Operation: FCC octane optimisation

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FCC octane optimisation

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The fluid catalytic cracking unit (FCCU) at the Tüpraş Izmir Refinery was designed in 1972 for a feed rate of 93 m^3/hr and is made up of heavy vacuum gas oil (HVGO) and lubrication oil extracts. The FCC was originally designed in a side-by-side configuration with a bubbling bed regenerator operating in partial burn, a riser-disengager with rough cut cyclones, and feed injection at the base of the riser. Various revamps have been performed to renovate the regenerated catalyst standpipe and wye section from hot-wall to cold-wall design, installation of a new regenerator air grid, and a wye premix feed distributor. The feed nozzle was later changed to a wye Optimix feed distributor as part of the 2018 revamp project.

The feed quality of the Izmir FCCU can vary with between 1 – 3 wt% feed sulfur, which results in a maximum sulfur content of FCC gasoline of 2800 ppm. Cat naphtha is sent to a Prime G unit for post treatment to decrease the recombined light cat naphtha (LCN) and heavy cat naphtha (HCN) product sulfur to 30 wppm. From there it is blended to gasoline pool. While the product sulfur is decreased, a decrease is also observed in research octane number (RON) and motor octane number (MON) values, of up to 2.8 and 0.8 respectively. This occurs since some of the olefin components undergo hydrogenation in the reactors along with targeted diolefin and sulfur components.

It was the desire of Tüpraş to explore different methods to mitigate or offset this loss of octane to maintain good properties for final cat gasoline sent for product blending. After a careful selection process considering various options, a plant trial was performed at Izmir refinery with **INTERCAT™ ISOCAT™ HP** from Johnson Matthey. The trial was performed over two months (3 February – 27 March 2015) with the objective to boost gasoline octane with minimal increase in LPG yields. By the end of the test, 16 t of **ISOCAT HP** had been loaded into 96 t of circulating catalyst inventory. The aim of the trial was to measure additive performance when the additive concentration in the FCC inventory was 10 wt%. This concentration was achieved and maintained for approximately 14 days to make up the steady-state portion of the trial.

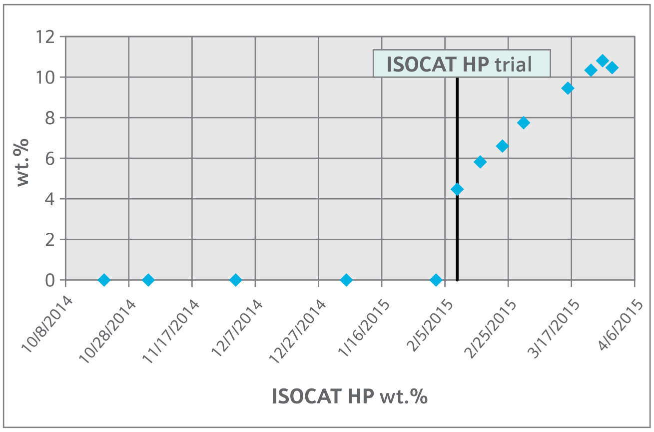

Figure 1. ISOCAT HP additive concentration.

Technology

Standard ZSM-5 additives traditionally have a low silica:alumina (Si:Al) ratio to maximise cracking. When the alumina content of the ZSM-5 crystal increases it means there are more acid sites for catalytic cracking reactions. Independent of alumina content, the ZSM-5 crystal also promotes isomerisation reactions. These reactions do not require acid cracking sites but utilise the shape-selectivity of the ZSM-5 crystal to increase branching in the gasoline cut.

Johnson Matthey's **ISOCAT HP** additive is designed to have a very high Si:Al ratio of approximately 10 times that of standard ZSM-5. The additive, therefore, has a lower intrinsic activity for catalytic cracking whereas isomerisation reactions are still promoted through the presence of the ZSM-5 crystal structure. As a result, gasoline octane is increased without the production of high amounts of LPG olefins. Tüpraş did not require extra LPG at the time of the trial, meaning that the additive proved itself as a good solution to produce extra octane whilst retaining liquid product yields (i.e. increase gasoline octane barrels).

As well as the common requirement to regain the FCC naphtha octane value as a result of reductions during hydrotreatment, there are other situations where boosting gasoline octane can be of particular interest to the refiner. These include when hydrotreatment of the FCC feed results in low base octanes, or low cracking severity results in the same situation. Changes in the catalyst formulation to give extra protection from metals, such as increases in rare earth levels or zeolite-to-matrix (Z:M) ratio, can reduce gasoline octane and create a need to boost it back to previous levels. Some refiners can look for a temporary additive solution during periods of outage of other downstream equipment, such as alkylation, MTBE/ETBE or reforming, to maintain the octane balance of the refinery.

