GRACE

SuRCA® Catalyst Reduces Gasoline Sulfur at Three Japanese Refineries

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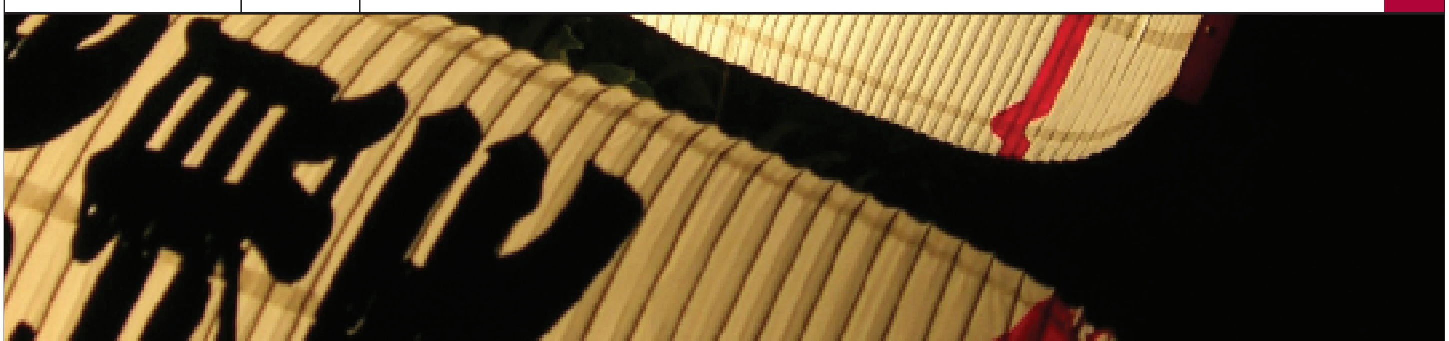


Background of Gasoline Sulfur Regulations in Japan

Refiners in Japan are challenged by increasingly stringent regulations on refinery emissions and product properties. Japanese refiners began supplying gasoline that contains 10 ppm sulfur (0.001 weight percent) on January 2005. This is much more stringent than the 50 ppm government regulation that was imposed January 1, 2005, which was a 67% reduction from the 2004 level of 150 ppm. The oil industry in conjunction with the automotive industry moved to reduce sulfur in fuels years ahead of tighter government regulations in order to reduce CO_2 emissions. The Japanese government is requiring the oil industry to meet the 10 ppm gasoline sulfur standard nationwide by 2008 to reduce carbon dioxide emissions in line with the Kyoto Protocol (Figure 1).

Of Japan's 5.42 million barrels of total gasoline imports in the first six months of 2004, about half came from South Korea. South Korea is also planning to reduce sulfur content in motor fuels but regulations will take effect after the Japanese limits outlined in Figure 1. Currently in South Korea, the maximum sulfur content in gasoline is 130

