hydrotreater. The blue data show an unmistakable improvement for the new KF 757 STARS catalyst, compared to the previous catalyst. It’s rare to see such clear separation in commercial data. This unit was on its way to doubling cycle life.

When Akzo rolled out STARS in 1998, they released a lot of pilot plant and commercial data that made it very clear this was a breakthrough innovation. Four years later, in 2002, STARS catalysts were in 60 commercial units.

Then in 2004, when ultra-low sulfur diesel came in the USA, STARS catalysts and similar competitive products swept through the industry by stampede, in what was to be a billion dollar innovation.

### **Type II catalysts**

The name STARS is an acronym which stands for Super Type II Active Reaction Sites. The science behind STARS involves forming a stable cobalt moly disulfide nanostructure called a Type II reaction site. Type II technology is what made STARS a breakthrough; and to really understand the story of this billion dollar innovation, we have to turn the clock back further, to research done by Haldor Topsoe in the 1980's. Figure 2 is an excerpt from a 1984 Haldor Topsoe paper presented at the 9<sup>th</sup> Iberoamerican Symposium on Catalysis, Lisbon, Portugal, July 16, 1984. There are 2 lines on the chart; the lower line is labeled Type I, and the upper line Type II.

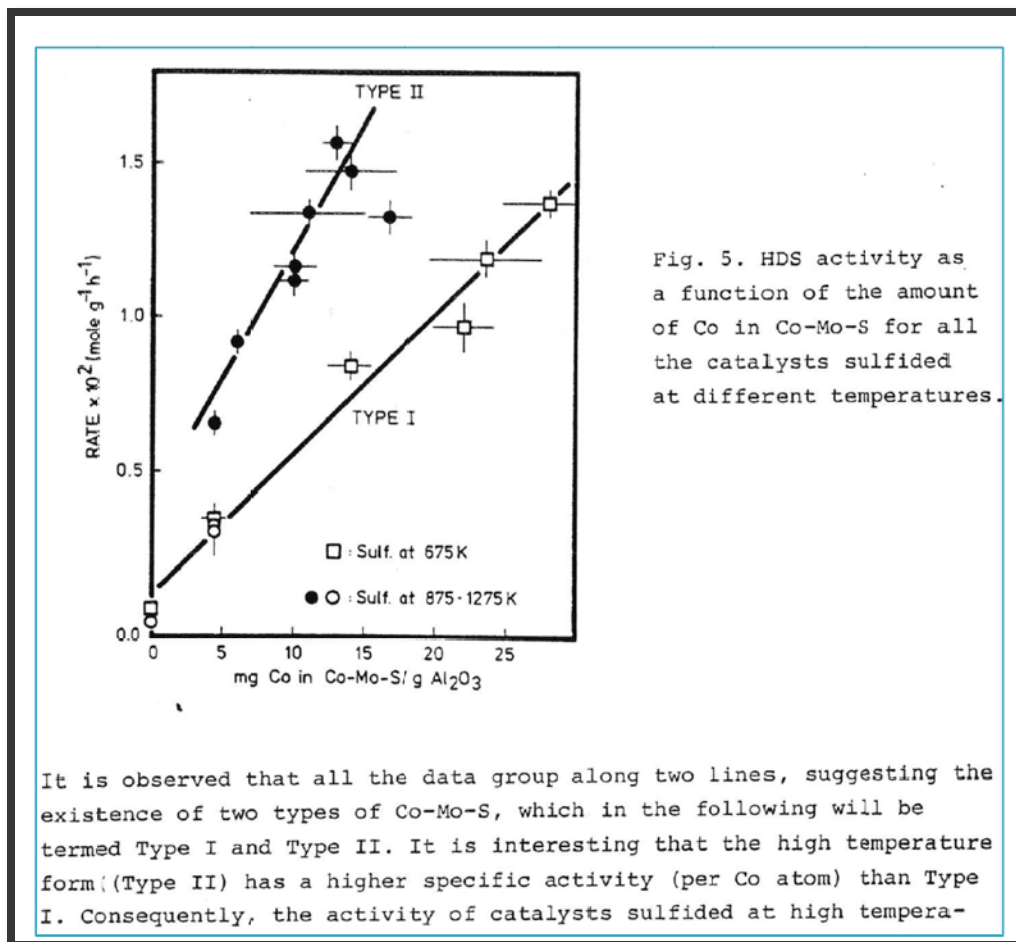


Figure 2 Excerpt from Haldor Topsoe paper presented at 9<sup>th</sup> Iberoamerican Symposium on Catalysis, Lisbon, Portugal, July 16, 1984 (ref 2) shows high activity of Type II active sites compared to Type I

I will read the text below the chart, it says, quote "It is observed that all the data group along two lines, suggesting the existence of two types of Co-Mo-S, which in the following will be termed Type I and Type II. It is interesting that the high temperature form (Type II), has a higher specific activity per Co atom, than the Type I." End quote.

I believe this is the first time the term "Type II" ever appeared in print with reference to the high activity of Type II active sites. The steep slope of the "Type II" line showed the connection between the "Type II" nanostructure and its high activity. That discovery by Haldor Topsoe in 1984 laid the foundation for a billion dollar innovation.

So in fact the stampede that occurred in 2004 should be called the *Type II catalyst stampede*. It was a billion dollar innovation that eventually involved all the catalyst suppliers and all refiners, and swept the entire market.

Still today our industry is benefiting from Haldor Topsoe’s discovery of Type II activity in 1984, from Akzo and Albemarle’s great commercial innovation of STARS catalysts in 1998, and from the work of all the catalyst suppliers who continue to develop and deliver improved catalyst technology to the industry.

