
Question 50: How is your company planning to meet Tier 3 gasoline regulations?

WRIGHT (Hunt Refining Company)

Currently, our gasoline runs at 12 ppm sulfur. There are two sour components: our LSR (light straight-run) and butane. Some approaches we are contemplating for compliance are hydrotreating the LSR, reducing the sulfur via dilution, or restarting an out-of-service Merox unit.

EPSTEIN [Flint Hills Resources, LP (FHR)] Our company includes two refineries. Flint Hills Resources Pine Bend Refinery will increase the amount of hydrotreating in gas oil hydrotreaters to remove sulfur from fuel products to meet these regulations. Flint Hills Resources Corpus Christi Refinery is reconfiguring its ultra-low-sulfur gasoline unit in order to meet these requirements.

McARTHUR (Phillips 66) Our compliance strategy varies by refinery. We are using different strategies. Our West Coast sites are generally already at a Tier 3 performance level. We have some unit revamps to allow for higher severity operation of our FCC feed hydrotreaters. We have some new Merox (mercaptan oxidation) units we are installing; and where necessary, we are adding some additional hydrotreating capability.

MORELAND (Valero Energy Corporation) For the 14 Valero refineries, three are not affected by Tier 3, either in Europe or California. Prior to Tier 3, Valero met gasoline sulfur requirements with FCC pretreat only at three of our refineries that process light sweet crudes. For two of those three refineries, we are going to build grassroots gasoline desulfurization units; and at the third, we have shut down the FCC unit. So, for compliance with Tier 3, all Valero refineries will have FCC gasoline hydrotreating or post-treat units.

Additionally, I would like to add that for Tier 3 gasoline, a lot of our frontend studies have had to do more with how we deal with the crude unit naphtha than with the FCC gasoline naphtha. In many of our cases,

the crude unit naphtha is not hydrotreated to meet the 30 ppm pool, but must now be hydrotreated to meet the 10 ppm pool. Tier 3 will require refiners to hydrotreat a lot of straight-run naphtha.

DOMINIC VARRAVETO (Burns & McDonnell)

My question regarding Tier 3 compliance has to do with the strategy or use of credits and how that fits in for any of the operating companies represented on the panel or in the audience.

MORELAND (Valero Energy Corporation)

Since the EPA has allowed us to use five years' worth of credits, Valero has sufficient credits built up that may allow us to delay startup of those two grassroots units I referred to earlier.

MEL LARSON (KBC Advanced Technologies, Inc.)

Considering not only Tier 3 but also the emissions requirements, I am curious why more FCC feed hydrotreating will not be the preferred option. Feed pretreating improved stack emissions compliance as well as fuel side issues. And just a comment: It seems like that is the direction the industry is moving: to zero flue gas sulfur that you get two for one, lower emissions, and increased hydrogen content of feed improving conversion flexibility and selectivity. And if you are building new FCC pretreat capacity, it will justify expense on a per-barrel basis versus the lower pressure post-treat units.

WENDY WILDENBERG [Flint Hills Resources, LP (FHR)]

We found that managing hydrogen recycle and hydrogen purity can keep our deactivation rates low. Even though we are more severely hydrotreating, it seems like our Crude people keep finding harder and harder things for us to hydrotreat. [Laughter] So at FHR – Pine Bend, we have been enjoying very low deactivation rates. But, like I said, it requires a lot of management, catalyst strategy, and careful management of higher hydrogen purity/higher hydrogen recycle. Kevin has asked me about run-length and product sulfur. One example is our heavy coker, heavy vacuum gas oil hydrotreater that has minimal catalyst deactivation. This unit shut down after three years at the scheduled turnaround, but it could have gone longer. It has been averaging 0.05 to 0.07 wt% product sulfur with 3.5 wt% sulfur feedstock, so it is doing well.

MORELAND (Valero Energy Corporation)

Do you still get all the way to 10 ppm on FCC gasoline with feed from that cat feed hydrotreater?

WENDY WILDENBERG [Flint Hills Resources, LP (FHR)]

We get to 30 ppm or less on the FCC gasoline from that feedstock. We have two gas oil hydrotreaters that hydrotreat 100% of the gas oil that Flint Hills Pine Bend runs. The lighter feedstock goes to the 900-psig unit, and the heavier feedstock goes to the 600-psig unit. So we managed these units and their catalyst strategies very diligently.

MORELAND (Valero Energy Corporation)

In our refinery in Wilmington, California refinery, we are running similar coker gas oil and HVGO to produce FCC feed with 500 to 700 ppm sulfur content. We typically only get a two-year cycle.

