

Good morning.

Each year my company sponsors a catalyst testing program that involves pilot plant testing of competitive hydroprocessing catalysts, and we issue an annual report on each year's work. Independent Catalyst Test Report 2015 is our sixth annual report. The 2015 program focused on FCC gasoline desulfurization, and the title of my talk today is Pushing the limits of FCC gasoline desulfurization.

FCC gasoline desulfurization

- Goal: desulfurize FCC gasoline with minimum octane loss
- Uses conventional naphtha hydrotreating
- Uses selective catalysts to minimize olefin saturation

The goal of FCC gasoline desulfurization is to desulfurize FCC gasoline with minimum octane loss. The process uses conventional naphtha hydrotreating and selective catalysts to minimize olefin saturation and octane loss.

Commercial status

- Got off the ground in 1999
- There are now 300 units in the world
- Most are Scanfining (ExxonMobil) or Prime G (Axens) units
- Revamps and new builds are ongoing

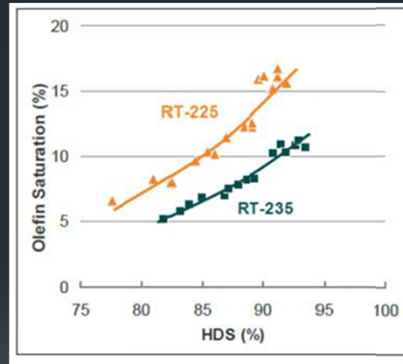


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This process has been studied since the 1970's, but it didn't get off the ground commercially until 1999 with the introduction of clean fuels mandates in the United States. There are now 300 such units in the world. Most of them are Scanfining or Prime G units licensed by ExxonMobil and Axens. The units are often called "gasoline post-treaters". There is continued interest in increasing the performance of these units, especially with Tier 3 gasoline regulations coming into effect in the United States. Tier 3 regulations require most refiners to make an average 10 ppm S gasoline starting in January 2017.

FCC gasoline desulfurization catalysts are⁴ designed for *olefin retention selectivity*

- Excerpt from ExxonMobil presentation
- Shows ExxonMobil pilot plant data - *olefin retention selectivity*



Excerpt from XOM presentation



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FCC gasoline desulfurization catalysts are designed for olefin retention selectivity.

This is an excerpt from an ExxonMobil presentation that shows the idea nicely. It is a chart of % olefin saturation versus % desulfurization for two catalysts. You want to get your target desulfurization with minimal olefin saturation, so that more high-octane olefins remain in the desulfurized product.

This chart shows that the RT-235 catalyst is more selective, that is it gives lower % olefin saturation for a given level of desulfurization. This kind of chart pretty much defines the performance of a selective desulfurization catalyst, and we will be looking at this kind of data through this whole presentation.

Independent catalyst test report 2015 (ICT 2015)

- Side-by-side pilot plant tests of competitive catalysts
- Catalysts are ranked on activity and selectivity
- Includes competitive analysis
- Includes new insights on the process