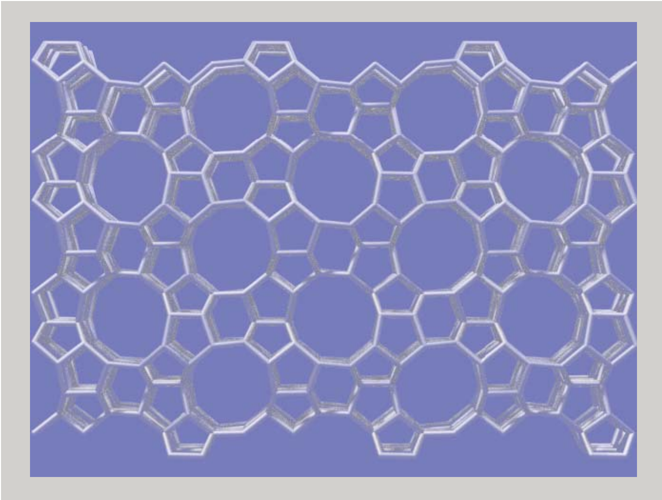

Figure 2. The shape-selectivity of ZSM-5 crystal pores and channels.

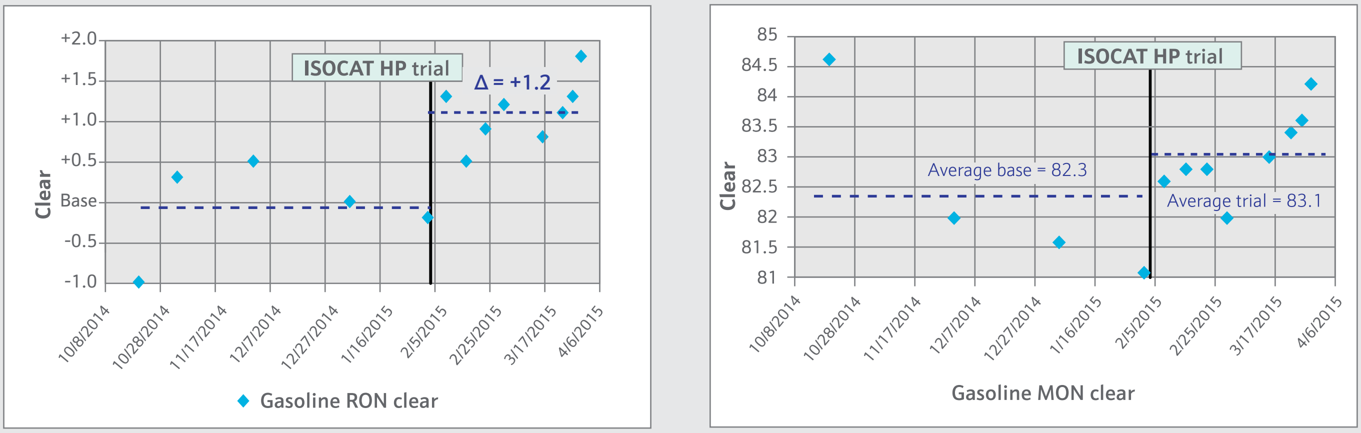

Figure 3. Time plots show octane response during **ISOCAT HP** trial.

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Trial

In the trial it was observed that base gasoline octane was highly sensitive to unit operating parameters such as riser outlet temperature, Ecat rare earth content and gasoline cutpoint. Variations in LPG yield and RON were further magnified if the starting riser outlet temperature and gasoline cut point are lower, for example. Therefore, delta RON and LPG amounts need to be evaluated according to different riser outlet temperatures and other constant conditions. The hydrogen-transfer potential of the main catalyst is key in both determining FCC gasoline octane and the effectiveness of ZSM-5 additives to produce LPG. The hydrogen transfer potential increases with more rare earth on zeolite and higher Z:M ratio of the catalyst.

The key feed properties that can impact gasoline octane and ZSM-5 effectiveness are the general indicators of feed crackability and aromaticity. On the one hand, feeds that are highly crackable, as indicated by low feed density (S.G.) and high UOP K factor, can show good ZSM-5 upgrade potential due to the creation of abundant intermediates suitable for ZSM-5 cracking. On the other hand, aromatic feeds can produce a high base octane should a high proportion of aromatic species transpire in the final gasoline product. Finally, the hydrogen content of the feed can also have an opposing impact. Low hydrogen feeds indicate high aromaticity with the outcomes discussed above. Hydrogen rich feeds, perhaps indicating the hydrotreatment of the feed, may result in a low proportion of reactive olefinic intermediate material for ZSM-5 cracking, and also a lower base octane due to a relative absence of precursors of gasoline olefins and aromatics.

