Application Note AN-PAN-1026

Online analysis of mercaptans and hydrogen sulfide from crude oil, following ASTM D3227 and UOP163

Aside from their unpleasant odor, sulfur compounds are environmentally damaging and promote corrosion. Desulfurization can happen at many points in a petroleum refinery, from the crude feedstock to the distillate streams. While lighter impurities (including mercaptans and sulfides) are removed via hydrotreating, heavier sulfur compounds are removed with hydrocracking after the hydrotreating process.

This Process Application Note details the online analysis of hydrogen sulfide (H_2S) by potentiometric titration according to ASTM D3227 and UOP163. The Metrohm Process Analytics **2060 TI Ex Proof Process Analyzer** with its customized sample preconditioning system can be implemented in many areas within a refinery. This solution ensures that the catalysts in the reactors are not exhausted, and it limits corrosion further on in the distillation unit. The process analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas.

INTRODUCTION

Fossil fuels are known for their sulfur content, which originates from the decomposition of dead organisms over millennia. Mercaptans (thiols) and hydrogen sulfide (H_2S) are two sulfur compounds present in crude oil that contribute to its characteristic odor. In the refining process, these can lead to increased corrosion in distillation equipment at high temperatures. Additionally, excess sulfur dioxide ($SO_{2(g)}$, a pollutant) can be emitted after combustion if sulfur is present in the refined products. Therefore, it is best to remove as much sulfur as possible early in the refining process.

Sulfur compounds are present throughout the entire boiling range of hydrocarbons in crude oil. Depending on the size and bond strength of these compounds, different desulfurization treatments are available. Lighter impurities (including mercaptans and sulfides) can be removed via *hydrotreating* in a reactor with a catalyst (generally cobalt molybdenum) and hydrogen under high temperature and pressure. Heavier sulfur compounds can be removed with *hydrocracking* after the hydrotreating process. *Desulfurization* (Figure 1) can occur at many points within a refinery, from the crude feedstock to the distillate streams.

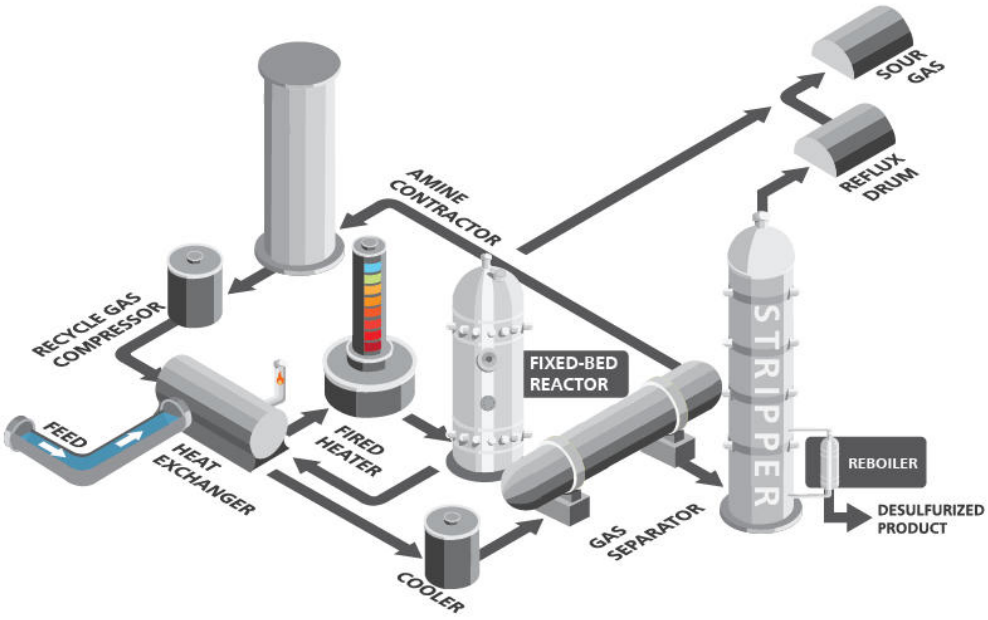

Figure 1. Schematic diagram of a typical hydrodesulfurization (HDS) unit in a petroleum refinery.