I will come back to this story of Type II catalysts shortly. But first, let’s fast forward to 2014, and look at today’s catalyst market from the refiner’s perspective.

### **21<sup>st</sup> century catalysts - A refiner’s perspective**

Today there is an abundance of catalyst brands. Figure 3 shows a partial list of names you’ll hear if you start shopping for hydroprocessing catalysts.



Brim	Stars	Centinel Gold	Encore	Guardian	Ace
Hytreat	Ascent	Phoenix	Stax	Smart	Centinel
Opticat	React	Hybrim	Nebula	Protect	Sulficat
Ascent Plus	Totsucat	Refresh	Centera	Xpress	Impulse

Figure 3 Brand names of some hydroprocessing catalysts

Within most brands, there are several different flavors of products. By flavors I mean, for example, CoMo or NiMo, high density or low density, high metals or low metals, trilobes or quadrilobes, and stacked beds.

When you take all the brands and multiply by all the flavors, you have 200 options.

If you were a busy process engineer needing to select catalyst, how would you deal with 200 options that are presented to you with conflicting claims? From your perspective, it looks bewildering. You would be forced to simplify things.

You could stick with the incumbent. That is simple, safe, sure, the path of least resistance.

You could try something new, but that seems like “rolling the dice” when you have so many options and no basis to judge the conflicting claims.

Or you could do some independent testing. That option is being used increasingly today, and it is more accessible than ever before.

### **Independent testing**

These pilot plants are used for independent catalyst testing at the company called C Solutions LTD. in Thessaloniki, Greece. They are designed specifically for side by side independent testing of competitive hydroprocessing catalysts, and they run around the clock for only that purpose.



Figure 4 Hydroprocessing pilot plants at C Solutions LTD., Thessaloniki, Greece

### **Site-specific proprietary projects**

C Solutions does lots of *site-specific proprietary projects* for refiners. Each site-specific project is sponsored by a single client, usually for a specific VGO or hydrocracking unit that requires a tailored test program.

With a site specific proprietary project, you send two drums of your unit's feed and four candidate catalysts to C Solutions, one of your people will work with C Solutions to plan and oversee the tests, C Solutions will run the program on your feed and you will draw your conclusions.

The pilot plant test itself typically lasts 30 days, and you'll need about 6 months lead time to plan the program, deliver the feed and catalysts, and complete a 30-day pilot plant test on 4 catalysts.

Lots of refiners are doing this kind of project today with great success.

