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The Shell DENOX system for low temperature NO_x removal

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Abstract

Shell has developed a low temperature DENOX system which consists of a high activity granular SCR catalyst and a low pressure drop lateral flow reactor. The Shell DENOX system achieves more than 95% NO_x reduction with minimal ammonia slip. The Shell DENOX system can be installed at the low temperature end of the flue gas stream and, therefore, represents a more economical solution compared to retrofitting of honeycomb type catalysts in the high temperature window.

Keywords: Nitrogen oxides; DENOX system

1. Introduction

Increasing concerns about the effects of air pollution on the environment and public health have resulted in strict environmental legislation and restrictive emission standards for nitrogen oxides. Nitrogen oxides (NO, NO_2) contribute to the formation of acid rain and smog, while nitrous oxide (N_2O) contributes to global warming (green house effect) and the depletion of the ozone layer [1]. The emission of nitrogen oxides can be reduced by primary measures, which aim to abate the formation of NO_x in a given process, or by secondary measures, which are aimed at removing the NO_x from the flue gas. Although primary measures are relatively inexpensive, their effect on NO_x emissions is not sufficient to meet legislation in countries with high environmental standards.

Deep removal of NO_x requires secondary measures such as selective catalytic reduction (SCR) of NO_x with ammonia. Since its introduction in the early 70's, SCR has found wide-spread application in Japan, Germany and the USA. Conventional SCR systems are based on titania honeycombs promoted with tungstenia or vanadia, the honeycomb structure ensuring a low pressure drop. The operation temperature of the conventional honeycomb SCR catalysts is typically 300 to 400°C. This high operation temperature is a drawback for retrofit applications. In contrast, Shell has developed a low temperature add-on SCR system that operates at temperatures between 120 and 350°C [2,3].

2. The Shell DENOX system

The Shell DENOX system (SDS) consists of a proprietary V/Ti-type catalyst and a lateral flow reactor (LFR) (Fig. 1). The commercial Shell DENOX catalyst is produced in the catalyst manufacturing plant in Gent (Belgian Shell) [4]. In

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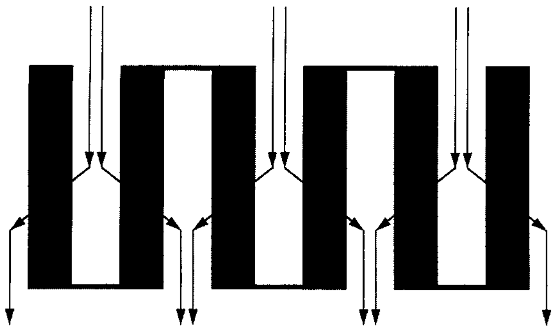

Fig. 1. SDS: lateral flow reactor.

order to meet pressure drop requirements, the catalyst is used in an LFR. The LFR is essentially a fixed bed type reactor consisting of numerous shallow slabs of catalyst. In addition to the low pressure drop (2–50 mbar) and the possibility of quick catalyst (un)loading, the high catalyst utilization makes the LFR very attractive with respect to size and cost. The LFR allows flexible designs based on desired conversion, pressure drop and even plot size. In the SDS the catalyst volume determines the NO_x conversion, whilst the pressure drop is determined by the module design. This independence of NO_x conversion and pressure drop differentiates the SDS from honeycomb catalysts. It allows SDS to be designed for a wide range of NO_x conversions and pressure drops.

The SDS achieves a high nitrogen oxides conversion and a low ammonia slip, at very low operating temperatures. Typical operating temperatures of commercial SDS applications range from 120 to 350°C, with space velocities of 2500–40 000 $Nm^3/(m^3$ catalyst h). As opposed to other low temperature SCR catalysts, which are based on noble metal, the SDS catalyst does not show N_2O formation (detection limit 5 ppmv) up to at least 300°C. In SDS designs, the minimum operating temperature is limited by the dew point of ammonium salts, such as ammonium nitrate [5,6] and ammonium sulphates [7].

3. Comparison with honeycomb SCR systems

3.1. Activity

In honeycomb and plate type catalysts, the shape and dimensions of the catalyst are a compromise between mechanical strength, pressure drop and overall activity. The SDS catalyst is subject to fewer constraints, because the LFR meets the necessary requirements with respect to mechanical strength and pressure drop. Therefore, the catalyst has been optimized with respect to its SCR performance by taking full advantage of the additional degrees of freedom in catalyst manufacturing. Integration of reactor-design, catalyst manufacturing and catalyst testing has resulted in the development of a proprietary high-activity silica-based SCR catalyst. The catalyst activity is determined by measurement of the NO_x conversion in simulated flue gas. Nano-flow units are used to determine the intrinsic activity of the catalysts, whereas micro-flow units are used for SDS design validation and testing of the catalyst under customer conditions. Fig. 2 shows that the intrinsic activity of the Shell DENOX catalyst exceeds that of a typical titania-based honeycomb-type catalyst.

