

Increasing catalytic reforming yields

Case study where a CCR Platforming process unit increased profitability by changing to a high-density catalyst. Higher aromatic yields and the ability to load new catalyst without a unit shutdown helped to justify the costs

Mark P Lapinski, Joe Zmich and Steve Metro *UOP LLC*
Nungruetai Chaiyasit and Kosol Worasinsiri *PTTAR*

Since the commercialisation of the first UOP continuous catalyst regeneration (CCR) Platforming unit in 1971, these catalytic reforming units have become the preferred choice for converting naphthas into high-octane product for the gasoline pool, aromatics for petrochemicals production and hydrogen for clean fuels hydroprocessing. There are currently over 200 of these units in operation, with more than 50 additional units in various stages of design and construction. Many reforming units originally designed and built as semi-regen fixed-bed units have been revamped to continuous-regeneration units, with almost all new reforming units being the continuous-regeneration type.

The continuous burning of coke from the catalyst was a large step-change in reforming performance, since it permitted operations at low pressures and high conversions to achieve much higher product yields. Continuous innovation in both CCR catalyst and processing technologies has enabled even higher performance and profitability. Loading an improved catalyst remains one of the most economical methods for further improving reformer capabilities. Combining this with the on-the-fly reloading capability of CCR Platforming units, a new type of catalyst can be added to the unit while the older catalyst is withdrawn without shutting down the unit. Since production losses during catalyst reloading are minimised, the on-the-fly method enables the changing of catalysts with minimal processing penalty.

CCR catalysts

UOP's R-264 is the newest CCR Platforming catalyst on the market that allows continuous-regeneration units to increase throughput and/or yields while reducing coke production. Compared to UOP's R-130 series catalysts, R-264 consists of a higher-density alumina support with a tailored pore structure

“UOP's R-264 is the newest CCR Platforming catalyst on the market that allows continuous-regeneration units to increase throughput and/or yields while reducing coke production”

and a re-optimised metal/acid balance. These properties result in enhanced yield activity performance with approximately 20% less coke make. The catalyst can be operated in either a high activity mode to process more feed or achieve higher octane, or in a high yield mode to achieve higher yields. In addition, the tailored pore structure minimises very small pores, which allows for faster coke burning rates in the regenerator.

The R-264 catalyst has the ability to debottleneck units that are pinning constrained. Catalyst pinning is the condition where the force from the horizontal flow of feed across the downflowing catalyst results in the catalyst being held up against the centre pipe screen.² Pinning should be avoided since it impairs the reactant flow distribution, leading to lower conversion and significantly higher coke production. The catalyst's physical properties reduce pinning, allowing a higher feed throughput. As a result, the hydraulic capacity in many CCR Platforming units can be increased by approximately 10–20%, depending on whether the hydrogen-to-hydrocarbon (H_2/HC) ratio or recycle gas flow remains constant. The increased product volume from a higher feed rate results in significant increases in profitability.

The catalyst also has high chloride retention and high surface area stability compared to other commercially

available CCR Platforming catalysts. In terms of platinum costs, the total amount of platinum loaded in a reactor for the higher-density R-264 catalyst is similar to that required for the lower-density UOP R-134 and R-234 catalysts. This makes change-outs to R-264 economically attractive. Overall, R-264's properties allow it to be a drop-in replacement catalyst for most existing continuous-regeneration reforming units.

R-264 is used in both new and existing reforming units. The catalyst was first loaded in an existing European CCR reforming unit in 2004.³ Since then, it has been operating well in over two dozen CCR Platforming units worldwide.

With the ability to maximise yields, R-264 is preferred for almost all new CCR Platforming units for both motor fuel and aromatics applications. The industry trend for new CCR Platforming units has been towards larger-capacity units. The average capacity of a unit designed over the past few years has increased from 25 000 bpd (166 m³/hr) to 40 000 bpd (265 m³/hr). The high-density catalyst formulation facilitates smaller-sized reactors and smaller regenerators, resulting in lower equipment costs and project net present values. For designs that employ lower-density catalyst, the catalyst offers an economical means of obtaining additional capacity without capital expenditure.

