Application of the Criterion PS-40 CCR Catalyst At the ERE Refinery, Lingen, Germany.

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Abstract

In November 2000, the ERE Refinery at Lingen in Germany took an opportunistic decision to replace the incumbent PS-10 CCR catalyst with Criterion's more advanced PS-40. The new CCR catalyst allowed them to achieve a record maximum feedrate at a higher octane level without the need to revamp the regenerator. The benefits gained from the change-out paid for the catalyst in less than 3 months. This paper presents the experience with PS-40 at ERE

Introduction

The ERE refinery in Lingen, Germany, replaced the existing catalyst with Criterion's PS-10 in 1996. After 4 successful years (>200 cycles) in operation the PS-10 catalyst was far from the end of its life, with a surface area still greater than 140 m^2/g. However, ERE took an opportunistic decision to change to PS-40 to improve the margin on the CCR immediately. PS-40 catalyst is specifically designed to reduce paraffin cracking and therefore the coke-on-catalyst. The first generation CCR platformer at ERE had always been limited by the coke burning capacity of the regenerator section. Criterion proposed that replacement of the PS-10 with PS-40 would allow ERE to reduce coke make by approximately 40% therefore allowing the unit to increase throughput and at the same time, operate at higher severity to meet the octane needs of the refinery. This earlier than expected changeout would result in economic benefits, based on operating margin alone that would pay for the catalyst in less than three months.

ERE and Criterion mutually agreed that this was an excellent opportunity. Furthermore, the old catalyst would be replaced `on-the-fly` (while the unit is running), and the unit would maintain full severity throughout the catalyst replacement operation. This would allow the refinery to avoid an unnecessary shutdown until the mandatory quinquenial turnaround one year later. During this shutdown the PS-10 would be unloaded, density graded and replaced. The catalyst turnaround process was managed by Criterion with assistance from Cat-Tech and CRE, Luxembourg.

Since the change to PS-40, ERE have confirmed that increasing the throughput from 108 to 115 tonnes/hr and the Research Octane Number (RONC) from 100.5 to 101.5 will realise annual benefits of 10 Million Deutsch Marks (5 Million Euros). They also avoided a costly 3 million Deutsch mark (1.5 Million Euro) regenerator revamp. Furthermore, the reduction in platinum content on PS-10 to PS-40 also provided the refinery with a net return of 1.5 million Deutsch Marks (0.75 Million Euros). Therefore, the overall benefits will be approximately 14.5 Million Deutsch marks (7.25 million Euros) and the catalyst payback period (including platinum credits and avoidance of a revamp) was less than three months.

PS-40 CCR Catalyst

Our newest catalyst, PS-40, is designed to significantly improve refiner profits with higher C_5+ yield and better catalyst stability by lowering coke make on catalyst. With PS-40, coke on catalyst is reduced by 30 to 50 percent, with resultant increases in C5+ and hydrogen yield by 1 to 2 wt% and 0.2 wt% respectively. PS-40 provides the refiner more octane barrels and can have an even more substantial payback when used to debottleneck units with undersized regenerators. As with ERE, for refiners with first generation (and with some of the later generation) CCR reformers, PS-40 catalyst will reduce the constraint of the regenerator capacity. PS-40 enables the feed rate to be increased, the octane severity to be increased, or more difficult feedstocks to be processed.

Criterion's catalyst is made by a unique manufacturing technology to achieve the desired dispersion and distribution of promoter metals. A reforming catalyst is mainly composed of high purity alumina. Research has shown that high purity alumina is desirable to balance the dual functionality of metal and acid catalyzed activity. Criterion has developed proprietary technology to modify the alumina acidity of carriers used to make PS-40.

Coke Make Reduction
No Requirement to Revamp The Regenerator

The ERE platformer has a maximum catalyst circulation rate of 209 Kg/hr (460 lb/hr). The coke-burning limit is 13.8 Kg/hr (30.4 lb/hr) of coke resulting in a maximum coke-on-catalyst of 6.6 wt%. This is limited by the peak burn zone temperature of 620°C (1148 °F) at an oxygen level of 1.25%. Any increase in feedrate or octane would push the coke-on-catalyst greater than 6.6 wt% and the peak burn zone temperature would rise too high above the recommended 620°C. This would potentially cause damage to internals as well as catalyst.

In order to increase the throughput using contemporary `conventional` catalysts a revamp of the regenerator internals would be required to increase the coke burning capacity. This would allow the coke on catalyst to be increased. However, this tower internal revamp was estimated to be over 3 million Deutsch Marks (1.5 Million Euros).

Open literature has suggested that contemporary `low coke` catalysts to PS-40 would be able to reduce coke make by only 10%. Thus allowing the throughput to be increased marginally without a tower revamp. The licensor solution would be increasing the throughput by 15% with a combination of a new `low coke` catalyst as well as a tower revamp.

Criterion PS-40 has reduced the catalyst on coke from 6.6 wt% to 3.9 wt%; a significant 40% reduction allowing the refinery to achieve the desired operating objectives without need for capital expenditure and revamp of the regenerator.

