6. What catalyst and metallurgy design considerations are important when evaluating the co-processing of highly acidic renewable distillates? What can be done to mitigate carbon monoxide formation?

Bob Riley, Technical Sales Representative

There are two main types of acidic renewable “distillates” available: triglyceride based (animal fats or vegetable oils), or pyrolysis oils to be considered when co-processing is an option at the refinery. Grace is leading development of technologies to be utilized for the process of either of these types of oils in a petroleum refining environment.

Triglyceride based oils derive their acidity mainly from free fatty acids in the oils. The level of impact of corrosion on processing equipment will depend on the type of feedstocks (animal fats or vegetable oils) and their level in the overall blend going to the refinery processes. To evaluate co-processing of these oils in a hydrotreater, several other factors must be understood as well:

- Triglyceride based oils have a new suite of metals contaminants. They are typically lean in nickel and vanadium, but very rich in calcium, magnesium, phosphorous, and other transition metals. Left unchecked, these metals can have a strong detrimental effect on the catalyst bed. Grace Davison has studied the treating of these oils extensively, and recommends a pretreatment system to remove metals. Guard beds have been suggested, but the suitability of a guard bed depends on its size and the amount of oil to be processed; it is likely to require bed replacement much sooner than a typical VGO hydrotreating guard bed. The combination of a separate pretreatment system and an in-situ guard bed is typically the approach preferred for commercial operation.
- Triglyceride oils also contain between 10 and 15 wt.% oxygen typically. The removal of this oxygen creates a high level of water, carbon dioxide, and carbon monoxide, and due to the higher oxygen concentration, releases heat at a much higher rate than desulfurization of VGO. Care must be taken to ensure that the hydrotreating unit can handle additional heat release.
- Triglyceride oils release higher than typical amounts of water, carbon dioxide, carbon monoxide and propane when hydrotreated. One must review the downstream gas system to ensure that higher volumes of these products will be appropriately handled by the existing equipment.
- In this type of system, production of carbon monoxide happens via the de-carbonylation route. To minimize the production of carbon monoxide, some process conditions can be changed, including increasing the available hydrogen, and selecting a catalyst system that is designed for deoxygenation. However, if co-processing renewable stocks, these moves are likely to have an impact on the non-biobased portion of the feedstock, and must be evaluated against the reduction in carbon monoxide.

Pyrolysis oils are a wide class of oils that are produced via cooking biomass in an oxygen free environment. The level of acidity and other properties ultimately depends on the production process with a typical pH range from 2.0 to 4.0. These oils are newer to commercial markets, and experience is limited in being processed in existing refining equipment. It is safe to say that the points below do not apply to all commercially available oils, however the following points should be considered:

- These oils are typically very hydrogen deficient, and the average molecular weight can be quite large. They easily lay down on the surface of an extruded catalyst to condense (form coke), and thus coking and pressure drop increases in a hydrotreater is an important concern. Catalyst activity could be manipulated to a degree to compensate, but the range of compensation may not be wide enough, depending on the quality of the pyrolysis oil.
- There are often miscibility concerns when co-processing with standard VGO material. Phase separation could also ultimately lead to unintended coking in the unit, including the plugging of feeding equipment.
- These oils often have extremely high metals levels, and may need to be pretreated in some fashion to remove those metals.
- Another option is to consider processing these oils in other units in the refinery (FCC or coker). Though not without issues, these units may be more suitable to handle the metals levels and the coking tendency of pyrolysis oils.

In all cases, one should closely examine the blending percentage of the renewable oil to be co-processed as a key variable. Minimizing this percentage will minimize disruption to an existing unit. In addi-
tion, one should also closely examine the regulatory environment to determine if there are benefits to co-processing or if standalone processing (100% renewable) adds additional benefits in the form of tax credits.

79. What tools are being used to monitor the FCC performance? What are the key performance indicators (KPIs) and expectations?

Bob Riley, Technical Sales Representative

There are many tools that are available to monitor FCC unit performance. Most FCC operators monitor in process, or “as produced” yields and operating conditions, and additionally they complete unit mass balances at routine intervals (often weekly or more frequently).

