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ULSD: Ensuring the Unit Makes On-Spec Product

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ULSD: Ensuring the Unit Makes On-Spec Product

There is little margin for error in making clean fuels. This is especially true now as we expand the manufacture of ultra low sulfur diesel, in order to meet the new specifications. Consistency in all aspects of unit performance is essential.

BP operates 14 refineries. In these, a total of 20 diesel hydrotreating units are producing, or will soon produce, ultra low sulfur diesel. This represents a total of 30 reactors and 5 million pounds of catalyst installed. These units all require consistently high catalyst performance in order to avoid unscheduled outages in the unit.

This paper focuses on the importance of consistent catalyst quality. There are 2 main topics: First, we will describe BP's catalyst selection process. Second, we will present the results of a catalyst quality study focusing on the consistency of catalyst quality.

Implementing New Hydrotreating Catalysts

BP is fortunate to have many capable catalyst suppliers as our partners. These catalyst suppliers have been leaders in developing new technology to enable production of clean fuels. They all have strong research and development programs and outstanding people. They continue to develop new products at an expanding rate to meet the refining industry's needs.

As catalyst technology continues to advance, BP's strategy is to quickly find and implement new improved catalysts. For this to work, BP refineries must have full confidence that these new catalysts will always deliver the expected high performance.

BP has an ongoing catalyst testing program that is done at the Chemical Process Engineering Research Institute, or Cperi, in Thessaloniki, Greece. The program is operated by Cperi Solutions, LTD, which is a new company that has been formed as a spin-off business from the Chemical Process Engineering Research Institute. The catalyst testing program has only one purpose. It is to test and rank new catalysts so that the refineries can decide whether to use them.

Since 2001, BP has evaluated and ranked 25 different catalysts from 7 different suppliers in this program. The partnership with Cperi Solutions has led to fast and highly focused testing to produce up-to-date catalyst rankings.

BP's catalyst rankings are *generic* rankings. They are *managed by networks*, and they are *used for catalyst selection*.

The rankings are *generic* as distinct from unit-specific, and as distinct from site-specific. This means that the rankings are developed on a standard set of feedstocks, using a standard protocol. All refineries use the same rankings.

The catalyst rankings are *managed by networks*. This means the testing is funded and used by formal networks, specifically, the BP Hydroprocessing Technology Network and the BP Catalyst Procurement Network. The hydroprocessing network consists mostly of unit engineers who work at BP refineries. These are the people who operate BP hydrotreaters around the world. Similarly, BP's catalyst procurement network consists mostly of refinery-based procurement specialists who work as one team with the technology network.

The catalyst rankings are *used for catalyst selection*. Each unit engineer decides which performance tier is needed for his or her unit, and selects from catalysts in that tier. This may seem obvious; to say the rankings are used for catalyst selection. But in fact this part is often the greatest challenge. Switching to a new catalyst, from a different supplier, is filled with real and perceived risks. Unit engineers are often hesitant to switch away from a proven catalyst, or from an incumbent supplier with whom they are comfortable. They hesitate for good reason; Switching to a new catalyst is a big decision that carries risk.

But when pilot plant testing shows that a new catalyst is better than one currently being used, BP refineries want to use it. They need assurance that it will perform as expected. Providing this assurance is critical if we want to take full advantage of new catalyst technology for making clean fuels.

How can we assure consistently high catalyst performance?

First, the catalyst testing must be very reliable and reproducible. Second, the catalyst rankings must be credible, meaning they are fully accepted by the hydroprocessing technical network. Third, the catalyst quality must be consistent. This means the catalyst suppliers must always deliver batches of product that meets the expected performance based upon the samples tested.