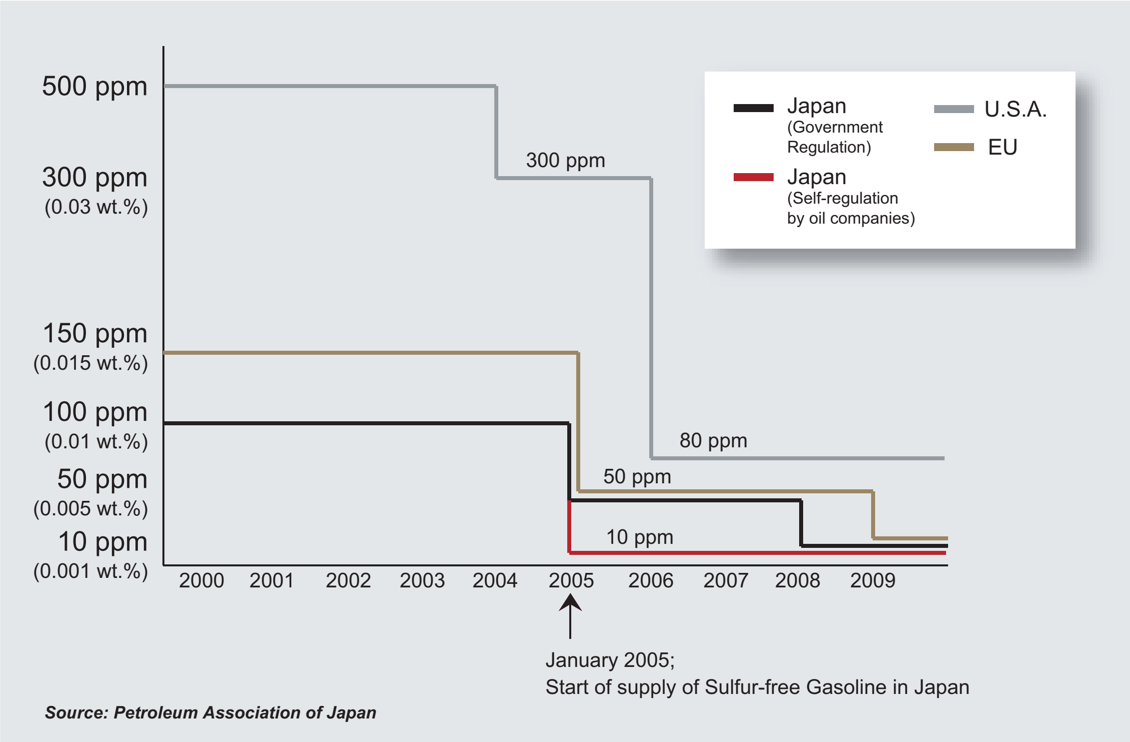


Figure 1: Gasoline Sulfur Regulations in Japan

ppm. On January 1, 2006 the limit will be lowered to 50 ppm, with no plan for further reduction. Unless South Korean refiners complete refinery upgrades to enable them to produce 10 ppm motor fuels, there is a potential for a shortage of low sulfur gasoline in Japan.

Production of Ultra-Low Sulfur Gasoline in Japan

Although refiners have a number of process options to reduce the sulfur level in FCC gasoline, the two most common are: (1) hydrotreating the feed to the FCC unit or (2) hydrotreating the FCC gasoline.

Hydrotreating the FCC feed improves gasoline yield and quality, while reducing the SOx emissions from the FCC unit, but this method is capital-intensive. Refineries wishing to process heavier, less expensive crudes in the future may also need to desulfurize the resulting higher-sulfur gasolines if feed hydrotreating capacity is insufficient. Furthermore, manipulation of process feed sulfur alone may not be sufficient to meet future gasoline performance standards. Benzene and MTBE are regulated to a maximum of 1 vol.% and 7 vol.% respectively in gasoline year round. From early 2005, summer RVP has been self-regulated at <65 kPa.

Most refiners in Japan have elected to heavily hydrotreat FCC feedstocks and therefore base gasoline sulfur levels are extremely low by worldwide standards. The sulfur content of FCC gasoline blended into the gasoline pool typically must be 15 ppm or less, but varies with each refinery.

Figure 2 shows the percentage of refiners in Japan who have elected to install FCC gasoline hydrotreaters to date as well as a projection for 2007.

In Figure 3 the percentage of refiners who have chosen to achieve 10 ppm sulfur operation by modifying FCC

