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Sulfur reduction: What are the options?

Refiners must choose the technology that makes the most sense to them, weighing initial capital expenditure, operating costs and product performance

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Sulfur reduction in gasoline. People have been talking about it for years. Refineries have been planning and working to meet all the various regulations as the sulfur specifications keep getting lower and harder to reach. Refineries today are scrambling to meet not only the low sulfur requirements, but also the imminent ultra-low sulfur mandates. Billions of dollars will be invested in the next few years to attain these sulfur levels. The big questions in everyone's mind are:

- What to buy?
- How much to spend?
- What will be the payout?
- Can the investment be delayed or staged?
- Will the investment made for 30 wt ppm be stranded capital or can it be modified to later reach 10 wt ppm?
- And, most importantly, will any of the sulfur treating technologies currently available actually work?

Many new technologies are being offered today to meet the sulfur reduction demands being presented. Unfortunately, the majority of them are unproven in commercial refineries. Whether refiners were in total disbelief that the low sulfur regulations would actually come to pass or the ability to remove sulfur just took that long to be developed, the technologies that refineries are betting on are pretty much just that—a bet. This is a huge bet for an industry that inherently hates to take risks. The future of their gasoline pool depends on the correct choice. Mistakes could set them back millions of dollars and years of work.

Regulatory trends. The United States Environmental Protection Agency (EPA) will require most refineries and distributors to meet EPA Tier 2 regulations beginning in the next three to four years. This regulation will require refiners to meet a 30 wt ppm sulfur limit as compared with today's average of 330–340 wt ppm. Staged reductions must start in 2004. Early compliance in 2000-2003 will generate "sulfur credits," which can be used to partially offset the estimated $8-billion cost to refiners to comply with the new limits.[1]

European regulations call for levels of 50 wt ppm sulfur by 2005, with some EU governments advocating even lower sulfur levels prior to that time. Many European governments are giving tax credits to refineries if they beat an earlier, 2004 deadline.

Future legislation in both the U.S. and Europe may require sulfur levels as low as 10 wt ppm in the gasoline pool, a level that very few of today's technologies can meet without significant operating costs. Various lobbying groups such as the automotive industry are also demanding zero sulfur in fuel. Most people believe this means meeting less than 5 wt ppm in the gasoline pool as a practical matter. Table 1 illustrates the regulatory trends for sulfur reduction.

What is the solution? Each technology for sulfur reduction must be reviewed with deliberation and care. Regardless of what each company offering a technology choice may say, not all methods are appropriate for every application.

TREATMENT OPTIONS

Since the primary contributor of sulfur to the gasoline pool is FCC gasoline (approximately 90%), FCC gasoline is the main focus of many refineries' sulfur treatment efforts. The two primary ways to attack the sulfur in the FCC gasoline pool are pretreatment and post-treatment. Utilizing special catalysts in the FCC may reduce sulfur levels, but these catalysts cannot meet the requirements mandated by Tier 2 regulations.

Pretreatment. FCC feed pretreatment using hydrotreating may be a viable option some refineries may choose. FCC feed hydrotreating improves overall liquid yield as well as quality and reduces the SO_X emissions from the FCC unit.

Pretreatment of the FCC feed is probably the most expensive way to reduce sulfur in gasoline. Estimates range as high as $1,500–$2,500/bbl to pretreat the FCC feed. All of this money will probably not allow the refinery to meet the 30 wt ppm sulfur specification required for the Tier 2 regulations, much less meet a possible future 10 wt ppm sulfur specification.

Table 1. Gasoline sulfur specifications[5]

Property		North America		Europe		World Fuels Charter
		EPA 2006	CaRFG3*	Current	2005	
Sulfur	wt ppm	30 max	15 max	150 max	50 max	30 max

*CARB Phase 3 proposed averaging limit.