Catalyst Testing

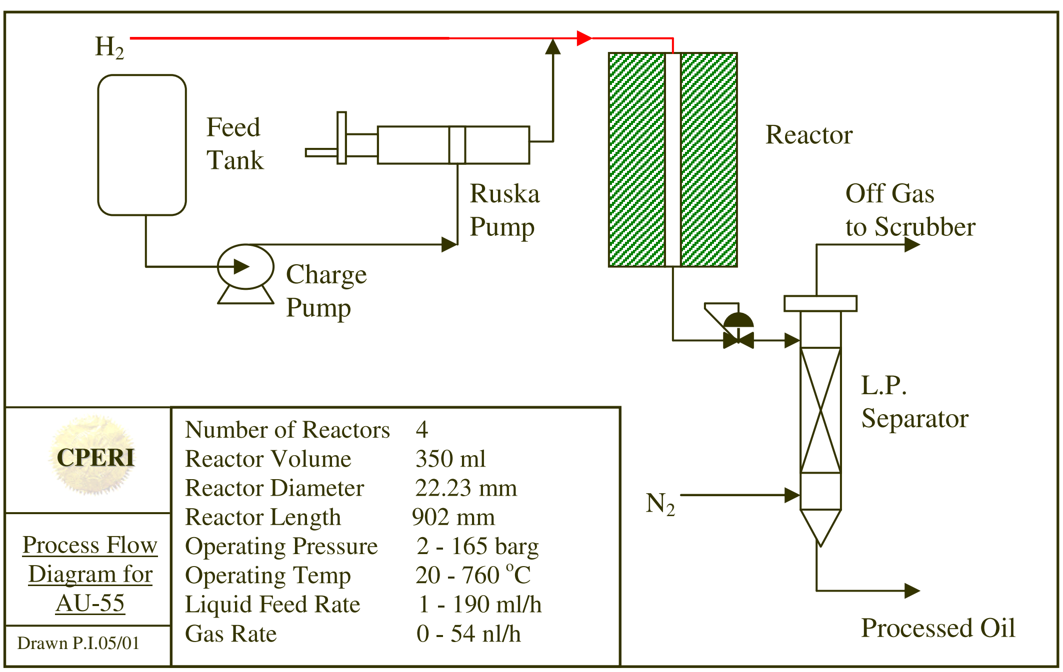
The first step is reliable catalyst testing. In order to satisfy the different requirements from all of the refineries in a single program, BP's Hydroprocessing Network has established standard feeds for catalyst testing. The diesel catalyst test uses two standard feeds. They are a straight run light gas oil, and a 30% light cycle oil blend.

Table 1 Standard Feed Properties

	Light Gas Oil	30% Light Cycle Oil
Specific Gravity	.8645	.8713
Sulfur, wt%	1.02	0.93
Nitrogen, ppm	127	178
Hydrogen, wt%	13.0	12.6
Aromatics, wt%	31	37
Distillation ASTM D86 30% /50%/90% (C)	284 / 299 / 346	276 / 295 / 346
Distillation ASTM D86 30% /50%/90% (F)	544 / 571 / 654	529 / 564 / 654

The testing is done in Cperi Solution's AU 55L pilot plant. This unit has four isothermal reactors which operate in parallel with once-through hydrogen:

Figure 1: Cperi Solutions Pilot Plant Configuration



The test protocol is a 38 day pilot plant test consisting of a sequence of 12 different conditions. Each of the 12 conditions is a different combination of feed and reactor conditions.

Table 2: BP Diesel Hydrotreating Catalyst Test Protocol

BP - CPERI Diesel Hydrotreating Catalyst Test Protocol								
	Pressure		Temperature		LHSV	H2/oil		
Condition	(psig)	(bar)	(F)	(C)	Vo/hr/vc	(scf/b)	(nm3/m3)	Feed
1	812	56	650	343	2	900	152	100% LGO
2	812	56	650	343	1	900	152	
3	812	56	650	343	2	6000	1012	70% LGO& 30% LCO
4	812	56	650	343	2	900	152	
5	812	56	650	343	1	900	152	
6	812	56	700	371	2	900	152	
7	812	56	700	371	1	900	152	
8	464	32	650	343	2	900	152	
9	464	32	650	343	1	900	152	
10	464	32	700	371	2	900	152	
11	464	32	700	371	1	900	152	
12	812	56	650	343	2	900	152	

Each condition is held for 3 or 4 days. The test proceeds through this sequence in stepwise fashion. The straight run light gas oil is fed in conditions 1 and 2. Conditions 3 through 10 are on the 30% light cycle feed. Hydrogen pressure is set at 812 psi, and is held there through the first seven conditions. Then there is a block of four low pressure conditions, at 464 psi. Pressure is increased back to 812 psi for the final condition 12. Temperature is varied between 650F and 700F. Space velocity and gas-to-oil rate are also varied.

