The FCC unit as a propylene source

The FCCU is an important source of propylene production. Additives are essential to optimise the flexibility to respond to today's and tomorrow's challenges

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Propylene has often been considered as "the other olefin", implying a relative unimportance compared to ethylene. However, this view is rapidly changing, with annual worldwide production now in excess of 65 million tons and worth more than $25 billion.[1]

The supply and demand balance is also tightening, as propylene demand growth is forecast by SRI Consulting to exceed 4.5–5.0% per year over the next five years, led by Asia with even stronger growth at nearly 6% per year. This exceeds the forecast growth rate of ethylene by about 0.5%. The consequence of these different growth rates is that by 2015 propylene will form 40% of the total olefin demand.[1]

On the supply side of the balance, propylene is a by-product of ethylene plants and refineries. Currently, about 61% is produced in ethylene plants, 34% in petroleum refineries and less than 3% in on-purpose propylene-only production plants.

Ethylene plants, however, have very limited flexibility for increasing the relative yield of propylene. Table 1 shows that feedstock selection essentially determines the yield ratio, and even the heaviest gas-oil feeds will only produce about 37.5% propylene. In 2005, the average was only 29% propylene, and most of the relative future growth will need to be met from refinery sources.

In refineries, while cokers and visbreakers produce some propylene, the majority comes from FCC units. Indeed, it is only in refineries with FCCUs that the scale of production supports the investment in recovery of propylene as a separate product. Propylene production in refineries is also increasing as refiners struggle to blend FCCU naphtha and propylene polymer gasoline into the gasoline pool due to increasingly restrictive product specifications. The major advantage the FCCU has over steam crackers is its high degree of flexibility in low-cost feedstock selection and product yields. The FCCU operator can use a combination of operating conditions, catalyst selection and additives that can be adjusted to suit the current economics. All these factors combine to make propylene ever more important to refinery and FCCU economics.

Steam cracker production ratio

Feed	Propylene/ethylene	% propylene
Ethane	<1	<1
LPG	0.33–0.46	25–32%
Naphtha	0.40–0.57	29–36%
Gas oil	0.53–0.62	35–38%
2005 average	0.40	29%

Table 1

Commercial ZSM-5 yields

	Base case	With 5% Super Z	Difference
Operating condition			
Riser outlet temperature, °C	505	505	–
Regenerator temperature, °C	695–700	695–700	–
C/O	7.9	8.0	0.1
HCO recycle ratio	0.30	0.34	0.04
Products yields			
Dry gas	3.8	3.9	+0.1
LPG	29.5	33.2	+3.7
Propylene in LPG, wt%	37.0	39.0	+2.0
Propylene	10.9	12.9	+2.0
Gasoline	30.0	26.0	-4.0
Diesel	26.5	26.9	+0.4
Slurry	2.6	2.2	-0.4
Coke + loss	7.6	7.8	+0.2
Light ends	86.0	86.1	+0.1

Table 2

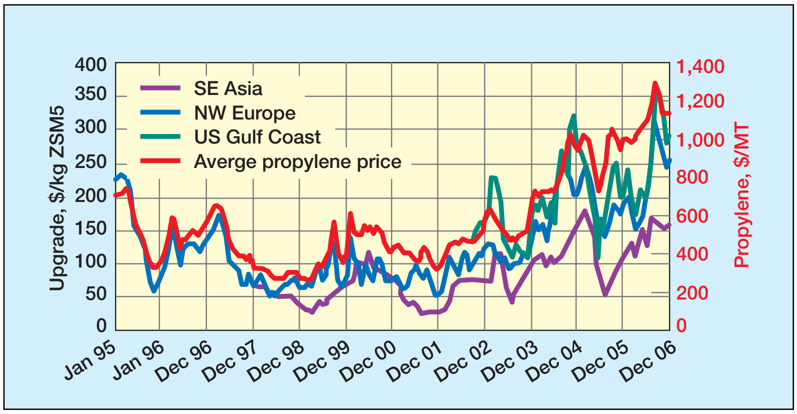

Figure 1 Regional ZSM-5 margin trends

This increasing importance of propylene to FCCU economics can be demonstrated using a simple model based on the commercial yields shown in Table 2. These come from a high-propylene yield unit running resid feed.[2] They illustrate what a unit designed for this type of operation can achieve, and how using incremental high-activity ZSM-5 additive can further enhance the propylene yields.