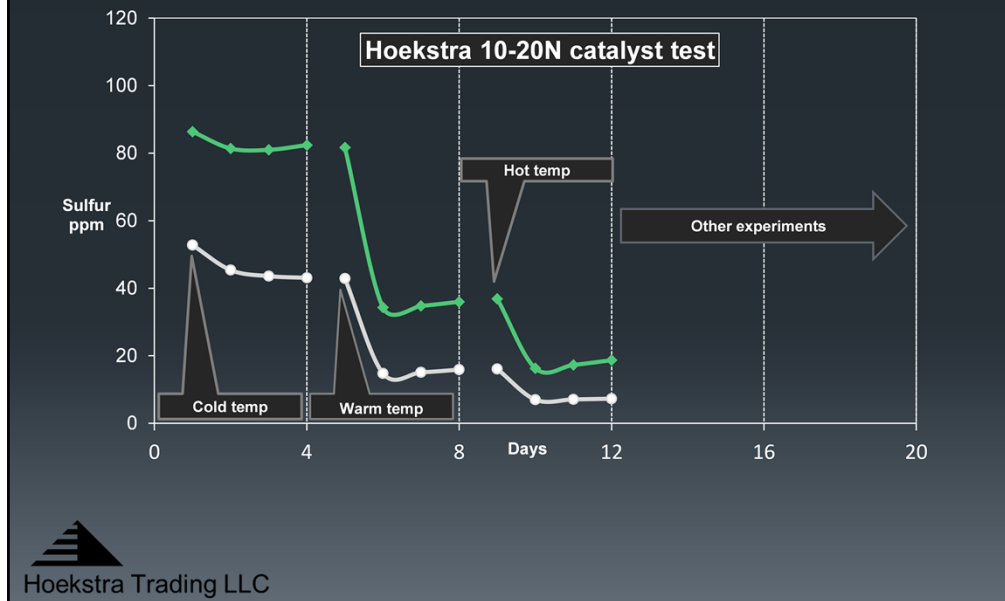
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Independent Catalyst Test Report 2015 is the annual report on the work we did in 2015 which involved side by side pilot plant testing of competitive catalysts for this process. In it, we have ranked the catalysts on activity and selectivity for use in catalyst selection.

Our report also includes competitive analysis based on study of open literature on this process, and it includes new insights on the process that will be valuable to those interested in meeting Tier 3 gasoline requirements. Now I will show you some of the results from our pilot plant tests.

ICT 2015 - desulfurization activity

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This chart shows product sulfur versus time for the first 12 days of our pilot plant test. Data are shown for two catalysts, one in green and another in white. The test is a 20 day test using a sequence of five test conditions, each test condition is held for four days. The first 4 days are at a low temperature which we call the cold condition, then we increase the temperature to the warm temperature for days 5-8, and then hot temperature for days 9-12.

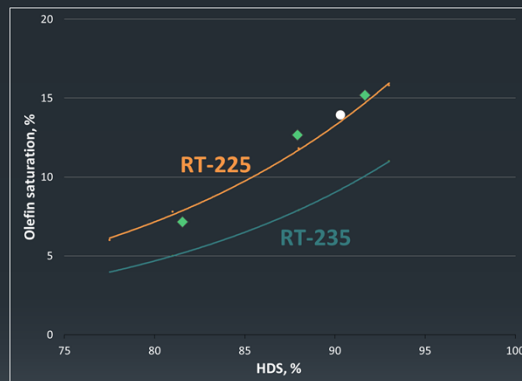
You see here, as we go from cold to warm to hot temperature, the green catalyst goes from 80 ppm product sulfur on day 4, to 40 ppm on day 8, to 20 ppm on day 12 at the hot temperature. The white catalyst is much more active for desulfurization. At the same 3 temperatures, it produces product sulfur of 40 ppm, 15 ppm and 8 ppm.

So you see our tests covered a wide range of product sulfur, from nearly 100 ppm product sulfur to under 10 ppm product sulfur, as we varied temperature at 3 levels, for test catalysts that have different activities.

This chart is all about desulfurization activity, what about olefin retention?

ICT 2015 - olefin retention selectivity⁷

- Green and white data points are from ICT 2015 tests of competitive catalysts
- Trendlines are XOM pilot plant data for RT-225 and RT-235