Example of Catalyst Test Results

To show an example of actual test results, Haldor Topsoe has offered to release some data for their TK 574 and TK 576 BRIM catalysts. We will focus now on four of the test conditions; these are conditions 4, 5, 6, and 7.

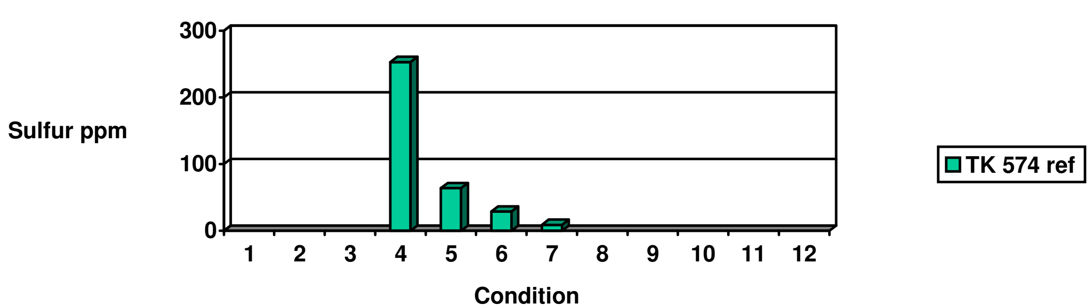
Table 3: Operating conditions for example

BP - CPERI Diesel Hydrotreating Catalyst Test Protocol								
	Pressure		Temperature		LHSV	H2/oil		
Condition	(psig)	(bar)	(F)	(C)	Vo/hr/Vc	(scf/b)	(nm3/m3)	Feed
1	812	56	650	343	2	900	152	100% LGO
2	812	56	650	343	1	900	152	
3	812	56	650	343	2	6000	1012	70% LGO& 30% LCO
4	812	56	650	343	2	900	152	
5	812	56	650	343	1	900	152	
6	812	56	700	371	2	900	152	
7	812	56	700	371	1	900	152	
8	464	32	650	343	2	900	152	
9	464	32	650	343	1	900	152	
10	464	32	700	371	2	900	152	
11	464	32	700	371	1	900	152	
12	812	56	650	343	2	900	152	

The feed during this stage of the protocol is the blend with 30% LCO, the pressure is 812 psi, and the temperature is 650 F and then increased to 700 degrees F. Space velocity is also varied during this stage of the test.

Figure 2 shows the product sulfur levels achieved at conditions 4 through 7 for Haldor Topsoe's TK 574 CoMo catalyst. The feed for these tests was more severe than feeds used earlier in BP's catalyst test program.

Figure 2: Product sulfur at various run conditions



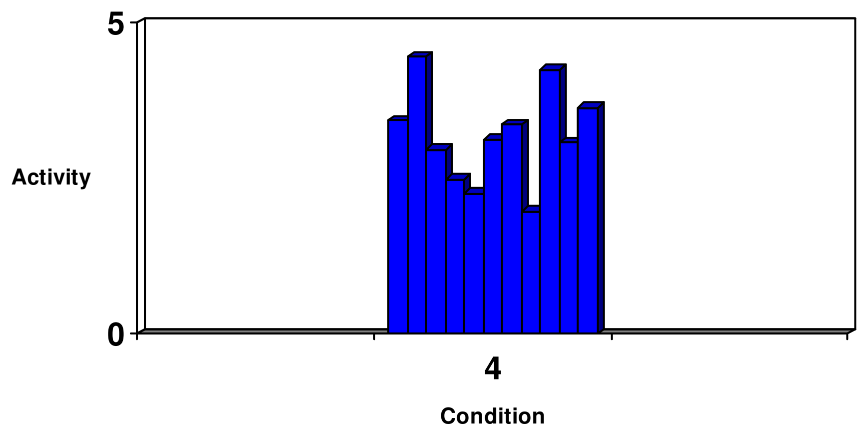
As we move from condition 4 to condition 7, the reaction severity, in temperature and space velocity, is being increased in stepwise fashion. The product sulfur decreases from a high of 258 ppm at condition 4, down to 8 ppm at condition 7.

