Application Note AN-PAN-1026

Analysis of hydrogen sulfide and mercaptans derived from crude oil

Online determination according to ASTM D3227 and UOP163

Sulfur compounds in petroleum products not only have an unpleasant odor, but they are also environmentally damaging and promote corrosion. Desulfurization can occur at many points within a refinery – from the crude feedstock to the distillate streams. While lighter impurities (including mercaptans and sulfides) can be removed via hydrotreating, heavier sulfur compounds can be removed with hydrocracking after the hydrotreating process.

This Process Application Note details the online analysis of hydrogen sulfide and mercaptans by potentiometric titration. Many areas within the refinery can benefit from the implementation of a Metrohm Process Analytics 2045TI Ex proof Process Analyzer with a customized sample preconditioning system to ensure the catalysts in the reactors are not exhausted and to limit corrosion in the distillation unit. The 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 which contribute to its characteristic odor. In the refining process, these can lead to increased corrosion in distillation equipment at the high temperatures used. 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 on 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.

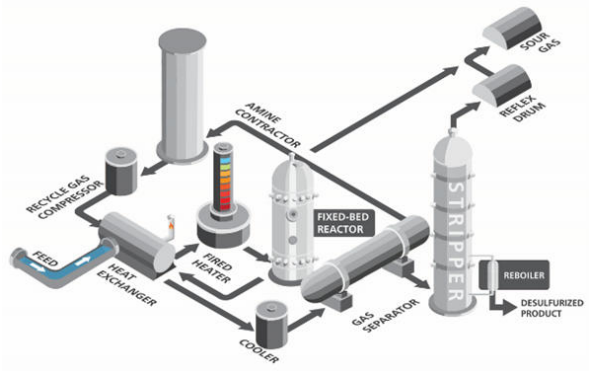

Figure 1. Schematic diagram of a typical hydrodesulfurization (HDS) unit in a petroleum refinery.

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

By using online process analyzers, 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, the time of response to corrosion formation is fast and immediate warnings are delivered in case of out-of-specification readings.

The Metrohm Process Analytics 2045TI Ex proof

Process Analyzer (Figure 2) with a customized sample preconditioning system could be implemented in many areas within a refinery to ensure that catalysts in the reactors are not exhausted and to limit corrosion further on in the distillation unit. The analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas.

Figure 2. The 2045TI 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 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 such as: salt in crude oil, ammonia, phenol, bromide index, saponification value, halogens, acidity, and many more in different areas of a refinery (e.g., water in crude desalting).

Table 1. Oil refinery measurement parameters

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

CONCLUSION

Crude oil contains several percent by weight of sulfur compounds. They not only have an unpleasant smell, but they are also environmentally harmful and corrosive which is why they must be largely removed during refining. The 2045TI Ex proof Analyzer with a flexible sample pretreatment system is the ideal solution for a very wide selection of petrochemical refinery applications. This process analyzer fulfills EU Directive 94/9/EC (ATEX95) and is certified for Zones 1 and 2. The 2045TI Ex proof Analyzer monitors mercaptan and H_2S content in crude oil in accordance with ASTM D3227 and UOP163.

RELATED APPLICATION NOTES

AN-PAN-1001 Online analysis of hydrogen sulfide and ammonia in sour water stripper
AN-PAN-1014 Online determination of salt in crude oil by automated process analysis
AN-PAN-1037 Online thermometric titration of acid number (AN) in oils (ASTM D8045)
AN-PAN-1047 Inline monitoring of water content in naphtha fractions by NIRS
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 (e.g., no exposure of operator to dangerous and explosive environments)
- Guarantee compliance with environmental standards

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CONFIGURATION

ADI 2045TI Ex proof Analyzer

The ADI 2045TI Ex proof Process Analyzer is used in hazardous environments where explosion proof protection is a critical safety requirement. The analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone-1 and Zone-2 areas. The analyzer design combines a purge/pressurization system with intrinsic safety electronic devices. The air purging phase and permanent overpressure prevents any potentially explosive atmosphere in the ambient air from entering the analyzer enclosure. The analyzer smart design avoids the need for purging large analyzer shelters and can be located at the production line in the hazardous zone.

Titration, Karl Fischer titration, photometry, measurements with ion selective electrodes, and direct measurements are all possible with this Ex-p version.