Local gas – the source of hydrogen in Tarnów

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Prosimy cytować jako: CHEMIK 2012, **66,** 10, 1095-1102

Introduction

Hydrogen is one of the key intermediate products used in the production processes in Zakłady Azotowe in Tarnów-Mościce S.A. It is used as the component of the synthesis mixture for the production of ammonia, as well as in the hydrogenation in cyclohexanone production systems.

Currently hydrogen in Azoty Tarnów is produced in two systems employing the processes of vapour reforming of natural gas. Starting from 2005, the feature distinguishing the hydrogen and syngas production systems in Tarnów from other Polish installations has been the use of nitrided natural gas from local sources as the raw material.

Natural gas from local sources as the distinctive feature of Azoty Tarnów in Polish chemical industry

Before 2000 the hydrogen and ammonia production capacity at Zakłady Azotowe in Tarnów-Mościce S.A. have been adjusted to the needs of the Works. The turnpoint for the company's hydrogen balance was the shutdown, due to economic reasons, of the PVC production plant and the methane incomplete combustion system in 2001. The Works faced the challenge of operating with a continuous, structural deficit of ammonia, which originated from the deficit of syngas production capacities.

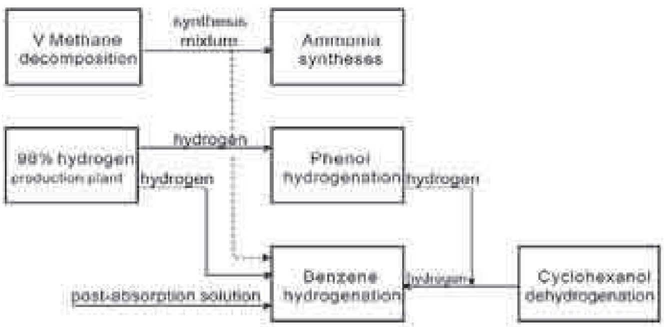

Fig. 1. Current flow chart of hydrogen production and use in Azoty Tarnów

Faced with this challenge, the company has relatively quickly gained appropriate competences allowing it to successfully purchase ammonia both on domestic and Eastern markets. The decisions concerning securing the hydrogen and ammonia stocks for Azoty Tarnów after the shutdown of the methane incomplete combustion system were prepared in the context of rapidly changing concepts for privatisation of both the company itself and the entire great chemical synthesis sector. The changing concepts affected the ammonia balance in the target configurations of the Nitrogen Works' operation and in consequence, the planned production capacities of the new hydrogen plant in Tarnów.

In the analyses of the issue two concepts of reconstructing the syngas source in Tarnów clashed: one assuming that the ammonia synthesis systems in Tarnów would be used in full capacity, the other based on procuring some of the required ammonia volumes from third-party sources. The final decisions on the production capacities of the new hydrogen plant in Tarnów have been made taking into consideration the volumes of natural gas available from local sources and assuming partial consolidation of Poland's fertiliser industry. The core of the adopted strategy of securing hydrogen and ammonia stocks for Azoty Tarnów maximisation of the share of hydrogen and syngas produced from the nitrided gas from local sources, which is cheaper than system gas, as well as supplementary deliveries of ammonia from third parties, mainly from the affiliated companies of Azoty Tarnów Capital Group, i.e. ZAK S.A. and ZCh Police S.A.

The reason of the relatively lower price of gas from local sources is its chemical composition. The level of contamination of this gas makes it impossible for using in the gas system. The necessary condition for using this material in the vapour reforming processes has been the appropriate design and adjustment of the system.

Modernisation of the existing systems for the purpose of using local deposits of natural gas

The idea of using natural gas from local sources for chemical processes in Azoty Tarnów has been discussed already in the 1990s, when skyrocketing prices of natural gas from the so-called Russian basket, as well as successful drills for gas in the vicinity of Tarnów, opened the doors for alternative solutions that would yield measurable profits. First works on implementing solutions for using nitrided gas begun in 2004 with concluding the agreement with Biprozat Design Office for drawing up the construction and technical design for the task "Use of natural gas from local sources." The primary concept assumed using nitrided gas only as fuel gas in the main system of the ammonia process line, i.e. syngas production system. It was decided to divide the task into two stages: at the first stage the furnace of the reformer of the syngas production system would be supplied with mixed gas. At the second stage, the methane-rich natural gas would be replaced with gas from local sources, following the modernisation of the furnace burners.

