JM ProcessWise webinar

Manage propylene and butylene in the FCC

Q 01. We are running at reduced feed rate and taking the opportunity to run much more atmospheric residue to the FCC. Our ecat vanadium is now over 5000 ppm and nickel is over 2000 ppm – what impact will this have on ZSM-5 additive?

A 01. At these levels, vanadium and nickel effect on ZSM-5 particle itself is almost negligible, however vanadium increases the rate of deactivation of the Zeolite Y in the base catalyst, so we anticipate higher fresh catalyst additions will be needed to maintain activity. In addition, base catalyst addition rates may also need to be increased to control Ecat metals levels, especially if the unit is WGC constraint. End result is ZSM-5 will effectively be flushed from the unit by the higher base catalyst replacement rate. To compensate for this flushing effect, ZSM-5 additions would have to be increased. Johnson Matthey also offers **CAT-AID**™ additive to minimise vanadium detrimental effect.

Q 02. Lots of people think all ZSM-5 additives are equal. What is different about your additives?

A 02. R&D efforts include projects to improve activity, stability and selectivity. Consequently, JM can offer high activity additives, additives that selectively produce propylene, additives that selectively produce butylenes, and additives that selectivity produce octane.

Q 03. Why does the ZMX additive make more C4 olefins while ZSM-5 makes more C3 olefins?

A 03. **ZMX**™ contains a JM proprietary zeolite, which has microporous channels that are intermediate in pore size between ZSM-5 and Zeolite Y. The larger pore diameter of **ZMX** compared to ZSM-5 leads to cracking slightly larger gasoline range olefin molecules on average. The different zeolite is more selective to C4 olefins compared to a ZSM-5 zeolite.

Q 04. Our FCC is already at gas handling limit, how could you reoptimize the unit to enable ZSM-5?

A 04. If the limit is on the WGC, gas composition needs to be understood. WGC handles inerts (N_2, CO_2, CO, O_2), H_2, C1, C2, H_2S, LPG and a small amount of C5+. First, to reduce H_2 loading, you would need to reduce dehydrogenation reactions which are typically catalysed by feed metals depositing on the base catalyst. You would explore the possibility to reformulate your base catalyst to a more metal tolerant catalyst, in order to minimise the catalyst contribution to the gas make. Ni is also commonly passivated by injection of antimony (Sb). Reduction in dehydrogenation activity of 30-50% typically observed with Sb. Secondly, C1 and C2 are formed primarily by thermal cracking reactions. To reduce C1 and C2, you would need to minimise thermal cracking, which typically results from: High riser temperature, poor feed atomization, bad catalyst distribution in the feed mix zone, etc. You would probably re-optimize reactor temperature vs. cat/oil vs. cat activity. If you lower reactor temperature, this will significantly reduce gas make. The conversion can be recovered by increasing cat/oil and or cat activity. One side benefit of increasing cat circulation is that this will also lower regenerator bed temperature and reduce thermal cracking in the feed zone. More inerts will be carried from the regen, but gas reduction due lower thermal cracking will be much more significant. All of these actions should help to utilize ZSM-5 which is more LPG selective and makes no dry gas. Finally, some FCC units use different additives for summer and winter operations. For example, a high activity ZSM-5 additive may be used in winter while an additive that improves gasoline octane with less incremental LPG olefins (**ISOCAT**™) may be used in summer.

Q 05. You mentioned APC / digitalisation solutions are available with your additive addition systems. Can you tell us more?

A 05. To assist the additive and catalyst inventory management, Johnson Matthey has patented a technology called **AIM TECHNOLOGY**™ (Automatic Inventory Management). This system automatically tracks the onsite inventory of FCC catalyst and additives and allows remote monitoring of loader operation by refinery personnel. The system continually tracks the number of days of inventory remaining on site and can alert the refinery and JM of the need to reorder. The access to the loader data is made via a secure password protected web site. With **AIM**, diagnostic information is available for JM to perform remote troubleshooting. Often, loader issues can be diagnosed and resolved remotely.

Q 06. We operate a C4-Alkylation plant and are in the position of being long on butenes, can you advise us how can we increase our isobutane yield?

A 06. To answer, we need to understand where the isobutane comes from. As said in the presentation, cracking reactions produce olefins, while competing hydrogen transfer reactions saturate olefins to paraffins. Isobutane is formed in two steps: (1) Feed / gasoline gives isobutylene via cracking and (2) a part of this isobutylene converts into isobutane via hydrogen transfer. To maximise step 1, rate of cracking (making isobutylene) should be maximised in the same way we described in the webinar, i.e. maximising conversion via higher reactor temp, higher cat-to-oil and higher catalyst activity. Then to maximise step 2, hydrogen transfer reactions (converting isobutylene to isobutane) should be maximised, by doing the opposite optimisation we described in the webinar (increase LPG olefins). In this case, we would rather reformulate the base catalyst to a catalyst having higher rare earth on zeolite, higher UCS.

Q 07. In the presentation there is mentioned several scenarios how ZSM-5 could affect economics. May I ask you, whether JM specialists have experiences and could indicate the highest amount of ZSM-5 which could be effectively added with positive impact on maximization of propylene or generally on petrochemical streams? Of course, if there is some limit. For example, is it possible to add ZSM-5 in amount 20% or more? Do you have this experience?

