BOOSTING NITRIC ACID PRODUCTION

Dr. Nina van Gellecom, Messer Group, Germany, explains how oxygen application can increase nitric acid plant efficiency and capacity.

Nitric acid is an important raw material for the production of fertilizers. The yearly output worldwide amounts to an estimated 60 million t. Approximately 80% of that is used for the production of the fertilizer chemicals ammonium nitrate (AN) and calcium ammonium nitrate (CAN).

The majority of the global industrial nitric acid production utilises a process invented by Wilhelm Ostwald in 1902: the catalytic oxidation of ammonia followed by the oxidation of the emerging nitric oxide and its subsequent absorption in water. The production process and the plants have been improved over the years, and optimisation continues to

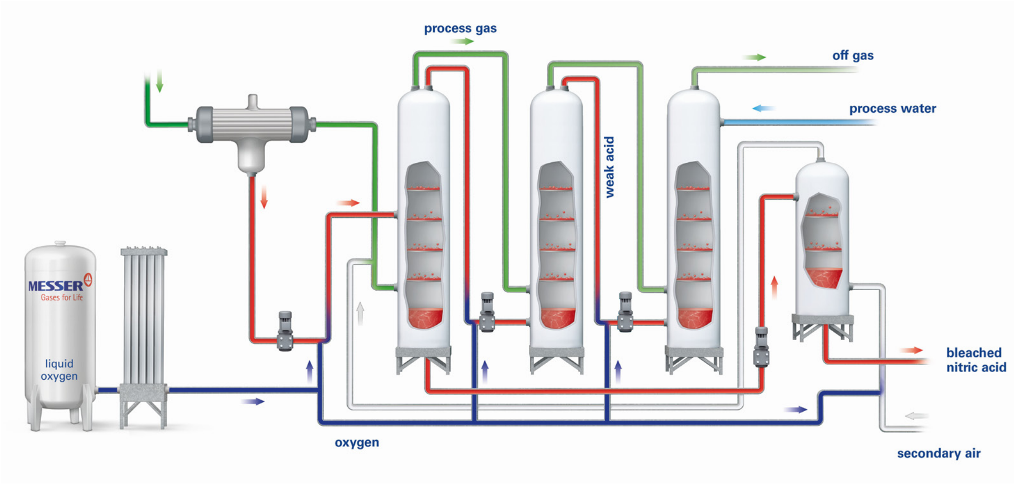

Figure 1. Flow chart of nitric acid production with different introduction points.

Figure 2. A nitric acid plant with oxygen application.

improve process efficiency and the ecological footprint by focusing on energy efficiency.

However, many plants are not equipped with the latest technology, especially in Europe. There are many older plants with optimisation potential that could become urgent cases due to the stricter regulatory limits for emissions that have emerged in recent years, and further restrictions can be expected in the future. Operating older plants without improving efficiency can have negative effects on economic balance that become worse over time.

Oxyboost options

With the new solution, nitric acid producers have a choice between two options of oxygen application in the production process:

- Increase efficiency and lower nitrogen oxide (NO_X) emissions.
- Increase capacity by up to 10%.

The additional oxygen enhances the oxidation of nitrous acid and nitrous oxides in the liquid and gaseous phases of the process. The essential parameters for using the gas successfully and efficiently are the right choice of injection point, oxygen quantity and the injection system. The points of injection depend on the option chosen, and the type of plant and the configuration of the process are also of importance. For increasing efficiency, the gas must be dosed into the liquid phase and injected at carefully chosen points in the acid lines, either between the absorption columns or in the line between the cooler-condenser and absorption tower. To increase capacity, most of the oxygen has to be injected into the secondary air stream (Figure 1).

Increasing efficiency and reducing NO_X emissions

The transformation of ammonia into nitric acid involves the seven reaction steps shown below, of which reactions number 2, 6 and 7 are particularly affected by oxygen. The injection of additional quantities of oxygen at specific points in the production process leads to increased efficiency and reduced NO_X emissions.

Under standard conditions, reactions 6 and 7 are very slow and rather insignificant.