Catalyst Ranking

When the full protocol is run on different catalysts, a comparative data base is developed showing competitive performance of different catalysts over a range of conditions. This is the data base used to develop BP's rankings.

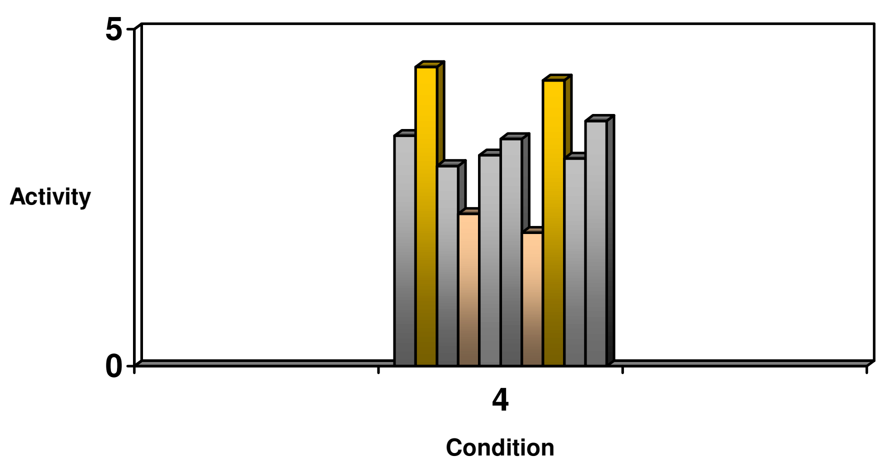
Figure 3 shows desulfurization activity for ten different catalysts as measured at condition 4.

Figure 3: Ranking Catalyst Performance



On the Y axis, the product sulfur measurement at condition 4 has now been converted to relative desulfurization activity. So a higher bar means a more active catalyst. The different bars represent different catalysts. With data like this, catalysts are clustered into tiers. It is not always easy to decide where to draw the lines to separate the tiers. These ten catalysts were grouped by BP into three tiers, as indicated in Figure 4.

Figure 4: Ranking Catalyst Performance



Two of the catalysts, represented by gold bars, ended up in Tier 1. Six of the catalysts, the silver bars, were called Tier 2. Three of the catalysts, the bronze bars, were called Tier 3. Lines were drawn where there were significant gaps in the data.

After drawing lines between tiers, BP does not further differentiate the performance of catalysts within a tier. This means that small or inconsistent differences between catalysts are not considered in catalyst procurement. All catalysts within a tier are considered equal.

When deciding how to separate catalysts into tiers, there are actually 12 sets of data like this to consider, one such comparison for each of the 12 test conditions of the protocol. As conditions are varied through the test sequence, some variables cause the catalyst rankings to change.

For example, changing hydrogen partial pressure causes the rankings to change. Different ranking tables are then made for different pressures, one table for low pressure units, and one table for high pressure units.

Figure 5: Different ranking tables for different pressures

Low Pressure (<40 bar = 580 psi)
Tier 1
Tier 2
Tier 3

High Pressure (>40 bar = 580 psi)
Tier 1
Tier 2
Tier 3

For BP's rankings, the cutoff point for switching tables is 40 bar (580 psig) hydrogen partial pressure.

