Integrated Solutions to Improve Pygas Hydrogenation Reliability

Introduction

Ethylene production through pyrolysis (steam cracking) produces several by-products, including a naphtha-range C5+ stream. The C5+ cut is referred to in the industry as pyrolysis gasoline or pygas. Left in its raw form, the stream has limited commercial value owing to its high reactivity and low stability. However, the stream contains many high-value components, such as isoprene, benzene, toluene and xylenes.

Extracting these components can be highly economical. To do so requires multiple steps, including distillation, hydrotreating, and extraction. Although multiple processing arrangements are possible (depending on the desired final product slate), pygas processing typically involves two hydrotreatment stages. The first stage involves hydroprocessing the feed to remove diolefins, alkenylaromatics (styrene) and some olefins in preparation for optimal downstream processing. The second stage involves olefin and sulfur removal from all or a specific cut of the first-stage product. This processing prepares the feed for aromatic extraction and/or motor gasoline pool addition.

The two hydrotreating steps can be problematic and negatively impact process reliability, forcing production losses as well as additional operating and maintenance costs. Chronic problems such as reactor plugging (pressure drop build-up), short catalyst cycles, and/or off-spec product have led to frequent shutdowns, catalyst regenerations, and/or catalyst changes. In this article, pygas processing issues will be examined in detail by reviewing specific commercial examples, presenting the solutions and subsequent results.

Example 1, Reactor Plugging (pressure drop build-up)

As mentioned, a raw pygas stream is highly reactive, containing a wide variety of potential gum-forming materials such as diolefins and alkenylaromatics. The gums can form in the raw pygas during transit and storage, or during the first stage hydrogenation. These gums contribute to catalyst fouling, pressure drop increase across the reactor and ultimately reactor shut down. The build-up in pressure drop can be gradual (over several weeks or months) or dramatic (within hours). Dramatic pressure drop build-up is typically related to poor feed quality. Gradual pressure drop can be traced to feed quality, as well as attributed to problematic operation of the first stage hydrogenation reactor.

The commercial operation reflected in Figure 1 presents pressure drop data versus time across a first stage pygas reactor. This specific application processed a raw C5+ stream across CRI Catalyst Company’s 10% nickel trilobe catalyst. In Figure 1, a new charge was installed into the reaction system at “time zero”. Shortly after start-up, a gradual pressure drop increase was apparent. After 28 weeks, the pressure drop reached the process limit, and the reactor was shut down. The unit operator conducted an in-situ hot hydrogen strip of the catalyst bed, and the reactor was placed back on-stream. The hot hydrogen strip effectively reduced the pressure drop, but the subsequent cycle lengths continued to decrease.
Analysis of the pressure drop problem identified two potential contributors. The first was the quality of the feed, and the second was the reactor operating conditions.

The site did not generate its own feed, but instead purchased and processed pygas from third-party sources. The purchased feeds were subject to variability in quality due to how they were stored, treated, and transferred. The nature of the purchased feeds (potential for gums and other foulants) suggested the need to modify the reaction system to accommodate the variation in quality.

The second and initially less apparent cause for pressure drop build-up, is the reactor conditions. Specifically, CRI identified a strong correlation between the concentrations of inlet reactives (dioresins), inlet temperature, and catalyst activity on the fouling rate of the catalyst bed. A highly reactive feed combined with high temperatures can easily result in polymerization, leading to pressure drop build-up and consequential activity loss.

To address the problems, the reactor bed was modified through the installation of both inert and active grading. The operator installed a layer of inert medallions, designed with a high capacity for particulate capture while maintaining low pressure drop. The active grading was CRI’s KL6656 HC4.8, a low-activity, hollow cylinder, nickel catalyst. The active catalyst grading material is designed to react away (hydrogenate) the most reactive components (polymer promoters) in a high tolerance zone (optimal void space). Figure 2 displays the differences in void space associated with the grading materials and the actual catalyst bed.

In addition to the top bed grading modification, changes were made to the process operating conditions. The concentration of inlet reactives was reduced by increasing the recycle ratio (diluting the feed with reactor product). Although this solution appears simple, CRI incorporated detailed models to assess the impact of an increase in recycle ratio on other key reactor performance controls such as liquid velocity, optimal inlet temperature, differential temperature and the overall LHSV, etc. Of notable concern, increased recycle can reduce reaction activity. CRI thoroughly assessed the impact of recycle adjustments, the addition of specialized grading and the corresponding reduction in catalyst bed size to assure the changes yielded acceptable reaction system activity.

In this specific example, implementation of the changes had a dramatic effect. Pressure drop build-up was almost eradicated. The elimination of unscheduled shutdowns to conduct in situ hot hydrogen strips gave way to scheduled “opportunistic” hot hydrogen strips during normally scheduled plant shutdowns. Figure 3 shows the initial performance following the implementation of the mentioned changes.
Example 2, Off-Spec Product

In this example, the application processes a C6 to C8 pygas feed in two stages to prepare the stream for downstream aromatic extraction. For efficient extraction unit operation, the target bromine index of the product stream is 400 mgBr/100g or less. This target proved difficult to achieve, and at times production adjustments were necessary due to limitations in reaction system activity.

The stream was processed in two stages. The 1st stage reactor operated with a target outlet styrene concentration of <0.25 wt% and an outlet diene concentration of < 0.5 g I2/100g. The 2nd stage reactor processed the product stream from the 1st stage reactor, hydrotreating the sulfur and reducing the olefins to the target levels mentioned above. Typical for pygas units, the 1st reactor operated in trickle phase, while the 2nd reactor operated in gas phase.