R-262 catalyst

A small number of CCR Platforming units operate under severe or non-standard conditions and experience a diminished metal function. For example, a few units operate with higher sulphur in their naphtha feedstock. Sulphur is a known poison to platinum in catalysis. The R-262 catalyst was designed specifically for the above types of CCR Platforming applications and contains a higher platinum level than R-264. The higher platinum content in R-262 maintains the proper metal function in

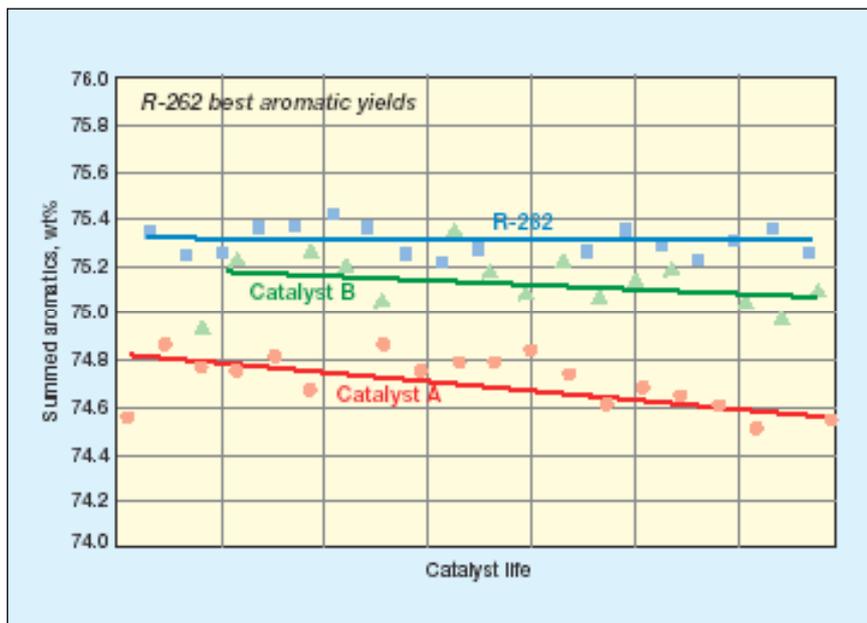


Figure 1 Pilot plant results for CCR Platforming catalysts under high sulphur conditions

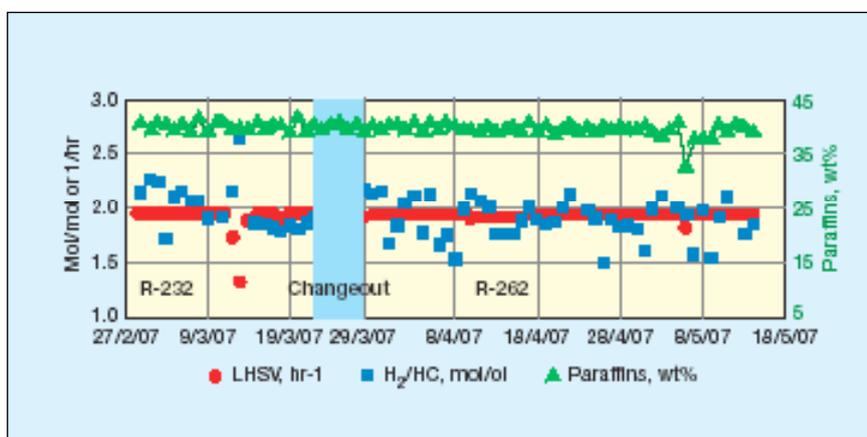


Figure 2 PTTR feed and process conditions

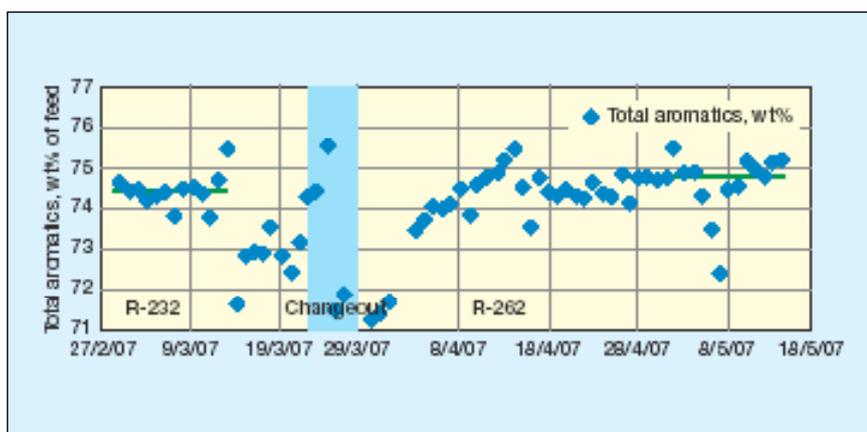


Figure 3 PTTR reactor temperatures and octane

these applications, maximising the C₅+, aromatics and hydrogen yields. Like R-264, the R-262 catalyst can be operated in either high activity or high yield modes.⁴

Case study

The R-262 catalyst was put into service in March 2007 at the PTT Aromatics and Refining Public Company Limited

(PTTAR), previously The Aromatics (Thailand) Public Company Limited (ATC), in Map Ta Phut, Thailand. PTTAR operates a UOP CCR Platforming unit at the feed rate of 26 362 bpd (175 m³/hr) with a pressurised CCR regenerator. The naphtha feed to the unit typically consists of approximately 85% N+2A with an ASTM D86 endpoint of 320–329°F (160–165°C). The feed also

contains higher sulphur than typical for a CCR Platforming unit. The catalyst in the unit prior to the change-out was UOP's R-232.