1. $4NH_3 + 5O_2 \leftrightarrows 4NO + 6H_2O$
2. $2NO + O_2 \leftrightarrows 2NO_2$
3. $2NO_2 \leftrightarrows N_2O_4$
4. $6NO_2 + 3H_2O \leftrightarrows 3HNO_3 + 3HNO_2$
5. $3HNO_2 \leftrightarrows HNO_3 + H_2O + 2NO$
6. $2HNO_2 + O_2 \leftrightarrows HNO_3$
7. $2N_2O_4 + O_2 + 2H_2O \leftrightarrows 4HNO_3$

The basic idea of increasing efficiency with oxygen has been described several times before: EP 0 799 794 A1 proposed feeding oxygen or an oxygen-enriched gas downstream to the reactor, but upstream to the absorption column.[1] In EP 1 1013 604 B1, oxygen is fed to the process stream in a way that creates a significant interface between gas and liquid.[2] According to US 4 235 858 B1, cold oxygen is fed into the absorption tower.[3] However, the most important parameter is the right choice of the introduction point. Hence, a more effective method of applying oxygen in the production process of nitric acid was developed and patented by Messer Group as EP 2953894 B1/WO 2014121938 A1.[4]

Case study: increasing efficiency in Eastern Europe

The new technology was implemented in a nitric acid line of a customer located in southeast Europe (Figure 2). It is a 730 tpd

Stamicarbon plant commissioned in 1968, and the oldest of the three units operated by the customer. The plant uses Stamicarbon 4 bar(g) monopressure technology and operates with two oxidation columns and two absorptions columns in order to achieve reasonable absorption efficiency. The towers are filled with Raschig rings.

The plant showed insufficient absorption efficiency, which resulted in high NO_x values after absorption. The customer had to feed relevant quantities of ammonia to the $DeNO_x$ system based on selective catalytic reaction (SCR) to reduce the emissions to meet the current European Union (EU) limit of 90 ppm. For limiting NO_x emissions in hot weather conditions, the plant had to be operated at reduced capacity and summer shutdowns were partially prolonged.

To make production efficient again under all weather conditions and to comply with EU regulations, substantial investments seemed inevitable. The options involved installing a completely new $DeNO_x$ system, or at least a new $DeNO_x$ catalyst, combined with improved cooling for the absorption towers.

As an alternative to substantial investment the company offered the oxygen injection technology, promising a number of advantages:

- Significant reduction of NO_x values before and after $DeNO_x$, enabling regulation-compliant emission.
- Less shutdown time due to excessive emission levels.
- Higher production rate proportional to improved absorption.
- Reduced ammonia consumption in the $DeNO_x$ plant.
- Low investment.

According to patent EP 2953894 B1/WO 2014121938 A1, four injection points (Figure 3) were chosen for the trial run, which can be done with practically no investment because the test run is performed with mobile equipment (Figure 4). Figure 5 shows the preparation of one of the introduction points.

The tests were carried out in September and October 2017, when the NO_x values after absorption were approximately 1700 ppm. The NO_x flow is directed to a selective catalytic reduction plant which reduces the NO_x emissions to 90 ppm by reaction with ammonia.

Figure 6 clearly shows the effect of the oxygen dosed. To get a clear picture of this specific setting, the ammonia flow was held at a constant rate of approximately 185 kg/hr which resulted in NO_x values after $DeNO_x$ of approximately 230 ppm. The blue line shows the oxygen flow directed to the plant through the four injection points.

When the oxygen flow was started with 260 Nm^3/hr and the chosen settings, the NO_x values went down partly but remained volatile. The oxygen flow was then shut down briefly. At this point the NO_x emissions peaked to maximum scale value. After a recalibration of all systems, the oxygen flow was restarted with 310 Nm^3/hr. The NO_x emission values dropped almost immediately from 220 ppm to 20 ppm (indicated with a red arrow in Figure 6) and they remained at this level constantly for as long as oxygen was dosed. The ammonia consumption in the $DeNO_x$ plant could be reduced by 50 kg/hr. Analyses showed that the NO_x values after absorption decreased from 1700 ppm to 1150 ppm thanks to the injection of additional oxygen. The set-up, which was proven to be optimal for the specific plant during the trial, is used as a blueprint for the custom-made installation package.