The design works continued until June 2004. Then the necessary modernisation works commenced, followed by system trials and process line start-up at the turn of October and November. The success of the task and the obtained results convinced the engineers to modernise further methane-rich natural gas-powered systems. Thus, at the turn of 2005 and 2006 the 98% hydrogen production plant and the dolomite-milling plant were modernised.

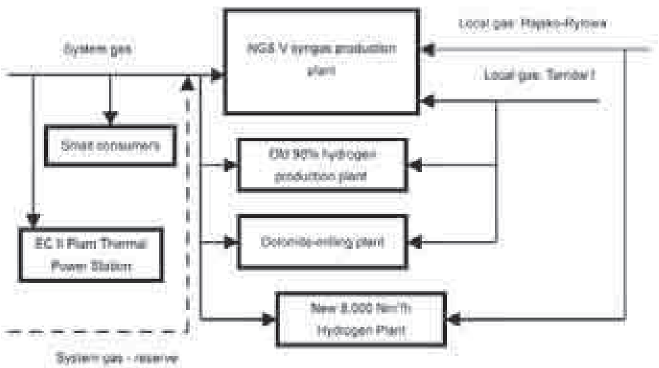

Fig. 2. Schematic diagram of supply for systems using methane-rich and local natural gas in Azoty Tarnów

The next step, which eventually allowed over 45% share of local gas in the total gas consumption balance by Azoty Tarnów, was the project of using this gas for the technological process of syngas production. This objective was accomplished in 2007 with the assistance of the Fertilizer Research Institute which prepared the technological design of this solution. The implemented technical and technological solutions yield considerable economic profits, arising directly from the cost difference between the two gas types. Furthermore, in a sense Azoty Tarnów now have a diversified structure of natural gas supply, which protected them for a number of times from temporary reductions of gas supply from the East. Also, Azoty Tarnów have become the main consumer of significant gas volumes with insufficient quality for the gas system for individual consumers, supplied by PGNiG S.A.

Based on those experiences and taking the opportunity created by new wells and successful prospecting of gas deposits in Tarnów region, the company Zakłady Azotowe w Tarnowie-Mościcach S.A. has been able to launch new investment tasks, such as the construction of the new hydrogen production plant, thanks to which the share of nitrided gas used by the nitrogen works currently amounts to more than half of the total gas consumption in the total methane consumption balance in the Works.

Construction of the new hydrogen production plant

Process technology as an example of a system prepared for using alternative sources of supply

The hydrogen production process can be divided into 4 process units:

- Sulphate removal from natural gas
- Conversion of natural gas (methane) with vapour
- High-temperature CO conversion
- Hydrogen purification – pressure swing adsorption (PSA).

Sulphate removal from natural gas

The objective of the sulphate removal process is to remove sulphate compounds from natural gas, including: hydrogen sulphide, carbon oxysulphite, sulphides, disulphides, mercaptans, whose maximum concentration must not exceed 40 ppm. Those compounds are very strong poisons, especially of vapour reforming catalysts. It is recommended that natural gas, processed in modern reformers operating under heavy thermal loads and high pressure, does not contain more than 0.02 ppm of sulphur.

Low sulphur concentration can be achieved by the classic high-temperature hydrodesulphurisation (HDS) process in which the organic sulphur compounds are first hydrogenated on a NiMo catalyst and the resulting hydrogen sulphide is then absorbed on active zinc oxide. Sulphur compounds are hydrogenated at 350- 400°C, 2- 4 MPa, 100 - 3,000 h^{-1} and hydrogen concentration of 2-5%.

Conversion of CH_4 and CO with vapour

The process of CH_4 conversion with vapour occurs at approx. 740 - 850°C on a Nickel catalyst in a decomposition furnace, while the conversion of CO occurs at 320- 420°C on a Fe-Cr-Cu catalyst in a high-temperature converter. The following molecular entities may appear in the reaction product: CH_4, H_2O, H_2, CO, CO_2, and C.