Traditionally, oil and oil product analysis can be monitored by laboratory titration with silver nitrate by using a sulfide-coated silver electrode as the indicator electrode. However, this methodology does not provide results quickly and requires human intervention to implement the laboratory analysis results into the process. Online process analysis allows for constant monitoring of oil quality without long waiting times in the laboratory. This ensures more accurate and representative results, delivered directly to the control room.

By using online process analyzers like the 2060 TI Ex

Proof Process Analyzer (Figure 2), operators gain the most representative, up-to-date information they need to accurately identify trends, reduce downtimes, and address operational issues before costly problems arise. In addition, these analyzers respond quickly to corrosion formation, and immediate warnings are delivered in case of out-of-specification readings.

Figure 2. The 2060 TI Ex Proof Process Analyzer is certified for Zone 1 and Zone 2 areas.

APPLICATION

The mercaptan and H_2S content in crude oil is determined online by a two-endpoint argentometric titration based on ASTM D3227 and UOP163. Endpoint 1 corresponds to H_2S and endpoint 2 to the mercaptans.

REMARKS

Other online applications are available for the petrochemical industry. These include salt in crude oil, ammonia, phenol, bromide index, saponification value, halogens, acidity, and many more.

Table 1. Measurement parameters for the analysis of crude oil in refineries.

Parameters	Untreated	Treated
Mercaptans	100–500 mg/L	0–50 mg/L
H_2S	0–100 mg/L	0–1 mg/L

CONCLUSION

Raw oil contains several percent by weight sulfur compounds. Aside from having an unpleasant smell, they are environmentally harmful and corrosive. For these reasons, they must be largely removed during refining. The 2060 TI Ex Proof Process Analyzer with its flexible sample pretreatment system is suitable for a wide variety of refinery applications. Not only can it monitor mercaptan and H_2S content in accordance with ASTM D3227 and UOP163, it can also be used to determine ammonia, halogen, and phenol content, as well as the bromide index, saponification, and acid number (AN). The analyzer fulfills EU Directive 94/9/EC (ATEX95) and is certified for Zones 1 and 2.

RELATED APPLICATION NOTES

AN-PAN-1001 Online analysis of hydrogen sulfide and ammonia in sour water stripper
AN-PAN-1014 Automated online determination of salt in crude oil according to ASTM D3230
AN-PAN-1037 Online measurement of the acid number (AN) in oils with thermometric titration (ASTM D8045)
AN-PAN-1047 Monitoring water content in refined products inline with NIR spectroscopy
AN-PAN-1052 Online process monitoring of octane number during catalytic reforming by NIRS following ASTM D2699 and ASTM D2700

BENEFITS FOR TITRATION IN PROCESS

- **Protection of company assets** with built-in alarms at specified warning limits to prevent corrosion.
- **Safer working environment** for employees (corrosive and hazardous environments).
- **Guarantee compliance** with environmental standards.

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CONFIGURATION

2060 TI Ex Proof Process Analyzer

The **2060 TI Ex Proof Process Analyzer** is an intrinsically safe wet chemistry process analyzer for process monitoring in gas or dust zoned hazardous environments rated as zone 0, 1 and 2, or 20, 21, and 22. It complies with EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas. Its design combines a purge and pressurization system with intrinsically safe electronic devices. The air purging phase and permanent overpressure prevent potentially explosive atmospheres from entering the analyzer enclosure.

The analyzer's design eliminates the need for purging large analyzer shelters, allowing for direct installation at the production line within hazardous zones. It supports various kinds of techniques, including titration, Karl Fischer titration, photometry, ion-selective electrode measurements, and direct measurements.