Figure 2: FCC Gasoline Hydrotreater Units in Japan

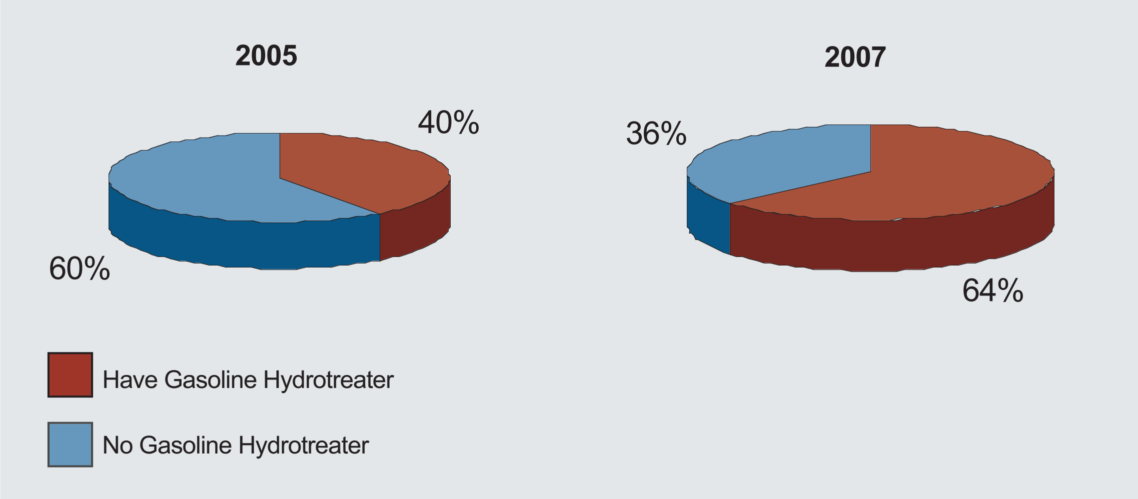
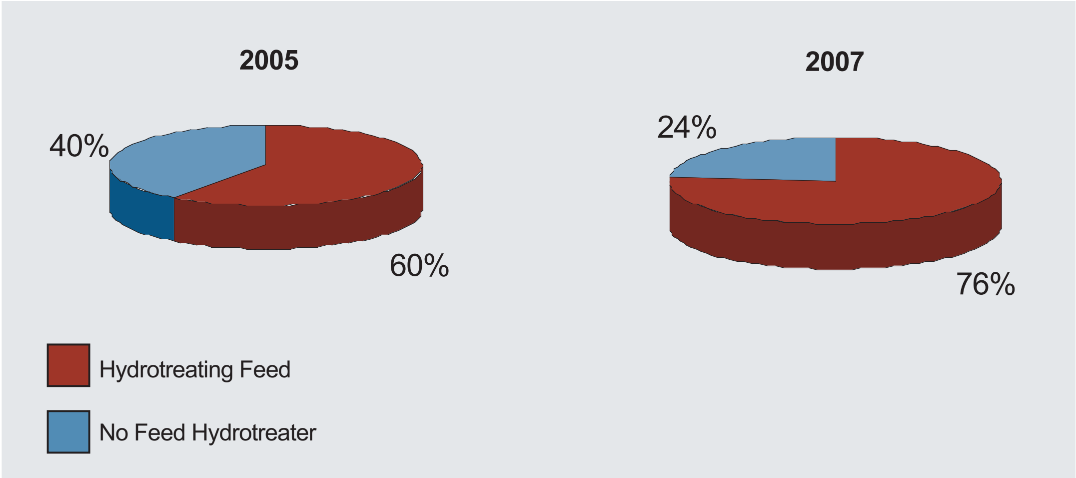


Figure 3: FCC Feedstock Modifications in Japan



feed properties is depicted. There are some refiners who will employ both strategies to meet the gasoline sulfur limits.

Potential Benefits of FCC Gasoline Sulfur Reduction for Refiners in Japan

The sulfur content of FCC feed that has been hydrotreated ranges from 700 ppm to upwards of 3000 ppm. The severity of the hydrotreating operation needed to achieve these levels limits the life of the FCC feed hydrotreating catalyst to one to two years. The use of *SuRCA* (Sulfur Reduction Catalyst) in the FCC unit reduces gasoline sulfur levels by 20-35 percent. By using *SuRCA*, FCC feed sulfur could be increased and the refiner would achieve the same FCC gasoline product sulfur as was produced on the lower sulfur feed. Increasing FCC feed sulfur is accomplished by reducing severity on the upstream FCC feed hydrotreater. Reducing severity of hydrotreater operation will extend the life of the FCC feed hydrotreater catalyst.

SuRCA catalyst technology can also be used to reduce the severity of FCC gasoline hydrotreaters. Lower sulfur in the feed to the gasoline hydrotreater allows lower severity operation to achieve a given product sulfur level. Lower severity has the benefit of reducing octane loss across the gasoline hydrotreater.

Other benefits of FCC gasoline sulfur reduction technology include the potential to increase cut point (T90°) of the FCC gasoline, which increases gasoline yield. Some refiners in Japan are also hydrotreating only a portion of the FCC gasoline stream and using *SuRCA* catalyst to optimize overall refinery production of low sulfur gasoline.