Of primary importance is the net product value produced by running the FCC. This is most often examined using mass balanced data from the unit, in conjunction with refinery specific product and feed values (pricing). In many refineries, FCC profitability is driven by overall volume gain, so this is an important KPI.

Unit reliability is also a very important profitability parameter, and (along with a strong routine maintenance program), many refiners monitor in process operating parameters to ensure that limits are not being exceeded. Some of these parameters are directly measured in the unit, and some are calculated using in-process or mass balanced data.

Measured parameters include unit temperatures (at various points in the unit, including reactor outlet, regenerator bed, reactor and regenerator dilute phases, and others), unit pressures (reactor & regenerator), wet gas compressor suction and power, regenerator emissions, and slide valve / standpipe differential pressures.

Calculated parameters, which are important to monitor, include yield selectivities (yields / conversion), coke make, superficial velocities (especially in cyclones), and catalyst circulation (or cat-to-oil ratio).

The recommended ranges for all of these parameters are specific to the FCC unit's configuration, feed and catalyst type, and operating strategy.

As a service to its customers, Grace provides routine technical service reports, including equilibrium catalyst analysis. These reports can be a critical tool to monitor FCC unit performance, and to troubleshoot the various problems that can arise in typical FCC unit operation. They are most effectively used when they are incorporated into routine operating reviews with the catalyst supplier. During the reviews, recommendations are often made to adjust operating strategies or fresh catalyst formulation to address future operations or issues that are expected/anticipated for the refinery. These routine reviews are a critical component of the successful operation of the FCC.

The catalyst KPI’s include cracking data (ACE or MAT), physical properties of the catalyst, and chemical analysis of the catalyst. As with yield and operating KPI’s the expectation for these KPI’s varies greatly depending on the feed processed, unit design, catalyst type, and operating strategy of the refinery.

In addition, equilibrium catalyst data can be used to benchmark unit performance against similar units, feed types, catalyst types, or a number of other variables. Advanced analytical tools and methods have been developed by catalyst suppliers to understand how age distribution, cyclone performance, contaminant metals, and other variables may impact the performance of the FCC catalyst. These analyses are typically performed “on request” as problems arise.

80. We are considering severe hydrotreating of our FCC Feed. What yield shifts or unusual operating problems might we expect? What can be done to address these issues?

Bob Riley, Technical Sales Representative

Severe hydrotreating of the FCC feed offers a mix of benefits and challenges for the typical FCC operator. Benefits can include dramatically lower sulfur content in products, lower flue gas SOx or NOx, and improved yields; however the price for these benefits is often a dramatically lower coking tendency of the feedstock. Many units which operate with severely hydrotreated feed struggle to make enough coke to maintain heat balance within unit circulation constraints. In addition, one may see slurry yield decrease to minimum acceptable levels, increased bottoms circuit fouling due to the lower volumes, heat removal limits in the gas concentration units due to higher volumes of light and wet gases, and lower overall product olefinicities.

To counteract that challenge, several operating changes are possible. These include:

- Use of higher activity FCC catalyst – For units which will run severely hydrotreated feed for long periods of time, reformulation to a higher activity FCC catalyst is often the most cost effective means of increasing the ECAT activity, and bringing the unit into heat balance.
- HCO recycle – HCO can be recycled to the reactor to aid in additional coking and to increase the heat requirement on the reactor side. This strategy causes an economic penalty when the unit is operating at maximum fresh feed rates, as fresh feed will need to be backed out.
- Use of regenerator torch oil – Torch oil is often used in the regenerator to add additional heat. However, the severe hydrothermal environment, coupled with the high velocities
near the injection point(s), creates a very challenging environment for FCC catalyst particle integrity. In addition, many refineries use LCO material as torch oil, which is a substantial hidden cost.

- Use of the fired air heater – Some units will activate the fired air heater to reduce the heat requirement in the regenerator. In some cases, this air heater does not offer a great deal of flexibility in its duty, so its use can “swing” the unit from very low regenerator temperatures to much higher regenerator temperatures.

- Reduction in stripping steam – Some refiners elect to reduce stripping steam, sending some unstripped hydrocarbon with the catalyst into the regenerator. While this is a viable source of heat on the regenerator side, it results in a net loss of total liquid volume, and unit profitability can suffer. Additionally, the hydrogen-rich unstripped hydrocarbons burn rapidly creating local hot spots which can deactivate the catalyst.