### **Standardized multi-client testing**

A new approach is *standardized multi-client testing*. This is used for ultra-low sulfur diesel (ULSD) units. You don't need to run your own site specific proprietary project for diesel units. We have standard feeds and a standardized pilot plant test for this.

Five years ago, Hoekstra Trading sponsored the industry's first standardized multi-client catalyst testing program for ULSD catalysts, working with a group of independent refiners. Since then, we have tested 8 more catalysts each year at C Solutions using the same standardized test; so we've now tested 32 catalyst samples over 4 years in this program.

This is an *open market program*, meaning all our test results are available, now, to anyone. The cost per client for 30 days/year of testing is one-fifth the cost of doing your own proprietary program because the test is standardized, it is limited to ULSD, and the cost is shared across multiple clients.

Our standardized pilot plant test is a 15-day test. Figure 5 shows some product sulfur data from the first 6 days of the test.



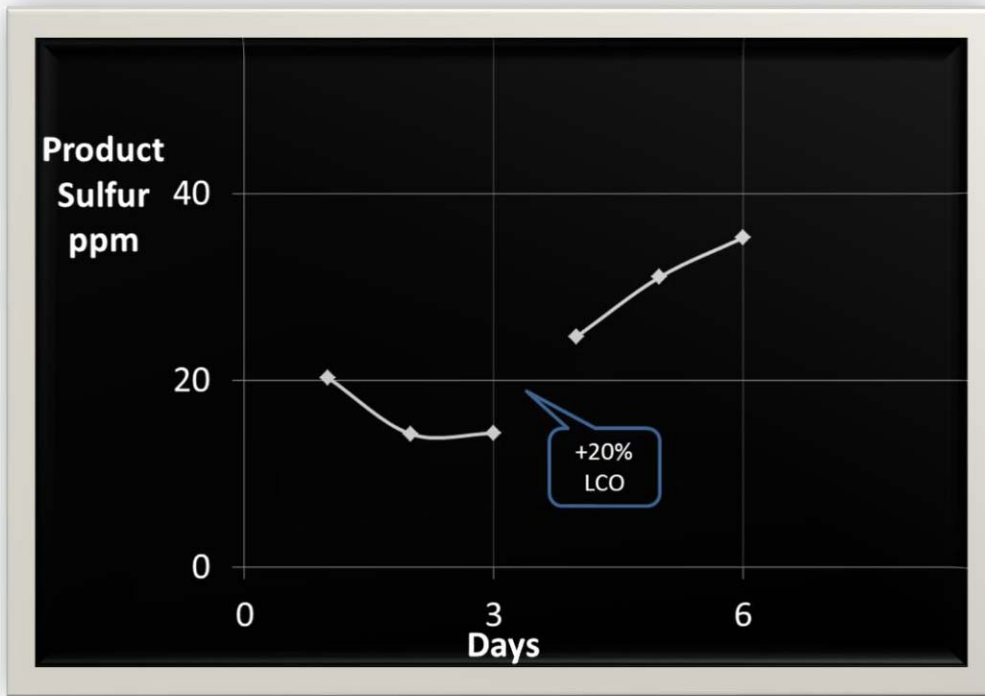


Figure 5 Product sulfur vs. time for days 1-6 of Hoekstra Trading's 15-day standardized ULSD pilot plant test

The test begins with a 3 day segment on straight run feed and then a 3 day segment on 20% light cycle oil feed, at constant temperature and pressure. On straight run feed this catalyst lines out at 15 ppm sulfur by day 3, then when 20% LCO is added, the product sulfur increases in response to the more difficult feed reaching 35 ppm by day 6. This data is for our original benchmark catalyst.

Figure 6 below includes data for a competitor's catalyst, in bronze, with higher product sulfur all six days. The higher sulfur means the bronze catalyst has lower activity than the silver catalyst.