The refinery immediately used this reduction in coke-on-catalyst to increase throughput from an average 108 to 115 tonnes/hr (7%) as well as increasing the octane from an average 100.5 to 101.5. They were also able to treat at least 9 tonnes/hr of the more difficult `Heavy Naphtha. The average coke on catalyst is now 5.8 wt%, still not at maximum (6.6 wt%). It is estimated that had the refinery decided to increase the throughput alone, then a least +20% would have been achievable; all this without a regenerator tower revamp.

Reduction in Platinum inventory.

The total inventory of the unit is approximately 50 tonnes of catalyst. Therefore, changing from the high platinum PS-10 catalyst (0.375 wt% Pt) to the low platinum PS-40 (0.3 wt% Pt), the platinum credit was approximately 1200 Troy ounce. At a market price of 600 Euros per Troy ounce, this was worth 0.75 Million Euros to ERE.

High platinum content catalysts are designed for first generation units that have small regenerators with less residence-time for oxychlorination and hence platinum re-dispersion. Therefore, a higher platinum content catalyst could alleviate the loss in performance associated with incomplete platinum dispersion. However, Criterion and ERE were confident that the regenerator at ERE could operate with the lower platinum content PS-40 catalyst and the unit would not suffer from performance problems. As a result, ERE decided to use PS-40 and apply the platinum credit to decrease the payout period.

CRII Group of Companies Manage the Changeout

The `CAT 360` concept of catalyst management has long been practised by the CRII group of companies. The idea that a single focal point can coordinate the catalyst manufacture, the loading and the catalyst recovery has been proven successful in many areas to lower the total cost of a turnaround.

In the reforming area, Criterion in conjunction with Cat-Tech and CRE Luxemburg provided the ERE refinery with a complete service which worked extremely well resulting in considerable time and cost savings and simplified logistics, and is worth looking into in more detail.

Once the catalyst had been manufactured and delivered to ERE in preparation for the change-out, a Criterion engineer was already on site working with Cat-Tech to organise the loading work-area and schedule. Criterion and Cat-Tech have carried out

numerous change-outs `on the fly` now and have improved the operation in several ways to help the refinery overcome several problems. Two examples of these improvements are the `catalyst cooler` and the `de-humidifier tent`. Both of which help the operation run more smoothly and drive the maximisation of severity during the catalyst replacement. (Details below).

a) Catalyst Cooler

Once the line underneath the flow control hopper has been broken and the incline of the discharge pipe has been set correctly to ease the flow of catalyst, the cooler then comes into operation. A water-jacketed unit is connected to the pipe work which accepts catalyst coming directly from the drying zone at >300C (too hot to handle). After passing through the cooler the catalyst is stored for a short period in flow bins and is cooled enough so that the catalyst can be moved away from the site immediately

This benefits the refiner in two ways, firstly the obvious problem of handling hot catalyst is relieved and secondly, the `drying air` can be left in the regenerator. This does not upset the complicated heat balance in the unit and provides for a smoother regenerator operation.

b) De-Humidifier Tent

Fresh catalyst is very hygroscopic, i.e. it can pick up a lot of moisture from the atmosphere during loading and introduce this into the system if it is not protected. Our experience has shown that whether the catalyst is supplied in oxide or reduced form the recycle gas moisture content can rise to above 100 ppm. This is unacceptable when normal operating levels are 15-25 ppm. At levels of 100 ppm moisture several problems will occur. Chloride is stripped from the catalyst thus upsetting the water/chloride balance, promoting cracking; increasing LPG make and reducing C5+ yield. This is difficult to redress, since the amount of chloride required to compensate the loss is difficult to estimate. In addition, the coke on the catalyst increases significantly. This results in the need to reduce the catalyst circulation, reduce the operating severity and ultimately prolong the changeout period.

Cat-Tech have developed a tent, which is dehumidified, therefore the atmosphere inside the tent is controlled to a certain level of humidity, which is less then that of the ambient air. This can help in a high moisture atmosphere.

ERE's turnaround proved that the use of this tent was a success, and as can be seen by the chart below, the moisture in the recycle gas never exceeded 53 ppm. The unit was able to maintain maximum octane and capacity throughout the catalyst replacement.

C5+ and Hydrogen Selectivity and Activity

At ERE, the reduced paraffin cracking function of PS-40 will generate between 0.5 million octane barrels and up to 0.2 wt% extra hydrogen. The severity and throughput were increased directly after the reduction in coke make. Therefore, soon after the change out, the unit was operating at 10% more feed and 1 octane number higher. In conclusion, the yields of hydrogen and C5+ have remained roughly equivalent even at the higher severity when compared to the lower severity operation.

PS-40 met all yield guarantees as confirmed by two consecutive test runs. The data was also used to tune a new kinetic model for PS-40 operation compared to PS-10. Using this model we are able to estimate what the yield would have been at the lower throughout and octane. The table below shows the results. Basically, the table shows that at higher throughput and octane the PS-40 produces equivalent yields to PS-10. At the same throughput and octane target the yields are +2.0 wt% and 0.2 wt% for C5+ and hydrogen respectively.

