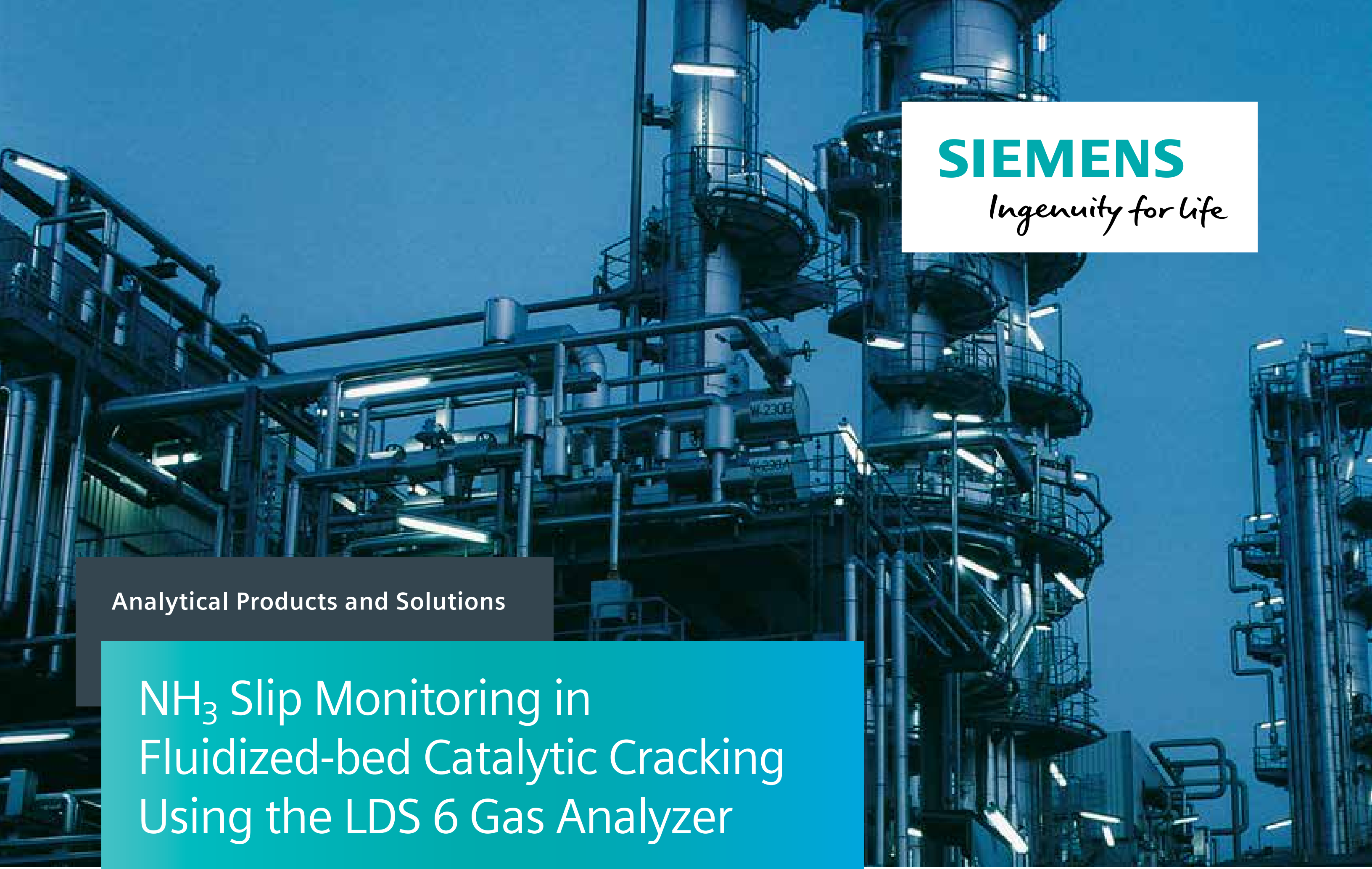

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NH_3 Slip Monitoring in Fluidized-bed Catalytic Cracking Using the LDS 6 Gas Analyzer

Fluidized catalytic cracking (FCC) units are used in refineries to convert low value heavy oils into more valuable lighter compounds. Cracking units are sources of emissions of pollutants (e.g. NO_x) and must comply with concentration permits set by local or federal authorithies. Modern technologies are applied to reduce the content of pollutants and to monitor certain gas compounds (here: NH_3) in the exhaust gas.

The **LDS 6 in-situ laser gas analyzer** offers the best possible capabilities for this application. It is installed directly in the process gas flow and delivers fast and accurate ammonia concentration data. The data are used to prove compliance with the permits as well as to control and optimize the denitrification process.

This Case Study presents details of the corresponding LDS 6 application in the petrochemical industry.