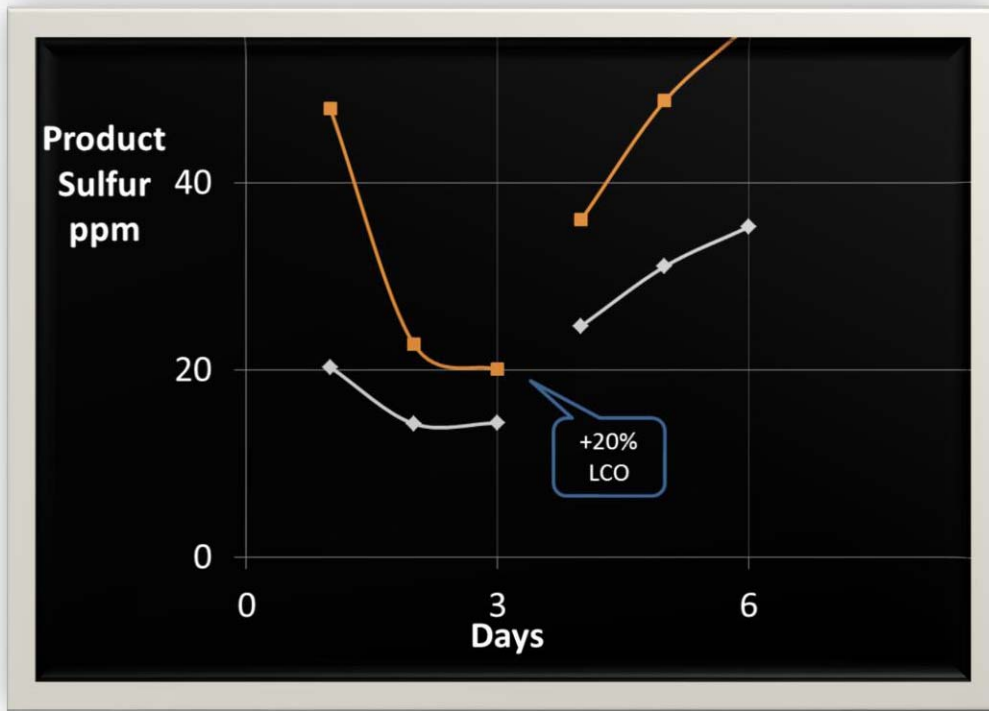


Figure 6 Product sulfur vs. time for 2 competitors' catalysts, days 1-6 of Hoekstra Trading's standardized test

Figure 7 shows data for all the fresh catalysts tested in our first year program, in 2010.

