Increasing FCC yields with oxygen enrichment

With the demand for diesel increasing faster than that for gasoline and other refined products, an increase in FCC distillate yield can provide a low-cost route to capturing margins opportunities. Oxygen enrichment can help to achieve these goals

Jack Olesen
Praxair

A relevant question posed by refiners at the recent NPRA Q&A in Orlando and the ERTC in Vienna was concerned with how to configure the FCCU towards higher distillate-to-gasoline ratios. Other related and equally important issues were concerned with ways to manage light cycle oil (LCO) production, bottoms recycling and the use of oxygen enrichment to improve FCCU profitability.

Straight-run diesel recovery

Considering the importance of major diesel-producing units in today's market, such as the hydrocracker, higher diesel yields are also possible with FCC operations. The first thing a refiner should consider is how much straight-run (SR) diesel is in the combined feed to the FCCU. It is not unusual to find up to 20% diesel-range boiling material in the FCC feed, and the target should be to get this down to 5%. SR diesel does not crack that well in the FCCU and the quality of the LCO is worse than the quality of the virgin diesel going into the unit. Then there are the obvious operational changes that can be made on the unit, such as lowering catalyst activity, increasing the matrix surface area (lower Z/M) and reducing the riser temperature.

Trade-offs: higher CSO production

The trade-offs in pursuing this route (ie, reducing severity to increase LCO production) are that the main fractionator bottoms, often referred to as slurry or clarified slurry oil (CSO), increase at a faster rate than the LCO. These increases are at the expense of gasoline and LPG. If the reduction in LPG or alkylation unit feed is a concern, the refiner should consider using a ZSM-5 additive.

In order to quantify these changes, one must first bear in mind that, as with everything in FCC operations, these changes will be unit specific. For example, Praxair recently completed a study for a 30 000 bpd FCCU that was planning to increase LCO make. Dropping the riser temperature 40°F and lowering catalyst from 71 MAT to 63 increased LCO by 3%, but CSO also increased by 5%. This is probably not a good economic trade-off.

To provide better economic trade-offs, changing the catalyst matrix activity to compensate for a lower riser temperature and other previously noted changes has been considered. However, in this case, when making the previously discussed changes and raising the matrix surface area by 80 m^2/g, LCO did indeed increase by 4%, but CSO increased even more than the LCO. The larger volume of CSO can be mitigated by taking a heavy cycle oil (HCO) draw and sending that stream to the hydrocracker, if one is available. Otherwise, the refinery should consider recycling the fractionator bottoms (ie, bottoms recycling), preferably the HCO portion if that can be drawn off separately.

Bottoms recycling

While bottoms recycling was practised in the past before high-activity zeolite catalysts were available, this option may re-emerge into a future trend. Why? If there are going to be substantial increases in LCO make, recycling HCO, or recycling HCO plus CSO (if there is no separate HCO draw), will almost always have to be considered. The recycle should be injected into the riser through separate nozzles that are preferably located above the fresh feed injection nozzles. At the same fresh feed rate, the FCCU will have to be able to handle the additional volume from the recycle and have sufficient air blower capacity to deal with the increased coke make.

Of concern is the increase in slurry at lower conversion unless the recycle stream is put into service. The recycle stream can be as high as 20% of the fresh feed rate. This volume of recycle is necessary to keep the CSO make constant relative to the higher conversion base case. Even with a coke-selective bottoms cracking catalyst system, the type of molecules that are being cracked will increase the coke make.

Air blower constraints

If there is no additional capacity in the air blower, options to remedy this constraint include:
— Diverting some of the heavier FCCU feed to a hydrocracker
— Adding more air blower capacity
— Using oxygen enrichment to supplement the air blower.

When implementing oxygen enrichment, the refiner should first determine if there are any permitting issues related to emissions or allowed coke burning rates. Praxair has supplied oxygen enrichment systems for over 25 years and is currently supplying about 20 FCCUs. In the past, the reasons for enrichment were to increase feed rate or conversion, have the ability to process heavier feedstocks, or reduce regenerator velocity for increased time between turnarounds.