Since the existing R-232 catalyst was operating beyond more than 550 cycles with good platinum dispersion and on-target chloride level, an economic case was needed to justify the early replacement of the catalyst. PTTAR's goals were to maximise the aromatic and hydrogen yields at the current feed rate, but also to have a catalyst system that was flexible and could be utilised for higher throughput in the future. To help develop a justification, PTTAR's naphtha feed was sent to UOP's research and development centre for characterisation and pilot plant testing. Pilot plant runs were conducted on several UOP catalysts with the PTTAR feed at typical PTTAR process unit conditions. To ensure the best catalyst would be identified for its operation, the H₂S partial pressure was set in the pilot plant to match PTTAR's at the inlet of reactor No. 1. All the pilot plant runs were done in an accelerated stability test format by increasing the temperature to maintain the target octane as a function of time. Under the high sulphur conditions, the pilot plant results showed that the R-262 catalyst had the highest aromatic yields and the highest yield stability (Figure 1). This catalyst was ultimately selected by PTTAR for its new operation.

Detailed discussions were held between PTTAR and UOP covering unit operations when changing from a low- to high-density catalyst and the procedure for reloading the catalyst on-the-fly. For unit operations, only very minor adjustments are needed for operating with a high-density versus a low-density catalyst on CCR Platforming units.

For reloading, the design of the CCR Platforming unit permits on-the-fly reloading while the unit continues to convert feed to products. Fresh catalyst is added to the unit while the old catalyst is removed. UOP has had experience with over 50 on-the-fly-type reloads, including changing from low- to high-density catalysts. The on-the-fly catalyst change-out is specifically utilised when a catalyst needs to be replaced between routine turnaround maintenance and inspections (about every three to four years). For PTTAR, the reason for the catalyst replacement was to realise the increased yields and profitability from a higher performance catalyst. A shutdown at PTTAR was not an option in 2007, so the on-the-fly capability was critical.

Another consideration for the reload project was managing the platinum costs. Since platinum costs have been rising dramatically in recent years,

increases in the reactor platinum inventory can be a significant cost for a refiner. Since PTTAR was already operating with the higher platinum, low-density R-232 catalyst, there was no increase in platinum requirement when switching to R-262. On a total volumetric fill cost basis, the platinum content of the R-262 catalyst was equivalent to R-232, making the investment platinum neutral.

Based upon the UOP pilot plant yield results, technical proposal, discussions, experience and change-out plans, PTTAR was able to justify the catalyst replacement to R-262. The on-the-fly reload was successfully completed in March 2007 with on-site UOP service expertise. PTTAR was able to maintain 90–100% of its feed rate during the approximately one week change-out period.

To demonstrate the performance differences, data was obtained before and after the catalyst replacement while process conditions and feed quality were kept as similar as possible. Figure 2 illustrates that the feed properties and conditions were similar before and after the catalyst change-out. Figure 3 shows that the R-262 catalyst resulted in a 7°C lower weighted average inlet temperature (WAIT), while Figures 4 and 5 demonstrate an increase in total aromatics and hydrogen yields for the R-262 catalyst. To gauge the profitability from the change-out, PTTAR performed an economic evaluation examining the product yields, values, energy usage and the benefit of high chloride retention for the R-262 catalyst versus the R-232 catalyst both at start-of-run (SOR) and before change-out. Based upon actual performance, PTTAR calculated an economic benefit of \$3.1–3.8 MM \$/yr for the R-262 catalyst and payback of its investment within one year. At the time of writing, the R-262 catalyst continues to run very well in the high yield mode, exceeding expectations.