Economics of FCCU propylene production

Figure 1 gives the product upgrade value per kg of ZSM-5 for these yields for three regions using the appropriate Platts average prices. Superimposed is the cross-regional average propylene price. The ZSM-5 margin closely tracks the propylene price, showing how important this price is to ZSM-5 economics. The steep rise in this margin since 2003 is a major contribution to significantly improved overall FCCU margins.

Increasing FCCU propylene yield

What can the refiner do to maximise the propylene yield from the FCCU? Not surprisingly, high propylene yields follow from high conversion and selective cracking. Using a combination of unit and catalyst design plus additives, refiners can substantially increase the propylene yield from the process.

Unit design Unit design changes are only an option when designing a grassroots project or revamping an existing unit. For propylene maximisation, the reactor/regenerator design objectives should be a high cat-to-oil ratio and high riser temperature to give a high conversion, and short contact time for selective cracking. Good catalyst activity maintenance is also important, since it increases conversion and improves selectivity, while allowing greater flexibility in catalyst design.

Light ends handling capacity is crucial when designing for maximum propylene. Areas such as the wet gas compressor, amine treating and fractionation should be sized to ensure the economic maximum propylene recovery is achieved. For revamps, switching tower internals and possibly even overhead refrigeration may be warranted, particularly when ethylene recovery is also intended.

Catalyst design The constant replacement of the FCCU catalyst is a significant part of the inherent flexibility of the process compared to the relatively fixed yields from a steam cracker. However, in designing a catalyst, there are always diverse needs, which force compromises and limit this flexibility. Inevitably, there are trade-offs, but high activity with low coke selectivity is usually a good starting point on the way to high conversion. For residue operation, the right balance between bottoms upgrading and metals tolerance is critical, while for propylene selectivity low hydrogen transfer activity has to be traded against stability. Added to this is the need to retain flexibility to respond to short-term opportunities and constraints. It is in this area in particular that the separation of base catalyst and additive functions can have a major impact.

Additive design Additive systems allow the refiner to compensate for the compromises in catalyst design, while still offering synergistic benefits and enhanced flexibility. For example, bottoms-cracking additives can increase conversion without coke penalties, while metals-trapping additives aid catalyst activity maintenance.

ZSM-5

Although ZSM-5-based additives were first used to boost the gasoline octane rating during the phase-out of lead in the US and Europe, they have now become the key lever used by refiners to increase olefins production. ZSM-5 is now regularly used in over 50% of FCCUs worldwide. The reason for this is that while there are alternative methods for increasing gasoline octane and LPG yield, such as raising the reactor temperature, using ZSM-5 offers the advantage that the cracking reactions it promotes are very selective, and hence the desired yield and octane shifts are achieved with no increase in undesirable C_2- and coke yield.

ZSM-5 zeolite has a unique three-dimensional structure, with very small pores compared to the Y-zeolite in normal FCCU catalyst. This makes ZSM-5 zeolite "shape-selective" for cracking the long chain (C_6-C_{10}) olefin molecules in FCCU gasoline (it also cracks the equivalent paraffin molecules but at a much slower rate). The products of these cracking reactions are predominantly C_3= and C_4=, with a small amount of iC_4. It is the removal of these low-octane components, along with isomerisation reactions occurring in the ZSM-5 cage, which results in a significant increase in gasoline octane.

ZSM-5 is also effective in boosting the propylene yield, even when used with a high Re_2O_3 content FCC catalyst, because it cracks olefins before they can react with hydrogen to form a paraffin.

ZSM-5 technology developments

There have been a number of advances in ZSM-5 technology in recent years, such as changes in the zeolite Si-to-Al ratio and increased activity.

In gasoline-focused refineries, increasing the Si-to-Al ratio in ZSM-5 is used to alter the ratio of cracking-to-isomerisation rates. Additives such as Isocat produce similar octane gains to traditional ZSM-5 additives, but at a reduced LPG yield. This is ideal for those units with LPG-handling constraints.

Where olefin production is more important, ZSM-5 additive activity increases have contributed to enhanced yields. These advances have come from two sources and are particularly important when using high levels of additive. Major improvements in binder technology have increased the zeolite accessibility and stability, and provided higher activity per unit of zeolite. This was demonstrated in the switch from Intercat (Johnson Matthey)'s original Z-CatT Plus product to Penta-Cat and has improved the cost-effectiveness of using ZSM-5. Combining this with the second advance — namely, an increase in the ZSM-5 concentration of the additive — resulted in additives such as Z-Cat HP. This uses the same type of zeolite as Penta-Cat, but at an increased zeolite loading and hence higher activity per particle. These developments continue with Super Z as the latest product and highest activity additive.