Similarly, ranking tables may divide catalysts based on feed type, or product sulfur level, if the data say that is necessary. It is still a generic ranking, with the same set of tables for all refineries. But, as a BP unit engineer, you must decide which table to use based on the feed and operating conditions of your unit. If your diesel hydrotreater operates below 40 bar hydrogen partial pressure, then you will use a low pressure table, and if it is an ultra-low sulfur diesel unit operating above 40 bar, you will use a high pressure table.

Catalyst Quality Assurance

In doing this work, it is obviously important to understand the variance of catalyst quality when testing the same catalyst type from the same supplier. This requires understanding the repeatability of catalyst test results. Also, because of the high performance requirements for ultra low sulfur diesel, it is important to consider the consistency of catalyst quality as it is produced over time.

To address this issue, the BP Hydroprocessing and Procurement networks sponsored a catalyst quality study. Haldor Topsoe offered to participate in the study. We will now present results of this cooperative project between BP, Haldor Topsoe, and Cperi Solutions.

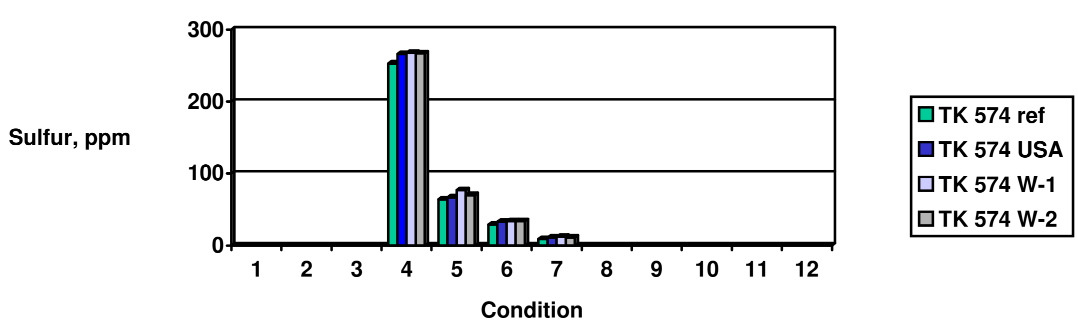
Four samples of TK-574 were tested in BP's 38-day pilot plant protocol – The first sample was the TK-574 pilot plant reference sample, which gave the results shown in Figure 2. The second sample, TK-574 USA, is a sample taken from a commercial shipment as received by a BP refinery in the USA. Samples TK-574 W-1 and W-2 were samples taken from a different commercial shipment as received by a BP refinery outside the USA.

TK-574 Catalyst Samples for Catalyst Quality Study

- Sample TK-574- ref — Pilot plant reference sample
- Sample TK-574-USA — Commercial shipment to BP Refinery in USA
- Sample TK 574-W-1 — Commercial shipment to BP Refinery outside USA
- Sample TK 574-W-2 — Commercial shipment to BP Refinery outside USA

Figure 6 shows the results for the four catalyst samples.

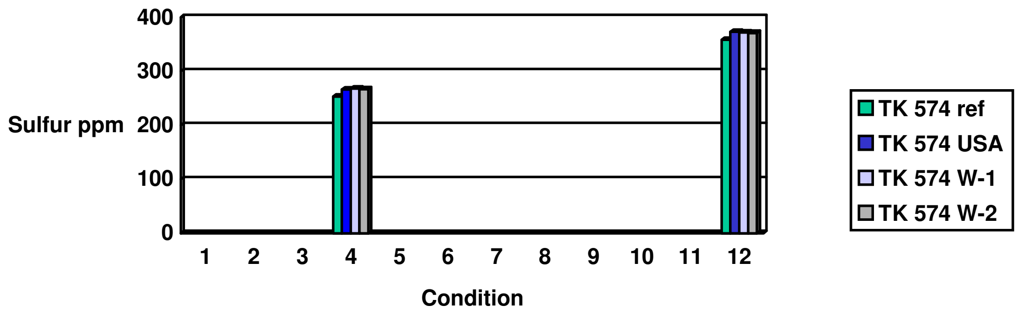
Figure 6: Product sulfur at various run conditions



The commercial shipment samples tested essentially the same as the pilot plant reference sample. The differences between the four samples are very small. This variance is well within the normal variance that we see for a single catalyst, and much smaller than the differences seen between catalysts ranked in different tiers.