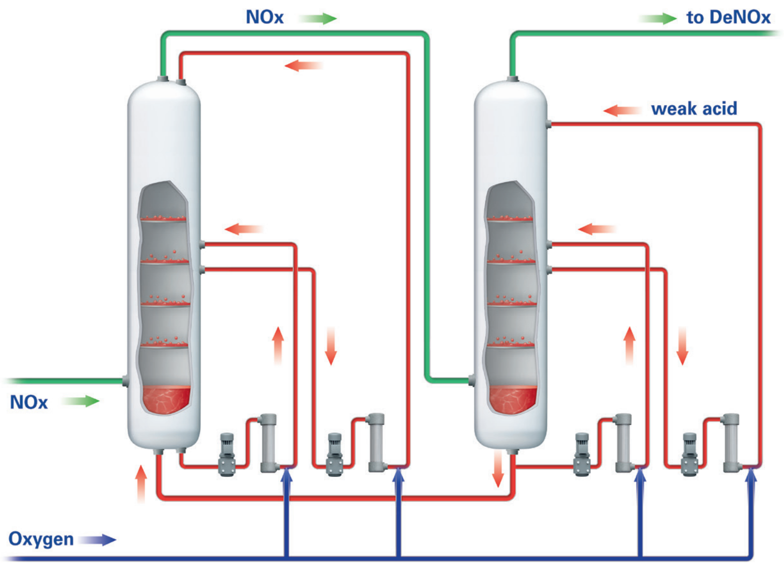

Figure 3. Flow chart of the last two absorption towers at NA line 2 with four injection points.

Figure 4. Test equipment including a mobile tank, vaporisers, fundaments, regulation skid and flexible hoses.

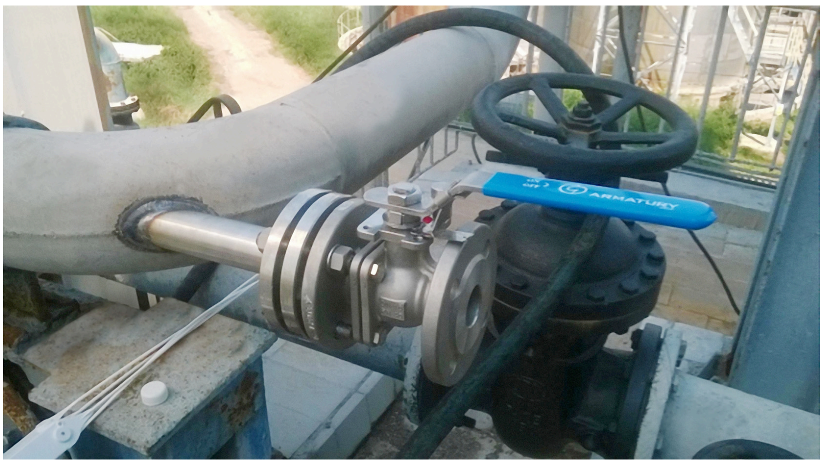

Figure 5. Preparation of one of the injection points.

Absorption was improved and downtime substantially reduced. In contrast to the previous situation, the plant now constantly works at full capacity in hot periods. The production of nitric acid rose slightly by 260 kg/hr (calculated as 100% nitric acid), which is proportional to the improved absorption. The sum of the reduced ammonia consumption for the SCR (-50 kg) and the slightly higher output due to improved absorption (+260 kg/hr) equates to considerable economical benefit, while NO_X emissions were efficiently cut to comply with EU regulations. The substantial reduction of downtime generates additional value which is not included in the benefits discussed.

Reducing NO_X emissions

The technology was tested and further optimised in a dozen industrial-scale trials. During the latest of these, a reduction of the NO_X level after absorption by 1000 – 1500 ppm was shown, and depending on plant efficiency and configuration, even higher reduction rates are possible. It should be noted that the oxygen application can also be economically beneficial for plants with better absorption levels than in the case study. As oxygen for NO_X treatment offers relevant cost savings towards ammonia, cost reduction is a logical consequence of using the gas. Requiring only a small investment, the break-even point is reached quite quickly in most cases. Additionally, the ammonia fed to the burner is used to a higher degree, which simultaneously reduces emissions and increases product output.