Additive synergies

	Base e-cat	BCA-110 Plus	Super Z ZSM-5 additive	Blend of 60% Super Z & 40% BCA-110 Plus
Total additive concentration	–	10%	10%	10%
Conversion, wt%	75.6	77.5	76.0	76.8
C_2-	2.4	2.6	4.1	3.6
LPG	24.7	25.4	34.6	33.0
Total gasoline	44.7	45.4	33.7	36.3
LCO	15.6	15.0	15.1	15.1
Bottoms	8.7	7.6	8.8	8.1
Coke	3.8	4.0	3.7	3.8
ΔLPG	0.0	0.7	10.1	8.6
Expected LPG increase if no synergistic effects present				6.3

Table 3

ZSM-5 synergy with other additives

A controlled separate addition of catalyst and additives allows the synergistic effects from combinations of ZSM-5 and other additives to be exploited. The following laboratory study for a refiner needing to maximise their LPG yield demonstrates this effect. This investigation compares the yields achieved by adding 10% of a bottoms-cracking additive (BCA-110 Plus); 10% of a high-activity ZSM-5 additive (Super Z) and 10% of a 40:60 blend of BCA-110 Plus and Super Z.

Table 3 shows how the two additives in combination give increased conversion and propylene yield over the level expected from an average of the individual contributions. On the commercial unit, the refiner can gain enhanced flexibility as well by adding the additives separately.

ZSM-5 additive activity range

In selecting a ZSM-5 additive, the refiner needs to consider both the fresh activity and how well

