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Taking back what's yours: Extractive desulfurization minimizes octane loss in FCC naphtha hydrotreating

Generating octane barrels has always been a tough road for refiners. In 2020, this road got a lot tougher with olefin saturation and octane destruction being collateral damage as refiners strive to achieve the sulfur limit in the gasoline pool.

In the U.S., the Tier 3 day of reckoning has come. After 3 yr of utilizing accumulated sulfur credits, refiners must meet a 10-ppmw total sulfur limit in their gasoline blending pool this year. The alternative is to purchase credits from refiners who have met compliance requirements.

Are refiners able to meet this new limit? Between October and November 2019, sulfur credit prices skyrocketed from \$800/credit to more than \$4,000/credit.[1] This is a good indication that the task has been difficult to achieve.

Through crude selection and capital investment in hydrotreating facilities, some refiners are able to meet the 10-ppmw-sulfur average limit in the gasoline pool. Unfortunately, they are finding that doing so has created another costly problem: the reduction of octane in their blending pool.

FCC naphtha makes up a significant portion of both the volume and octane number in the blending pool in the U.S., as with other gasoline markets. Whereas low-octane, straight-run, paraffinic naphtha can be easily hydrotreated with minimal impact on naphtha properties, high-octane, highly olefinic FCC naphtha presents a special challenge. Unfortunately, when hydrotreating FCC naphtha, one side reaction is the hydrogenation of these olefins to paraffins. Worse yet, when treating at high severity to reach 10-ppm sulfur, the rate of olefin hydrogenation increases with every ppm of sulfur removed from the naphtha. TABLE 1 represents a typical FCC naphtha.

Note that more that 40% of this naphtha is olefinic, and most of the olefins are in the C_5–C_7 carbon number range. As the naphtha hydrotreatment severity is increased to achieve the sulfur limits, more than half of these olefins can hydrogenate to paraffins. So, what happens to the octane number? TABLE 2 gives an idea.

Clearly, there is a high price to pay for saturating these molecules. With the technologies available, either the refiner must make up lost octane barrels with high-priced alkylate or platformate, or purchase high-priced sulfur credits.

A game-changing tool. Solvent extraction technology for the removal of sulfur and the preservation of olefins can solve some of these challenges. The technology[a] is a fractionation and extraction process designed to fractionate a middle cut from the refiner's FCC naphtha. It segregates the olefin-rich material from the FCC naphtha hydrotreater feed and sends it to a proprietary extraction process, as shown in FIG. 1.

Operations and engineering specialists accustomed to aromatics or lubes extraction units will be familiar with the flow diagram for this process; however, this extraction process utilizes a proprietary solvent blend and customized fixed tower internals to maximize extraction of sulfur species from the mid-cut naphtha, generating an olefin-rich raffinate that meets Tier 3 sulfur. The separate liquid/liquid extraction and distillation steps in this process are significantly more energy efficient than extractive distillation alternatives.

The solvent is specially formulated to reject olefins and absorb sulfur species, particularly thiophene, that dominate the mid-cut naphtha. TABLE 3 shows the relative solubilities of aromatic and sulfur species in the solvent, compared to the olefin and paraffin species present in the mid-cut naphtha stream.

TABLE 1. Example of FCC full-range naphtha

C	nP	iP	O	N	A	Total	Olefin, wt%	Olefin wt% of total naphtha
4	0.1	0	0.6	0	0	0.7	87.5	1.6
5	1.2	7.8	18	0	0	26.9	66.8	**44.2**
6	1.1	5.9	11.9	2	0.8	21.6	55	**29.3**
7	0.9	2.2	4.3	3.2	3.7	14.3	30.3	**10.7**
8	0.4	2.7	3.6	1.8	6.4	14.9	24.2	8.9
9	0.3	1.6	1.4	1.3	7.8	12.3	11.2	3.4
10	0.2	0.7	0.7	0.2	4	5.7	11.7	1.5
11	0.3	1.5	0.1	0	1	3	5.4	0.4
Total	**4.4**	**22.2**	**40.6**	**8.6**	**23.6**	**99.4**		**100**

TABLE 2. Component octane numbers for C_5–C_7 olefins and paraffins

Component	RON	MON	(RON + MON) ÷ 2
n-Pentene	90	77	84
n-Pentane	62	63	62
i-Pentene	103	82	93
i-Pentane	92	90	91
n-Hexene	90	80	85
n-Hexane	25	26	25
i-Hexene	100	83	92
Methylpentane	76	74	75
C_7 olefins (average)	90	78	84
Methylhexane	52	52	52

The result is a process that produces an olefin-rich raffinate with less than 10-ppm sulfur that can be sent directly to the blending pool, and a sulfur-rich, olefin-lean extract that is sent to the naphtha hydrotreater, dramatically decreasing olefin saturation and minimizing octane loss.

