

# The Evolution of the Ammonia Synthesis Catalyst 'AmoMax®-Casale'

John D'Alessandri<sup>a</sup>, Ermanno Filippi<sup>a</sup>, Sergio Panza<sup>a</sup>, Marvin Estenfelder<sup>b</sup>, Stephan J. Reitmeier<sup>b</sup>, Andreas Reitzmann<sup>b</sup>, Pierdomenico Biasi<sup>a\*</sup>, and Rene Eckert<sup>b\*</sup>

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**Abstract:** Despite the Haber-Bosch process being more than 100 years old, only incremental improvements have been achieved until recently. Now, by combining the catalyst expertise of Clariant and the engineering knowledge of Casale, a breakthrough has been realized. AmoMax®-Casale is a new ammonia synthesis catalyst jointly developed by Casale and Clariant particularly for use in Casale ammonia converters. AmoMax®-Casale is a customized evolution of the well-known, wustite-based catalyst, AmoMax® 10. While retaining the same superior resistance to ageing, poisoning and mechanical strength, AmoMax®-Casale is significantly more active. This feature allows to reduce the loop recycle rate and the loop pressure and/or to increase the ammonia production. The higher activity of AmoMax®-Casale contributes to improve the overall operating efficiency either by saving energy, or by increasing the plant capacity significantly. This article will describe in detail the successful development of AmoMax®-Casale, explain advantages and commercial benefits based on concrete plant simulations and share the start-up experience of the first commercial reference.

**Keywords:** Ammonia catalyst · Casale · Clariant · Haber-Bosch · Reactor design



**John D'Alessandri** joined Casale in 2014 as a laboratory technician. He was able to develop new mechanical tools for catalyst testing as well as new testing procedures. In 2021 he was promoted to Lab. Manager and started to be in charge of different projects and of the annual budget of the Casale Laboratory.



**Sergio Panza** graduated in chemical engineering from Polytechnic University of Milan in 1998. He worked for one year in the research field at ETH Zurich. Since 2001 he is part of Casale Group. His current position is Technology Manager in the Syngas Process Department. Sergio has 6 granted patents and several patent applications in his career.



After his PhD in industrial engineering, **Pierdomenico Biasi** carried out research activities as a Post-Doc at the Abo Akademi University, Finland. He then moved to the plastics industry where he was responsible for developing brand new TPE (Thermo Plastic Elastomers) formulations. He joined Casale in 2014 where he was able to co-develop the AmoMax®-Casale in collaboration with Clariant. Since November 2018 he

leads the activities of the fundamental research team for Casale SA.



**Rene Eckert** holds a PhD in chemistry from Ruhr-Universität Bochum, working in the group of Prof. Schüth at Max-Planck-Institut für Kohlenforschung. He joined Clariant in 2017 after a period of Post-Doc research at the Max-Planck-Institut. Rene leads R&D projects in the area of ammonia synthesis and manages a lab team and lab-scale technical equipment.



**Ermanno Filippi** graduated in chemical engineering from Milan Polytechnic. He joined Casale in 1985 as a Process Engineer, before being promoted to Process Group Manager. Subsequently he became Head of Process and Technology Department and Head of Research and Technology Development Department. He presently holds the position of CTO of the company. Ermanno Filippi is author of several technical papers and patents



**Stephan J. Reitmeier** holds a PhD in chemistry from the Technical University of Munich. He joined Süd-Chemie (now Clariant) in 2010 as R&D Group Leader working on zeolites and aromatics separation. Since 2018, he is Head of the Department 'Syngas Applications' focusing on catalyst development for methanol, ammonia and watergas shift applications. Stephan is author of a number of publications and patents.