FCC Gasoline Sulfur Species Comparison

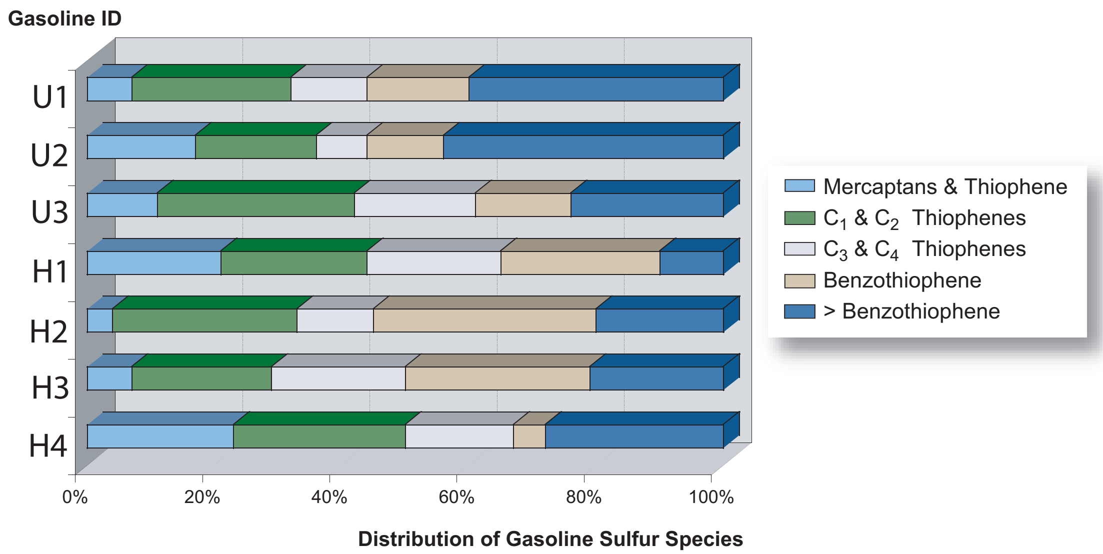
In a typical FCC gasoline sulfur species distribution, the presence of heavier, ringed sulfur species such as benzothiophene and alkylbenzothiophenes (boiling at 430°F+) is dependent upon the cutpoint of the gasoline sample and the efficiency of fractionation between gasoline and LCO products.

FCC feed type and FCC operating conditions do not influence the types of sulfur species present in FCC gasoline. The relative quantity of each of the sulfur species is related only to the feed sulfur content. A hydrotreated or severely hydrotreated FCC feed may have only a few ppm of each of the sulfur species present in the FCC gasoline product and a very low total sulfur level (less than 50 ppm). In comparison a feed that is not hydrotreated may have a couple hundred or even a thousand ppm of sulfur in total, which is spread out among the typical species.

To illustrate these cases Davison has normalized gasoline sulfur species distributions. By normalizing, the sulfur distribution curves for multiple samples can be easily compared. Figure 4 shows a comparison of sulfur species in gasoline from seven FCC units processing unhydrotreated and hydrotreated feeds. The total sulfur in the three gasoline samples produced from unhydrotreated feeds ranges from 750 to 1870 ppm. The total sulfur in the four gasoline samples produced from hydrotreated feeds varies from 20-120 ppm. Notably benzothiophene and heavier sulfur species are present in all seven gasoline samples regardless of feed type or treating.

Grace Davison's *SuRCA* gasoline sulfur reduction catalysts reduce the sulfur species present in full range FCC gasoline. Sulfur reduction is more difficult as sulfur species become heavier, ringed, and boil at temperatures approaching typical LCO boiling range material. Sulfur reduction performance of *SuRCA* will be influenced by significant percentages of these ringed compounds in FCC gasoline. However, as long as hydrotreating FCC feed does not shift the contribution of ringed species to the total gasoline sulfur in the resultant product gasoline, the 20-35 percent range of sulfur reduction performance observed commercially for *SuRCA* would be anticipated for even severely hydrotreated FCC feeds.

Figure 4:
Comparison of Gasoline Sulfur Species Distribution for Unhydrotreated and Hydtrotreated FCC Feedstocks



Gasoline ID	T90°F	FBP°F
U1	399	472
U2	390	484
U3	444	475
H1	359	423
H2	399	449
H3	375	447
H4	324	401

Commercial Performance of *SuRCA* Catalyst

Grace Davison FCC gasoline sulfur reduction catalyst and additive technologies have been used in more than 65 applications worldwide since 1995. Currently there are seven long-term users of *SuRCA*. The average use for these long-term users is 615 days.

