In-line H_2S analysis during sulphiding

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Real-time, in-line analysis of the H_2S concentration during hydroprocessing catalyst activation with DMDS Evolution E2 reduces the risk of exposure to toxic gas and helps to better manage the sulphiding procedure.

Hydroprocessing catalyst activation is generally performed on site, at the refinery, using a sulphur chemical that is able to decompose to H_2S at low temperature (at 200°C and above) so the metallic oxides are smoothly and fully converted to sulphides. This maximises the initial catalyst activity and catalyst lifetime.

Dimehyldisulphide (DMDS) offers the best economical compromise in terms of physical and chemical properties, and over the years it has become the standard sulphiding agent. To ease this temporary use of DMDS at refineries, over the last 20 years Arkema has developed a global and integrated service, covering logistics, handling and safety aspects.

Last year, in keeping with its policy of innovation, Arkema introduced an in-line H_2S analyser to helps refiners perform the sulphiding of hydroprocessing catalysts with DMDS Evolution E2. During this critical period, temperature ramp-up and DMDS Evolution E2 flow rate have to be adjusted, depending on the H_2S concentration in the recycle hydrogen.

Traditionally, refiners manually obtain every hour the H_2S concentration information with H_2S reactive tubes. However, due to the high toxicity of H_2S and the flammability of hydrogen, this measurement is a risky operation and the refinery has to dedicate workforce to this task during the busy unit start-up period. Moreover, the accuracy of the result depends on the experience of the operators, and a faster response analysis than every hour would be welcome to anticipate decisions for a quicker and more efficient catalyst activation.

Thanks to Arkema's know-how in handling this dangerous gas and its extensive experience in hydroprocessing catalyst sulphiding with DMDS Evolution E2, it has designed (patent filed) an in-line H_2S analytical tool that addresses all these concerns:

- Accurate and continuous measurement of H_2S concentration, from 0.03 % to 5%
- Tightly closed system, without any risk of exposure to H_2S to workers.

The core of this equipment is a spectrometer that benefits from the latest advances in electronics and signal treatment to drastically improve the sensitivity and selectivity of the H_2S determination in a complex gas.

EQUIPMENT DESIGN AND IMPLEMENTATION

A day before the start of the catalyst activation, a full set of analytical equipment is delivered with the current equipment required to inject DMDS. All the electric H_2S analyser equipment complies with one of the most severe European ATEX certifications (EC II 2 G EExd IIC T4) and can be implemented safely inside the hydroprocessing unit.

Sampled at high pressure, the pressure of recycle hydrogen containing H_2S is reduced to almost atmospheric pressure before entering the analyser. The outlet gas that exits the analyser is injected into the flare network of the refinery to avoid any atmospheric release. All gas connections are achieved with high-pressure hoses and quick couplings for a fast and safe implementation.

Figure 1 Arkema's H_2S analyser implemented on site

Safety aspects of this design have been checked and approved by all major European refiners, and no accident has been reported since the launch of this service.

CASE STUDY

In May 2017, a Western Europe refinery had to change 350 MT of hydrocracking catalysts due to normal catalyst deactivation, and they ordered 73 MT of DMDS for their in-situ catalyst sulphiding. This DMDS amount represents a 45% contingency compared to the stoichiometric amount of DMDS (50.4 MT) required to convert metallic oxides to sulphides. This level of contingency is a usual practice for refineries that want to be able to manage any event during the activation process without being limited by DMDS availability. Arkema includes this delivery flexibility in the Carelflex service package.

Figure 2 represents with injection time the DMDS flow rate and the H_2S concentration continuously measured by the in-line analyser. Since it was the first time this refinery had used such equipment, reactive tubes were used four times to confirm the H_2S concentration indicated by the analyser. An excellent match was obtained with the two methods and gave high confidence in the new equipment.

The overall sulphiding procedure and DMDS flow rate were optimally managed by the refinery, and the continuous indication of the H_2S concentration was particularly useful:

- **Anticipation of H_2S breakthrough period:** thanks to the low detection level (300 ppmv), the H_2S breakthrough (defined as more than 5000 ppm H_2S) has been noticed over one hour before its occurrence, after around six hours of DMDS injection. Therefore, as soon as the 5000 ppmv H_2S concentration was reached, the refinery could increase the inlet reactor temperature from 220°C to over 300°C and reduce the DMDS flow rate. Compared to previous activation, the refinery saved around one hour during this critical period of H_2S breakthrough.
- **Optimal management of DMDS injection rate after H_2S breakthrough**: after H_2S breakthrough, the refinery has to keep a minimum H_2S concentration (2000 ppmv) to prevent the catalyst from irreversible reduction with hydrogen, and the refinery also wants to avoid high concentrations of H_2S (>30 000 ppmv) because of potential damage to the metallurgy and the recycle compressor. However, H_2S concentration stabilisation at typically 10 000 ppm is not as easy, because H_2S results from the balance between catalyst consumption (full conversion of metal oxides to sulphides) and H_2S formation, either from DMDS or from sulphur species in the feedstock. Hence, a continuous measurement of H_2S concentration and its rate of decrease or growth is helpful to decide when and how much the DMDS flow rate needs to be adjusted.