\*Correspondence: Dr. P. Biasi<sup>a</sup>, E-mail: p.biasi@casale.ch; Dr. R. Eckert<sup>b</sup>, E-mail: rene.eckert@clariant.com; <sup>a</sup>Casale SA, Via Giulio Pocobelli 6, CH-6900 Lugano, Switzerland, <sup>b</sup>Clariant Produkte (Deutschland) GmbH, Arabellastr. 4a, D-81925 Munich, Germany



**Marvin Estenfelder** holds a degree in chemical engineering from Karlsruhe Technical University and completed his PhD at the university's Institute for Chemical Process Engineering. In 2003, he joined Süd-Chemie (now Clariant) to lead research and development in the area of Selective Oxidation Catalysts. He is author of a number of patents and publications, mostly in the field of Selective Oxidation catalysis.



**Andreas Reitzmann** holds a PhD from the Institute of Technical Chemistry, Technical faculty University Erlangen-Nürnberg. He was Assistant Professor and Head of Research Group at the Institute of Chemical Process Engineering at University Karlsruhe (KIT) from 2000 to 2007. In 2007 he moved to Süd-Chemie (now Clariant) as Project Manager. Since 2011 Andreas is the Head of R&D Center,

Business unit 'Catalysts' of Clariant in Heufeld, Germany. He is author of 40 publications and holds 8 patents and patent applications.

## 1. Introduction

The importance of ammonia in the world economy is well known considering its paramount role as fertilizer in the worldwide food supply; additionally ammonia synthesis is also at the heart of the so-called green ammonia process. Ammonia is also widely used to produce other chemicals and finally it is becoming interesting in the field of application as energy carrier.<sup>[1]</sup>

In the fertilizer industry, Clariant is a catalyst supplier with a wide range of products for many licensors including Casale; analogously Casale is a process licensor with a wide range of technology solutions covering all the sections of ammonia, urea, nitric acid, ammonium nitrate and complex fertilizers plants. For ammonia synthesis Casale has a series of unmatched products in terms of overall performance, reliability and efficiency, and dozens of Casale ammonia converters are presently operating with Clariant catalysts.

Casale's and Clariant's mission is focused on a continuous enhancement of the supplied products and solutions to achieve the targets of better performance, lower energy consumption, reduction of the CO<sub>2</sub> footprint, and a long and reliable operation of the processes using their products.

It must be noted that catalyst and ammonia converter internals are parts of the same final product (ammonia synthesis converter) but sometimes their development and improvement follow parallel paths without taking advantages of possible synergies that could create value for the final customer.

Starting from this idea Casale and Clariant co-operated with the goal of developing a new catalyst to be suitably utilized inside the Casale ammonia synthesis converter in the most efficient and reliable way.

## 2. The Development of an Evolutionary Ammonia Synthesis Catalyst

Catalytic ammonia synthesis from H<sub>2</sub> and N<sub>2</sub> represents one of the most important industrial reactions today.<sup>[2]</sup> The catalyst used in this reaction is made from iron oxide with small amounts of other oxides added as promoters to enhance activity and stability. Despite the Haber-Bosch process being more than 100 years old, only incremental improvements have been achieved until recently.<sup>[3]</sup> Combining the catalyst expertise of Clariant and the engineering knowledge of Casale, a breakthrough has been realized leading to the new ammonia synthesis catalyst AmoMax®-Casale.

The new catalyst is based on Clariant's successful and superior catalyst AmoMax® 10 with more than 100 references worldwide and is customized for Casale reactors (patent pending) with significantly improved activity compared to state-of-the-art iron-based catalysts. When introducing a new catalyst into the market, performance evaluation is of utmost importance, but simple catalytic tests in powder form are not representative enough for industrial applications and only suitable for screening purposes. Therefore, a precise and rigorous methodology must be applied.