Table 2. Sulfur treating technology comparison

Technology	Octane loss	Volume loss	Sulfur reduction	Hydrogen cons.	Commercial unit*	Add'l pros	Add'l cons
Feed HDS	No	N/A	May not meet 30 wt ppm	High	Many	1) Impr. liquid yield 2) Red. SO_X emissions	Highest initial capital cost
Catalytic distillation hydrotreating	Yes	No	10–30 wt ppm	Yes	1st started up in May 2000	—	1)Catalyst cost 2) May produce recomb. RSH 3) High capital cost
Conventional hydrofining with octane recovery	No	Up to 5%	10 wt ppm	Yes	Operating since 1991	—	1) Catalyst cost 2) Total olefin sat and Rvp increase
Selective cat naphtha hydrofining	Yes**	No	10 wt ppm	Yes	Yes	—	1)Catalyst cost 2) May produce recomb. RSH
Dual-catalyst reactor	Yes	No	10–30 wt ppm	Limited	First startup for unit producing 10 wt sulfur expected in 2001. Several other units in operation	No need for additional product sweetening	1) Catalyst cost 2) Includes diolefin sat and interstage strip 3) May produce recomb. RSH
Low pressure fixed-bed hydroprocessing	Yes	0.3–2%	10 wt ppm	Yes	Yes	—	1)Requires MTBE (or equiv.) addition for max yield case to recover octane. Octane neutral case does not 2) Total olefin sat and Rvp increase
Olefinic alkylation	Yes	Yes	10 wt ppm	No	One	—-	Catalyst cost
Sorbent	No	Yield is almost 100% of original stream	10 wt ppm	Low	Small-scale startup in 2001	No recomb. RSH formed	1) High initial capital cost 2) Sulfur yielded as SO_2
Extractive mass transfer ***	No	No	10 wt ppm	No	No	1) Cost savings compared to HDS as final polishing step 2) Preserves octane	1) Chemical costs 2) RSH removal only

* Not enough published data exists regarding feed and product sulfur levels to determine if these units can meet the 30 wt ppm sulfur requirements with the existing commercial units.
** Can be reduced when used in combination with extractive mass transfer technology.
*** Must be paired with a selective hydroprocessing unit.

(All information in Table 2 is reproduced from published articles regarding each technology.)

Post-treatment. Post-treatment offers the refiner the largest number of options for treating sulfur. A variety of technologies are available, ranging from catalytic distillation to selective hydrotreating to adsorption systems. Many of these are still unproven in full-scale units or have very few units in operation to measure their actual capabilities. Installation costs for each unit also vary widely as do the operational costs in both utilities and octane losses. Every refinery choosing one of these options will have to carefully consider the pros and cons of each technology before making its decision—and hope that the technologies work as well as advertised. Table 2 compares properties for the technologies summarized in the following discussion.

Catalytic distillation hydrotreating. One of the earliest technologies to come into the market was selective hydrotreating via catalytic distillation. The single-bed system reportedly achieves 90% desulfurization of FCC gasoline while maintaining high yield and minimum octane losses. Distillation is a significant benefit of this technology when used as a pretreatment step, whereby light sulfur compounds are reacted and removed with the bottom product. This can eliminate the need for caustic treating the light FCC gasoline fraction downstream of the fractionation steps. Several of these units are currently operating. The first was built in 1994.

An additional process involving catalytic distillation in combination with hydrodesulfurization reportedly reduces the sulfur approximately 95% in FCC gasoline. This is accomplished using a dual-bed system with hydrogen injection into a distillation column. The light ends are fractionated in the upper low temperature zone while the heavy ends are concentrated into a high temperature zone. The primary goal is to maintain olefin saturation, but still desulfurize. Reported results show an octane loss of less than 1.0.

The two systems are used in combination by running the FCC gasoline first through the single-bed column and then through the dual-bed column for maximum sulfur reduction. In the first column, mercaptan sulfur reacts with excess diolefins to produce heavier sulfur compounds. The remaining diolefins are partially saturated to olefins by reaction with hydrogen. Bottoms from the first column are fed to the second column where the mid and heavy naphtha are catalytically desulfurized in the two separate reaction zones. Hydrogen is added to each column at typical reformer hydrogen pressure levels.