Oxygen enrichment levels

In terms of the range of possible enrichment levels, most of the FCCUs supplied by Praxair enrich to 23–28% oxygen, although levels up to the mid-30% have been reported. Praxair has no specific oxygen enrichment limit and we treat any enrichment that results in greater than 23.5% oxygen as if the system were exposed to pure oxygen. For most units, the practical enrichment limit becomes the regenerator temperature or the ability of the downstream recovery system to handle the higher charge rate and conversion. The regenerator temperature limit has often been addressed with a catalyst cooler. For situations where there is 20% recycle, oxygen enrichment is very practical. For example, in the previously discussed case, the level of enrichment required was about 23%.

Therefore, taking into account all of the previously noted issues surrounding bottoms recycling and LCO production, a certain level of LCO increase can be expected. Referring again to the previously discussed case that Praxair studied in detail, the change in LCO was from a base case of about 10% to about 18%, while keeping the CSO constant. However, Praxair did not model the use of ZSM-5 to keep LPG make constant.

Implementation

While the increase in LCO at constant CSO and 23% oxygen enrichment is very attractive, refiners may nonetheless be concerned with the amount of time required to implement oxygen enrichment. This depends on whether the refiner is close to an oxygen pipeline or not. Where pipeline oxygen is available, it would realistically take about nine months to implement. There are the usual permitting and HAZOP processes that need to be handled first. The equipment involved is relatively simple and consists of an oxygen metering skid, an oxygen flow controller tied into the control room instrumentation to control and monitor the process effectively and safely, and the injection quill that goes in downstream from the main air blower (MAB). If there is no oxygen pipeline, the refiner would have to consider a liquid oxygen system or an on-site air separation plant. Timing for liquid oxygen would be similar to the pipeline case. In addition, there would need to be a site for installation of liquid oxygen tanks and a vapouriser. The timing to build an air separation unit is currently about 24 months. Praxair builds, owns, operates and maintains the unit and then sells the oxygen directly to the refiner. The oxygen cost is competitive with the cost of pipeline oxygen.

There is concern with regard to an expected octane drop in the FCC gasoline at reduced unit severity, which is another reason to consider ZSM-5 to maintain FCCU gasoline octane and keep the alkylation unit full.

Impact on emissions

It is well understood that NO_x reacts with CO to produce N_2 and CO_2. With oxygen enrichment, there is less inert nitrogen in the regenerator and hence the CO partial pressure is higher, leading to reduced NO_x. As for SO_x, if the refiner is using a SO_x additive, the performance should increase. This is because the SO_x additive captures the SO_3 and the higher oxygen partial pressure drives the SO_2 to SO_3.

With regards to future CO_2 limits and carbon capture and sequestration (CCS) requirements, the development of "green FCCUs" may become a possibility. Praxair is looking into this topic in co-operation with FCC licensors, since we have a lot of history with CO_2 handling due to the acquisition of Liquid Carbonic several years ago. To be sure, while the equipment we are accustomed to may be similar, the operation might be dramatically different.

Petrochemical interface

Oxygen enrichment does not only apply to FCCs, but also to sulphur plants for capacity expansion or backup purposes and process heaters for improvements in efficiency and throughput. In addition to oxygen, hydrogen is supplied either by pipeline or by on-site steam methane reformers (SMRs).

More recently, a process for reducing NO_x and or CO coming out of the regenerator is in development. This process would have application in meeting emission requirements for full-burn or partial-burn units. In the petrochemicals arena, hydrogen is being recovered and purified, which might otherwise be burned as fuel. In the next issue of *PTQ*, a detailed article on energy and hydrogen utilisation audits will be featured.

Jack Olesen *is Senior Business Development Manager for Praxair in the US Gulf Coast region. He has over 30 years' experience in the industry. Olesen earned a BS degree at University of California Irvine, and MS and PhD degrees in chemistry at University of Colorado. Email: jack_olesen@praxair.com*