### 2.1 Materials and Methods

To reliably validate a new catalyst, laboratory-scale tests should be representative of the industrial catalyst. Thus, catalytic and mechanical tests are performed with the final form and shape of the catalyst. During catalytic tests, the temperature profile in the catalyst bed is measured and correlated with the heat exchange between oven and reactor. Subsequently, a systematic modelling of the obtained data is applied to understand the performance of the catalyst under industrial conditions. The information acquired is used to compare the new catalyst with the best available state-of-the-art catalyst technology. In case of superior activity of the new catalyst, as a next step, in-depth mechanical stability characterizations are performed to confirm the robustness of the catalyst. This includes simulations and experiments of friction between the catalyst pellets/granules and the walls of the reactor, crush strength and simulations of start-up/shut-down of industrial reactors. If the catalyst passes all the mechanical tests, proof of concept is achieved, and it is considered ready for scale-up. Transferring the catalyst recipe from lab to production scale is a highly complex process with numerous important parameters, which must be considered by the catalyst manufacturer. After a successful scale-up, the catalyst is prepared for shipment. To ensure it maintains its mechanical integrity and activity after transport from the production site to the plant, samples are taken during transportation, sent to different analytical laboratories and precisely analyzed. The catalyst is then validated with the same catalytic and mechanical tests applied during the proof of concept phase. If all the parameters are confirmed, the catalyst is finally ready for the market.

## 3. AmoMax®-Casale Catalyst Characterization

### 3.1 Performance Tests

#### 3.1.1 Activity

Laboratory results for the catalytic activity are reported in Fig. 1. The test conditions were:

- Tubular reactor, tests performed on granules;
- Pressure: 150 bar and H<sub>2</sub>:N<sub>2</sub> = 3;
- Temperature: 300, 330, 360, 380, 400 and 420 °C.

The results show how the new AmoMax®-Casale outperforms magnetite- and wustite-based state-of-the-art ammonia synthesis catalysts over the whole relevant temperature range. Especially, the gap to the standard magnetite catalyst is drastically increased.

Based on the test results, a kinetic model was created which fits very well the experimental data (Fig. 2).

#### 3.1.2 Poison Resistance

The performance with different O<sub>2</sub> concentrations in the feed was tested at different temperatures with the following results (Fig. 3):

- The oxygen poisoning behavior of the new catalyst is similar to the reference catalyst at all measured O<sub>2</sub> concentrations (compare dotted versus full line).
- The deactivation observed due to oxygen poisoning corresponds to observations in commercial plants. Despite the higher activity, AmoMax®-Casale offers superior performance regardless of oxygen concentration.

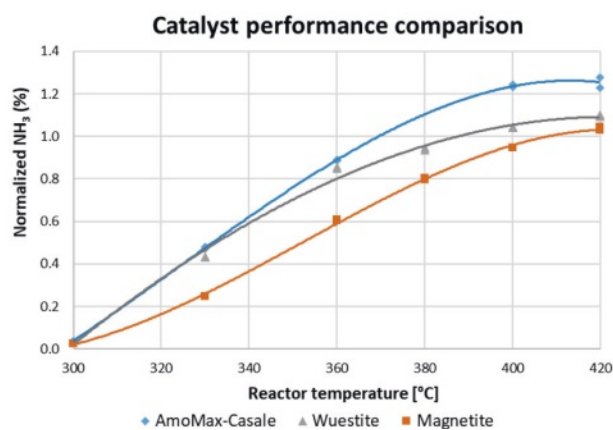


Fig. 1. Comparison between state-of-the-art magnetite-based catalyst, wustite-based reference catalyst and AmoMax®-Casale.

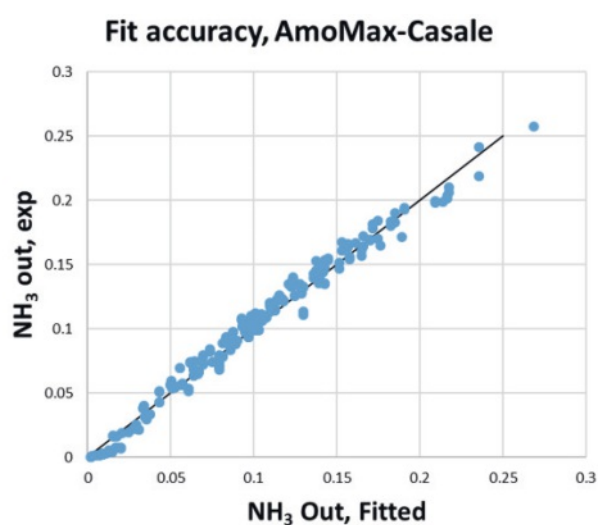


Fig. 2. Comparison of simulated and experimental data.