Fluidized-bed Catalytic Cracking (FCC)

Fluidized-Bed Catalytic Cracking (FCC) is the most important and widely used refinery process for converting low value heavy oils into more valuable gasoline and lighter products. The typical FCC process will convert 75 % or more of the heavy oils to gasoline and lighter products. Originally, chemical cracking was accomplished by heating the oil to high temperatures (thermal cracking), which nowadays has been almost completely replaced by catalytic cracking.

FCC units are sources of NO_x (and SO_x) emissions. Emissions from refineries are regulated in many parts of the world and their reduction and monitoring is of increasing concern worldwide. Even though petroleum refining represents only a few percent of the total NO_x emission rate, these emissions are typically concentrated in a small area and, therefore, the subject of advanced gas cleaning and gas monitoring measures.

Various techniques for flue-gas denitrification can be applied. The suppression of NO_x formation directly in the boiler or NO_x reduction by post-combustion abatement will involve use of an ammonia compound (e.g. ammonium hydroxide or urea). Ammonia is mostly used as a reducing agent to convert nitrogen oxides to nitrogen and water at high temperatures. Under real conditions, a small amount of NH_3 will remain unused during the process and slip through to the atmosphere. This NH_3 slip concentration must be monitored continuously to comply with environmental regulations.

Additionally, minimizing the NH_3 slip means optimizing the denitrification and provides a possible cost reduction to the process operation.

Application task

The cracking process (Fig. 1)

The fluid catalytic cracking unit (FCCU) receives heavy oils and residues from different parts of a refinery (atmospheric and vacuum distillation units) as feedstock. The purpose of a FCCU is to crack heavy molecules into lighter and more valuable compounds. This is an endothermic process which takes place in a vertical tube reactor with ascending flow (riser). The fresh and the recycle feeds are preheated and enter the unit at the base where they are mixed with hot regenerated catalyst. The feed is vaporized and the mix of catalyst and hydrocarbon vapor travels up the riser into the reactor. After the cracking into lighter products, such as gasoline and LPG, light gas oil and fuel gas, the spent catalyst is stripped from the hydrocarbons and fed to the regenerator.

The hydrocarbons leave the reactor for separation in the main column.

Regenerator and waste heat boiler

The reaction also produces carbon (coke) which remains on the catalyst particle and rapidly lowers its activity. In order to recover its activity, it is regenerated by burning off the coke with air. This is done in a continuous move from the reactor to the regenerator and back.

Burning off the coke from the catalyst particles does also increase their temperature thus providing energy for the following cracking process.

The flue gas leaving the regenerator contains a large quantity of CO (carbon monoxide) which is burnt to carbon dioxide in a CO furnace called "The waste heat boiler" to recover the available heat.

NO_x reduction and NH_3 slip

The combustion exhaust leaving the waste heat boiler contains a large amount of NO_x which, depending on the local environmental permits, must be reduced to very low levels anywhere from 50 to 1 ppm, before it is released to the atmosphere. This is achieved by directing the exhaust through either a selective catalytic (SCR) or a selective non-catalytic (SNCR) reduction unit (see text box), where NH_3 is injected into the process to react with NO_x and form nitrogen and water. However, under real operating conditions, the process is not always perfectly balanced and some un-reacted NH_3 can pass through the system to the atmosphere and is often referred to as "NH_3 slip".

The SCR process

Nitrogen oxides (NO_x) formed in combustion processes are efficiently reduced to water and nitrogen in the selective catalytic reduction (SCR) process. Ammonia (NH_3) or urea $CO(NH_2)_2$ is introduced to the flue gases upstream of a heterogeneous catalyst where the reduction takes place. The SCR process is normally operated in the temperature range of 300 to 400 °C.

The SNCR process

For the selective non catalytic reaction (SNCR) process, ammonia (NH_3) or urea $CO(NH_2)_2$ is introduced to the flue gases in the hot combustion zone where the reduction of NO_x takes place spontaneously. Depending on the type of the reducing agent, the SNCR process is typically operated in the temperature range of 800 to 950 °C. At temperatures below the optimum temperature, the reaction rate is too slow, resulting in an inefficient NO_x reduction and too high ammonia slip. Above the optimum temperature, the oxidation of ammonia to NO_x is getting significantly high and the process tends to produce NO_x instead of decreasing it.