Note: This chart shows 4 of 20 data points from ICT Report 2015



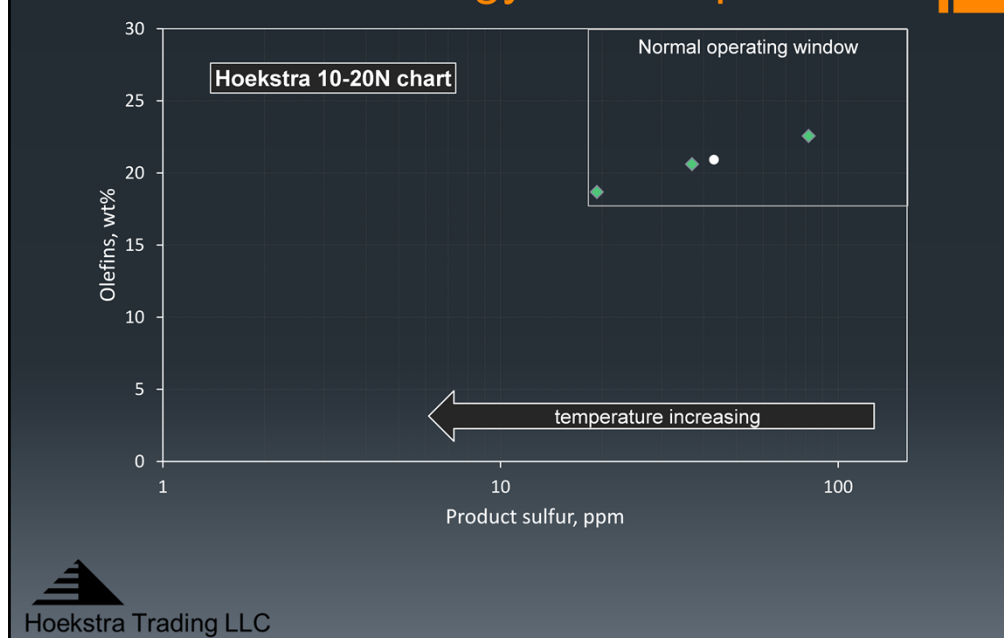
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Here we again see the curves from the ExxonMobil presentation, for the RT-225 catalyst and RT-235 catalysts, they show the % olefin saturation charted against % desulfurization. We converted our product sulfur data from the last chart to percent desulfurization, and plotted our four data points as percent desulfurization on the horizontal axis, and we show here the % olefin saturation we measured, and these fall along the RT-225 curve. The white data point, for the more active catalyst at the cold temperature also falls along the same RT-225 curve. So we say the green and white catalysts have the same olefin retention selectivity, even though they have very different desulfurization activity.

With the white catalyst we tested, you can get the same desulfurization, and the same olefin retention selectivity at much lower temperature, compared to the green catalyst.

Now if you're still with me, (ASK), you realize we also have data for the white catalyst at the higher temperature. Where is that data? Well it falls much higher up and to the right on this chart, and we end up getting squashed in the corner. So I will show those data points shortly but they will be plotted on a different kind of chart.

ICT 2015 Technology landscape charts⁸



I call this a landscape chart because it shows a broader perspective on activity and selectivity. Instead of plotting % desulfurization on the x axis, I am showing the product sulfur, in ppm on a logarithmic scale. This gives plenty of space to the left to see what happens as we move deeper in desulfurization. On the vertical axis, we have the %olefins remaining in the product. This is not percent olefin saturation, it is the absolute amount of olefins remaining in the product. This is how we will look at activity and selectivity data from now on. On this chart, going left means higher conversion, and a higher curve means more olefins retained, means a more selective catalyst.


The box in the upper right indicates the normal operating window for the process. Here again, we see our four data points, three for the green catalyst, the product sulfur ranges from 80 ppm at the cold temperature down to 20 ppm at the hot temperature, and the more active white catalyst gives 40 ppm product sulfur at the cold temperature, and there is no difference in the olefin retention selectivity of the catalyst.

Now looking within this window, for any test catalyst, we can place its data points for product sulfur and olefin content and compare it using the green as a reference. We did that for all the catalysts we tested, we did see significant differences in activity and selectivity, and this gives our catalyst ranking chart:

ICT 2015 Catalyst ranking grid ⁹

Delta Selectivity	
Delta Activity	Base selectivity
	-5 wt% olefin saturation
	-20°F
	-10°F
	0°F
	+10°F
	+20°F
	+30°F

Test catalysts are placed in this grid



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Each catalyst we tested is placed in this grid, based on where its curve fell on the landscape chart. We have vertical tiers indicating delta activity in terms of the equivalent reactor temperature required to get a target product sulfur. We saw two distinct tiers of olefin selectivity. So this ranking grid summarizes the main performance factors important for catalyst selection.