The first unit using the dual-bed system started up in May 2000 to treat heavy FCC naphtha. The mercaptan levels in the gasoline product have been low enough that the refinery has been able to blend and ship gasoline with no further treatment required.

Conventional hydrofining with octane recovery and selective cat naphtha hydrofining. Another approach is to fractionate the FCC naphtha into two or three streams—light cat naphtha (LCN), intermediate cat naphtha (ICN) and heavy cat naphtha (HCN)—and treat those streams individually. The ICN and HCN can be combined and selectively hydrotreated to achieve less than 100 wt ppm sulfur with very little loss of octane. If the endpoint of the LCN is kept relatively low (150°F), a significant portion of the sulfur in this stream will be light mercaptans, which can easily be treated using caustic extraction. Utilizing caustic treating for this stream prevents any loss of octane that would occur if it were hydrotreated. The total full-range naphtha stream can also be selectively hydrotreated if a gasoline splitter is not economically justified.

Two commercially proven technologies have been developed for treating the ICN and HCN streams. The first process approach uses an octane recovery technology that is very similar to a conventional gasoline hydrofinisher or distillate desulfurization unit. The process involves complete saturation of olefins via hydrotreating followed by octane recovery via isomerization to higher octane components (primarily isoparaffins). Here, octane retention is the main advantage. The main disadvantage is the loss of C_5^+ volumetric yield that accompanies the relatively severe octane recovery step.

This process has been commercially proven, with the first unit implemented in 1991. New catalyst improvements have been implemented since the 1991 startup to improve volume retention while maintaining octane.

The second process technology, selective cat naphtha hydrofining process, is a catalytic hydrodesulfurization process that uses a proprietary catalyst developed for the selective removal of sulfur from naphtha with minimum hydrogenation of olefins and octane loss. Commercialization of this process was announced in 1998. A second generation of this technology can achieve product sulfur levels between 10 and 50 wt ppm using a conventional hydrotreating process configuration and a new, highly selective catalyst. One of the features of this process is that to minimize olefin saturation and octane losses, the severity of hydrotreating may be reduced, allowing the formation of recombinant mercaptans. These are formed when H_2S reacts with olefins.

A modeling system has been developed by the licensor that revolves around octane loss and recombinant mercaptan formation. This modeling system is essential to predicting the formation of recombinant mercaptans so they can be effectively dealt with downstream of the unit. If the recombinant mercaptans formation is not taken into account, the sulfur specification may not be easily met without significant octane losses required by running at higher severities.

The second generation of this technology can achieve 10 wt ppm sulfur, while in many cases reducing the octane loss by as much as 50% from the original technology with some incremental investment.[2]

Dual-catalyst reactor. This technology was developed to remove sulfur from heavy to mid-range naphthas with modest octane loss and high gasoline yield. Increased requirements for sulfur reductions have led to another generation of this technology that utilizes a dual-catalytic concept. The second-generation technology includes a selective hydrogenation reactor upstream of a splitter with the dual-catalyst reactor system just downstream of the splitter. The main reactions taking place in the reactor are hydrogenation of diolefins, isomerization of the olefin's double bond and conversion of mercaptans to heavier sulfur species.

Staged investments may be possible allowing the first investment to produce sulfur specifications ranging from 50–150 wt ppm. The full implementation will reportedly meet the 10–30 wt ppm sulfur requirements. This technology allows the reduction of olefins in the gasoline pool in the range of 10 to 15 vol%. Olefins may be further reduced, but this would require higher hydrogen consumption and higher octane loss.

The first two units utilizing this technology were expected to start up in Germany in 2001.

Low pressure, fixed-bed hydroprocessing. This method utilizes proprietary, low-pressure, fixed-bed hydroprocessing technology to selectively reconfigure the lower-octane components of its gasoline-range feedstock. The licensor states that it enables refiners to hydrotreat the sulfur-containing components of a gasoline pool while also controlling the octane of the hydrotreated product. The process can independently control both the octane and product sulfur, which eliminates the octane penalty typically associated with hydroprocessing.[3] This flexibility is achieved by the use of a catalyst system that reportedly promotes an array of octane-enhancing reactions.