SuRCA is unique patented technology that can be built into any Davison FCC catalyst. This allows formulation flexibility to meet a wide range of yield and operating objectives. *SuRCA* provides full range gasoline sulfur reduction in the range of 20-35%, even with heavily hydrotreated FCC feeds. Some commercial applications have also observed up to 25% LCO sulfur reduction.

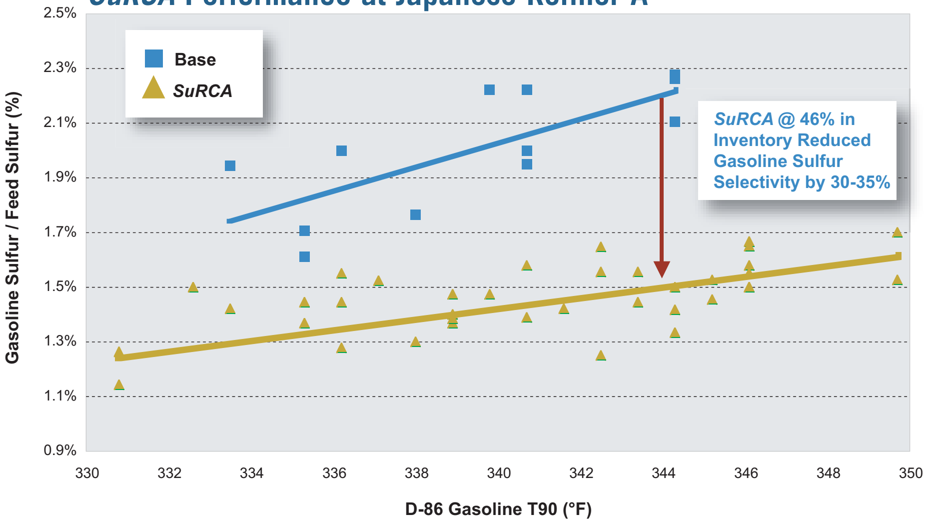
SuRCA catalyst can be "baseloaded" into the FCC catalyst inventory to achieve targeted sulfur reduction performance more quickly.

Table I is a list of refiners that have used *SuRCA*. The **RED** Refiner denotes hydrotreated feed. Average gasoline sulfur reduction observed in these hydrotreated feed applications is 27%.

Table I
Commercial *SuRCA* Applications

	Region	Regen	Unit Design
Refiner 1	AP	PB	EXXON MOD IV
Refiner 2	NA	FB	UOP SBS
Refiner 3	NA	FB	SINC. SBS
Refiner 4	NA	FB	SINC. SBS
Refiner 5	NA	FB	UOP VENTED RIS
Refiner 6	NA	FB	UOP HIGH EFF.
Refiner 7	NA	PB	UOP SBS
Refiner 8	NA	FB	UOP SBS
Refiner 9	NA	FB	EXXON FLEXI
Refiner 10	NA	FB	SINC. SBS
Refiner 11	NA	FB	KEL ORTHO B
Refiner 12	NA	PB	UOP OFFSET HT
Refiner 13	NA	FB	EXXON MOD IV
Refiner 14	NA	PB	UOP STACK
Refiner 15	NA	FB	EXXON MOD IV
Refiner 16	NA	FB	EXXON MOD IV
Refiner 17	NA	FB	UOP OFFSET
Refiner 18	NA	FB	UOP SBS
Refiner 19	NA	PB	UOP SBS
Refiner 20	NA	PB	KEL MOD III
Refiner 21	NA	PB	UOP STACK
Refiner 22	NA	FB	EXXON MOD IV
Refiner 23	NA	PB	UOP STACK
Refiner 24	NA	FB	EXXON MOD IV
Refiner 25	NA	PB	UOP SBS
Refiner 26	AP	FB	SHELL DESIGN
Refiner 27	AP	FB	UOP RISER SBS
Refiner 28	NA	FB	KEL MOD II

Figure 5
***SuRCA* Performance at Japanese Refiner A**



The patented sulfur reduction chemistry of *SuRCA* catalysts provides a mechanism to reduce gasoline sulfur molecules during the cracking process, and converts the gasoline sulfur to H_2S. In all commercial trials to date, the incremental H_2S has not been measurable.