- Higher FCC catalyst addition rates – For units that process severely hydrotreated feeds intermittently, catalyst reformulation may not be practical. However, a short term increase to the FCC catalyst addition rate can increase the equilibrium activity and bring regenerator temperatures up, which will allow the unit to maintain heat balance.

Each of these methods should be evaluated for both its feasibility in a given refinery and for its economic impact to the plant. It is often the case that higher catalyst addition rates, or a high activity catalyst reformulation, is the most economically favorable option.

81. Is there experience with continuous torch oil and/or air preheater firing and for what reasons? What are the demonstrated effects from doing either of these?

Bob Riley, Technical Sales Representative

The use of “dry circulation” is a common event in many refineries. Often upstream or downstream problems in a refinery can cause the FCC to pull feed, and during these times, many units elect to continue “hot” catalyst circulation to avoid a complete thermal cycle on the FCC. Typically, these events are short-lived (up to about one week). During this time, refiners may add fresh, or more typically, equilibrium catalyst to the unit to maintain catalyst bed levels.

Using torch oil creates a severe hydrothermal environment, with temperatures at the nozzle tips often eclipsing metallurgical recommendations, and velocities well over 100 ft/s. These nozzle tips are often buried in the dense bed of the regenerator, causing areas of severe stress on the catalyst particles. Attrition and catalyst deactivation are the outcomes of this activity.

The use of torch oil or fired air heating while feeding oil is less common. In units that process severely hydrotreated feedstocks, opera-

We have noted one refinery that, after a turnaround, started up on a substantially lighter feed. This unit started up using the fired air heater and did not turn it off, as the new lighter feed resulted in an unacceptable drop in regenerator temperature. Catalyst addition rates were increased, and eventually, the unit reformulated to a higher activity catalyst. This reformulation, along with other moves in the operation, allowed them to discontinue the use of the fired air heater.

Another refinery with a similar short-term “lightening” of the feedstock elected to fire torch oil to maintain heat in the regenerator. This unit continued this practice until they shut down for a planned turnaround. They observed increased fines generation, and complete destruction of the torch oil nozzle tip. After their turnaround, the refiner reformulated to a more active catalyst to remove their dependence on torch oil to keep the regenerator hot.

89: With the increase in rare earth costs, many units have decreased the rare earth oxide (REO) content or used rare earth substitutes in their FCC catalyst. What is your experience with these in terms of activity maintenance, delta coke, conversion, attrition, and yield selectivities? How have operating conditions changed?

Ann Benoit, Technical Service Representative

Rare earth plays a key role in FCC catalyst and has been traditionally used in stabilizing zeolite which preserves catalyst activity and modifies selectivity. Rare earth has also been successfully utilized

![FIGURE 1: As Rare Earth on Catalyst Decreases, LPG Yield Will Increase]
as a contaminant metals trap, reducing deactivation caused by vanadium.\textsuperscript{1} There are several different avenues one could take to lower rare earth on catalyst with wide ranging impacts on FCCU yields and selectivities.

The following avenues will be discussed:

1. Lowering rare earth on zeolite
2. Lowering rare earth and using a rare earth substitute
3. Lowering rare earth used for metal traps

Simply lowering rare earth on zeolite with no other changes made to the catalyst system will typically reduce catalyst activity at similar catalyst additions. Conversely, higher catalyst additions will be required to maintain similar catalyst activity. If activity/conversion is maintained, catalysts with lower rare earth will typically be more LPG selective than gasoline selective. The graph below showing this relationship was presented at the 2012 Cat Cracking seminar. The data are pilot plant yields from merely reducing rare earth on an FCC catalyst with constant zeolite and matrix input.\textsuperscript{2}

For further information on the function rare earth plays in FCC catalyst and yield selectivities please refer to the Grace paper “Role of the Rare-Earth Elements in Fluid Catalytic Cracking”.\textsuperscript{1} One thing to note is that removing rare earth from FCC catalyst typically provides relief in catalyst expenses, but is not necessarily an economical solution as most FCC operations cannot accommodate lower activity and/or product value.\textsuperscript{3}