Increasing plant capacity

In most nitric acid plants, the main air compressor's output is a limiting factor for production capacity. Normally, when operating at its maximum output, production cannot be further increased without massive investment. The concept for a capacity increase is based on an oxygen enrichment mainly at two different points of the plant combined with a re-arrangement of the air flows. A capacity increase of up to 10% can be generated without investing in a larger or additional compressor or fan.

The flow of secondary air to the bleaching column can be reduced if certain elements can be guarenteed:

- The air stream must contain enough oxygen for the reactions.
- The air stream must have sufficient total flow for efficient stripping.

This is balanced with an oxygen enrichment in the secondary air stream, which gives the customer the opportunity to redirect a certain amount of compressed air from the secondary air to the primary air stream. The enrichment of the secondary air stream with oxygen was also described by Watson et al. in 1980.[5] The percentage capacity increase provided by this method strongly depends on the split of air streams. In most cases, a ratio of 85:15 for primary and secondary air has proved to be optimal. An additional injection point in the recycle flow from the bleaching column to the absorption tower promotes oxidation in the intermediate stages of nitric acid production in this stream and intensifies the following absorption.

The concept can be applied with flexibility. The oxygen-fuelled capacity increase can be implemented for greater output in times of high demand; oxygen injection can simply be reduced or switched off when no additional capacity is needed.

Increasing capacity in practice

A well-known nitric acid producer operates a modern dual pressure plant in Eastern Europe and wishes to increase capacity permanently by approximately 10% to increase their fertilizer production. According to the specialists' in-depth analysis of the site, this technology will enable an additional production of 50 tpd of nitric acid (calculated as 100% nitric acid). Over 300 working days, the additional yearly yield adds up to approximately 15 000 t. The amount of ammonia needed for the reactor will also rise by 10%, and costs for oxygen, as well as process and cooling water, must also be taken into account. Discounting these costs, the company will achieve additional revenues of several €100 000/yr.

As gas applications cause mainly operational costs – investments are only needed for a gas regulation skid, lances and piping – the payback period will be short.

Conclusion

Oxygen provides an opportunity for improving process efficiency while lowering emissions or increasing plant capacity. In contrast to different methods, this can be done without big investments. The method is safe, easy to install and handle and can be applied in a flexible way. Prior to taking the final decision, a test run with mobile equipment is usually done for evaluating the optimal set-up for the individual plant. **WF**

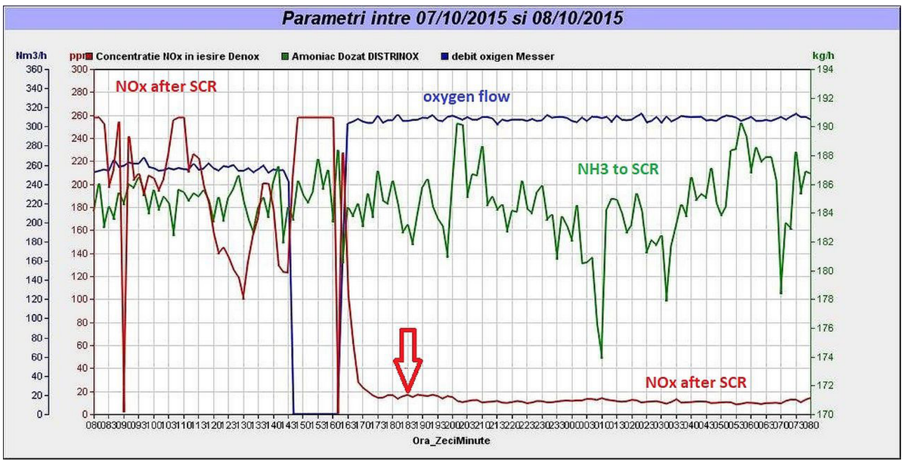

Figure 6. Plot of NO_X values, ammonia consumption and oxygen flow. The red line indicates NO_X emissions after $DeNO_X$ (limit value: 90 ppm). The green line indicates NH_3 consumption for $DeNO_X$, which was kept at approximately 185 kg/hr. The blue line indicates oxygen consumption, which started at 260 Nm^3/hr and increased to 310 Nm^3/hr. NO_X emission values decreased to 20 ppm.

References

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