The main goal of our 2015 program was to define this grid, and place the test catalysts in it, so that our clients have a good objective, independent basis to choose a catalyst. That goal was accomplished, and if you are interested in this process, our report will certainly be of great value for you in considering what catalysts you might want to use in your FCC gasoline desulfurizer in the future.

Pushing the limits

- Studying the detailed chemistry of the process
- Pushing severity to make ultra low sulfur gasoline



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But in our 2015 program, we went beyond just ranking the catalysts, we also studied the detailed chemistry of the process, and we measured what happens when you push severity to make ultra low sulfur gasoline. We didn't stop at just total sulfur and total olefin content! In fact, we gathered seventy five hundred data points showing what happens to over 300 individual compounds in this process. You'll be happy to know I don't intend to show you all 7,500 data points. I will start with just some additional detail on the four data points we have been looking at so far.

Pushing the limits

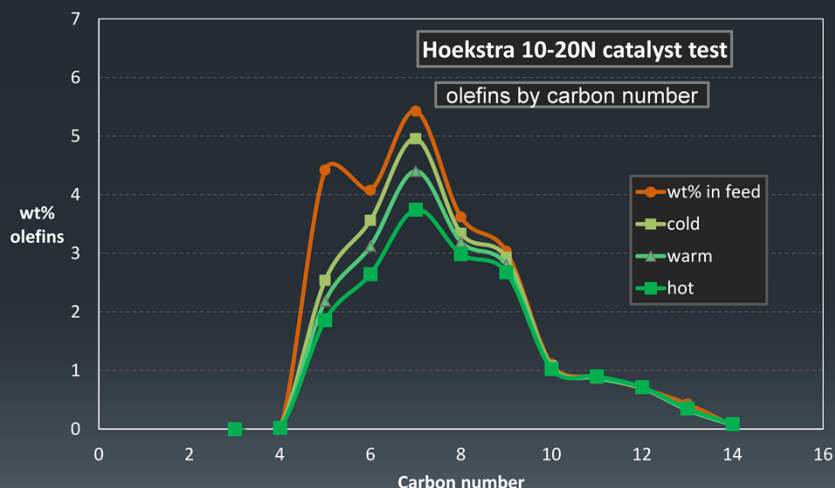
Reactivity of compound groups



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First, instead of just looking at total olefin content, we will look now at the reactivity of olefin compound groups broken down by carbon number.

ICT 2015 – olefins by carbon number¹²



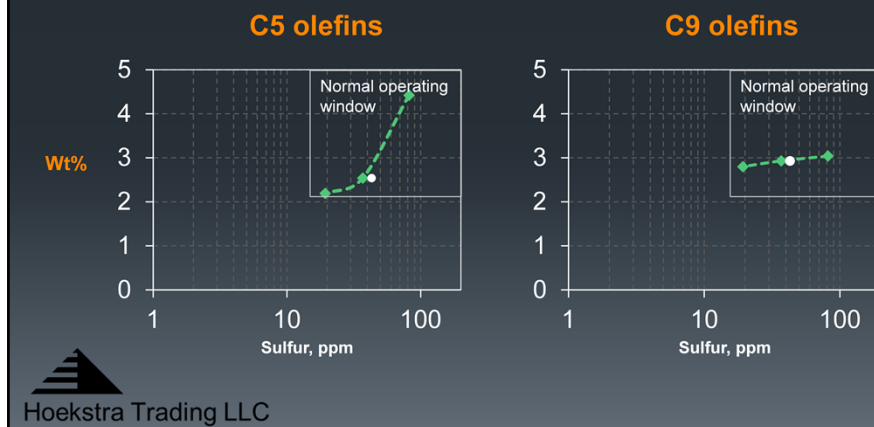
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This is the distribution of olefins by carbon number for the feed and those three product samples at the cold, warm, and hot temperatures for the green catalyst. Looking first at the orange curve for the feed, it shows that C5 and C7-olefins are present in the highest concentrations, and the feed contains some olefins all the way up to C14 olefins.