Other feed contaminants also play a role in determining final gasoline octane value. Sodium increases hydrogen transfer reactions by poisoning the strong acid sites.[1] The mechanism is a selective poisoning of stronger acid sites of zeolite-Y leaving weaker acid sites more strongly represented. These weak acid sites tend to be more closely spread and therefore bi-molecular reactions, such as hydrogen transfer, are more likely to occur. Iron poisoning of the catalyst inventory is also likely to reduce gasoline octane due to the formation of a diffusional barrier, increasing the probability for hydrogen transfer reactions through increased intra-particle residence time.

Through the trial at Tüpraş İzmir refinery, feed properties were in a similar range to base case data and the fresh catalyst formulation was not changed.

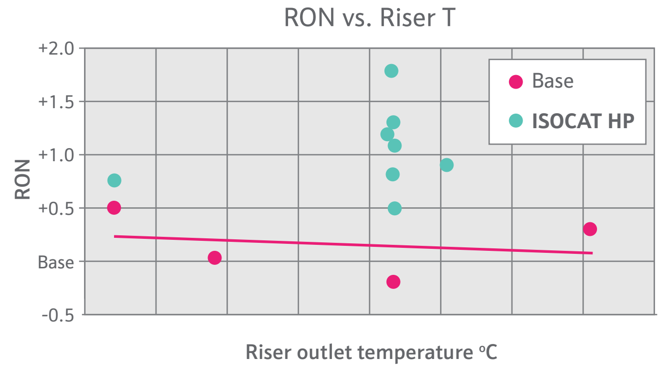

Figure 4. Cross-plots showing RON octane increase at fixed single variables during the **ISOCAT HP** trial, riser outlet temperature (˚C).

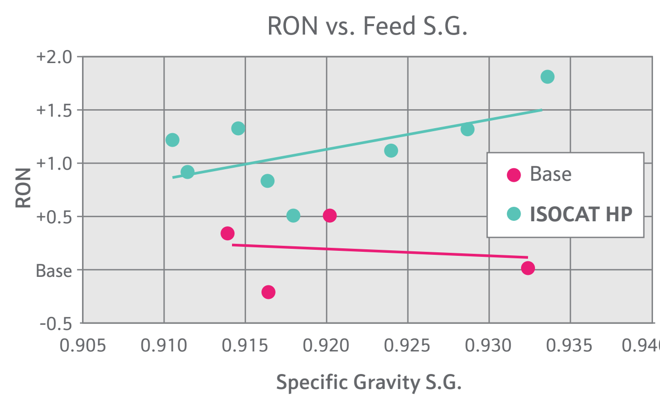

Figure 5. Cross-plots showing RON octane increase at fixed single variables during the **ISOCAT HP** trial, specific gravity.

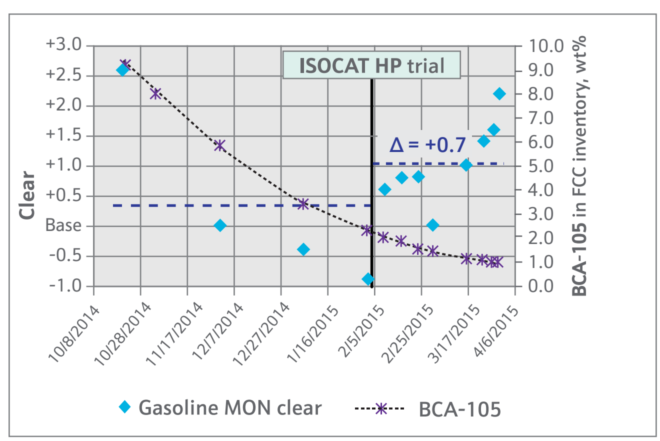

Figure 6. Impact on gasoline octane following conclusion of **BCA-105** trial.