If installed with a new hydrotreater, the technology can reduce the required throughput of the hydrotreater by up to 40% and reduce hydrogen requirement by up to 50%. For refiners with existing hydrotreating units, the technology will recover 2 to 4-plus octane units in the full-range FCC naphtha pool, reduce hydrogen consumption, reduce operating severity and consequently extend the run life of the unit.

Commercial example. A refiner installed the process in its existing FCC unit. Prior to installation, the refiner had been separating its 17,000 bpd of FCC naphtha into light and heavy cuts, and then desulfurizing the fractions with caustic and hydrotreating, respectively.

A new mid-/heavy-cut splitter was installed, with a targeted 100°C (212°F) cutpoint. The new, 6,800-bpd mid-cut naphtha stream was sent to the new unit, with resulting performance as shown in **TABLE 4.**

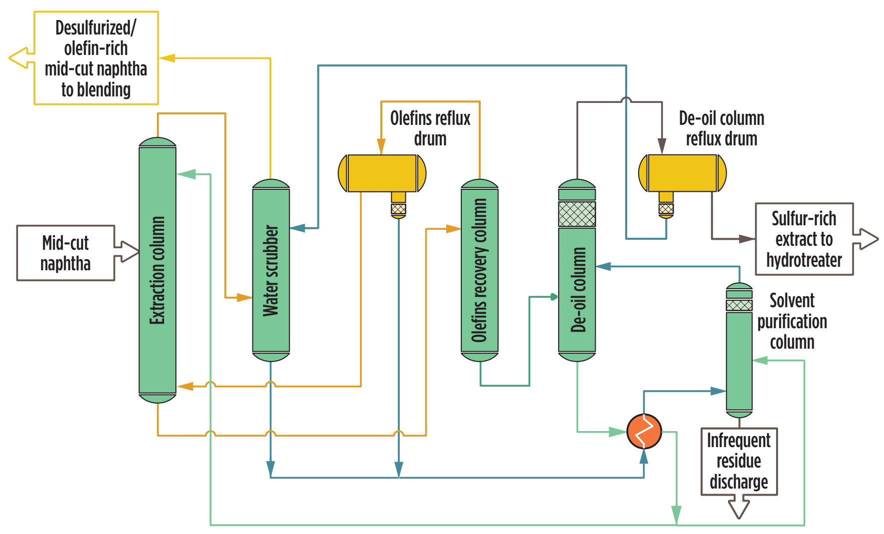

FIG. 1. Process flow diagram of the new FCC naphtha sulfur extraction process.

TABLE 3. Relative solubilities of hydrocarbon and sulfur species in the proprietary solvent

Hydrocarbon	Benzene	Toluene	Cyclohexane	Every other hydrocarbon
Relative solubility	8	4.8	2	< 1
Sulfide	Thiophene	Methylthiophene	Thioether	Mercaptan
Relative solubility	10.5	5.2	5	4.7

TABLE 4. Commercial unit results for the new FCC sulfur species solvent extraction process

Commercial unit, 6.8 MMbpd	**Naphtha feed**	**Raffinate to blending**	**Extract to naphtha hydrotreater**
Flowrate, MM lb/hr	70.6	58.7	11.9
Percentage, wt%	100	83.1	16.9
Olefin content, wt%	43.9	48.6	20.7
Olefin flowrate, MM lb/hr	30.9	28.5	2.4
Olefin split, %	100	**92.1**	7.9
Sulfur content, ppmw	380	8	2,212.4
Elemental sulfur split, %	100	1.8	**98.2**

RON loss in the full-range FCC gasoline blending pool dropped to less than 1 number after treating vs. 4 numbers before the installation of the unit. In addition, the new 8-ppm-sulfur raffinate stream was sent directly to blending, bypassing hydrotreating. At $0.98/bbl of octane,[2] this project recovered more than $18 MM/yr in octane value. Similar results have been demonstrated in commercial operation of the unit at other refineries.

Takeaway. Due to the millions of dollars per year at stake, much effort has been spent on optimizing desulfurization vs. octane loss in FCC naphtha hydrotreating processes. Commercial implementation of this extraction technology demonstrates that there is a low-cost, efficient means of desulfurizing naphtha while preserving olefins and dramatically reducing octane loss from hydrogenation. Refiners can keep the octane barrels and "take back" their post-Tier 3 future. HP

NOTE

[a] The technology is offered by Koch Industry affiliates INVISTA Performance Technologies and Koch Glitsch under the trade name of ExoS technology.

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