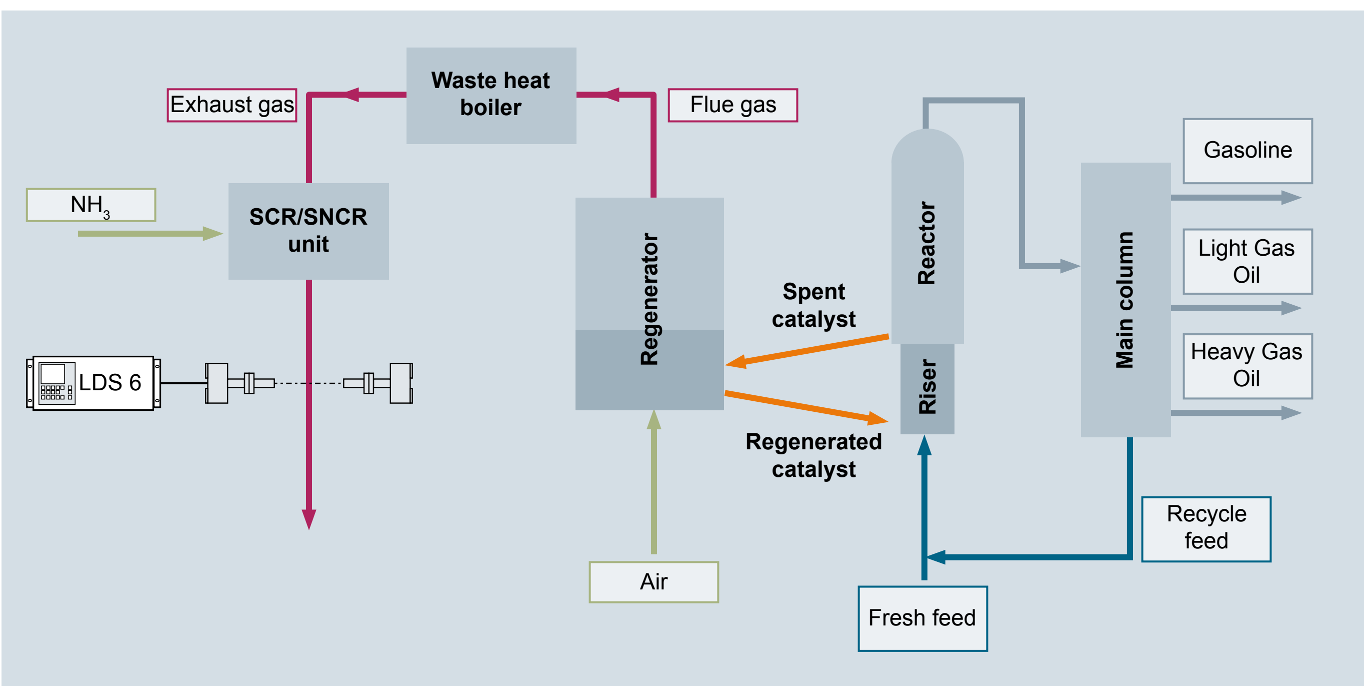

Fig. 1: Fluid catalytic cracking flow chart with LDS 6 in-situ laser gas analyzer

Measuring task
Measuring task is to determine continuously, with high accuracy and reliability the concentration level of NH_3 in the exhaust gas downstream of either a SCR or a SNCR type denitrification unit.

The Siemens LDS 6 tunable diode laser in-situ gas analyzer (Fig. 2) is very much suited to accomplish this task. It routinely measures NH_3 in a range as low as 0 to 45 ppm. LDS 6 is availabe in specific versions to meet best the application requirements of a SCR or a SNCR unit.

LDS 6 gas analyzer

LDS 6 (Fig. 2) is a diode laser-based in-situ gas analyzer for measuring specific gas components directly in a process gas stream.

LDS 6 consists of a central unit and up to three pairs of cross duct sensors in a transmitter/receiver configuration. The central unit is separated from the sensors by using fiber optics. Regardless how hostile the environment is, the analyzer can always be placed outside any hazardous areas. Measurements are carried out free of spectral interferences and in real-time enabling proactiv control of dynamic processes.

Full network connectivity via ethernet allows remote maintenance.

Key features include:
- In-situ principle, no gas sampling
- Three measuring points simultaneously
- Ex-version available (option)

LDS 6 is designed for fast and non-intrusive measurements in many industrial processes. Measuring components include: O_2, NH_3/H_2O, HF/H_2O, HCl/H_2O, CO/CO_2, ...

Application solution

In the actual application, either in homogenities in the catalyst efficiency throughout the cross section can be monitored by using several measurement channels. Alternatively, more than one $DeNO_x$ column can be monitored with only one central unit. It is installed in-situ directly downstream the catalyst, see Fig. 1.

