BASF

Customised bed solutions with new Quattro catalysts

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BASF has produced sulphuric acid for various industrial applications since 1866 and has been producing catalyst for the sulphuric acid process since the early 20th century. A first patent for a vanadium pentoxide catalyst was granted to BASF in 1913. Today, BASF is operating six sulphuric acid and 13 sulphonation plants with inline SO_2 oxidation units worldwide all using BASF's in-house catalyst technology with world class plants operating at emission levels below 50 ppm SO_2. The last 15 years have brought new challenges such as tighter emission regulations and cost pressure to the sulphuric acid market. This has led BASF to be on the forefront with cutting-edge research into one of the oldest catalysts of the portfolio.

Customer focus

In alignment with the new strategy of BASF, the focus on sulphuric acid producers and their needs is ever greater, driving improvements of catalyst technology. BASF works directly with customers to make sure customers achieve the best performance under the specific design and operation conditions of their reactors. This is enabled through BASF's state-of-the-art testing facility and analytics combined with more than 150 years of research and experience.

New extruded shapes

Sulphuric acid catalysts are generally produced by extrusion of a precursor paste to yield shaped catalyst bodies. The extrusion process not only defines the shape of the catalyst bodies, but also impacts other crucial properties such as pore structure and mechanical stability of the catalyst. These properties are also related to the fluid properties of the precursor paste in the extrusion device. Eventually, the extrusion process has to cope with pastes of varying composition for different catalyst types. Fluid properties of precursor paste and control of the entire extrusion process are strongly determined by the specific design of extrusion dies. Especially the detailed design of internals of the dies has a significant impact on quality and capacity of extrusion. This becomes an immediate challenge, when entirely new shapes for a catalyst family shall be extruded and new dies have to be found.

Fig. 1: BASF Quattro catalyst.

Table 1: **Customers' challenges addressed by the new BASF Quattro catalyst**

Typical issues	Can Quattro help?	How?
High emission levels	Yes	Higher geometric surface area resulting in better SO_2 conversion.
Production capacity bottleneck	Yes	Higher geometric surface area allows for increased production rates at historically high conversion levels.
Limited bed height	Yes	Higher geometric surface area allows for higher space-time-yield.
Low ignition temperature	Yes	Higher geometric surface area resulting in better SO_2 conversion at low temperature.
Wider operational range	Yes	The low activity of the Quattro catalyst allows for a much wider operational range.

Source: BASF

Commitment and continuous progress in extrusion technology has been a key for successfully turning a lab idea into an established and reliable commercial product. Here, BASF can make full use of the Technology Verbund with in-house competence on computational fluid dynamics (CFD) and metal powder 3D-printing technology to develop and optimise dies for extrusion devices. This is evidenced by an international patent family filed by BASF on extrusion dies for catalyst production (WO2019/219892 A1).

In 2016, after years of catalyst development, BASF launched 04-115 with the Quattro geometry (Fig. 1, WO2016/156042 A1 and WO 2019/170406 A1) leading to 5-8% increased plant capacity in the first commercial application. Many additional customers have chosen the Quattro geometry since, all benefiting from performance improvements.

In early 2020, BASF introduced the Quattro catalysts 04-110 and 04-111, the newest members of the Quattro family. These vanadium-based catalysts allow sulphuric acid producers to boost production capacity significantly, reduce SO_2 emissions, extend turnaround schedules and shorten start-up time leading to significant cost savings. These latest developments allow customised catalyst bed solutions to be created for unique applications worldwide. Continuous innovation and creative thinking continue to define BASF as a global innovation leader in catalyst research.

Table 2: **Conversion at DOMO Caproleuna plant 2016-2019**

Conversion comparison BOSS 100 (%)

Date of measurement	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5
Quattro					
26.10.2016	58.3	80.8	90.6	99.5	99.84
16.05.2017	57.8	78.3	89.7	99.5	99.84
25.04.2018	47.3	66.3	88.3	99.2	99.79
26.02.2019	48.4	67.3	87.7	99.1	99.78
11.09.2019	48.2	67.1	87.5	99.1	99.80

Source: BASF

Table 3: **04-115 Quattro properties vs. star rings**

	Star Ring 04-115	Quattro 04-115
Packing density, kg/m³	450	450
Relative geometric surface area, %	100	130
Relative pressure drop, %	100	105-110
Cutting hardness, N	>70	>110
Attrition, %	<2.0	<1.0
Active range, °C	390-630	370-630
Ignition temperature, °C	340	330

Source: BASF

04-115 Quattro development and application

In 2017, first long-term results from the Quattro catalyst development were described and demonstrated:

- 5-8 % increased production capacity;
- increased conversion with increased SO_2 feed content and reduced O_2/SO_2 ratio;
- no increase in pressure drop across the 04-115 Quattro bed;
- flexibility across varying O_2/SO_2 ratios.