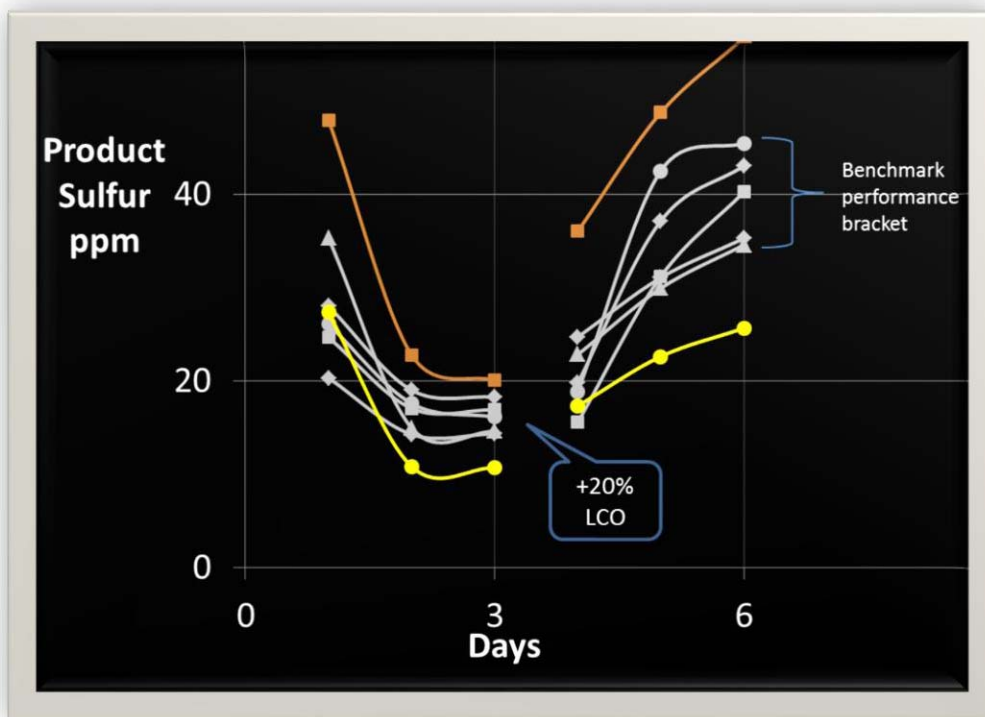


Figure 7 Product sulfur vs. time for competitive fresh catalysts, days 1-6 of Hoekstra Trading's standardized test

### Ranking catalyst performance

We ranked these catalysts into three tiers. The cluster of catalysts shown in silver defines the benchmark bracket. The catalyst in bronze color, with highest product sulfur, ranks a tier below benchmark in activity. The gold catalyst, with lowest product sulfur, won the 2010 gold medal for most active catalyst in our 2010 program; that was ART's 420DX, a second generation Type II CoMo catalyst.

This relative ranking, into three tiers, held up through the whole 15 day test. The cluster of silver catalysts never showed consistent separation so they were not subdivided further; they were collapsed to a single tier.

We don't split hairs when ranking catalysts. We look for clusters and gaps that define clear break points that hold up across a range of feeds and conditions.

### The power of catalyst rankings

We have seen big differences among the many competitive Type II catalysts tested in this program, and some results have been surprising. Research in the 1980's showed that placing a cobalt atom at the right spot in the Type II nanostructure increases the activity per cobalt atom by a factor of 50, and more recent development has

multiplied that factor further. So there is lots of leverage in getting a higher percentage of the promoter on the sweet spot which is why catalysts keep getting better as suppliers develop better catalyst preparation technology.

From the refiner's perspective, these competitive product rankings are powerful in your catalyst selection process. Now you have some reliable hard data, from side-by-side tests on a reliable independent test track, with different competitors' products, apples-to-apples. You can consider putting something new in your unit without feeling like you're "rolling the dice".

In short, you are in position to make a much better decision, much like when you use Consumer Reports before choosing an expensive new vehicle or a high budget purchase for your home.

### **Independent Catalyst Test Report**

Our standardized multi-client program delivers an annual report called Independent Catalyst Test Report.

The graphic features a dark blue background with the title "Independent Catalyst Test Reports 2010, 2011 & 2012" in white serif font. Below the title, a white rounded rectangle contains the heading "OUR REPORT WILL HELP YOU:" followed by three bullet points: "Simplify catalyst selection", "Choose the right catalyst with confidence", and "Save hundreds of thousands on your next catalyst purchase". To the right of the text, three overlapping report covers are shown. The top cover is for "Independent Catalyst Test Report 2012" and lists sections: "Section 1 - Results of pilot plant run G4-3LP", "Section 2 - Results of pilot plant run G4-B", and "Section 3 - Analysis of product performance claims".

Figure 8 Independent Catalyst Test Report

Each year's report contains a year's worth of new data and rankings for eight more catalyst samples. Four of these annual reports, representing our first four years of work, are available now for immediate delivery, and the fifth will be released in 2014.

A big advantage of the standardized multi-client program is that there is no extra work for you. You only need to sign up, take the time to accept delivery, and start putting this new database to work for you.

### **Benefits of independent testing**

A one tier improvement in performance is worth \$1-5 million/year in a typical ULSD unit, and \$10 million plus per year for a hydrocracker. You can get 20% lower catalyst cost by opening your business to more suppliers and newer catalysts. These bottom line benefits can be realized immediately with no capital investment and no real risk. That has been proven, many times over.

With independent testing you gain confidence in your decisions, and you can be more flexible in catalyst supply. Whether it's site specific or standardized testing, you are naturally led toward a more flexible strategy which is beneficial for many reasons. One reason is that the catalyst market is prone to be hit from time to time by unpleasant surprises.