Furthermore, in pilot plant testing of Grace products showing near 50% reduction in gasoline sulfur, the incremental H_2S has also not been measurable. This is due to the fact that the amount of sulfur in the FCC gasoline actually converted to H_2S via a 25-35% reduction is on the order of tens to hundreds of ppm for unhydrotreated feeds (or less than twenty ppm for heavily hydrotreated feeds), and this amount is insignificant compared to the H_2S produced in the base cracking process.

Commercial Examples of *SuRCA* Use in Japan

Japanese Refiner A

The FCC feed is 45,000 barrels per day of 100% hydrotreated VGO. This unit operates in partial burn mode. The customer was interested in gasoline sulfur reduction to meet the Japanese 10 ppm sulfur limits.

The Refiner reached 53% turnover to *SuRCA* at the end of a 3-month trial.

SuRCA catalysts provide a mechanism to reduce gasoline sulfur molecules during the cracking process.

Sulfur reduction was determined by normalizing for gasoline endpoint. Gasoline sulfur reduction at 53% turnover was 30-35%, as observed in Figure 5.

With ~0.2 wt.% sulfur FCC feed with *SuRCA* in inventory, and undercutting of the gasoline to 330°F T90˚, the total pool sulfur was above 10 ppm when FCC gasoline sulfur was combined with the sulfur from the balance of the gasoline pool. Increased hydrotreater severity would have been required to meet <10 ppm “sulfur free” gasoline pool specifications.

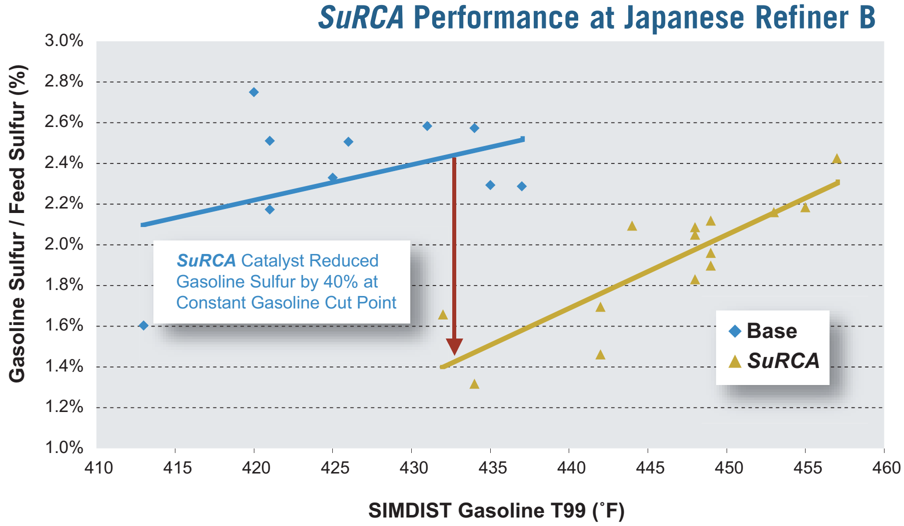
With ~0.1 wt.% low sulfur FCC feed with *SuRCA* in inventory, and undercutting of the gasoline to 330°F T90˚, the total gasoline pool could meet the <10 ppm “sulfur free” gasoline pool specification with FCC gasoline. When FCC gasoline was combined with the balance of the gasoline pool, total pool sulfur was lower. Alternatively, benefits of lower severity hydrotreater operation or higher gasoline endpoint could be considered.

SuRCA catalyst replaced a competitor catalyst and in addition to the 30-35% gasoline sulfur reduction, conversion was higher for *SuRCA* than the base catalyst.

Japanese Refiner B (Ongoing User)

This FCC unit also processes 100% hydrotreated VGO feed. The unit

Figure 6
***SuRCA* Performance at Japanese Refiner B**



charge rate is 40,000 barrels per day and it is a full burn operation.

With the use of *SuRCA*, there was an observed 35-40% reduction of the gasoline sulfur/feed sulfur ratio.