Conclusion

A strong case was developed by UOP and PTTAR for replacing PTTAR's R-232 catalyst with the new high-density R-262 catalyst. Pilot plant testing with PTTAR's feed and operating conditions was very important in demonstrating the new catalyst performance prior to investment. The on-the-fly method was a critical enabler, since a unit shutdown and associated production loss were not a viable option. After a successful reloading, PTTAR realised a significant economic benefit due to the increased aromatic and hydrogen yields from the R-262 catalyst. In the future, the R-262 catalyst with its increased activity and reduced pinning properties will enable a higher throughout, which will provide significantly more volumes of aromatic

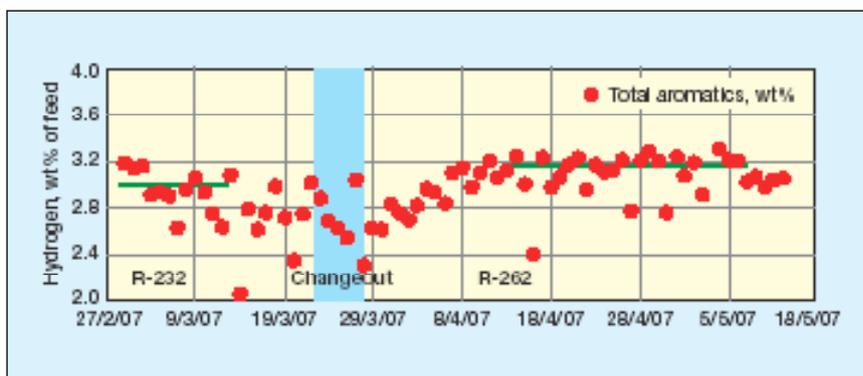


Figure 4 PTTR aromatic yields

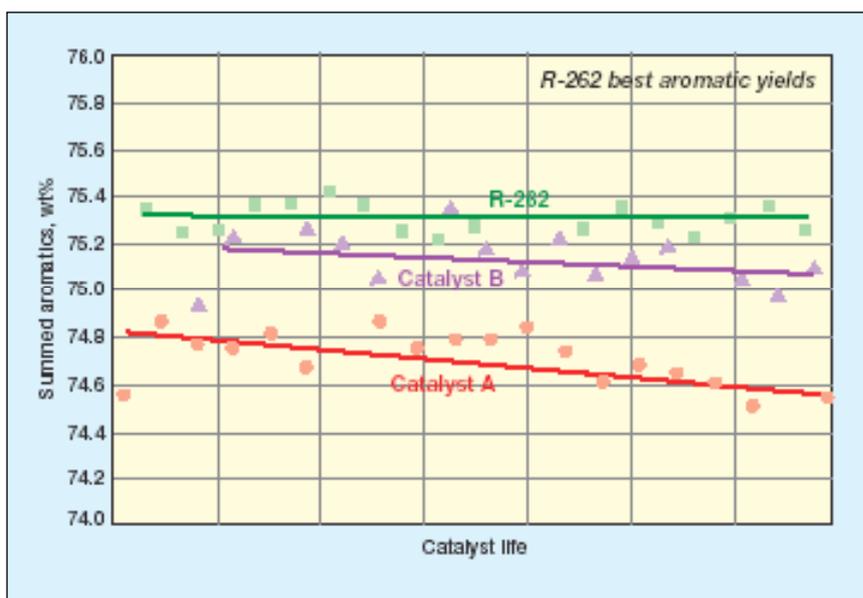


Figure 5 PTTR hydrogen yields

products and further economic benefits.

Platforming, R-264, R-134, R-234, R-262, R-232 are marks of UOP.

References

- 1 Lapinski M P, Baird L, James R, UOP Platforming Process, Ch. 4.1, *Handbook of Petroleum Refining Processes*, 3rd ed., McGraw Hill, New York, 2004.
- 2 Lapinski M P, Rosin R R, Anderle C J, *Hydrocarbon Engineering*, 9, 9, September 2004, 29.
- 3 Lapinski M P, Moser M D, Proffitt R G, *Hydrocarbon Engineering*, 11, 11, November 2006, 59.

“In the future, the R-262 catalyst with its increased activity and reduced pinning properties will enable a higher throughout, which will provide significantly more volumes of aromatic products and further economic benefits”

4 Metro S, R-262 Catalyst Technical Sheet, www.uop.com/objects/R262.pdf, 2007.

Mark P Lapinski is group leader of the Platforming development group at UOP LLC. Lapinski has a BS degree in chemical engineering from the University of Illinois and a PhD from the University of Texas. Email: mark.lapinski@uop.com

Joe Zmich is leader of UOP's catalyst services and sales support group in Platforming and isomerisation technologies. Zmich has a BS degree in chemical engineering from Purdue University. Email: joe.zmich@uop.com

Steve Metro is business manager in the catalysts, adsorbents and special ties group at UOP LLC. Metro has a BS degree in chemistry from Northeastern Illinois University. Email: steve.metro@uop.com

Nungruetai Chaayasit is process engineer at PTTAR, Thailand. Chaayasit has a BS degree in chemical engineering from King Mongkut's Institute of Technology Ladkrabang and MS degree in chemical engineering from Chulalongkorn University.

Kosol Worasinsiri is process engineer at PTTAR, Thailand. Worasinsiri has a BS degree in chemical technology from Chulalongkorn University.