### **Mini-crises in the catalyst world**

We call these mini-crises in the catalyst world. For example, the catalyst supply crunch of 2004, the molybdenum price spike and crash of 2005-07, and the rare earth price spike and crash in 2010-12.

We call these mini crises because they upset your plans; they put your selection process into crisis mode, and sometimes cause panic buying and overspending of catalyst budgets. As one example, Petroplus, who was an inflexible catalyst buyer, overspent their catalyst budget by \$20 million dollars in 2011, and that nasty surprise was cited in their financial reports as a key factor in their going extinct in January 2012. There's no doubt, a more flexible catalyst strategy could have helped them a lot.

Your plans also get altered by new crudes, new specifications, tight margins, and changing feed and hydrogen costs. These changes cause faster development of new catalyst brands and flavors. Today's new flavor may or may not be the next breakthrough, but regardless, it adds to the list of options to consider.

Our reports also contain focused catalyst market research not available anywhere else, to help you navigate the choppy waters of the catalyst business.

## **A challenging purchase**

From the refiner's perspective, catalyst is a challenging purchase today. Forty years ago, most refiners developed their own catalysts and had whole teams of in-house catalyst experts. Now this is a third party purchase. Some engineers spend months sorting through piles of brochures and presentations without the benefit of any objective data or in-house catalyst knowhow. Most engineers will work very hard to make the right decision for their unit, but too often they end up confused and frustrated.

It shouldn't be that way. We have helped many dozens of engineers choose catalysts and we know when they see good independent test data, they're hooked. It's not only engineers who get hooked, its procurement managers too – because some refiners spend over \$100 million dollars per year on catalyst, that's a big third-party, spend, and there's a lot you can do to manage it.

When a team gets together and leads their company to a better way of doing this important work, it's rewarding for everyone involved.

Speaking of challenges, I want to talk briefly about two obstacles we've had to clear on the way to acceptance of our standardized multi-client testing program.

## **A culture of secrecy**

The first obstacle is a culture of secrecy that is deeply woven into the orthodoxy of catalyst testing.

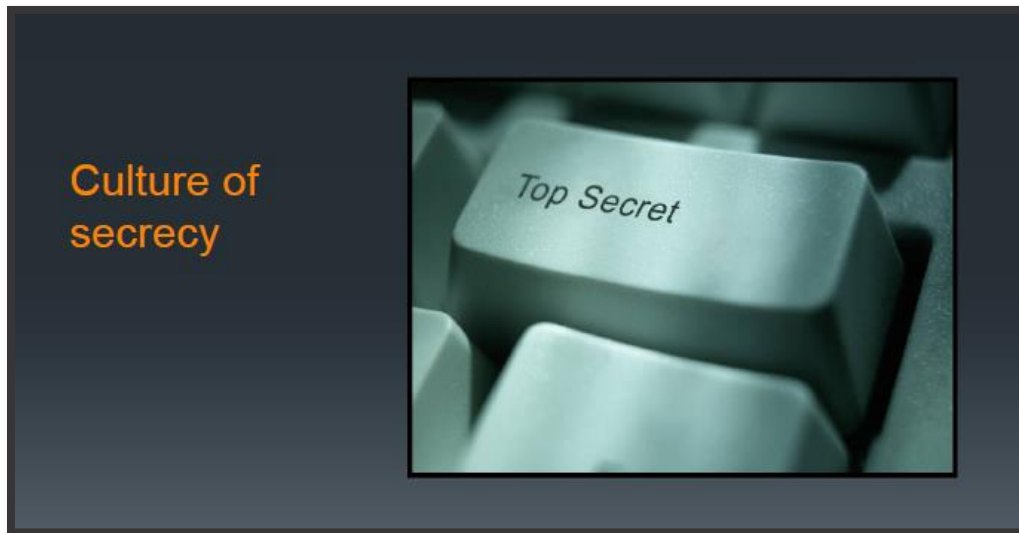


Figure 9 A culture of secrecy has been an obstacle in open market independent catalyst testing

Catalyst testing has always been veiled in secrecy. Our open market, multi-client program lifts that veil by making independent test data openly available to everyone.