3.2. Pressure drop

Using the LFR, it is possible to meet pressure drop requirements by increasing the number of catalyst slabs. Furthermore, the LFR allows the use of small catalyst particles, which reduces the effects of pore diffusion limitations and results in a high catalyst utilization. The SDS can, therefore, be designed for any pressure drop, without affecting the NO_x conversion. The design of SDS is thus more flexible compared to honeycomb systems, where the design parameters, catalyst utilization and pressure drop are dependent variables.

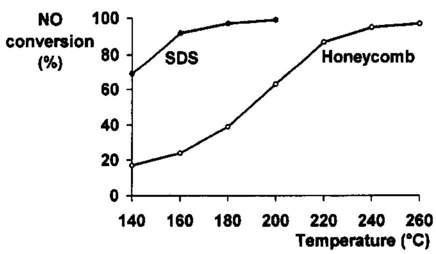

Fig. 2. Intrinsic activity for Shell DENOX catalyst and typical Honeycomb type catalyst.

Table 1
Comparison of SDS and honeycomb type SCR systems

Performance issue	SDS	Honeycomb
Activity	Optimized intrinsic activity Low operating temperature, small catalyst volumes	Compromise between activity and other design parameters High operating temperature, large catalyst volumes
Pressure drop	Low pressure drop and high NOx conversions	Low pressure drop, but poor catalyst utilization
Catalyst utilization	High catalyst hold-up and good contact between gas and catalyst	Poor catalyst utilization at deep NO_x and NH_3 removal
Catalyst deactivation	Low dust Operating temperature has to be above dew point ammonium sulphates End-of-pipe: no fouling of down-stream equipment	High dust Operating temperature is well above dew point of ammonium sulphates Potential for fouling and corrosion of waste-heat boiler

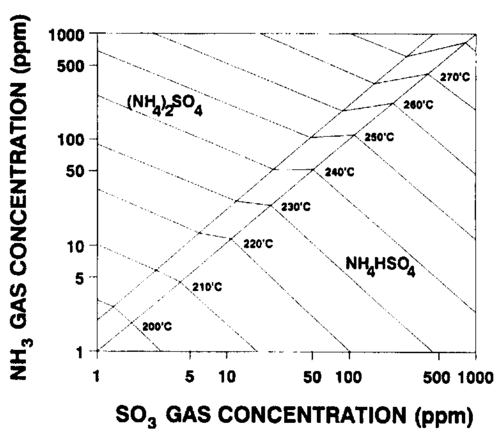

Fig. 3. Ammonium sulphate deposition: Equilibrium partial pressures of NH_3 and SO_3.

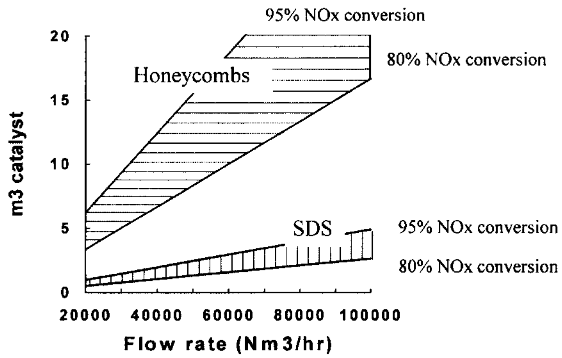

Fig. 4. Required catalyst volumes for SDS and honeycomb type SCR systems (350°C).

3.3. Catalyst utilization

An additional advantage of the LFR is the higher catalyst hold-up as compared to conventional honeycomb type systems. The increased amount of catalyst per unit volume of the reactor facilitates a high conversion of NO_x on a small plot size. Furthermore, the combination of a granular type catalyst and a LFR allows a better contact between off-gas and catalyst. With SDS the gas is forced through the thin catalyst slabs instead of through parallel channels in honeycombs. The turtuosity of the gas channels in the LFR catalyst slabs provides a better catalyst utilization, resulting in deep NO_x removal and minimal NH_3 slip.

3.4. Catalyst deactivation

The SDS has been developed for the treatment of relatively clean gases with low dust concentrations, whereas the straight open channels of the honeycomb type catalysts allow the treatment of dust containing gases. Furthermore, at very low operating temperatures (<200°C), made possible by the high intrinsic activity of the SDS catalyst, ammonium sulphate deposition can cause catalyst deactivation (reversible). The deposition of ammonium sulphates can be prevented by operating at somewhat higher temperatures. Honeycomb SCR systems operating at 300–400°C do not suffer from deposition of ammonium sulphates on the catalyst surface, but deposition in the cooler parts of the down-stream waste heat boiler can cause serious fouling and corrosion [8]. These problems are prevented by operating the SDS as an end-of-pipe system at intermediate temperatures.

The SO_2 deactivation of the SDS catalyst has been investigated in order to define the minimum operating temperature for low concentrations of SO_2. The formation and deposition of ammonium sulphates depend upon a number of catalyst parameters, such as SO_2 oxidation activity and pore size distribution, as well as on the exact operating conditions, such as temperature and NH_3 and SO_3 partial pressures (Fig. 3). Under typical operating conditions, the effects of temperature and SO_2 inlet concentration on SDS catalyst activity and stability have been investigated. Depending on the SO_2 partial pressure in the flue gas a certain minimum SDS operating temperature has to be maintained.

