DMS Exact-S® FAQs

DMS Exact-S® Grade is an important sulfidation agent for ethylene manufacturers. It effectively regulates carbon monoxide (CO) generation during steamcracking and helps to control the formation of coke in the furnace.

Over the years, Gaylord Chemical has fielded questions from our customers and a list of Frequently Asked Questions is categorized below.

Performance

Proper dosing of a high quality sulfidation agent is important to maximizing run length between decoking cycles.

Which sulfidation agents for ethylene production are commercially available?

The most widely used sulfur chemicals have been dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). Polysulfide oils, mercaptans and hydrogen sulfide have been used to a lesser extent.

What is the most important feature of a sulfidation agent?

From a performance standpoint, sulfidation agents appear to all work in the same way: they decompose at cracking temperatures to provide sulfur species which interact with the coil surface and free radicals formed during cracking. It could be argued that the most important feature of a sulfidation agent is really cost effectiveness: when adjusted for differences in sulfur content, which sulfur agent is most economical?

Is the sulfur content of a sulfidation agent important?

As all sulfidation agents do basically the same thing, sulfur content of the sulfidation agent is not particularly important. Techology licensors typically prescribe a dosing level of *ca.* 100 ppm during normal operating conditions. This requires the furnace engineer to simply adjust the flow rate of the sulfidation agent when changing from one having lower percent sulfur level.

As an example, an engineer switching from DMDS (%S 68%) would simply increase the flow of Exact-S (%S 51.6%) such that 100 ppm/w sulfur is fed into the furnace steam header. DMS is more effective than DMDS from a cost standpoint, an important motivating factor for such a switch.

Why is purity of the sulfidation agent important?

Steamcracking operations require a non-stop stream of sulfur chemicals to operate efficiently. The contribution of process contaminants by feedstock, furnace steam, and all additives should be minimized. Specifically, the impurities below can cause significant process problems for the reasons listed:

Specification Item	Potential Impact	DMS Exact-S® result
Carbon Disulfide (CS_2)	Hydrogenation catalyst poison	<10 ppm
Total Nitrogen	Indirect measure of NO_2: cold box hazard	<20 ppm
Hydrogen Sulfide		<200 ppm
Water		<700 ppm
Methyl Mercaptan		<500 ppm
Representative Analysis		
Iron (Fe)	Acceleration of coking rates; pyrophoric iron sulfide	25 ppb
Mercury (Hg)	Process safety; explosion potential	3 ppb
Potassium (K)	Radiant coil damage	<50 ppb
Sodium (Na)	Coil damage associated with chromium removal	<50 ppb
Phosphorus (P)	Radiant coil damage	<50 ppb
Vanadium (V)		7 ppb
Carbonyl Sulfide (COS)	Hydrogenation catalyst poison	non detected
Free water (ASTM 4176)		Clear, bright, free of particulate matter (CBP)

DMS Exact-S® carefully controls levels of problematic impurities and is the purest sulfidation agent available.

It is useful to remember that a world-class ethylene facility (1,500,000 MTA capacity) can consume over *one million pounds per year* of sulfidation agent. Even at low dosage levels, poor quality sulfidation agents can contribute to process contamination problems.

Is the decomposition temperature of sulfidation agents important?

The complete decomposition temperatures of the most popular sulfidation agents – DMS and DMDS – is about 675°C and 575°C, respectively. This is well under standard cracking temperatures, which range from about 825 – 950°C. Both DMS and DMDS are completely decomposed in the furnace.

There is some evidence that DMDS, which is slightly less thermally stable than other sulfidation agents, can actually *accelerate coking* relative to other sulfidation agents. Presumably this is due to the ability of DMDS to increase rates of noncatalytic coking– a potential disadvantage.

What are the decomposition products from DMS and DMDS?

The decomposition profiles of sulfidation agents under steam cracking conditions has not been studied in a comprehensive way. An early study (2) lists the decomposition products for DMS as methane, methyl mercaptan, and H_2S, and the decomposition products for DMDS as methyl mercaptan, H_2S, methane, ethylene, ethane, and 'heavier sulfur compounds'.