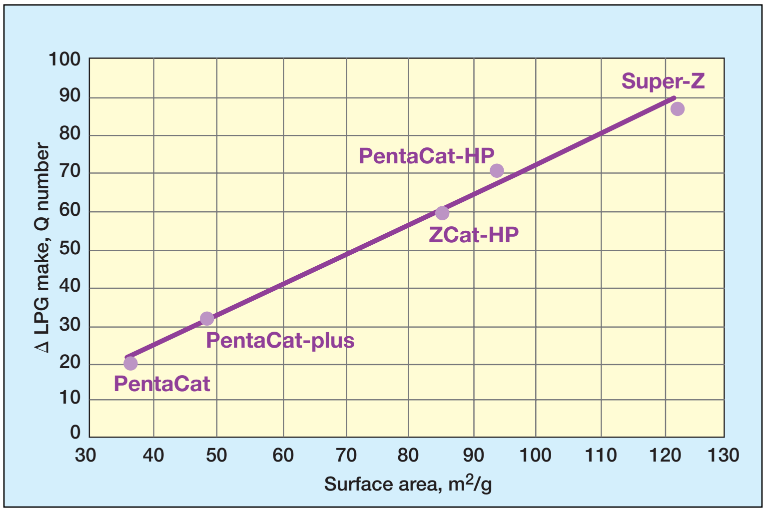

Figure 2 Intercat standard ZSM-5 additive range

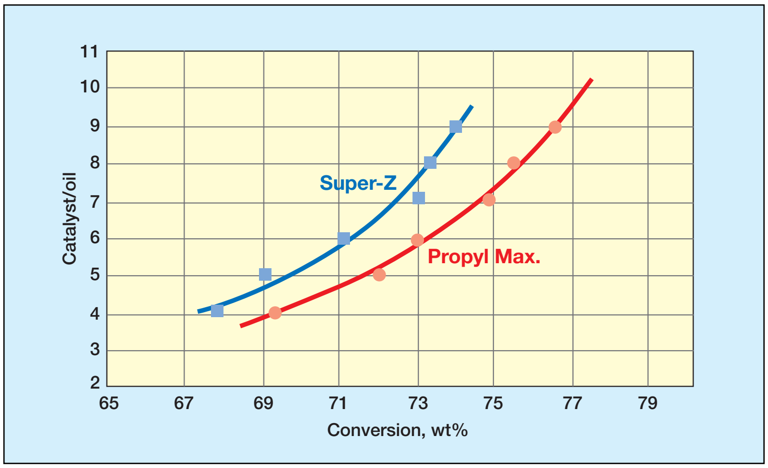

Figure 3 Propyl Max coke vs conversion

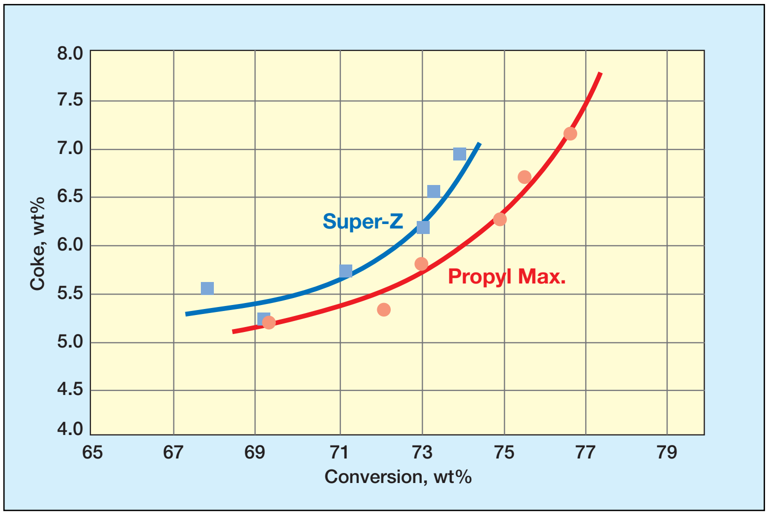

Figure 4 Propyl Max cat-to-oil vs conversion

that activity is maintained in use. The higher-activity additives are useful for those units with catalyst dilution concerns or circulation constraints, but for some units lower-activity additives are appropriate.

Intercat (Johnson Matthey) uses a proprietary "Q Number" quality-control test to ensure their standard ZSM-5 additives have consistent activity and deactivation characteristics. This compares LPG production from every ZSM-5 additive production batch against a laboratory standard sample. Figure 2 shows how the Q Number can also be used to compare standard ZSM-5 additives.

ZSM-5 dilution effects

In units targeting high propylene yields, where additions of ZSM-5 additives are in excess of 10%, dilution of the base catalyst with the additive can become a problem. Ultra-high ZSM-5 zeolite content additives like Super Z are one approach. However, for the units with more than 15% ZSM-5 additives, Propyl Max has recently been introduced, which is specially formulated to enhance conversion as well as converting gasoline olefins to light olefins.

The laboratory data in Figures 3 and 4 show how Propyl Max increases conversion at constant coke relative to Super Z. Hence, Propyl Max gives increased propylene yield without coke penalty in dilution-constrained units, or less gasoline loss and improved bottoms upgrading in LPG-constrained units. Propyl Max is intended to maximise LPG with minimum conversion loss. This is because Propyl Max is designed to make gasoline olefin precursors to feed the ZSM-5, so it never runs out of feed.

Most current ZSM-5 additive users are not at the maximum activity grade, so switching to higher-activity grades is still an option. The following commercial data comparison is from a European refinery, which was already using ZSM-5 additives in its FCCU for increasing propylene production. Prior to the trial, it was using 7% of 25% zeolite content ZSM-5, in combination with 5% pre-blended, plus 2% separately added. In the trial, Super Z alone was added at the rate required to maintain a constant propylene yield. This was achieved with 4.8% of fresh catalyst additions. The refinery used high-quality mass-balanced test run data to evaluate the trial, which gives a very accurate comparison. The results in Figure 5 clearly show this 74% increase in propylene per kg of additive.