3.5. *Overall comparison*

The SDS and honeycomb type SCR systems are compared in Table 1. The combination of the separate performance issues and calculation of the required catalyst volume to achieve a certain degree of NO_x removal, within the boundary conditions of ammonia slip and pressure drop, result in significantly smaller catalyst volumes for the SDS as compared to the honeycomb type systems (Fig. 4).

4. Applications of the Shell DENOX system

The SDS is particularly suited for the treatment of NO_x-containing flue gases originating from the combustion of fuel-gas/natural-gas in heaters, furnaces, boilers, gas engines and gas turbines and for the treatment of NO_x-containing off-gases from chemical plants, such as caprolactam, nitric acid and catalyst manufacturing.

4.1. *Industrial furnaces*

Most industrial furnaces are highly heat integrated. For existing units, the application of the SDS as a low temperature add-on DENOX process has advantages over conventional honeycomb type systems, as breaking into the heat exchange system is not necessary. This results in a short down-time of the unit during installation of the SDS. Furthermore, the flexibility of SDS can be used to take account for the available plot size, potentially avoiding extensive reconstruction of the site. Consequently, the total installment costs of a SDS is usually lower than that of a conventional SCR honeycomb type system.

In 1989, the first commercial SDS was installed on six furnaces of a new ethylene cracker at Rheinische Olefin Werke at Wesseling (Germany). The unit has been operating successfully for more than five years now, with only limited catalyst deactivation and without a significant increase in pressure drop over the reactor.

In 1991, SDS was installed at a gas-fired refinery furnace in California. In this application with a flue gas containing 10 ppmv of SO_2 and an operating temperature just above 200°C, SDS achieves NO_x conversions of more than 90% and an NH_3 slip of less than 5 ppmv. The unit has been operating successfully for nearly 4 years now.

4.2. *Gas turbines*

The application of SCR to gas turbines is characterized by the large amounts of flue gas to be treated, generally exceeding 100 000 Nm^3/h, and stringent pressure drop requirements. Recent SDS catalyst developments have made it possible to meet the stringent pressure drop requirements for gas turbine applications in a cost effective way. The flexibility of SDS designs with respect to pressure drop and catalyst volume (NO_x conversion) is a clear advantage over conventional honeycomb type systems, where pressure drop and catalyst utilization are dependent variables (Fig. 4). The independent optimization of pressure drop and NO_x conversion offered by SDS results in significantly smaller catalyst volumes for SDS as compared to honeycomb systems. Four large gas turbines in the California area will be equipped with the SDS to meet the less than 9 ppm NO_x emission regulations.

4.3. *Chemical plants*

The flue gas originating from chemical plants often contains large amounts of NO_x, mainly present as NO_2. Therefore, this type of application requires high conversions of both NO and NO_2. The amount of flue gas coming from chemical plants varies widely between approximately 5000 and 50 000 Nm^3/h.

In 1991, a SDS unit was installed at the calciner of the Shell Catalyst Manufacturing Plant in Gent (Belgium). The flue gas of the calciner contains up to 10 000 ppm NO_x, mainly present as NO_2. Performance data of this SDS show NO_x conversions of more than 99%, at 260°C.

In 1992, SDS was installed at a caprolactam plant in The Netherlands. This unit has been in operation for more than two years with a reduction of NO_x emissions (mainly NO) to below 100 ppmv. Another caprolactam unit in South-Korea has been equipped with SDS and is scheduled for start-up in January 1995.

In 1995, SDS was started up at a South-African nitric acid plant. The unit is operating at atmospheric pressure, with a pressure drop of 5 mbar over the SDS reactor and a NO_x conversion of 95% at 180°C.

4.4. *Gas engines*

Two demonstration projects have been performed to evaluate the applicability of SDS for the treatment of gas engine exhaust gas. One of these projects was performed at EBA (Amsterdam electricity generating board), the other being done at Jenbach (gas engine manufacturer). Both projects employed a 500 kW gas engine. At EBA, the operating temperature was 120°C with a NO_x conversion level of 75%, whereas at Jenbach the operating temperature was 200–300°C with conversion levels above 83%. Typical for gas engines is the relative small size of the engine and the small amount of flue gas (100–4000 Nm^3/h).

4.5. *Waste incineration*

A further application of SDS is in the treatment of off-gas from waste incinerators. Here the temperature of the NO_x containing off-gas is generally low due to previous scrubbing processes. Re-heating the off-gas is expensive and the low operation temperature of SDS is a clear advantage. A SDS has been designed for a waste incinerator in the Netherlands and will be installed shortly.

5. Conclusions

The SDS comprises a high activity catalyst contained in a low pressure drop lateral flow reactor, and is particularly suited for relatively clean flue gases and low operating temperatures.

The system is characterized by its great flexibility with respect to NO_x conversion, NH_3 slip and pressure drop, giving it several distinct advantages over conventional honeycomb type SCR catalysts.

The SDS has been applied to refinery heaters, ethylene crackers and a number of chemical plants. Detailed engineering designs have been made for its application to gas turbines and waste incineration plants.

The retrofit Shell DENOX system is a cost effective way of reducing NO_x emissions.

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