The flow scheme for this technology is very similar to that of a conventional naphtha hydrotreater. Capital and operating costs are also similar to those of a hydrotreater. The cost savings involve the savings in octane by not requiring as much MTBE to maintain the octane or by taking a loss on yield, which is still less expensive than the addition of MTBE to a hydrotreated stream.

Olefinic alkylation. This technology concentrates on the thiophenes found in the naphtha stream produced by FCCs. Its basis is the conversion of thiophenes to higher boiling point compounds that can be readily removed from the gasoline stream.

The conventional method to remove thiophenes is hydrotreatment, which consumes hydrogen and results in losses in octane. This technology facilitates separation of the thiophenes by catalytically causing them to react with olefins present in the naphtha to produce heavier compounds. The higher boiling sulfur fraction is then removed by fractionation and added to the diesel refinery stream, where the sulfur can be removed by hydrotreating. Between 1% and 4% of the feed stream is separated and sent to the diesel stream.

This process is reported to remove up to 99.5% of the sulfur from the gasoline stream. Reported octane losses are 2 or less octane numbers. Product sulfur requirements of 10 wt ppm can be met.

The first commercial application of this technology has begun production. Two additional units are expected to come online in 2002.

Sorbent. This technology utilizes a proprietary sorbent to attract sulfur-containing molecules and remove the sulfur atom from the molecule. The sulfur atom is retained on the sorbent, while the hydrocarbon portion of the molecule is released back into the process stream. H_2S is not released into the product stream, which prevents the recombination reactions of H_2S and olefins to make mercaptans.[4] The sulfur is removed in an offgas stream as SO_2 that must be processed in the Claus unit.

This technology does not utilize any type of hydrotreating technology, so typical hydrogen concerns of high consumption rates and purity are not issues. In some cases, reformer hydrogen may be an acceptable hydrogen source.

Several advantages noted by the licensor include yield preservation, low octane losses, sulfur removal up to 10 wt ppm and long run lengths. This technology can treat the entire FCC naphtha stream or parts of the naphtha stream as required by the refinery.

The first commercial unit started up in 2001 at the developer's refinery. The unit processed 6,600 bpd of full-range FCC naphtha.

Extractive mass transfer (post-hydrotreater sulfur removal). A new liquid phase extraction technology has been developed utilizing a special mass transfer device and a specially formulated treating solution to substantially enhance the extraction of higher molecular weight (C_4^+) mercaptan compounds such as recombinant mercaptans produced after FCC gasoline hydrotreatment. Individual studies have shown that several of the available sulfur-treating technologies mentioned earlier have the potential for recombinant mercaptan formation as a trade-off to minimize olefin saturation.

This technology has been specifically designed to treat product streams from the hydroprocessing sulfur treating units to allow refiners to meet lower sulfur (10 wt ppm or less) standards without losing octane. Many of the sulfur-treating technologies will be able to meet the more stringent standards, but only if they run at higher severities, causing significant octane losses. The savings in octane losses frequently pay out the cost of the mass transfer systems in as little as one to three years.

Capital expenditure for a grassroots system utilizing this technology is 35–50% of the cost of most incremental second-stage hydrotreating systems. Operating costs per barrel can be over 60–70% less than hydrotreating. This technology also provides staged investment options for additional sulfur removal.

The main advantages are lower investment costs as compared to a hydrotreating polishing step for final recombinant mercaptan removal and no octane loss through the system. Using this technology also allows the other systems to be run at a much lower severity, thus retaining more octane throughout the system.

The treating solution utilized is a specially formulated solution produced from common chemicals found in the refining industry. There are no additional disposal requirements beyond those of most common chemicals. The system is also regenerative, so chemical usage is minimized.

Outlook. The possibilities for sulfur reduction are as varied as their results. Some technologies will perform better regarding loss of octane, while others will perform better regarding volume losses. Each will be required to meet the specifications mandated by the U.S. and international communities. The cost for some technologies in initial capital expenditure may be very high, while others may have very high operating costs. Regardless of refiners' reasonings, the choices will have to be made soon. ■

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