The green curves show the reduced amount of olefins in the products, at the three different test temperatures. The gap between the orange and the green curves is the conversion of those olefins, it is largest for the C5 olefins, in other words, the C5 olefins are the most reactive olefins. The loss of olefins is less as we move to the right, toward higher carbon number olefins. And, for all carbon numbers, the olefin content goes down progressively as we raise temperature from cold to warm to hot.

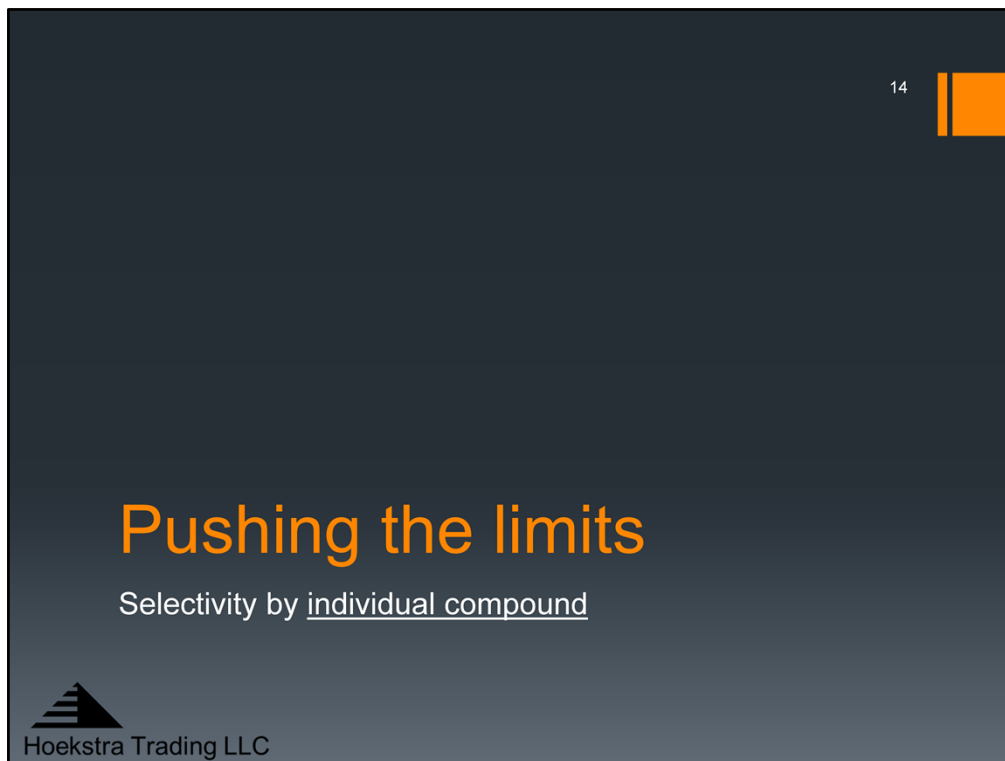
I don't know if this kind of data was available before, but none of my clients have seen this before, nor have I, so far as I know, this is new information for everyone.