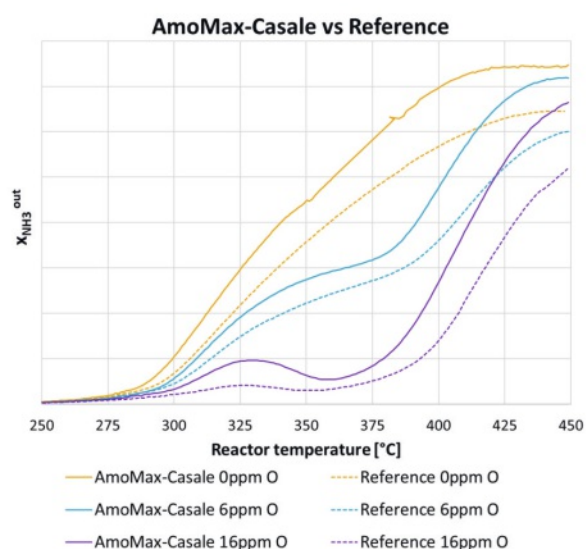


Fig. 3. Comparison of poison resistance in different oxygen concentrations.

### 3.1.3 Stability

AmoMax®-Casale shows an extraordinary stability in poisoning conditions. The performance was tested after each poisoning treatment and the activity was measured over time at fixed testing conditions without oxygen poisoning and after a stabilization period.

As shown in Fig. 4, AmoMax®-Casale has proven to be very stable compared to a wustite-based reference catalyst.

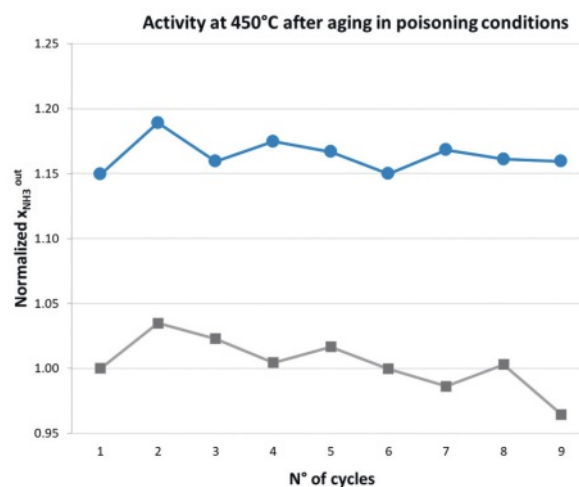


Fig. 4. Stability after aging in poisoning conditions.

### 3.2 Mechanical Performance Tests

Beside the pure activity and performance tests, Casale and Clariant also performed tests to assess the mechanical suitability of AmoMax®-Casale; in particular the main targets were to identify the intrinsic properties of the catalyst and how the catalyst would behave inside the Casale internals.

The tests performed to mechanically qualify the AmoMax®-Casale were:

- Crushing strength properties in Casale internals: AmoMax®-Casale has been tested with an in-house tool (so-called 'Casale wall tester', see Fig. 5) to assess the amount of powder produced due to friction of the catalyst with the Casale collectors. The AmoMax®-Casale crushing tendency has been compared with standard wustite and magnetite catalyst without identifying significant differences on the final values.
- Pressure drop: a test unit was set up to assess the pressure drop generated by the new catalyst and compared with standard catalysts used as references with the aim to evaluate the pressure drop inside an axial-radial bed. The results obtained were in line with the expectations and with the industrial pressure drop achievable in an industrial converter with a converter based on a standard catalyst (see Fig. 6).
- Shear stress test: basically, this test is designed to apply stress to a test sample so that it experiences a sliding failure along a plane that is parallel to the forces applied. Therefore, this test is important in order to assess the effect of the catalyst on the Casale internals; after several tests the parallel stresses created on the internal surface are comparable to the ones measured with standard catalyst (see Fig. 7).

