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REFINING DEVELOPMENTS

SPECIALREPORT

Improve sulfiding of hydroprocessing catalysts

An alternative safer, easier method to activate catalysts

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The catalyst in all hydroprocessing units in a refinery—hydrotreaters, hydrodesulfurizers and hydrocrackers alike—require sulfiding. Typically, a catalyst starts out in an inert/inactive form, with the active metals in the oxide form. The catalyst is sulfided by reaction of its active metals with hydrogen sulfide, which is produced *in situ* from a reaction between available sulfur in the feedstream and hydrogen, or more commonly from sulfur in the sulfiding agent. A defined quantity of sulfur is required to activate the catalyst.

Sulfiding catalysts. There are several ways to add sulfur to the catalyst. One that may appear attractive is to use naturally occurring sulfur in the feedstream; it avoids the cost of purchasing a sulfiding agent. For most catalysts, the greatest risk of this method is that the catalyst surface will accumulate coke before sulfiding is complete, thereby reducing overall catalyst activity and service life. The cost of reduced catalyst activity and lifetime greatly exceeds any savings on sulfiding agents. For many years, dimethyl disulfide (DMDS) has been used as a sulfiding agent. However, several hazards are associated with DMDS. DMDS is difficult to transport, store and apply, as presented in Table 1.

Alternative method. An alternative sulfur-rich material is now available, di-t-butyl polysulfide (DBPS). It has the advantage of having virtually none of the negative aspects or hazardous properties associated with applying DMDS. The DBPS molecule is a linear polysulfide chain with t-butyl end groups and is specifically manufactured for *in-situ* catalyst sulfiding.

Advantages. There are four clear advantages for refiners to choose DBPS over DMDS as a sulfiding agent:

• **Safety.** DBPS's high flash point—212°F (100°C)—reduces the fire hazard. In contrast, DMDS's low flash point of 61°F (16°C) presents a potential fire hazard in refinery usage. Therefore, DBPS imposes no special packaging, transportation or storage requirements. DMDS usually is stored under nitrogen pressure in closed containers to reduce its odor and hazards associated with its low flash point. Conversely, DBPS can be stored at the refinery in regular containers, and it does not need to be in a closed system.

Workers also appreciate working with DBPS because they are not required to wear special clothing beyond what is normally required for handling any chemical in a refinery. In addition, because the risk level is so low, the refinery's operators often inject DBPS with portable, low-pressure pumps.

• **Odor.** DMDS has an extremely unpleasant odor—primarily due to residual mercaptans from the production process. Spills can be a nuisance to the surrounding community as well as to refinery workers. On the other hand, when DBPS is used, there normally is a diesel-like smell associated with the product's chemistry. Neighbors and employees will appreciate it because the smell is not unpleasant and is virtually undetectable in an open-air environment.

TABLE 1. Comparison of DMDS and DBPS catalyst sulfiding methods

DBPS	Low odor and high flash point (212°F/100°C) mean excellent handling and worker safety properties and nonregulated transport. Low initial decomposition temperature (320°F/160°C) ensures good safety margin for catalyst reduction. Approved by catalyst manufacturers; rapidly growing global market share. Sulfiding usually complete in 1–2 hours less than with DMDS.
DMDS	Bad odor. Low flash point (61°F/16°C) requires DOT regulated transport and specialized handling. Initial decomposition temperature (392°F/200°C) is moderately high. Well-known and approved; the industry standard. Sulfiding usually complete in 18–36 hours.

• **Nonregulated transport.** Using DBPS may result in savings in on-site demurrage charges if there are delays in sulfiding at the refinery. Because of its low flash point, DMDS is Department of Transportation (DOT) regulated. Often, the driver must stay with the truck until the sulfiding is complete; higher demurrage charges result if there is a delay. In contrast, because of DBPS's flash point, the DOT has classified this sulfiding agent as nonhazardous for transportation; thus, the driver may leave the truck until the sulfiding is complete.

• **Reduced SO_x emissions.** The hydrocarbon byproduct of DMDS is methane, which accumulates in the hydrogen plus hydrogen sulfide (H_2S) recycle gas. This may reduce the hydrogen partial pressure below the required minimum, necessitating purge of the recycle gas and the addition of makeup hydrogen. The purge stream is commonly sent to a flare, producing undesired sulfure dioxide (SO_x) emissions from the H_2S contained in the purge gas. This also results in wasted hydrogen and H_2S. However, DBPS's hydrocarbon byproduct is isobutane, which normally exits the high-pressure separator with the liquid hydrocarbons and does not dilute hydrogen in the recycle gas.

Pilot-plant study. A pilot-plant study was conducted with two objectives. The first was to verify that catalysts sulfided with DBPS performed as well as catalysts sulfided with DMDS. The study data showed that there was no practical difference in the hydrodesulfurization activity of the sulfided catalyst regardless of whether DMDS or DBPS was used (see Fig. 1).*

The second goal was to determine if the lower decomposi-

TABLE 2. Comparison of chemical and physical properties of DBPS and DMDS

Property	DBPS	DMDS
Sulfur content (%wt/wt)	54	68
Decomposition temperature	320°F (160°C)	392°F (200°C)
Flash point (closed cup)	212°F (100°C)	61°F (16°C)
Odor description (vendor)	Low odor (diesel like)	Decaying cabbage

tion temperature of DBPS resulted in H_2S production at a lower temperature than DMDS. DBPS decomposes in the presence of hydrogen and catalyst to form H_2S at approximately 72°F (40°C) lower than the comparable DMDS temperature (see Table 2). In practice, DBPS's lower temperature permits sulfiding to begin at lower catalyst-bed temperatures. This lowers the risk of irreversible reduction of the catalyst by hydrogen due to exotherms and often decreases the sulfiding process time. It is to a refiner's advantage to use DBPS, particularly when considering the cost implications from reactor downtime and the reduced potential for catalyst damage.

Cons. One minor inconvenience of using DBPS is its lower sulfur content (54%) compared to DMDS (68%). This requires a small extra dosage of DBPS compared to DMDS to make the same amount of sulfur available to the catalyst (see Fig. 3).

Catalyst manufacturers worldwide cooperated with the testing and approval of DBPS as an alternative to DMDS. All of the participating catalyst manufacturers found that DBPS is an acceptable and efficient alternative to DMDS. There are a few exceptional applications in which certain catalyst manufacturers have not tested or approved DBPS. Overall, DBPS is safer, has less odor and is easier to handle than DMDS. As one refiner put it, "Why would I choose anything else?" **HP**

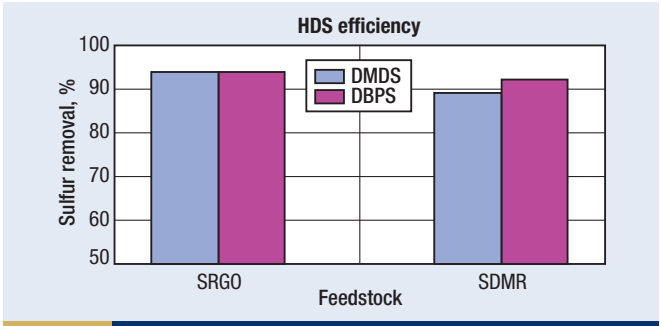

FIG. 1 Tests were run at average catalyst bed temperature of 675°F (357°C). Straight-run gasoil (SRGO), one of the feedstocks tested, contained 2.2% sulfur. Straight-run middle distillate (SRMD), another feedstock tested, contained 0.81% sulfur.

NOTES

* For more pilot-plant study details, send an e-mail request to dave.roberts@lubrizol.com.

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