WENDY WILDENBERG [Flint Hills Resources, LP (FHR)]

One other comment: We went back and looked at a lot of the deactivation times we had been doing and discovered that we had done a lot of it to ourselves. We were either cutting hydrogen too far or raising temperature too much. So, we really steadied down our temperature moves. We do not target the product sulfur and move temperatures around. We allow the sulfur to move around some to keep the temperature very steady, and then we are able to not deactivate. It was definitely helpful.

HENRIK RASMUSSEN (Haldor Topsoe, Inc.)

Tier 3 gasoline will be implemented January 2017, and refineries in the U.S. will be required to produce gasoline with an average product sulfur of 10 ppmw. The current spec is 30 ppmw sulfur on average. This can be achieved in a number of ways such as:

?Increased operating severity of the FCC pretreatment unit,

?Gasoline post-treatment, and/or

?Blending with sulfur-free gasoline from a gas to liquid process, like Haldor Topsoe, Inc.'s TIGAS™ technology based on methanol-to-gasoline (MTG) technology. This option will only to be viable as a partial solution and will have to be combined with either increased FCC pretreater severity or gasoline post-treatment.

A number of our clients have already successfully performed a test run with their existing FCC pretreatment unit using Topsoe's BRIM™ catalyst technology to reach Tier 3 by simply increasing the

operating temperature and producing a feed to the FCC with about 300 ppmw sulfur. The gasoline from the FCC will meet the 10 ppmw sulfur specification. Please see the below relationship between FCC feed sulfur and sulfur content in the FCC gasoline:

FCC Pretreatment: There are many additional advantages with the pretreatment option for meeting the Tier 3 gasoline:

?The result will be increased yield from the FCC because the increased operating severity in the FCC pretreat unit will also reduce the organic nitrogen to the FCC.

?The lower feed nitrogen will also improve the selectivity of the FCC catalyst.

?The reduced feed nitrogen will also reduce the FCC catalyst consumption.

?The SO_x and NO_x from the regenerator will be reduced significantly, which reduces the amount of FCC additives required to meet the emission limits.

?Better quality LCO and HCO from the FCC reduce the operating severity of the downstream diesel units or hydrocracking unit.

?The volume swell in the FCC pretreater will increase due to the increased aromatic saturation.

The above advantages will significantly increase the profitability of the refinery, which can easily offset the cost of reducing the cycle length of the FCC pretreat catalyst. In one recent test run, reducing feed nitrogen and/or the amount of FCC additive required to meet the emission limit resulted in an annual cost reduction of more than \$5 MM for the refiner. The other identified benefits furthermore increased the refinery profits by many multiples of the mention savings per year. In other words, there is a very significant ROI (return on investment) with the implementation of an environment regulation via the pretreatment route.

Gasoline Post-Treatment: There are several technologies in the marketplace today that can meet the Tier 3 specification by selective hydrotreating of the gasoline. The issue with this option is that it will also result in loss of octane barrels. Even though the catalysts used in these technologies are selective toward sulfur conversion, it is not possible to completely eliminate the octane loss. This technology will meet the regulation but will not offer a positive ROI. There are about 300 gasoline post-treatment units in operating globally today, and Topsoe has commercialized a portfolio of highly selective catalysts to meet this demand. The chart below shows how Haldor Topsoe, Inc.'s catalysts for gasoline post-treatment compared to other catalysts in the marketplace today:

Blending with MTG Gasoline:

Haldor Topsoe, Inc. licenses a process called TIGAS™ for converting natural gas to gasoline, which is commercially viable in the U.S. and Canada today due to the low price of natural gas (NG). The cost NG per barrel of gasoline produced is about \$25, or less than half of the cost of oil currently. The gasoline produced will meet all of the gasoline specifications; and as an added benefit, it will contain zero sulfur, making it an excellent blendstock. As mentioned, this solution cannot be used as the only means of getting from 30 to 10 ppmw because it will simply require too much blendstock; but, it could help close the gap. The following process flow diagram illustrates Topsoe's TIGAS™ technology for production of gasoline from natural gas:

WARD KOESTER (Shell Global Solutions)

Shell has evaluated the gasoline pool at each of its refineries to determine which require capital investment in order to meet the new Tier 3 specifications. It is recognized that FCC gasoline is the main contributor to sulfur in the gasoline pool at the refineries where capital investment is necessary. The focus at these sites has been on increasing the capability of the CDTECH-licensed units that were originally built with Tier 2 gasoline in mind. There has also been a focus on converting the heaviest part of the FCC gasoline into diesel to both upgrade its value and remove it from the gasoline pool altogether. For winter mode, butanes have also become more of a concern as their sulfur content is typically between 10 and 30 ppm. Caustic treating the butanes is not an option in many cases due to the >10 ppm levels of non-mercaptan sulfur found in this stream.

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