ICT 2015 - olefin selectivity by compound group



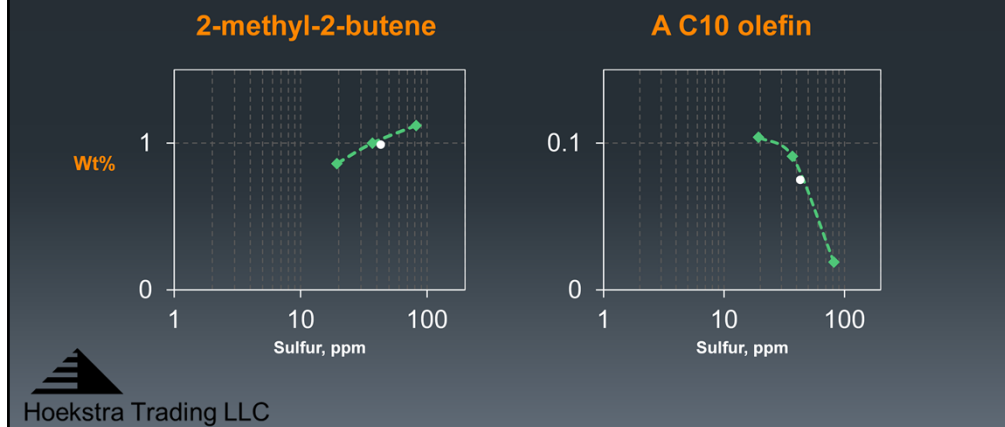
Here I am showing the above data charted on what I called a landscape chart, for the C5 olefins and the C9 olefins (Before we were looking at total olefins). You see the curve for the C5 olefins is steeper, indicating their higher reactivity compared to the C9 olefins on the right.

This is the exactly the type of data you would want in order to make a model to be able estimate effect of feed composition on olefin retention.



Our data go down another level of detail – we have these landscape charts for 300 individual compounds.

ICT 2015 - olefin selectivity by individual compound



Here is the data for 2-methyl-2-butene, it is a C5-olefin that happens to be present in high concentration in FCC gasolines. And on the right is the chart for a particular C10-olefin.

Who sees something different about this chart?

Its slope is opposite to the others. This particular C10 olefin is being formed in the process. The deeper you go in desulfurization, the more of this olefin you get. This is a peculiar result – We don't normally think about olefins being formed in this process, in fact, I have studied most of the available literature and I have never encountered any reference to the fact that some olefins are formed in this process. So this may be another new finding.

Pushing the limits

Selectivity for other hydrocarbon types

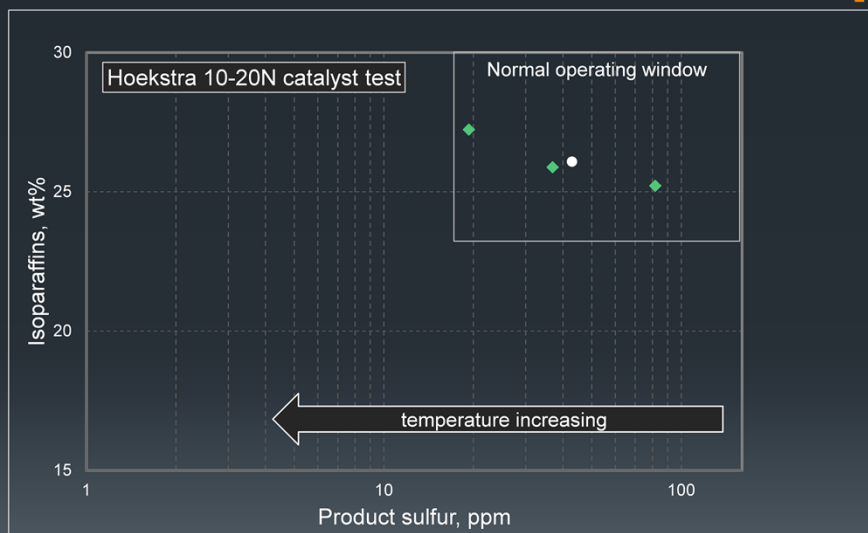


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We also have data for the other hydrocarbon types, besides just olefins. For example, what happens to isoparaffins in this process?

ICT 2015 - isoparaffin selectivity

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Total isoparaffins increase as you go deeper in desulfurization.

