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. NOx) and must comply with concentration permits set by local or federal authorities. Modern technologies are applied to reduce the content of pollutants and to monitor certain gas compounds (here: NH3) 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.

Fluoridized catalyst 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 NOx (and SOx) 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 NOx 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 NOx formation directly in the boiler or NOx 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 NH3 will remain unused during the process and slip through to the atmosphere. This NH3 slip concentration must be monitored continuously to comply with environmental regulations.

Additionally, minimizing the NH3 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.

NOx reduction and NH3 slip
The combustion exhaust 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.

The SCR process
Nitrogen oxides (NOx) formed in combustion processes are efficiently reduced to water and nitrogen in the selective catalytic reduction (SCR) process. Ammonia (NH3) or urea CO(NH2)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 (NH3) or urea CO(NH2)2 is introduced to the flue gases in the hot combustion zone where the reduction of NOx 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 NOx reduction and too high ammonia slip. Above the optimum temperature, the oxidation of ammonia to NOx is getting significantly high and the process tends to produce NOx instead of decreasing it.
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 available 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 proactive 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$_2$O, HF/H$_2$O, HCl/H$_2$O, 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 NH₃ 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 (NH₃ and NOₓ) emission. An optimized process input is the base of minimized emission.
- Keeping the legislative threshold values for NH₃ if required

Optimizing the SNCR process by controlling the NH₃ slip means:

- Reducing the consumption of ammonia or urea
- Keeping the legislative threshold values for NH₃ if required
- Stabilizing the process and avoiding peak emissions
- Minimizing technological drawbacks, increasing DeNOₓ efficiency
- Reducing the total nitrogen (NH₃ and NOₓ) emission. An optimized process input is the base of minimized emission.

Measuring conditions
Typical measuring conditions for the NH₃ 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.

<table>
<thead>
<tr>
<th>Conditions for NH₃ slip measurements in a FCC process using the LDS 6</th>
<th>SNCR principle</th>
<th>SCR principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas to be measured NH₃, NH₃/H₂O</td>
<td>0 ... 45 ppm</td>
<td>0 ... 50 ppm</td>
</tr>
<tr>
<td>Measuring range NH₃, NH₃/H₂O</td>
<td>± 1.4 ppm</td>
<td>± 1.5 ppm</td>
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<tr>
<td>Optional H₂O measuring range H₂O repeatability</td>
<td>0 ... 30 Vol.%</td>
<td>&lt; 25 g/Nm³</td>
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<tr>
<td>Dust load</td>
<td>± 0.1 Vol.%/m</td>
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<tr>
<td>Gas temperature</td>
<td>250 ... 350 °C</td>
<td>300 ... 400 °C</td>
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<tr>
<td>Typical opt. path length</td>
<td>2 ... 6 m</td>
<td>4 ... 8 m</td>
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<tr>
<td>Pressure</td>
<td>ambient</td>
<td></td>
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<tr>
<td>Required response time</td>
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<tr>
<td>Recommended purging mode</td>
<td>process side only, elevated flow</td>
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<tr>
<td>Purging media</td>
<td>instrument air, 2 ... 8 bar</td>
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<tr>
<td>MLFB gas code</td>
<td>C, D</td>
<td></td>
</tr>
<tr>
<td>MLFB application code</td>
<td>E</td>
<td>F</td>
</tr>
</tbody>
</table>

Table 1: LDS 6 measuring conditions for the FCC application

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