It is also useful to look at a comparison of catalyst performance between conditions 4 and 12 of the BP protocol. Conditions 4 and 12 are run on the same feed at the same conditions.

Figure 7: Product sulfur at various run conditions



The increase in product sulfur from 260 ppm at condition 4 to 360 ppm at condition 12 is essentially the same for all of the catalyst samples.

The deactivation measured in this way does not necessarily represent the amount of deactivation expected in commercial service. However consistency in catalyst stability, measured this way, is another useful indicator of consistent catalyst quality.

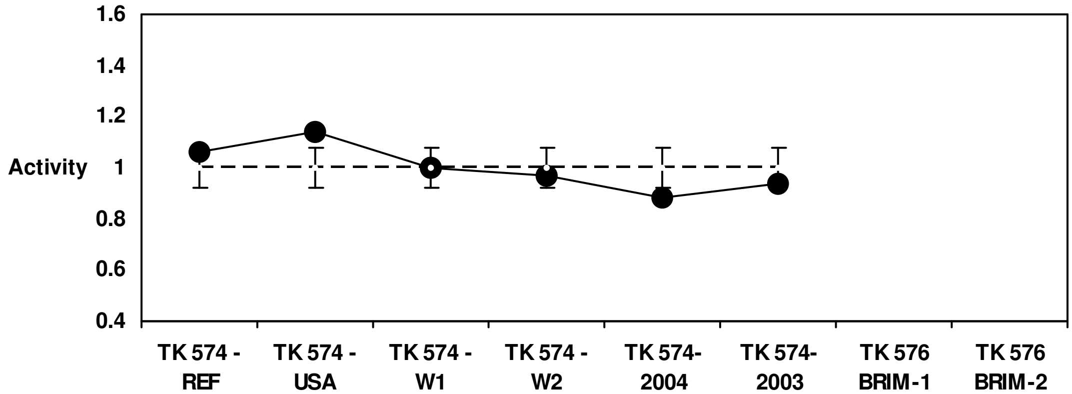
This study assured BP's Hydroprocessing and Procurement networks that Haldor Topsoe catalysts shipped to our refineries can be relied upon for consistently high quality.

Comparison of TK 574 and TK 576 BRIM

Finally, we present an analysis of variance that compares Topsoe's newest diesel hydrotreating catalyst, TK 576 BRIM, with this data on TK 574.

Figure 8 shows the measured desulfurization activity of the four TK 574 catalyst samples tested in the study that has been just described. On the Y-axis is the relative desulfurization activity measured at condition 4 of the BP test protocol. We have now added two more data points. These are from previous pilot plant tests on TK 574 samples. The horizontal line and error bars represent a plus or minus 10% interval around the mean of these data points.

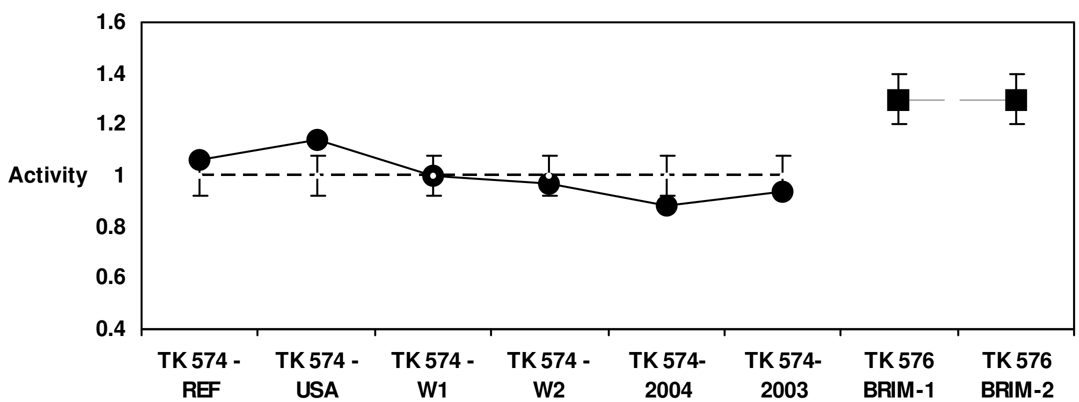
Figure 8: Analysis of Variance
Desulfurization activity at high pressure