### 4. Casale Internal Design Philosophy

Depending on the project type (new converter or revamping of an existing reactor), Casale can approach the ammonia synthesis converter in different ways.

In general for a new pressure vessel the main goals are:

- Full exploitation of catalyst;
- High reliability;
- Highest catalyst volume filling efficiency to reduce the final pressure vessel sizes;
- Easy access to internal baskets for maintenance or catalyst replacement.

While for a revamping, considering the possible physical constraints provided by the existing pressure vessel, the target is to



Fig. 5. Casale wall tester.



Fig. 6. Industrial pilot plant for pressure drop measurement.

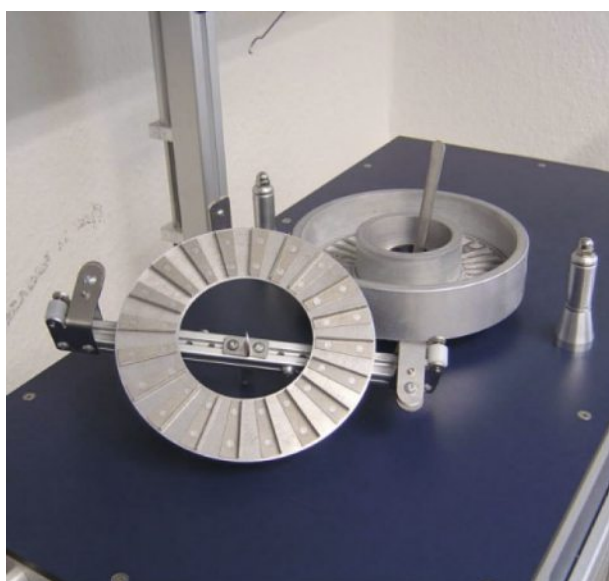


Fig. 7. Shear stress test unit.

provide the most efficient thermodynamic configuration combined with the maximum catalyst volume filling efficiency. Reliability is another paramount target while the access to the internal baskets is determined by the existing pressure vessel configuration.

For a new converter Casale usually adopts the well-known configuration based on three catalytic beds with interchangers between the 1<sup>st</sup> and 2<sup>nd</sup> bed and between the 2<sup>nd</sup> and 3<sup>rd</sup> bed, coupled with the use of Casale patented axial-radial internals.

In case of revamping the most frequent configuration is three catalytic beds with one or two interchangers; retrofitting an existing converter with Casale internals often means increasing the installed catalytic volume compared to the previous design.

The installation of a bottom exchanger is also quite common especially if the revamping or the installation of a new pressure vessel is taking place in an existing synthesis loop.

In general, the higher efficiency of Casale internals together with the well-known Casale cold-wall design allows the converter to operate at a lower thermal level, thus improving its expected lifetime. Independent control of each of the three beds' temperatures is foreseen since it is essential to obtain optimum operation of the converter at all times, *i.e.* with new as well as aged catalyst and at different plant loads, for maximum energy saving and thus highest return on the converter retrofit investment.

The new converter internal features are:

- A fixed cylindrical cartridge, which separates the catalyst baskets from the pressure vessel wall, allowing the vessel wall to be kept cool by flushing it with the incoming gas;

- First and second axial-radial flow type removable catalyst baskets for a three-bed design;
- A third (bottom) fixed axial-radial catalyst basket;
- Two internal heat exchangers.

