

# Mercaptans in Crude Oil

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# Agenda

- Mercaptan properties
- Mercaptan Scavengers
- Effect of temperature and time

# Odor of Mercaptans

<b>Hazard</b>	<b>Odor Detection Threshold</b>	<b>Hazard</b>	<b>Odor Detection Threshold</b>
Hydrogen Sulfide	0.0047 ppm	Carbon Disulfide	0.21 ppm
Methyl Mercaptan	0.0021 ppm	Methyl Alcohol	100 ppm
Ethyl Mercaptan	0.001 ppm	Kerosene	1 ppm
n-Propyl Mercaptan	0.00075 ppm	Ammonia	46.8 ppm
n-Butyl Mercaptan	0.001 ppm	Sulfur Dioxide	3.0 ppm

\*Data taken from "Hazardous Chemicals Data Book" by G. Weiss (1980)

# Properties of Mercaptans

Hazard	Physical State @ 15°C, 1 atm	Boiling Point (°C)	Vapor Specific Gravity	Toxicity By Inhalation (TLV)	Toxicity by Ingestion
Hydrogen Sulfide	Gas	-60.4	1.2	10 ppm	NA
Methyl Mercaptan	Gas	6.2	1.66	0.5 ppm	NA
Hydrogen Cyanide	Liquid	25.7	0.9	10 ppm	LD <sub>50</sub> = < 0.05 g/kg
Ethyl Mercaptan	Liquid	34.4	2.1	0.5 ppm	LD <sub>50</sub> = 0.682 g/kg
Carbon Disulfide	Liquid	46.3	2.6	20 ppm	LD <sub>50</sub> = 0.1 to 0.99 g/kg
n-Propyl Mercaptan	Liquid	67	2.6	NA	LD <sub>50</sub> = 1.79 g/kg
n-Butyl Mercaptan	Liquid	98.5	3.1	0.5 ppm	LD <sub>50</sub> = 1.5 g/kg
Automotive Gasoline	Liquid	60 to 199	3.4	NA	LD <sub>50</sub> = 0.5 to 5.0 g/kg
Kerosene	Liquid	200 to 260	NA	200 ppm	LD <sub>50</sub> = 5.0 to 15.0 g/kg

# Mercaptan Scavengers

- Mercaptans are less acidic and less reactive than H<sub>2</sub>S
- Typical hydrogen sulfide scavengers are ineffective at removing mercaptans from hydrocarbons
- Specialized chemistry with greater reactivity needed
  - SULFIX™ 9281
  - SULFIX™ 9284
  - SULFIX™ 9286

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# Mercaptan Scavengers

- Rapid reaction with lower molecular weight mercaptans
- Longer reaction time for longer chain or branched mercaptans
- Removal of other sulfur species:
  - Limited removal of carbonyl sulfide (COS) and dialkyl sulfides (RSR)
  - Some removal of carbon disulfide (CS<sub>2</sub>)

# Mercaptan Scavenger Test Methods

- ASTM D-3227, UOP-163
  - Titration methods using silver nitrate titrant
- Draeger Tubes (headspace measurement)
- Doctor Test
  - Lead solution & elemental sulfur used