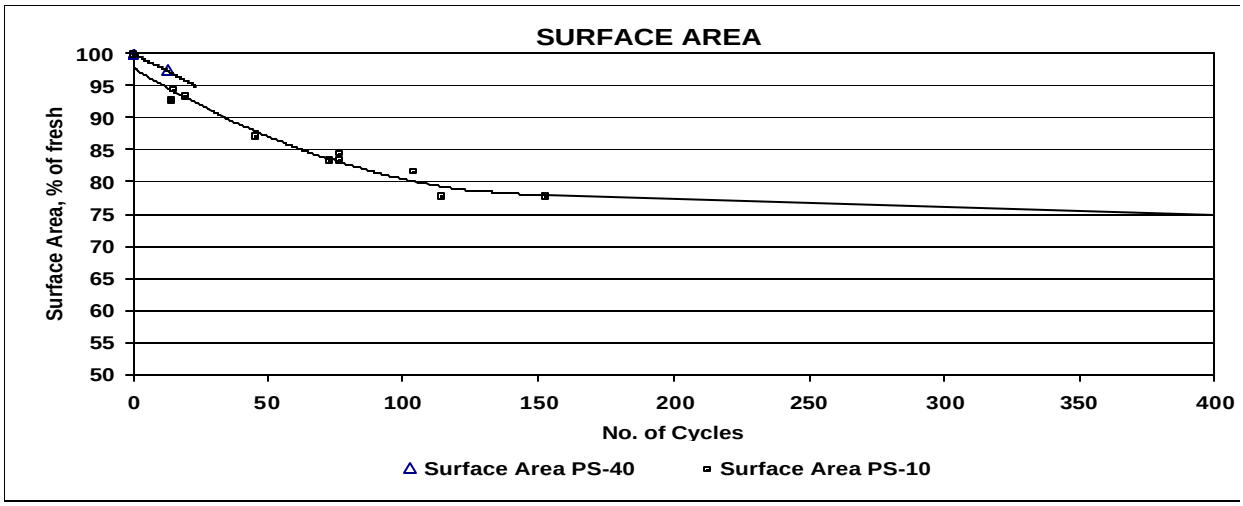
Table 1 – Commercial Selectivity and Activity of PS-10 vs. PS-40.

	PS-10	PS-40
Octane Barrels per year	Base	+0.5 Million
Hydrogen, wt%	Base	+0.2
Activity, °C	Base	Base

Surface Area Retention

Surface area retention for CCR catalysts is important for catalyst life. It is important for chloride retention and therefore yield profile. The chart below also shows the expected surface area decline profile for PS-10 and PS-40. Superimposed on the charts is the reduction is fresh catalyst surface area.

Chart 2 – Catalyst Surface Area



Physical Properties

The PS-40 catalyst physical properties are the same as that of the well-proven PS-10 series. Over 8 years in operation in several locations the PS-10 has proven to be the strongest catalyst on the market. This directly translates to low fines make due to low attrition rates and high crush strength distribution.

During the first 40 cycles (one year) the PS-40 has shown the same excellent strength as PS-10.

Conclusions

1) For CCR units where the regenerator has limited coke-burning capacity, Criterion PS-40 can allow substantial debottlenecking on throughout, provided there are no other operational limits.

2) The magnitude of coke reduction that is achieved will negate the need for a regenerator revamp.

3) The intrinsically lower coke making ability of PS-40 reduces the level of cracking to gas and LPG resulting in higher C5+ and hydrogen yields at the same RONC.

4) The lower coke making capability of PS-40 also gives the refiner flexibility to increase operating severity during periods when higher RONC is required.

Over 20 full charges of PS-40 have successfully been installed in CCR units worldwide. It is also fully compatible with other CCR catalysts and has been successfully used as a make-up catalyst in over 10 units using non-Criterion catalysts.

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Table 3 – ERE, Lingen CCR-Platformer Typical Operating Conditions

Main Process Parameter		
Average Throughput	t/hr	115
Liquid Hourly Space Velocity (LHSV)	hr^{-1}	2.0
Operating Severity	RONC	101.5
Hydrogen to Hydrocarbon Ratio (H_2/HC)	mol/mol	3.4
Weighted Average Inlet Temperature (WAIT)	°F/°C	968 / 520
Product separator pressure	psig / barg	130 / 9.0
Fines-make (wt % on catalyst circulation)	wt %	0.03
Chloride injection (as Cl)	Lb/hr / Kg/hr	0.88 / 0.4

Table 4 – ERE, Lingen CCR-Platformer Typical Feed And Product Qualities During PS-40 Operation

Feed		
Straight run naphtha	%	90.0
Cracked naphtha	%	10.0
Distillation ASTM D86, IBP	F/C	235/113
Distillation ASTM D86, FBP	F/C	365/185
N+2A	vol %	63.0
Product		
Delta C5+ Yield (PS-40-PS-10)	wt%	1-2
Delta H2 yield (PS-40-PS-10)	wt%	0.1-0.2
Octane	RONC/MONC	101.5/90.5