We also have these curves for the normal paraffins and naphthenes, all by carbon number and, in fact, by individual compound, which is how we get to 7,500 data points.

Because we covered a wide range of conversions and a wide range of catalyst activity, the data are revealing on possible ways to improve this process when extending it to deep desulfurization.

Pushing the limits

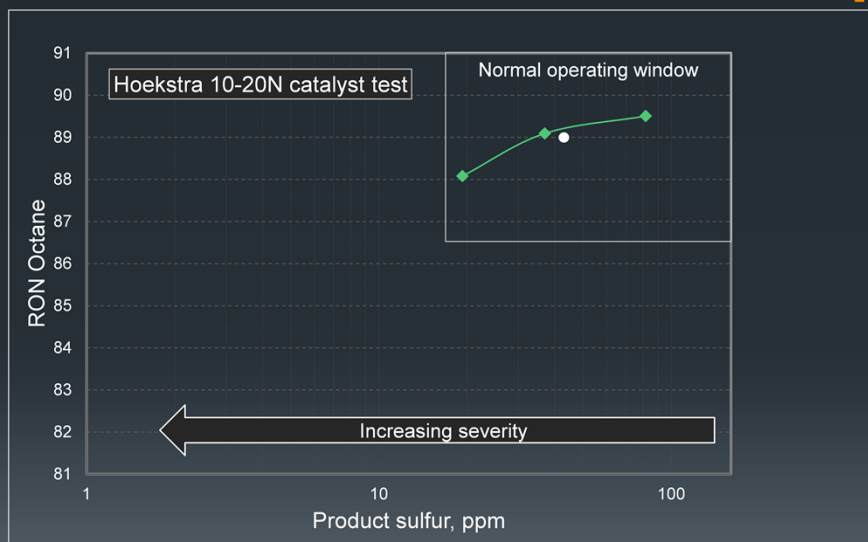
Increasing severity to make ultra-low-sulfur gasoline



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And this is my final topic , What happens when you increase severity to make ultra low sulfur gasoline, like the 10 ppm sulfur ultra low sulfur gasoline needed for Tier 3 next January?

ICT 2015 – octane retention selectivity¹⁹



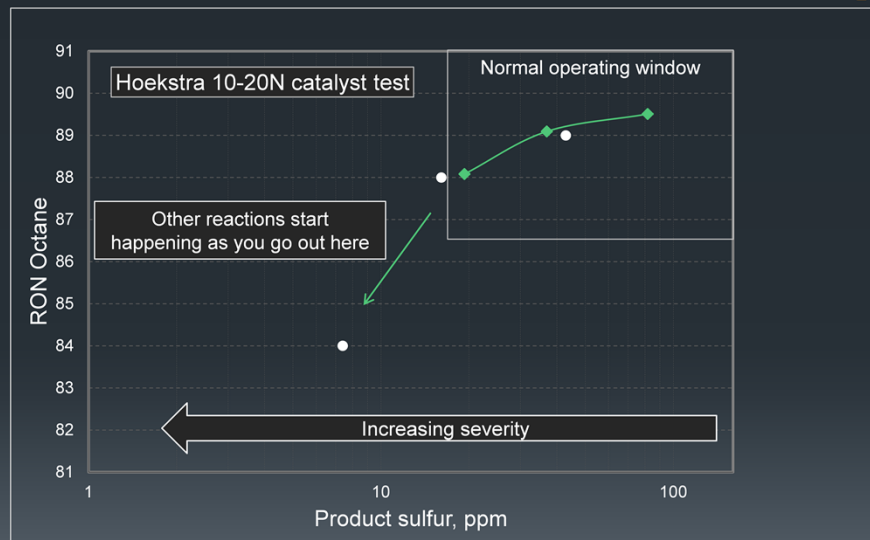
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Here are our 4 data points again, now I am charting the research octane number of the product on the landscape chart. And we have space on the left to see what happens to octane when you go to deep desulfurization.