# Mercaptan Scavengers

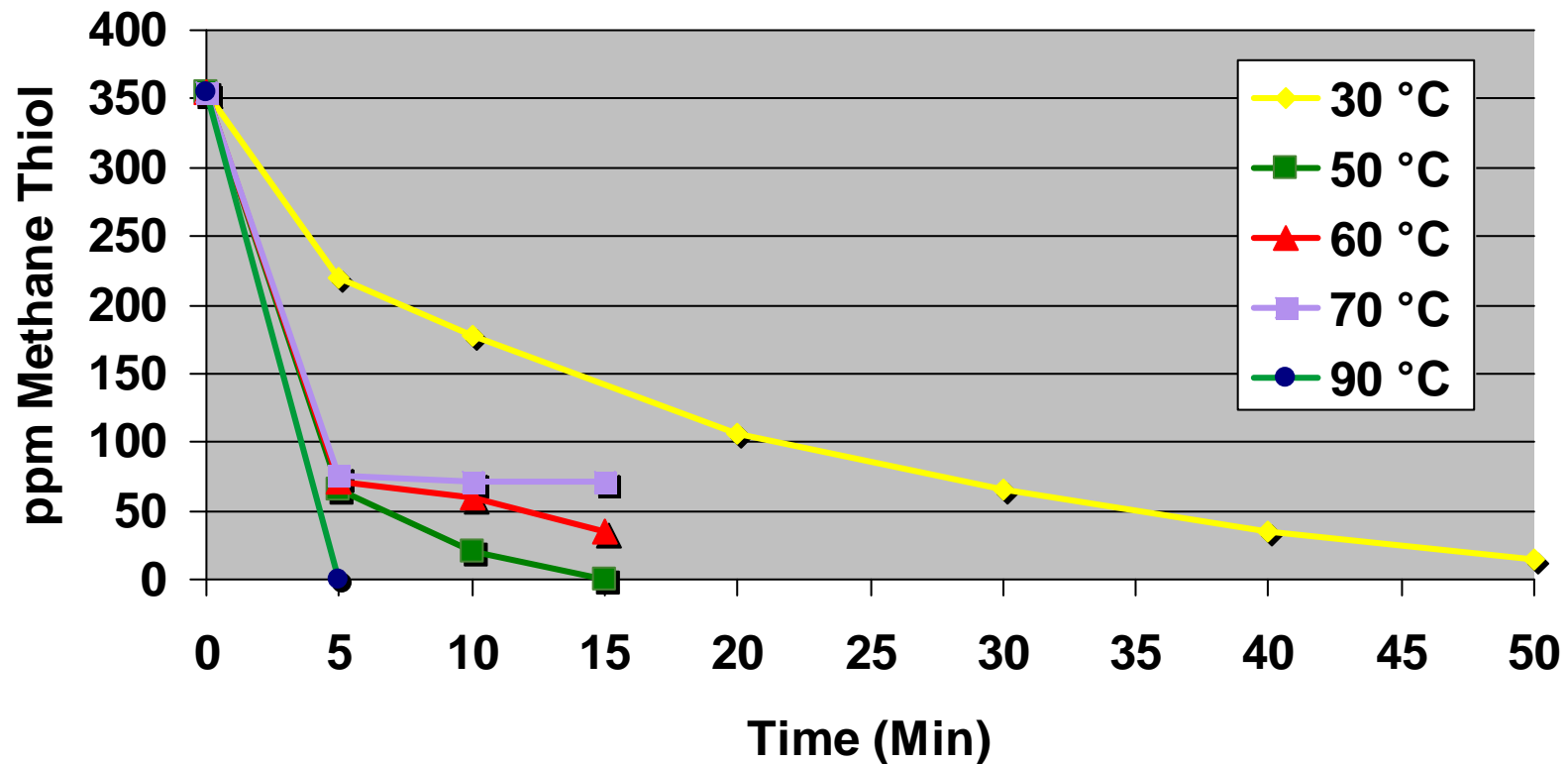
<b>Mercaptan</b>	<b>Untreated RSH (ppm)</b>	<b>ppm RSH Treated</b>	<b>ppm RSH Treated</b>
<b>Methane Thiol</b>	<b>115</b>	<b>24</b>	<b>67</b>
<b>Ethane Thiol</b>	<b>84</b>	<b>32</b>	<b>74</b>
<b>2-Propane Thiol</b>	<b>48</b>	<b>25</b>	<b>44</b>
<b>2 Methyl -2-Propane Thiol</b>	<b>6.5</b>	<b>4.7</b>	<b>6.1</b>
<b>2-Methyl-1-Propane Thiol</b>	<b>4</b>	<b>2.2</b>	<b>4.5</b>