Output from Johnson Matthey ZSM-5 estimate model on the effects of different ZSM-5 types using Tüpraş İzmir trial data							
Additive	ZSM-5 type	Concentration	Δ C3=	Δ LPG	Δ RON	Δ MON	Δ C3 = ΔRON
ISOCAT HP	Octane boost. min. LPG	8.2 wt%	1.5	2.8	1.2	0.5	1.26
SUPER Z	40% pentasil crystal	8.2 wt%	5.7	10.7	1.7	0.7	3.26
SUPER Z EXCEL	≈45% pentasil crystal	8.2 wt%	5.9	11.1	1.8	0.7	3.32

Table 1

Results

The trial of **ISOCAT HP** at Tüpraş Izmir refinery accomplished the targets set out. The gasoline octane value was increased for both RON and MON measurements. Octane increased shortly after the trial started thanks to the ability to baseload with separately added additives, thus achieving the required concentration in a rapid and efficient manner. The increase in octane during the trial at the refinery was 1.2 points of RON and 0.8 points of MON on average. Some outlier points indicate a large increase in the MON that can be attributed to the analysis method. This lower response of the MON metric is expected as MON increase with ZSM-5 type additives is typically half that of the RON delta.

It is important to measure the potential improvement in octane against other factors that affect gasoline octane held constant. Cross-plots allow the effect of **ISOCAT HP** to be viewed at fixed single variables. Over the parameters studied it is clear the additive provided an improvement in gasoline octane independent of the feed quality, operation, and Ecat properties at the time of the trial. As well as demonstrating that this rise in octane was not attributable to other factors, this method shows the gradient of the octane response as the concentration of **ISOCAT HP** builds in the inventory.

There were some particularities of this trial at Izmir that need to be taken into consideration when evaluating the results. The first was that the trial followed on from a trial of bottoms cracking additive, **INTERCAT BCA-105**™, in the previous period. The impacts of the additive on the base case used to evaluate the trial should be considered in terms of impact on key variables studied: gasoline octane and LPG yields. In this case, the use of BCA is likely to have resulted in a high octane measured in the base case. The reduction in Z:M ratio as a result of the use of this high matrix additive will have reduced the hydrogen transfer potential, thus preserving high octane-value olefinic molecules. In addition, as **BCA-105** contains no zeolite material, and therefore no rare earth, the total rare earth concentration on the Ecat would have been depressed through the decay phase of the **BCA-105** trial. Lower rare earth in the base case compared to the **ISOCAT HP** trial period would otherwise have translated into a reduction in gasoline octane in this period. Therefore, it can be said that the octane measured in the base case is artificially higher for these reasons, meaning the actual deltas witnessed during the trial could be more muted than they would be otherwise.

In addition to the impacts on gasoline octane value it is also important to review the effects on LPG yields. Although the high Si:Al design of **ISOCAT HP** dampens potential increases in LPG, it is likely that some gasoline cracking to LPG olefins will still be observed, particularly during the early stages of a trial when a large amount of fresh material has been loaded and is not yet equilibrated. For the trial at Tüpraş Izmir, LPG yields did increase moderately, alongside the more marked boost in gasoline RON and MON octane.

Although these results do show an increase in LPG with the additive, what would be the increase in LPG yield if a standard ZSM-5 additive was used instead? The Johnson Matthey estimate model can project the expected effects of other ZSM-5 types based on the operating data observed during this trial (Table 1).

As can be seen, the propylene and LPG produced by a 'regular' ZSM-5, i.e. Johnson Matthey **SUPER Z**™ and **SUPER Z EXCEL**, is higher than the **ISOCAT HP**. The benefit of **ISOCAT HP** can be seen by comparing the ratio of propylene increase per unit of octane. The additive is over 2.5 times more octane selective than regular, high activity ZSM-5 types, making it a strong application when LPG constrained but there is a high demand for gasoline octane.

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Conclusion

The trial of **ISOCAT HP** exemplified to Tüpraş the benefits that can be gained when implementing alternative ZSM-5 additive solutions in the FCCU. The trial proved the benefits of this enhanced octane selectivity additive, giving the Tüpraş refinery further profitability benefits. The economics of the trial and the period when it is suitable to use the additive depends on the price differential between LPG and gasoline, and the value applied to increases in gasoline RON and octane barrels. The benefit of the additive approach is to use the material only when economic and by performing a trial it gave the refinery planning group at Izmir refinery the information required to determine when it will be best deployed. Although activity effects will decay over time, with the half-life of the gasoline cracking reactions being shorter than the secondary octane boosting isomerisation reaction, in a low turnover unit, such as the Izmir FCC, the effect of such an additive can be observed in the unit for up to six months or until the concentration drops below 1 wt% in the inventory. Purging of the additive can be accelerated by increasing fresh catalyst addition, if this can be achieved within operational, logistical and economic constraints.

Reference

1. 'Controlling Contaminant Sodium improves FCC Octane and Activity,' Engelhard Corp., The Catalyst Report, TI-811

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