The catalyst beds have two cylindrical walls, one external (near the cartridge wall) and one internal, to contain and support the catalyst mass providing mechanical strength and to provide uniform gas distribution throughout the whole bed volume in order to get the best catalyst performance. Each of the three axial-radial baskets is designed with open top catalyst bed, which compared to conventional radial designs, has the following advantages:

- Utilizes efficiently the full volume of the catalytic beds, including the top layer;
- Easier mechanical construction, not requiring completely top sealed catalytic beds;
- Easier catalyst loading and unloading;
- Easy and controllable dense loading of the catalyst to obtain high and uniform bulk density.

To avoid any movement or spillage of the catalyst loaded in the top portion of the catalytic bed in upset conditions, proper means, such as slotted protection screens, are installed.

The material selection minimizes or avoids high-temperature hydrogen attack and nitriding phenomena that would affect the reliability and the life of the installed pressure vessel and internals.

The axial-radial flow pattern in the catalyst results in an empty cylindrical core around the converter centerline, which is the ideal location for the interbed heat exchangers. To save costly converter space, Casale adopts a special design that allows high heat transfer rates to be obtained with comparatively low pressure drop and eliminates vibration problems. The bottoms of the removable baskets are inverted dished heads. Besides simplifying the sealing problems, this arrangement allows better utilization of the converter volume (*i.e.* more catalyst can be packed in these baskets). The different interconnected metal parts, which combined constitute the internals, reach very different steady state temperatures in an operating converter. To cope with different thermal expansions, Casale only uses bellows expansion joints where they are easily accessible for assembly and disassembly (*i.e.* at the reactor top). For converter inner parts, since they are not easily accessible, Casale patented elastic seal rings are used (Fig. 8); in this way it is possible to reduce internal leakages with smaller axial dimensions and shorter length.

#### 4.1 Casale Internals Installation

In the case of the converter pressure vessel with fully open top configuration, this is unbolted to unload catalyst and remove the existing cartridge. The pressure vessel is then inspected, the stud bolts and gaskets seating surface are protected. A new cartridge is then lifted and installed inside the pressure vessel (Fig. 9). The expansion joint assembly on the converter outlet nozzle is installed and welded up to the cartridge bottom pipe, then the cartridge top cover is removed. After removal of the protection screen and lifting of the first bed basket, it is possible to unbolt and remove the thermowell pipes. To ensure a proper reading during converter operation, water moisture and dirt must be prevented from infiltrating the inside of the thermowell pipes: special care is therefore taken to plug and seal the thermowell pipe openings. Internal heat exchangers are already welded and in position inside the new cartridge; they are normally never removed during cartridge installation. Using the same procedure as for the first bed, the second bed basket is removed, and catalyst loading is started in the third bed. Special attention must be given during catalyst loading to preserve catalyst activity and the integrity of the converter internals. Oxidized catalyst is completely unreduced and does not present any risk of reaction with ambient air; conversely, pre-reduced and stabilized (RS) catalyst is obtained by the complete reduction of oxidized catalyst fol-

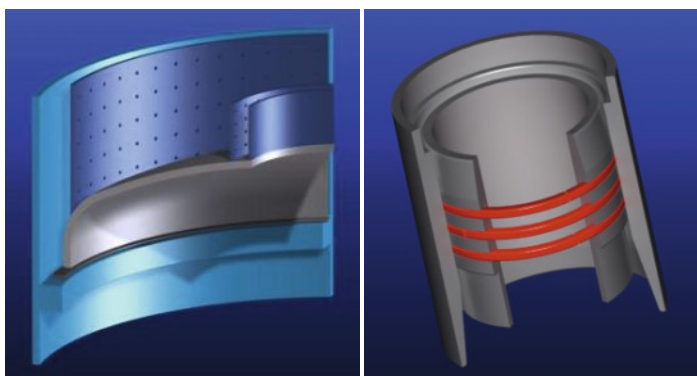


Fig. 8. Reverse dish bottom closure and elastic seal rings.

lowed by skin oxidation for safe handling and storage. Reduced and stabilized catalyst can react with air even at ambient temperature; if such a reaction occurs, the temperature can easily rise since the oxidation reaction is exothermic, causing both catalyst and converter internals damage. For these reasons, pre-reduced catalyst loading (converter first bed) must be performed under a nitrogen atmosphere. Special nitrogen connections are used to flush the converter and a temporary cartridge closure cover and polyethylene sheet are used to cover all areas where catalyst is handled.