Although the 2nd stage bromine index target was the ultimate production limiting factor, the underlying cause was poor performance of the 1st stage reactor. Poor conversion in the 1st stage reactor resulted in a more reactive feed to the 2nd stage reactor, making it difficult for the reactor to reach its olefin conversion targets.

Analysis of the 1st stage reactor identified several factors for the activity limitations: (1) undersizing of the reactor and (2) poor use of the existing catalyst bed. The reactor was initially designed with a target fresh feed based LHSV of 4.9/hr. Expansions to upstream ethylene production gave a corresponding increase to pygas production, increasing the LHSV in the 1st stage reactor to 8.5/hr. The reactor configuration included a poorly designed distribution system enabling channeling and mal-distribution in the reactor bed.

This maldistribution was apparent when plotting the temperature rise through the reactor as a function of bed position. In an adiabatic reactor with ideal distribution, temperatures in a 1st stage pygas reactor should increase from the inlet to the outlet of the bed. If temperatures prove erratic at the various measurement points, this is a strong indicator of poor distribution. Figure 4 is an example of poor reactor distribution.

To address these issues, three changes were implemented: (1) Installation of a new high dispersion (HD) tray from Shell Global Solutions. (2) A 16% increase in catalyst volume enabled by the installation of the new reactor internals. (3) Loading of a new high activity Pd catalyst.

The HD tray by Shell Global Solutions is a proprietary internal device designed to maximize catalyst utilization and total reactor volume. Unlike conventional trays, the HD tray creates a highly uniform spray pattern that mitigates bed channeling. In this case, as in several others, the design of the distribution system opened the doors for higher installation in the head space of the existing reactor allowing for increased catalyst volume. The 16% increase in volume accounted for a decrease in the LHSV from 8.5/hr to 7.3/hr; although a significant improvement, the 7.3/hr is still above the original design value of 5.9/hr. To compensate for the high LHSV, CRI’s highly active palladium catalyst, KL7763, was installed. CRI’s KL7763 SH has proven successful in commercial 1st stage pygas operations since 2001.

The combination of these innovative changes surpassed expectations. The 1st stage reactor produced a product with record low styrene and diol content, while operating at full rates and minimum feed temperature. The improvements in the 1st stage allowed the 2nd stage reactor to yield a product with a bromine index below 100. Figure 5 shows the dramatic improvement in the 1st stage reactor.
**Example 3, Activity Limitation**

In this final example, the operator’s pygas unit processed a C5+ cut in the 1st stage, and after separation, treated the C6 cut in a 2nd stage reactor, while sending the C7+ stream directly to the motor gasoline pool. In this arrangement, conversion targets for the 1st stage reactor were relaxed, targeting a styrene conversion of 75%, compared to a typical 1st stage reactor styrene target of 95% or higher.

Even when allowing for this relaxed specification, the 1st stage reaction exhibited severe activity limitations. The unit was equipped with two 1st stage reactors, one in service and the other operating as a spare. Typical cycle length was 6 to 10 weeks as shown in Figure 6. This unit was not equipped for in-situ hot hydrogen stripping or oxidative regeneration, requiring unloading of the 1st stage catalyst for ex-situ regeneration after every cycle. The unit design did not include recycle capability so actual reactor feed characteristics proved less than ideal. The non-ideal feed conditions lead to typical pressure drop increase from 10 psi up to 60 psi by the end of the short cycle.

Changes to motor gasoline regulations require hydrotreatment of the C7+ cut to reduce sulfur concentrations. For a 2nd stage C7+ reactor to function reliably, a higher styrene conversion target in the 1st stage would be necessary. Specifically, a 95% conversion would be needed, equating to a 116% increase in 1st stage reaction activity. Clearly, significant changes were needed to meet these new requirements.

The changes made to the 1st stage included optimization of all aspects of the reaction system. The biggest change was in the reactor configuration. Instead of one reactor on and one spare, the reactors were placed in series, doubling the catalyst volume and therefore doubling the reaction system activity. The addition of product recycle capability to improve the reactor feed characteristics, and inert/active grading minimized pressure drop buildup. Shell Global Solutions HD trays were installed, improving catalyst utilization from an estimated 65% to nearly perfect utilization. The reactors were loaded with CRI’s high activity palladium KL7763 catalyst. Additional improvements include improved thermometry, new on-line analysis for styrene conversion, and piping added to allow for in-situ catalyst regeneration through hot hydrogen stripping.

Once again, the results exceeded expectations; both pressure and activity limitations were essentially eliminated. Styrene conversion exceeded 95%, and pressure drop remained below 10 psi, with the cycle length increasing to > 3 years. Ultimately, a high maintenance unit with marginal product qualities was transformed into a low maintenance unit with exceptional product characteristics. Figure 6 shows temperature performance during the first five months of operation both before and after the modifications.

**Conclusions**

Processing of a pygas stream can be problematic due to the reactive nature of the stream. The potential exists for undesirable reactor performance in the form of short cycles through activity loss as well as polymerization and fouling induced pressure drop increase. Poor reactor performance contributes to off-spec product, production rate limitations, excessive catalyst regenerations and/or replacements. These concerns can be mitigated through optimization of the feed characteristics, the use of specialized grading and catalysts, and installation of high performance reactor internals. When properly designed and implemented, the result can be a highly reliable operating unit that meets or exceeds product specification targets.