DID YOU KNOW ARKEMA NOW PROVIDES AN IN-LINE H_2S ANALYSER SERVICE DURING HYDROPROCESSING CATALYST ACTIVATION?

Figure 2 illustrates this careful optimisation process on the DMDS flow rate during the sulphiding operation of a hydrocracking unit: after H_2S breakthrough, H_2S concentration in recycle hydrogen has been kept between 8000 and 15 000 ppm thanks to several DMDS flow adjustments.This monitoring has another benefit: it minimises the excess of DMDS used for the activation and leads to some significant economical savings. For this hydrocracking unit activation, 53.2 MT of DMDS was finally consumed, which is only 6% above the stoichiometric sulphur amount of the catalysts.

- **Valuable information to stop injection and disconnect DMDS equipment**: once more than the stoichiometric amount of DMDS is injected, how can you be sure the catalyst is fully sulphided? A convenient test is the following: DMDS injection is held for a while and H_2S is observed; since a fresh feedstock containing sulphur is continuously introduced, the H_2S concentration in the recycle hydrogen should increase due to the conversion of sulphur compounds in H_2S by the catalyst and no further H_2S consumption by the fully activated catalyst. **Figure 2** is an interesting demonstration of this test: DMDS injection was stopped after 18 hours and at first H_2S stabilised for two hours before increasing sharply. This test can be achieved safely and effectively thanks to the in-line H_2S measurement.

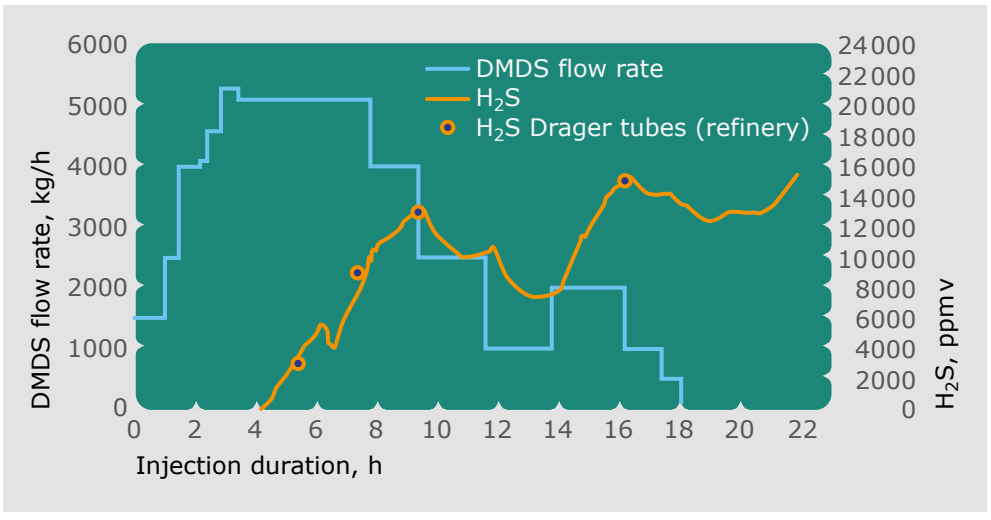

Figure 2 DMDS flow rate and H_2S concentration with time

CONCLUSION

The Arkema analyser has been used for monitoring H_2S in the recycle hydrogen of hydrocrackers units, gas oil hydrodesulphurisation units and naphtha hydrotreaters. This new service brings several advantages:

- **Safe equipment:** workers have never been exposed to any H_2S leak
- **High reliability and accuracy**: H_2S concentrations from the in-line analyser have always been in line with other analytical methods (reactive tubes, online gas chromatography and so on)
- **A useful tool to better manage the catalyst sulphiding operation according to catalyst manufacturer procedures and guidelines:** the continuous H_2S indication helps to anticipate DMDS flow rate changes, minimising DMDS consumption and sulphiding time significantly. ■

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