The development of the Quattro shape geometry addresses several common customer challenges when operating a sulphuric acid plant (Table 1).

In 2018 the DOMO Caproleuna Plant observed a decreased conversion over the first two beds of the sulphuric acid plant. Under normal conditions, this would have led to an increase in SO_2 emissions and potentially a forced shutdown to replace the catalysts in the first bed. However, BASF's Quattro catalyst in the 4th bed of the sulphuric acid plant was able to make up for the decreased conversion in the first two reactor beds, preventing a significant increase in SO_2 emission in the off-gas of the plant (Table 2).

In addition to the significant increase in geometric surface area of the Quattro shape geometry, which yields up to 30% higher activity, the mechanical properties of the Quattro catalyst have set it into a class of its own when compared to current state-of-the-art star-ring-type catalyst geometries (Table 2).

With 50% higher side-crush-strength and approximately 50% lower attrition compared to star-ring catalysts the predicted

Table 4: **Physical properties of the 04-115 Quattro catalyst after one year in the plant**

	Star Ring	Quattro after 1 year
Cutting hardness, N	>70	>90
Attrition, %	2.1	1.2

Source: BASF

loss on sieving for the Quattro catalyst is significantly lower than that of the star-ring type catalyst reducing refill costs.

The greatest attribute of the 04-115 Quattro catalyst is the wider operational range and the lower ignition temperature (Table 3). This allows for a much lower start-up temperature and a much broader operational range of the reactor.

The physical data taken from the DOMO Caproleuna plant also support the original lab data detailing the decreased attrition loss and the high mechanical stability of the Quattro catalyst (Table 4).

Fig. 2: BASF 04-111 Quattro catalyst.

Fig. 3: Reactor bed of Quattro catalyst.

04-110 / 04-111 Quattro development and application

Even though the 04-115 Quattro catalyst already shows a significant improvement compared to the state-of-the-art shape geometries, BASF is further committed to providing customers with the best possible solution for challenging demands such as improving throughput of existing units while decreasing SO_2 emissions to meet more stringent environmental requirements.

To meet this challenge, BASF extended the Quattro family to 04-110 and 04-111 Quattro (Fig. 2). As in the case of the 04-115 Quattro catalyst advantage is taken of the increased geometric surface area of the new shape geometry to push the production capacity of existing sulphuric acid units, providing a catalyst which requires a lower loading mass and offers a significant performance advantage compared to all standard star-ring type catalysts.

The most impressive outcome of the 04-110 and 04-111 catalyst shape geometry is the increased active range of the catalyst especially at low temperature. The decrease in ignition temperature is driven by the higher geometric surface area which allows more accessibility to the active sites at low temperature. This increases the active range of the catalyst.

Another major advantage is that sulphuric acid producers can lower the amount of catalyst required for a reactor filling while at the same time increasing conversion. This means pressure drop in the reactor can be decreased without compromising on conversion. In fact, this can even lead to the highly desirable situation of increased conversion with a lower pressure drop. The lower catalyst loading of the BASF 04-111 or 04-110 quattro catalyst is possible again due to the increased geometric surface area (Table 5).

Since 2016 the Quattro catalyst family has been installed in numerous plants globally, each time confirming the expected performance improvements described earlier: "Due to technical limitations we are not yet at full capacity, but the performance of the bed loaded with Quattro catalyst is already remarkable."

DOMO Caproleuna, Germany, loaded two additional beds with 04-111Quattro during the turnaround in 2020. Ulf Müller, Director Operations Inorganic Precursors and Fertilizers comments, "It is clear that the new catalyst has an excellent performance. With a capacity of 3% above the project load, we still have reserves in performance and conversion. So far, we could not detect an increase in pressure drop across the catalytic converter."

In summary, the 04-115, 04-110 and 04-111 BASF Quattro catalysts offer lower ignition temperatures, higher conversion and higher strength than conventional catalysts (Fig. 3). This directly translates into increased operational flexibility and significant cost reduction for sulphuric acid producers.

Table 5: **Quattro properties vs. star-rings**

	Star Ring 04-110	04-110 Quattro	Star Ring 04-111	04-111 Quattro
Packing density, kg/m³	450	450	450	450
Relative geometric surface area, %	100	130	100	125-135
Relative pressure drop, %	100	105	100	100-105
Cutting hardness, N	>70	>110	>70	>110
Attrition, %	<2.0	<1.0	<2.0	<1.0
Relative activity, %	100	130	100	125
Active range, °C	420-630	400-630	410-600	390-600
Ignition temperature, °C	380	360	360	350

Source: BASF