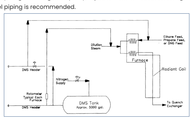
There have been reports that DMDS use can affect quench tower acidity in a way that may be attributable to SO_2 byproduct formation. If this occurs, it suggests that not all sulfur in the DMDS molecule is used productively; any DMDS sulfur converted to SO_2 introduces operational costs associated with quench water pH regulation. A recent paper has modeled the decomposition pathway for DMDS, which is indeed complex (3).

Dimethyl Sulfide (DMS) is a cost effective and proven sulfidation agent for steamcracking operations. The high purity of DMS Exact-S® helps to minimize the overall burden of feedstock impurities entering the furnace.

Engineering / Handling and Use

What does an injection system for DMS look like?

An injection system for sulfidation agents like DMS and DMDS is simple and is shown schematically below. DMS stored in a storage or smaller day tank is metered into the dilution steam header using nitrogen pressure or a small diaphragm or mag drive pump. Injection flow is measured using micromotion or coriolis meters. Stainless Steel piping is recommended.



How is DMS supplied and handled?

Gaylord Chemical supplies DMS Exact-S® internationally in 43,000 lb (19,454 kg) net weight quantities using IMDI ISO Containers. Both Top and bottom unloading options are available, using 3" BSP unload fittings.

Containers have a ½" nitrogen fitting and the recommended nitrogen unloading pressure is 10-30 lbs.

In North America, DMS Exact-S® can be supplied using Gaylord's fleet of dedicated trailers. DMS is placarded as UN1164 Flammable material.

Gaylord Chemical has considerable experience handling DMS. Our logistics, quality and engineering personnel are available to help.

Safety

How safe is DMS?
How does it compare to other sulfidation agents?

Dimethyl sulfide is the least toxic of all commercial sulfidation agents. It is even allowed by the US Code of Federal Regulations (CFR 21.172.515) as a synthetic food flavoring.

Exact-S® dimethyl sulfide is considerably less toxic than another sulfidation agent, DMDS. The comparative safety profiles are shown below. The higher LD-50 values for DMS indicate a *lower* degree of toxicity.

		DMS	DMDS
oral	LD 50	**3700 mg/kg**	290-500 (mg/kg)(rat)
skin	LD 50	**10,200 mg/kg (rat)**	> 2000 mg/kg
	TLV ACGIH :	**10 PPM**	0.5 ppm
inhalation	LC50	**40,250 ppm (4 hours, rat)**	1310 ppm (4 hours, rat)

Both DMS and DMDS are regulated as flammable substances.

What are physical properties of DMS?

Property	DMS Exact-S® result
CAS Number	[75-18-3]
Formula	$(CH_3)_2S$
MW	62.14
wt% S	51.50%
Boiling Point	38°C (99°F)
Vapor Pressure @ 25°C	502 mm Hg
Specific Gravity (20°C)	0.847
Water Solubility	0.4
Solubility in Water	2.0 max
Autoignition Temperature	209°C (409°F)
Flashpoint	-48°C (-54°F)
Henry's law constant	1.61×10^{-3} (25°C)
LEL	2.20%
Specific Heat @ 25°C (J/g/°C)	1.884
Viscosity, cP	0.29 (25°C)

A GHS-compliant Safety Data Sheet (SDS) can be **viewed here.** DMS is water-white liquid with a garlic- or onion-like odor. Like other sulfidation agents it is insoluble in water.

Small DMS spills can be cleaned using household bleach.

An extensive list of DMS physical properties can be **obtained here.**

DMS is a nontoxic sulfidation agent.

(2) J. Am Chem. Soc. **77**, 20 (1955) 5282-5285
(3) Mougon C, Hovelsehell, De Haan S, "Spent caustic treatment", *Hydrocarbon Processing*,April 2010, 61-66.