Five years ago, we started asking catalyst suppliers to provide test samples with the up-front understanding that the test results will be available to everyone. This stipulation of transparency came as a culture shock in the secretive world of catalysts. Our requirement for *open access to data* made it difficult for us to get samples to test in the standardized multi-client program.

But some suppliers quickly saw the value of our open market approach and they started providing test samples right away without requiring the data be held secret. Those suppliers confronted the unsettling fact that, for the first time, their catalyst might not finish first in every test their customers see. Those suppliers stepped up to our challenge; they put their products up for testing against competition on an open, fair independent test track with results available for all to see. Those suppliers now embrace the open market approach and are using our program proactively as a benchmarking tool to help improve their products. Other catalyst suppliers have since joined in to the open market approach.

### **Resistance to change**

A second obstacle for us has been resistance to change among refiners. What does this mean? It means many refiners allow their selection process to be paralyzed by too much red tape of various kinds.

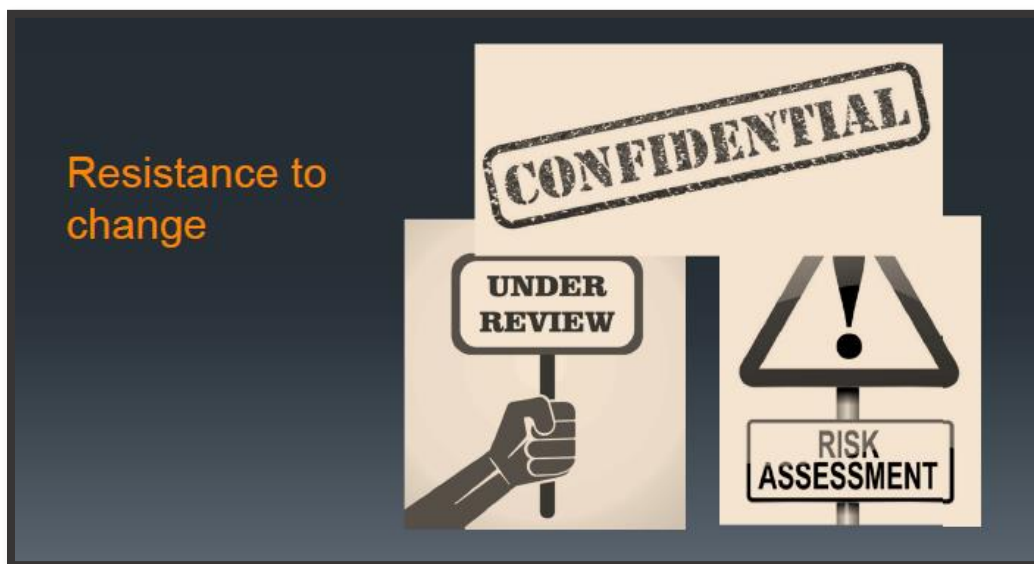


Figure 10 Resistance to change has been an obstacle to acceptance of open market independent testing



Resistance to change favors incumbents. Many refiners stay captive to favorite incumbents for years without seriously considering change. Even in the simple matter of buying our reports, which is a smaller decision by orders of magnitude, even that sometimes gets blocked by various internal obstacles and arcane restrictions, which usually serve to defend entrenched incumbents. Some companies won't allow their employees to look at competitive test data without first asking permission from their incumbent supplier.

Such rigid resistance to change is costly in today's catalyst refill market which is highly competitive and offers so many good competitive choices.

We encourage our clients to adopt an open, honest, straightforward approach to catalyst selection, and to focus their selection process on performance, price, service, and profitability.