The catalyst is always screened before loading: in fact, it is sieved to remove any dust before loading in the drums and shipment, however some dust can form during handling and transportation.

Catalyst loading is performed by using a dense loader (Fig. 10). The amount of catalyst loaded is recorded while regularly monitoring (every 1250 mm) catalyst distribution and bulk density (loaded catalyst weight and height are required) to maximize loaded catalyst bulk density.

After the third bed catalyst loading is completed, a relevant top protection screen is re-installed together with the second bed and gaskets. Catalyst loading on the second and first bed proceed as described for the third bed. Thermowell pipes and relevant stuffing boxes are also re-installed. During first bed loading, the bed temperature is carefully monitored to ensure that no oxidation occurs.

The cartridge cover is then re-installed and insulation sleeves welded in the main inlet nozzle and start-up/bypass nozzle. Finally, central pipe assembly and expansion joints assemblies are installed, and the pressure vessel is boxed up.

All welds are 100% checked by a dye penetrant test to ensure maximum reliability of internals. Installation of the new converter internals are accomplished smoothly in less than 15 days for a new converter, with no impact on plant scheduled shut-down time.

### 5. AmoMax®-Casale Operation in Casale Converters

As discussed previously the AmoMax®-Casale catalyst provides up to 30% higher activity compared with the standard wustite-based catalyst available on the market (reference catalyst). The combination and synergy of this catalyst with the best ammonia converter technology provided by Casale offers an unmatched design with the highest possible attainable performances, in terms of lower synloop operating pressure and higher ammonia conversion.

These benefits can be easily converted in energy saving, lower natural gas specific consumption or higher production if the limitation to a plant load increase is provided by the synthesis loop.

In the case of new converter, AmoMax®-Casale can be used in all designed beds boosting the performances and the expected life, a different layout could foresee a 1st bed based on standard catalyst (this bed is working with fresh and unreacted gas).

A new converter based on AmoMax®-Casale catalyst and Casale internals installed in a new synthesis loop would provide a smaller pressure vessel or as alternative a lower synloop circula-



Fig. 9. Cartridge lift and installation inside converter.



Fig. 10. Catalyst dense loading.

tion and therefore smaller equipment sizes with reduction of the relevant capex.

Viceversa in case of ammonia synthesis converter revamping, since AmoMax®-Casale is more efficient than the standard reference catalyst, this catalyst finds its logical application in the final bed of an existing converter. Often the AmoMax®-Casale can also be offered starting from the second bed of an ammonia synthesis converter. The application of AmoMax®-Casale in the first bed is usually not reasonable for an ammonia synthesis converter revamping considering that this basket is working with a very fresh gas (low ammonia concentration) and therefore the differences with a standard catalyst are not so significant.

In Table 1 the performance of a new ammonia synthesis converter pressure vessel designed with Casale internals and operated with standard wustite-based catalyst available on the market (reference catalyst) or AmoMax®-Casale catalyst are compared. The comparison is made according to the following boundary conditions:

- Same catalyst life;
- Same Casale internals;
- Same new pressure vessel;
- AmoMax®-Casale loaded in the 2<sup>nd</sup> and 3<sup>rd</sup> catalytic beds.

Therefore, also with an optimized ammonia converter internals configuration and based on the latest Casale technological improvements, the AmoMax®-Casale catalyst is able to provide an enhancement of the overall synloop performances.

The installation of this new catalyst inside a revamped converter can be even more effective considering that very often, an existing converter is working in conditions far away from the original ones, and therefore with a design and configuration no longer optimized for the current operation.