From this data we estimate the range of uncertainty on relative catalyst activity is plus or minus 10%, when measured on different samples of TK 574 produced at different times over a period of three years. This range includes many sources of variance in the measured catalyst activity including variance in actual production quality from batch to batch, pilot plant measurement errors, and analytical measurement errors.

In Figure 9, we have included the measured activity from two replicate runs on Haldor Topsoe's TK 576 BRIM catalyst.

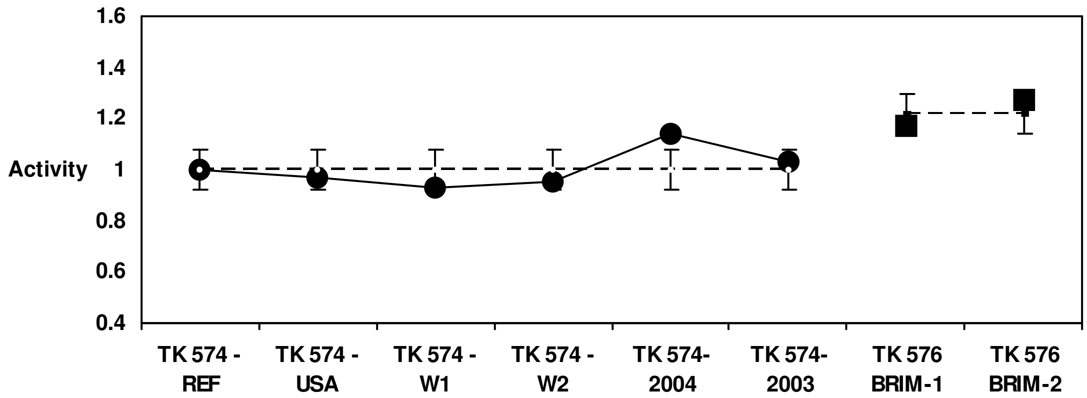
Figure 9: Analysis of Variance
Desulfurization activity at high pressure



Both runs on TK 576 BRIM gave a relative activity of 1.3. This is compared to 1.0 which is defined as the mean of the TK 574 result. There is clearly a gap between the two catalysts, and this gap can be readily distinguished from the variance within a tier. So these catalysts have been placed into different tiers.

This analysis can be done for any one of the 12 pilot plant test conditions. Figure 10 shows the same analysis for a low pressure condition:

Figure 10: Analysis of Variance
Desulfurization activity at low pressure



The mean of the TK 576 BRIM activity is 22% more active than TK 574. So also at low pressure, the data indicate the two catalysts should be placed into separate tiers.

As a result, BP's hydroprocessing network placed TK 576 BRIM in a higher tier than TK 574. Our refineries began ordering it very soon after it was introduced.

Conclusion

In the world of clean fuels, hydroprocessing catalysts are critical for making on-spec product. Consistently high catalyst quality is required. BP's catalyst testing program, managed by its Hydroprocessing and Procurement networks, enables BP to quickly implement and replicate new catalysts when they are introduced to the market. This program has been solidly established as BP's way of selecting hydroprocessing catalysts. It will continue to be used as new catalysts are introduced to the market. A quality assurance study done jointly with Haldor Topsoe has provided further assurance of the consistency of Haldor Topsoe catalysts.