A 07. JM has good experience here, a few conventional FCC do add >20% of ZSM-5 (typically not more than 30%). There is a diminishing return due to re-oligomerization of light olefins - which drives toward the thermodynamic eqm. distribution of olefins - see our "snakes & ladders" paper. In addition, there are specially modified types of FCC type processes that use 100% ZSM-5 catalysts. In these cases, the eqm. distribution is improved by operating at very high severity: RXT is generally very high (600C+), cat/oil ratios are very high (15+) and very high riser steam injection to the riser lowers the hydrocarbon partial pressure (e.g. 20% steam vs. usual 2-5%).

Q 08. If we decrease PPHC in the reactor, but due to the large unit size, gas residence time is also longer, how could we design an additive system to increase LPG olefins production?

A 08. It sounds like you may not have an advanced riser termination device (RTD) installed. Increasing steam to the riser not only lowers the PP of hydrocarbons, it also increases vapour velocities. Units without a RTD sill benefit greatly from the use of ZSM-5 additives in much the same way as risers with RTD installed.

Q 09. Do ZSM-5 additives exclusively crack gasoline olefins, or are they just highly selective toward olefin cracking with some paraffin and isoparaffin cracking still occurring?

A 09. Cracking of paraffin molecules with ZSM-5 is negligible in most FCC units. When ZSM-5 is in the unit, typically we see a decrease in both the olefin and paraffin content of gasoline. The paraffin reduction is especially noticeable when the base FCC catalyst has a high rare earth content. This is due to hydrogen transfer reactions. ZSM-5 cracks olefins which would otherwise have reacted via hydrogen transfer to form a paraffin.

Q 10. Generally, what is range of Catalyst to Oil ratio to get higher propylene yield?

A 10. In the first part of the presentation, we explored the process variable to be changed in order to get higher propylene yield. We explained increasing the cat-to-oil ratio is one of the three main optimisation possible. On the rules of thumb slide, we said increasing the cat-to-oil ratio by 1.0 point will increase the unit conversion by 1.5-2.5%. If you benchmark the conventional FCC units, cat-to-oil ratio varies between 4 and 10. Deep conversion units run at much higher cat-to-oil (15+). Process licensors offer various hardware upgrading options, for example recycling naphtha to the riser, to increase catalyst circulation.

Q 11. Does ZSM-5 come as premix supply to main catalyst or it can be separately added in the plant?

A 11. ZSM-5 can be pre-blended with the base catalyst, but the additive is best added separately to improve response time to changes in requirements. Separate addition allows a continuous optimisation, without having to over-load or under-load the fresh catalyst, as it would be the case if the ZSM-5 was pre-blended. On slide 30, we explored how ZSM-5 economics change over time. We showed in month N-1, the gross margin would be negative. Another re-optimisation needed. In month N+1, ZSM-5 gross margin would almost triple. This clearly demonstrates that only a separate additive addition gives the freedom to react to rapid changing economics and capture market opportunities.

Q 12. After existing FCC is revamp for maximising propylene, then plant can be operated for original yield before revamp? It's impact wrt catalyst?

A 12. It depends on the extent of the revamp. If the riser has been adapted to accommodate much higher steam rates, then that may be difficult to avoid. Likewise, if the revamp led to extremely high cat circ. that too would be difficult to avoid. But in principle operating in gasoline or diesel mode is still possible to some extent by lowering operating severity and use of a conventional catalyst without ZSM-5.

Q 13. What modification is required in the reformulation of base catalyst for straight run diesel cracking in a high propylene FCC?

A 13. Straight run diesel is run in many conventional FCC units (especially in North America) when the IBP of VGO is low (for example refiners run in excess of 20% of diesel range feed in the light end of the VGO). It is generally not as easy to crack as regular VGO. High Z/M ratio fresh catalyst with high ecat MAT is likely the best approach to pre-crack it for subsequent conversion to propylene by ZSM-5. The diesel that is not cracked serves to increase cat/oil which will boost overall conversion.

Q 14. Does feed Ni sits on ZSM-05/BCA as well along with base cat?

A 14. Yes, Ni is deposited on surfaces wherever there are mesopores large enough to host the hydrocarbon molecule that contains the Ni. Generally, this is toward the external surface of catalyst particles, because the metal containing hydrocarbon molecules are large and don't tend to penetrate catalyst particles deeply. ZSM-5 additives are designed without matrix activity, so they tend to be less loaded with Ni than the base catalyst. Bottoms cracking additives (and the base catalyst) can be designed with Ni-trapping alumina incorporated to help passivate the deposited Ni.

Q 15. What happen if we have SUPER Z and ISOCAT in unit at the same time?

A 15. **ISOCAT** promotes naphtha isomerisation reactions with less cracking than a standard Si/Al ZSM-5. **SUPER Z**™ (and other high activity ZSM-5 additives) also catalyses isomerisation, but the ratio of isomerisation to cracking is lower. The net result is that **SUPER Z** activity is higher than **ISOCAT** and would tend to dominate the performance of the mix. We don't normally recommend using such a mix unless the **ISOCAT** was used in large excess to **SUPER Z**.

We at JM would like to thank you for participating in this webinar.