Does anyone have an estimate of how much octane you might lose when you go from 30 ppm sulfur to 10 ppm sulfur by raising temperature on one of these units?

Does anyone have a guess?

ICT 2015 – octane retention selectivity²⁰

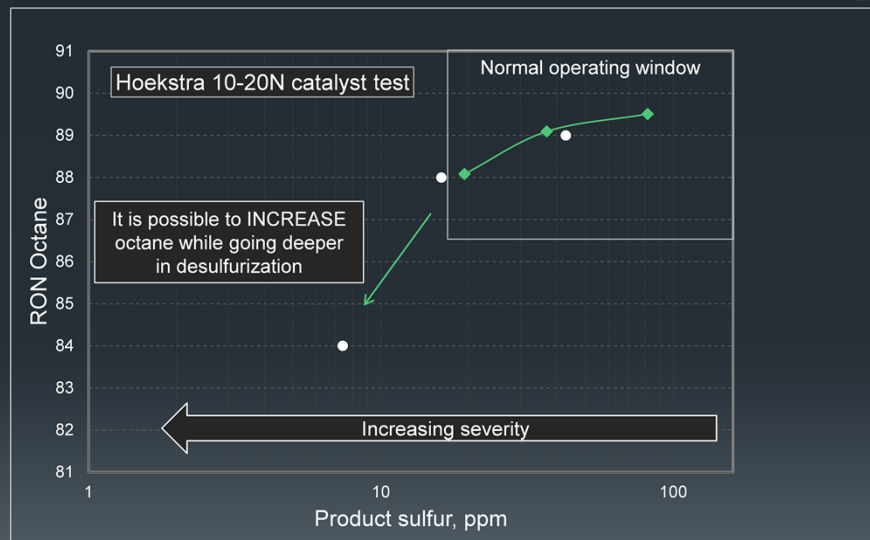


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Here we see the other two data points for the more active white catalyst at the medium and high temperatures. With the white catalyst at the high temperature, we made 8 ppm sulfur, and the research octane number went down to 84. For a unit currently making 30 ppm sulfur, that means pushing the unit to 10 ppm comes with a 5 RON octane unit loss on this feed.

Our detailed chemical analysis tells us why this large octane loss occurred. And we are also able to see that, at such high severity, different reactions, like the peculiar one I showed you, can become important for affecting octane.

ICT 2015 – octane retention selectivity²¹



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And our detailed data gives insights that suggest it is possible to reduce this 5 octane number loss – in fact, with the right catalyst and unit design, you could increase octane while going deeper in desulfurization.

Independent catalyst test report 2015

- Competitive catalysts have been tested
- They are ranked on desulfurization activity
- They are ranked on olefin retention selectivity
- Large improvements in desulfurization/octane performance are possible at deep desulfurization
- The report is available to anyone from Hoekstra Trading



To summarize, in Independent Catalyst Test Report 2015, competitive catalysts have been tested and ranked on desulfurization activity and olefin retention selectivity. Our data and catalyst rankings can certainly help any refiner improve the economic value contribution of your selective desulfurization units, especially in light of the coming tier 3 gasoline regulations.

This is a multi-client program that cost \$350,000. Because the cost is shared, the catalyst test report is available to anyone for \$75,000. If anyone in your company might be interested in getting this report, I encourage you to see me today.

Also, I must tell you of a recent development, which is that much of the detailed analytical data from this program has been purchased by one of our clients for their exclusive use. That client is Haldor Topsoe. Topsoe has been working to develop an improved process and they are now using our data to supplement that effort. Topsoe intends to offer an improved process and catalyst in 2016 that will deliver improved desulfurization/octane performance.

If any of you are interested in buying this report and/or speaking with Topsoe, please see me and I will help you set that up.

Thanks for your attention.

Thanks for your attention!

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Thanks a lot for your attention.

To request a copy of this presentation, please send me an E-mail or phone me at any time.

Thanks and have a good day