One alternative to lower rare earth while maximizing FCCU profitability is to use alternate materials and processing to stabilize the zeolite. Grace has recently added the REpLaCeR\textsuperscript{®} family to its catalyst portfolio. REpLaCeR\textsuperscript{®} is a collection of low and zero rare-earth catalysts which have been applied in a wide range of FCC applications.\textsuperscript{3} REMEDY\textsuperscript{®} catalyst, one of the REpLaCeR\textsuperscript{®} family of catalysts with low rare-earth content, has been proven to have similar unit conversion at similar catalyst additions, similar slurry/coke selectivity, similar Ecatal activity, and higher gasoline selectivity when compared to a moderate rare-earth containing catalyst. In one refinery example, the catalyst was reformulated from a traditional 1.5 wt.% rare earth catalyst, GENESIS\textsuperscript{®} GSR\textsuperscript{®}, to REMEDY\textsuperscript{®}2 GSR\textsuperscript{®}.\textsuperscript{3} As shown in Figures 2 and 3, the catalyst additions on a lb/bbl of feed basis were maintained with REMEDY\textsuperscript{®}2 GSR\textsuperscript{®} while maintaining similar conversion. Figure 4 shows both catalysts have similar coke selectivity.\textsuperscript{3} Also, REMEDY\textsuperscript{®}2 GSR\textsuperscript{®} proved to be more gasoline selective when compared to GENESIS\textsuperscript{®} GSR\textsuperscript{®} which is shown in Figure 5.\textsuperscript{1} It is also worth noting that the lower rare-earth catalyst reformulation in this example did not negatively impact catalyst retention.

With regard to rare earth being utilized as a metals trap, Grace has been successful in reducing rare earth by 40% without sacrificing activity or selectivity with the re-optimization of our IMPACT\textsuperscript{®} technol-
ogy, ResidUltra™. Commercial experience proves that unit performance is nearly interchangeable. In lab testing, ResidUltra™ and IMPACT® samples were deactivated with metals levels of 3000 ppm V and 2000 ppm Ni and tested side by side in the ACE unit over a residual feedstock. The constant conversion data is summarized in Table 1. In this scenario, relative to IMPACT®, ResidUltra™ has similar catalytic activity, the same hydrogen selectivity, slightly better coke selectivity, similar gasoline, similar LCO, and similar bottoms yield. ResidUltra™ yields slightly higher octane number and LPG olefins.

In summary, the means by which a catalyst supplier might lower rare earth may have no impact or a substantial impact on catalyst activity and FCCU yields and selectivities. Your unit objectives and constraints will dictate which catalyst reformulation best fits your FCCU.

References


2. 2012 Cat Cracking Seminar Q&A


90. Can ZSM-5 be used to make propylene from high metal resid feeds? What is the effect of Ni and V on this kind of operation?

Bob Riley, Technical Sales Representative

Yes, ZSM-5 additives are being used successfully, for example, in Asia and the Middle East, where the predominant FCC feedstock for maximum propylene FCC units is heavy, high metals resid. We have developed our AP-PMC and PROTAGON catalyst platforms to address the demands of these units. In addition, there are numerous resid applications around the world that target moderate propylene increases in which ZSM-5 additives are used. Regardless of the product to be maximized, the foundation for a superior resid cracking catalyst is coke-selectivity and bottoms cracking activity, and these are primary considerations in the design of these catalyst families. Grace’s ZSM-5 additives such as OlefinsMax® and Olefin-ultra® HZ are being used successfully in many resid units together with AP-PMC, Protagon, IMPACT®, Nektor® ULCC and ResidUltra™ in blend together with AP-PMC and PROTAGON max propylene FCC Catalysts as well as in blends with resid catalysts such as IMPACT®, Nektor® ULCC and ResidUltra™.

Industry experience indicates that high levels of Ni + V do not affect the performance of Grace’s ZSM-5 additives. Our customers have operated successfully with a combined Ni + V of up to 13,500 ppm. On the other hand, feed properties have a significant influence on product yields, including propylene selectivity.

Fundamental research has shown that ZSM-5 additives do not accumulate metals at the same rate as base cracking catalysts. This, in part, helps to explain why metals effects on ZSM-5 are not easily observed in commercial operation.