### The story of Type II catalysts

We now return to the story of Type II catalysts. I traced the story with three specific events, here's a review:

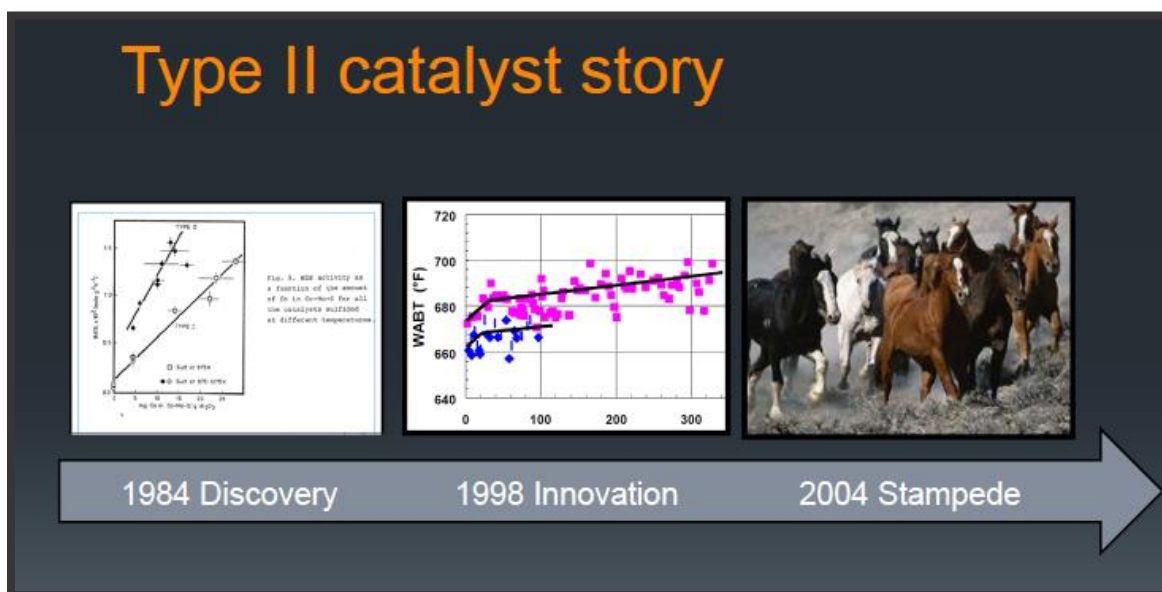


Figure 11 Timeline for Type II catalyst story

- First, the publication of a chart by Haldor Topsoe in 1984. That was the discovery event that triggered the development of early Type II catalysts.
- Second, Akzo's rollout of STARS catalysts in 1998. That was a great commercial innovation that raised awareness among refiners and provided compelling data to encourage refiners to start tiptoeing in.



- Third, the 2004 stampede. That was triggered by the looming deadline to make clean fuels and it led to a supply squeeze and 2-year waiting lists for Type II catalysts.

Looking at this timeline invites the question: Why did this take 20 years? Couldn't some starving refiners have used this billion dollar breakthrough sooner? Why did it take 20 years, lots of marketing buzz, and a government mandate, before our industry captured this billion dollar opportunity that was sitting on the shelf?

That's a good question for discussion at cocktail hour. Here is my theory, in a nutshell:

*With catalyst breakthroughs,  
Refiners move at glacial speed,  
Until there's a crisis,  
And then a stampede.*

### **Faster take-up of catalyst innovations**

I will finish this talk by again acknowledging the catalyst suppliers for their continuous development of improved products for refining. It is not only Akzo, Albemarle, Haldor Topsoe, and ART, who were mentioned by name, but all the catalyst suppliers are to be recognized as critical partners; the most proactive innovators in refining technology.

Our independent testing programs are helping refiners get better and faster at taking up catalyst innovations by providing:

- reliable independent test data
- catalyst rankings
- market research
- recommendations for catalyst selection

All this helps you:

- simplify catalyst selection
- choose the right catalyst with confidence
- save hundreds of thousands on catalyst purchases.

This is available today, it is affordable, and it works. It has been proven, many times over. We invite everyone to participate.

### **References**

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2. R. Candia, B.S. Clausen, H. Topsøe, Proc. 9th Iberoamerican Symposium on Catalysis, 1984, Lisbon, Portugal