LDS 6 advances for DeNOx control

- **Performance**
  Faster regulation than with other control instruments (e.g. FTIR) and therefore most efficient optimization. The in-situ approach allows representative measurements without side effects or cross interference.
- **Easiness**
  The central unit can be placed in the control room several hundred meters away from the measurement points by using fiber optic cables. Three measuring points can be handled simultaneously with one single central unit. No calibration is necessary in the field.
- **Robustness**
  The sensor pair at the measuring point contains a minimum of electrical and optical components to ensure highest reliability and availability. The residual maintenance is reduced to the cleaning of the sensor windows after several months of continuous operation. No optical realignment is necessary after cleaning.
- **Versatility**
  LDS 6 offers the option to measure the water vapour concentration of the flue gas in-situ and parallel with the NH_3 slip. This additional information is useful to detect leaks in the boiler's steam pipes faster and in an earlier stage than by e.g. the pressure drop. Also the compensation for the volume error in the result of extractive analyzers (e.g. as part of the CEM system) in the stack measuring at dry gas conditions becomes possible.

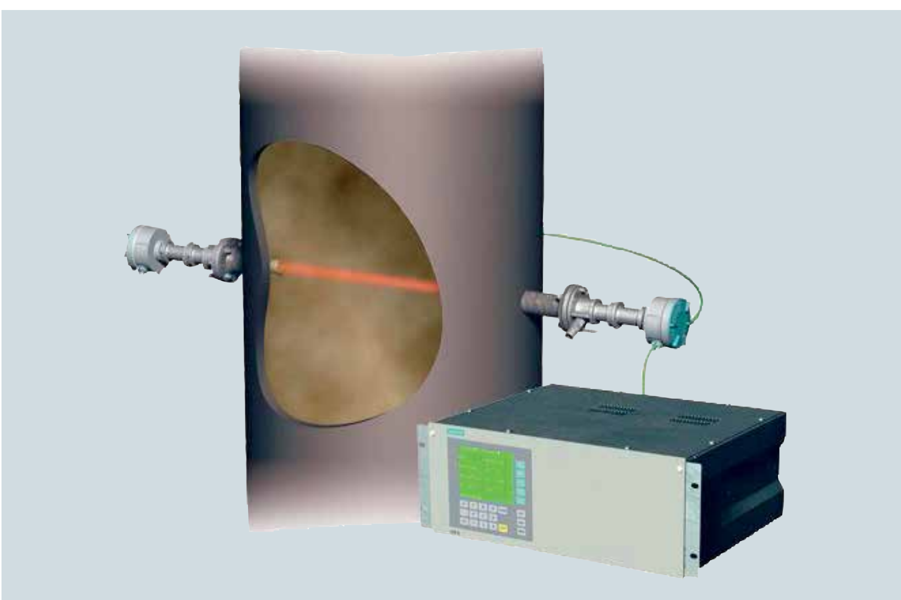

Fig. 2: LDS 6 laser diode in-situ gas analyzer

User benefits

Optimizing the SCR process by controlling the NH_3 slip means:

- Minimizing technological drawbacks such as ammonium bisulfate formation
- Optimizing maintenance intervals, decrease deterioration and replacement costs
- Minimizing plant runtimes with excess emission levels
- Reducing the total nitrogen (NH_3 and NO_x) emission. An optimized process input is the base of minimized emission.
- Keeping the legislative threshold values for NH_3 if required

Optimizing the SNCR process by controlling the NH_3 slip means:

- Reducing the consumption of ammonia or urea
- Keeping the legislative threshold values for NH_3 if required
- Stabilizing the process and avoiding peak emissions
- Minimizing technological drawbacks, increasing $DeNO_x$ efficiency
- Reducing the total nitrogen (NH_3 and NO_x) emission. An optimized process input is the base of minimized emission.

Measuring conditions

Typical measuring conditions for the NH_3 slip measurement in SCR or SNCR denitrification installations are shown in Table 1.

If the ranges of typical values are kept unchanged in the actual installation, the gas and application codes given in the last lines of Table 1 can be used for ordering the analyzer. In other cases, please contact your regional sales representative, or email ProcessAnalyticsSales.industry@siemens.com. User lists are available for different fields of application.

Conditions for NH_3 slip measurements in a FCC process using the LDS 6		
	SNCR principle	SCR principle
Gas to be measured Measuring range NH_3 repeatability	NH_3, NH_3/H_2O 0 ... 45 ppm ± 1.4 ppm①	NH_3, NH_3/H_2O 0 ... 50 ppm ± 1.5 ppm②
Optional H_2O measuring range H_2O repeatability	0 ... 30 Vol.% ± 0.1 Vol.%*m	
Dust load	< 25 g/Nm³	
Gas temperature	250 ... 350 °C	300 ... 400 °C
Typical opt. path length	2 ... 6 m	4 ... 8 m
Pressure	ambient	
Required response time	< 30 s	
Recommended purging mode	process side only, elevated flow	
Purging media	instrument air, 2 ... 8 bar	
MLFB gas code	C, D	
MLFB application code	E	F

① at 1 m, 15 Vol% H_2O, 300 °C
② at 1 m, 15 Vol% H_2O, 250 °C

Table 1: LDS 6 measuring conditions for the FCC application

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