Refiners in Japan are successfully using *SuRCA* to help cost effectively meet gasoline sulfur specifications.

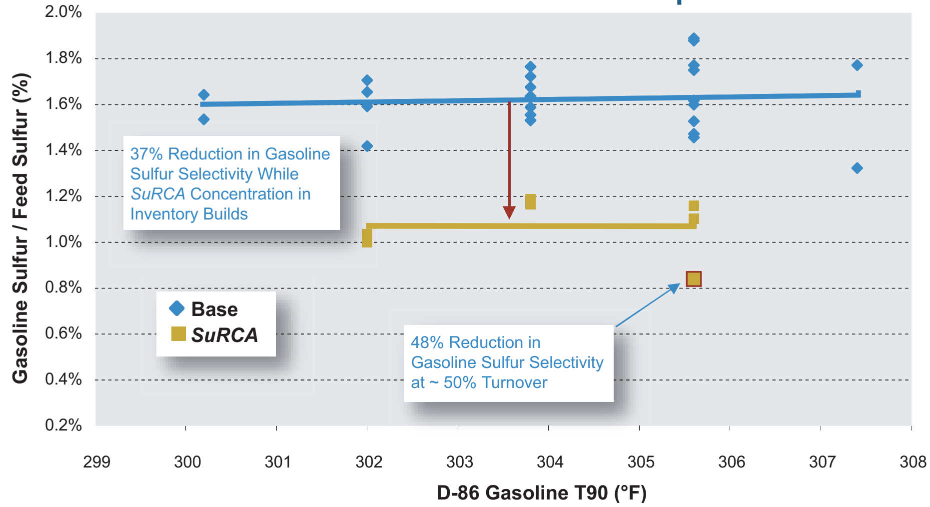
SuRCA was used over a base Grace Davison catalyst. Since the sulfur reduction functionality of *SuRCA* was simply applied to the base Grace Davison catalyst, the use of *SuRCA* did not change product selectivities or RON of the gasoline. Gasoline composition did shift with *SuRCA* (olefins in gasoline decreased, but aromatics and iso-paraffins increased) while RON was maintained. Yields and selectivities of any *SuRCA* catalyst can be adjusted through reformulation of the catalyst.

This refiner continues to use *SuRCA* today to allow them to either blend high sulfur coker gasoline into their gasoline pool or extend the catalyst life of their FCC feed VGO hydrotreater.

Japanese Refiner C (Ongoing User)

Refiner C is a 40,000-barrel per day unit operating in partial combustion mode. Feed to the FCC unit is a blend of hydrotreated VGO and <10% resid. They also have a gasoline hydrotreater to treat FCC gasoline.

Figure 7
***SuRCA* Performance at Japanese Refiner C**



A *SuRCA* trial was conducted for one month and at the end of the trial the Refiner observed a 35-40% reduction in the gasoline sulfur/feed sulfur ratio. This reduction was achieved at 50% turnover to *SuRCA*. Figure 7 shows the performance of *SuRCA*.

The reduction in sulfur may allow Refiner C to decrease the severity of the gasoline hydrotreater. The reduced severity in the hydrotreater would reduce the amount of RON loss across the hydrotreater, thereby increasing the RON of the hydrotreated stream.

In this unit, *SuRCA* replaced a competitor catalyst technology. With *SuRCA* at approximately 50% in inventory, coke selectivity was better, and conversion and gasoline yield was higher than the base, but RON was lower. The catalyst formulation will be adjusted to increase RON and they will continue to use *SuRCA*, replacing the competitor catalyst.

Conclusions

Refiners in Japan are successfully using *SuRCA* to help cost effectively meet gasoline sulfur specifications. *SuRCA* demonstrated an average of 35% reduction in gasoline sulfur at constant distillation conditions with extremely low starting gasoline sulfur levels. *SuRCA* performance with severely hydrotreated FCC feeds provides refiners in Japan using the technology the flexibility to adjust hydrotreater severity (FCC feed or FCC gasoline hydrotreaters), process higher sulfur feeds, or increase gasoline cutpoint. As a result of the success of *SuRCA* at Refiner B and Refiner C, *SuRCA* remains part of the refiners long term plans to meet the 2008 gasoline sulfur specifications.