**Tengiz Crude Oil, 1 Hr @ 50°C, 7,500 ppm Additive**



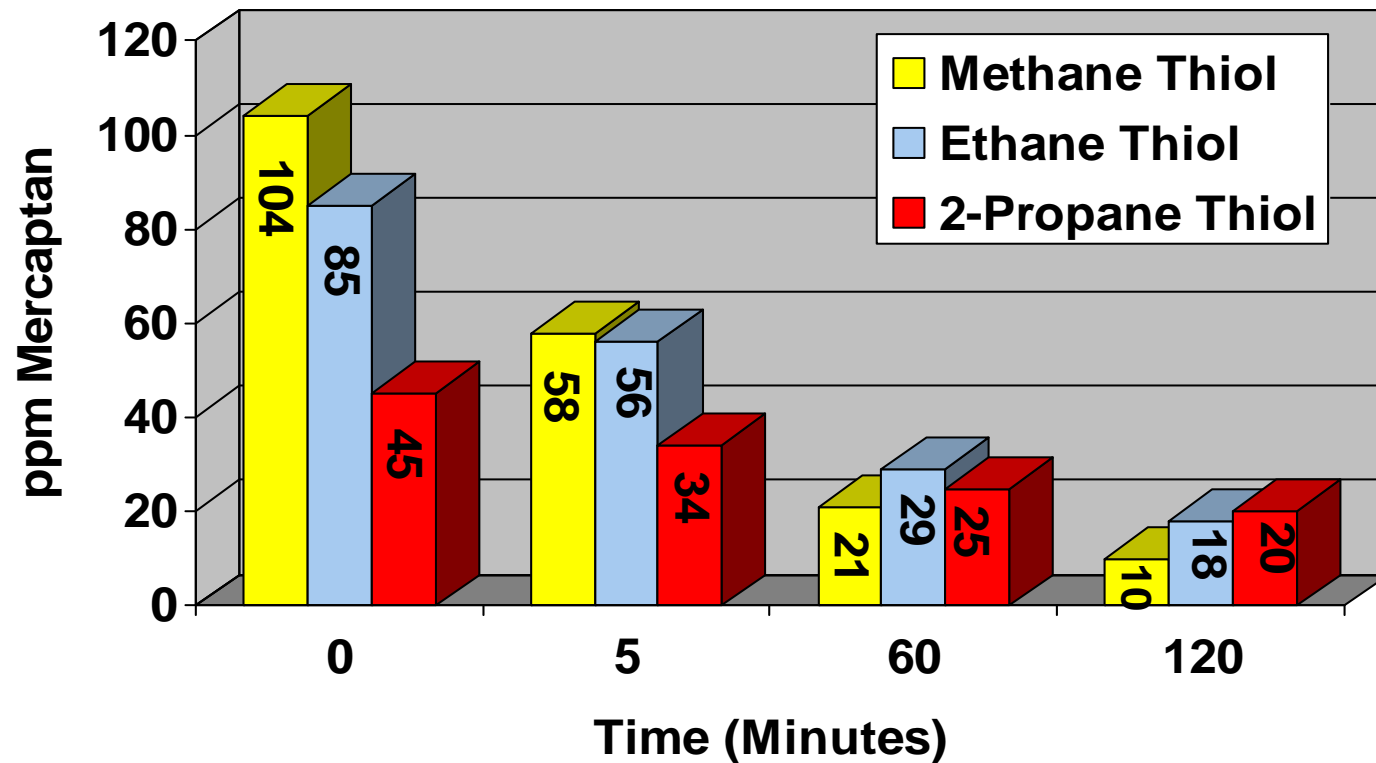
# Mercaptan Scavengers

## Scavenger Speed As A Function of Temperature



Tengiz Crude, SULFIX 9281 @ 1,540 ppm

# Mercaptan Scavenger Performance



Tengiz Crude, 50°C, 1,000 ppm SULFIX 9281

# Summary

- Mercaptans have low odor threshold
- Scavengers have partial success
- Scavenging improves with temperature and time