Table 1. AmoMax®-Casale comparison in new converter.

	Reference catalyst	AmoMax®-Casale
Internals	Casale	Casale
Production [MTD]	1,655	1,655
Operating pressure [kg/cm <sup>2</sup> g] <sup>a</sup>	140	134.5
Ammonia outlet [%mol]	17.7	18.4
Energy saving [kcal/MT]	–	>25'000

<sup>a</sup>Outlet converter

In this regard two different design configurations for a GIAP bottle shape and for a TEC bottle shape converter are presented (Fig. 11, Table 2, Table 3).

- Same catalyst life;
- Casale or competitor internals;
- Existing pressure vessel;
- AmoMax®-Casale loaded in the 2<sup>nd</sup> and 3<sup>rd</sup> catalytic beds.

The performance improvements in terms of energy saving and capacity increase are quite remarkable especially if compared with an ammonia synthesis converter design different than Casale.

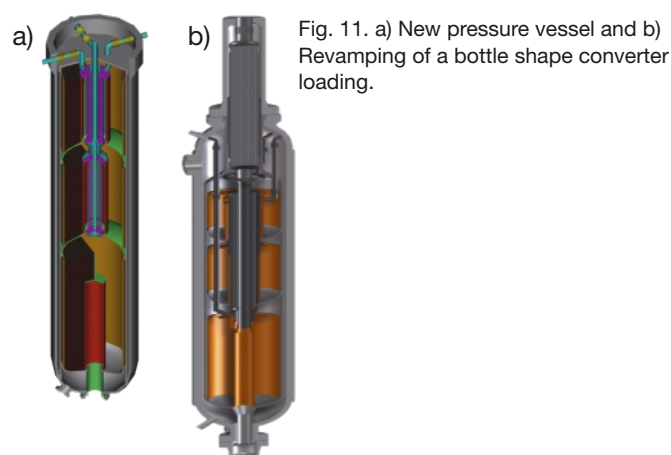


Fig. 11. a) New pressure vessel and b) Revamping of a bottle shape converter loading.

Table 2. AmoMax®-Casale comparison in GIAP revamped converter.

	Pre-re-vamping	Reference catalyst	AmoMax®-Casale
Internals	Other licensors	Casale	Casale
Production [MTD]	1400	1,870	1,870
Operating pressure [kg/cm <sup>2</sup> g] <sup>a</sup>	249	231.4	223.7
Ammonia outlet [%mol]	14.5	17.0	18.8
Chiller duties [Gcal/h]	7.2	9.5	8.6
Loop Circulation [kmol/h] <sup>b</sup>	35'700	38'100	34'100
Energy saving [kcal/MT]	–	163'000	>210'000

<sup>a</sup>Outlet converter, <sup>b</sup>inlet ammonia converter

Table 3. AmoMax®-Casale comparison in TEC revamped converter.

	Reference catalyst	AmoMax®-Casale
Internals	Casale	Casale
Production [MTD]	2100	2100
Operating pressure [kg/cm <sup>2</sup> g] <sup>a</sup>	226.1	217.4
Ammonia outlet [%mol]	20.7	21.7
Energy saving [kcal/MT]	–	>45'000

<sup>a</sup>Outlet converter

## 6. Conclusions

In a joint multidisciplinary effort involving process engineers, scientists, modelling engineers, and fluid dynamic engineers, Casale and Clariant created a new ammonia synthesis catalyst that was ready for the market in less than three years.

AmoMax®-Casale provides the following benefits to ammonia plants:

- Casale engineering adapted and optimized to use the newly developed catalyst;
- New catalyst efficiency index up to 30% more than wustite-based reference;
- Higher tolerance towards poisoning and aging compared to wustite-based reference;
- Energy savings, lower natural gas specific consumption or higher production if the limitation to a plant load increase is provided by the synthesis loop.

AmoMax®-Casale is now available on the market and has successfully been installed and started up in the first large-scale ammonia plant in the Americas.

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