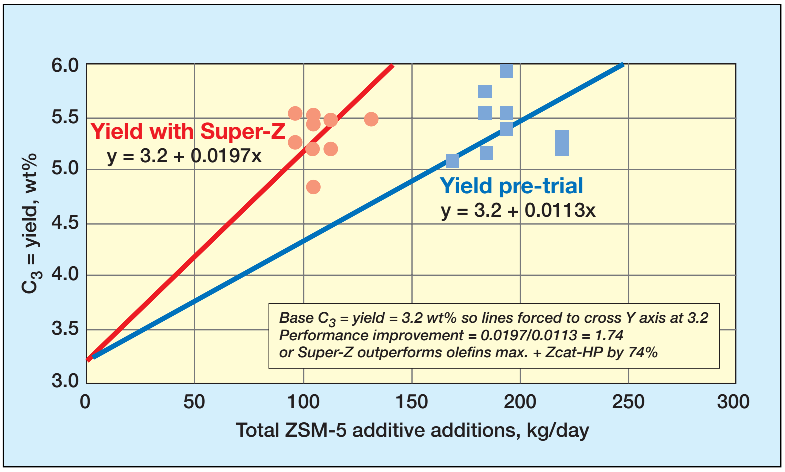

Figure 5 Commercial test of Super Z

Benefits of separate controlled addition rates

Adding fresh catalyst and additives on a continuous and reliable basis has always been an objective of FCCU operators. Continuous and precise separate additions allow the most efficient use of each catalyst component and, through smaller unit fluctuations, enable the FCCU to operate closer to its mechanical limitations. With the reduced deviation from targeted operation and more accurate activity maintenance, unit throughput and conversion can be maximised with greater flexibility in the choice of feedstocks.

Historically, it has been difficult to design systems that operate reliably for any length of time and, as a result, many refiners have switched to catalyst pre-blended with ZSM-5 additive and other additives. However, there are many hidden problems with pre-blending.

For example, the inventories in the supply chain at a fixed ratio of catalyst-to-additives prevent a quick response to changes in economics or FCCU operation (eg, gas compressor limits). There can also be operating problems when feed quality (vanadium) or catalyst addition rates vary over time due to the difference in the deactivation mechanism for Y-zeolites and ZSM-5 zeolites. This is because both Y-zeolite and ZSM-5 zeolite, in a low contaminant metals environment, deactivate hydrothermally at a similar rate. Therefore, with less than 2000 ppm vanadium on e-cat, both materials will deactivate at a similar rate, leading to a constant ZSM-5-to-Y-zeolite activity ratio, independent of the fresh catalyst addition rate or unit operating conditions. However, once the vanadium is over 2000 ppm, it accelerates the rate of Y-zeolite activity loss, but leaves the ZSM-5 unaffected. As the feed vanadium level varies, Y-zeolite activity in the unit will also vary at a constant fresh catalyst addition rate. The consequence is a variable ZSM-5-to-Y-zeolite activity ratio, resulting in non-optimum yields and product qualities. If the fresh catalyst addition rate is adjusted to keep Y-zeolite activity constant, the addition rate of ZSM-5 is changed and again leads to a variable ZSM-5-to-Y-zeolite activity ratio.

This problem has been seen in several locations and can be quite severe. Symptoms include:

- Wide variation in gasoline octane number and composition
- Unit inexplicably becoming gas compressor limited for several days at a time
- Wide variation in LPG production rate, especially on bad feeds
- The overall effect is to shift the FCCU operation away from the optimum.

Reliable, closely controlled separate addition of the correct amount of catalyst and additive every hour of every day should be the norm. Traditional loader designs have a large number of moving parts in regular contact with the catalyst, and after 6–12 months' operation often require almost continuous attention by maintenance personnel to cope with repeated breakdowns, instrument failures and catalyst spillages. In contrast, the proprietary Intercat (Johnson Matthey) catalyst-addition system contains only one regularly moving part in contact with the catalyst.

Typical commercial experience with the catalyst-addition system is greater than 99% availability, with only an annual check as planned maintenance. On average, there is just over one unplanned maintenance item per year. These are mostly trivial in nature, such as blown light bulbs, and involve minimal time and cost to repair, and reliability ceases to be an issue.

The accuracy and ease of monitoring of Intercat (Johnson Matthey)'s addition systems is because the system hopper is mounted on load cells, and the contents are weighed after each addition. The Intercat (Johnson Matthey) management system controller readjusts the loading schedule after each addition to meet the target daily rate. On a day-to-day basis, the addition rates from Intercat (Johnson Matthey) systems are usually well within 0.5% of target. This accuracy removes the necessity for hopper "dips" and bin/bag counts to assess how much catalyst has been added to the FCCU, and has allowed for the introduction of remote inventory management and consignment stocking of additives.

Summary

The FCCU is an increasingly important source of propylene production, and propylene price is becoming a major driver of the process economics. Hardware and catalyst design changes, which maximise conversion and selectivity, can increase the propylene yield, but ZSM-5 and other complementary additives are essential to optimising and retaining the flexibility to respond to today's and tomorrow's challenges.

Isocat (ISOCAT), Z-CatT Plus (Z-CAT Plus), Penta-Cat (PENTA-CAT), Z-Cat HP (Z-CAT HP), Super Z and Propyl Max are marks of Intercat (Johnson Matthey).

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