To the processes above the following stoichiometric model can be applied:

$$CH_4 + H_2O = CO + 3H_2 - 49.2\ \text{kcal}$$

$$CO + H_2O = CO_2 + H_2 + 10.1\ \text{kcal}$$

$$CH_4 = C + 2H_2 + 19.9\ \text{kcal}$$

$$2CO = 2C + O_2$$

Methane conversion is an endothermic reaction. The heat required for the reaction to take place is supplied by diaphragm heating of catalytic pipes with residual gas and local natural gas, according to the following reaction:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + Q$$

In order to reduce CH_4 concentration in the converted gas, a large surplus of vapour in the substrates should be used and the conversion process should be run at high temperature. The values of those parameters are determined according to the process economics and apparatus fastness. Conversion of methane with vapour increases the product volume with respect to the volume of substrates. Thus, pressure inhibits the course of the reaction.

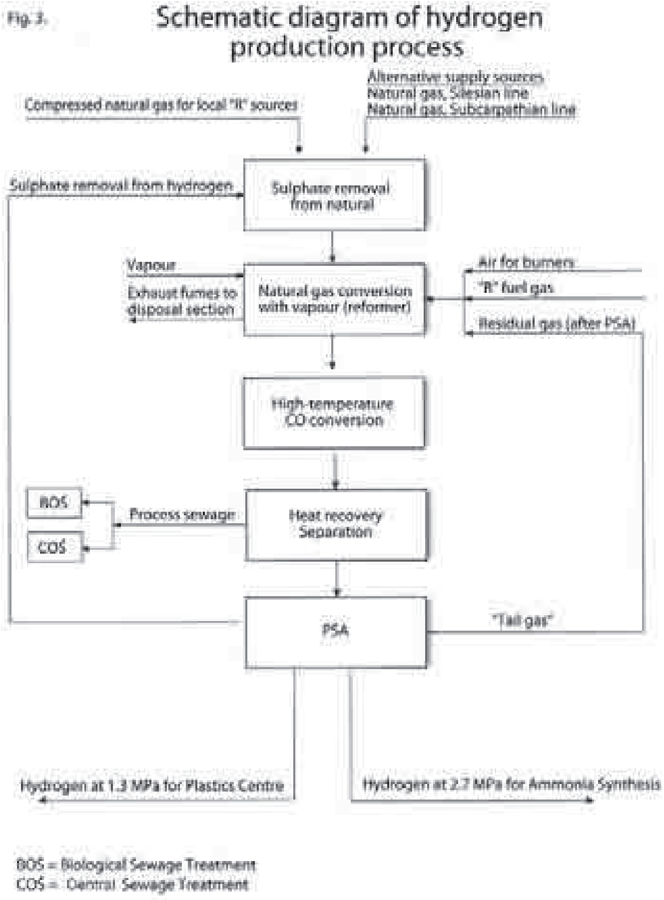

Fig. 3. Schematic diagram of hydrogen production process

The 8,000 Nm^3/h Hydrogen Production Plant has been designed to operate in three supply options:

- Option I – hydrogen production supplied with nitrided natural gas from Rajsko-Rylowa deposit
- Option II – hydrogen production supplied with system (methane-rich) natural gas
- Option II – purification of syngas supplied from the VRM system in the PSA unit..

The main raw material for the Hydrogen Production Plant is the local natural gas from Rajsko-Rylowa deposit.

The process natural gas in appropriate volume, at a specific pressure and temperature, is entered into the supply gas heater where it is heated by the process gas heat. The heated process gas is then directed to the hydrodesulphurisation unit, comprising two reactors – one filled with NiMo catalyst which catalyses the hydrogenation process of organic sulphur compounds to H_2S, and one filled with ZnO sorbent. The reaction of hydrogen sulphide with zinc oxide produces zinc sulphide which is absorbed in the catalyst bed. The hydrogen for the hydrogenation process is taken from the collector of hydrogen after PSA and added to the natural gas directed to the compressor supplying the system.

Desulphurised natural gas is directed to the mixer. Also, saturated vapour is supplied to the mixer. The mixture of vapour and natural gas in proper ratio and at a proper temperature is heated in the superheater and entered into the catalytic pipes of the reformer. The reformer has the structure of a roller. 48 catalytic pipes filled with nickel catalyst are located on its circumference. The furnace is heated from below by three centric burners. The main fuel for the burners is the residual gas from the PSA unit and nitrided natural gas. The air for the combustion process is sucked in from the ambient by the blower and heated to the required temperature in the exchangers.

The exhaust gases leaving the furnace are entered into the heat recycling section, where they are used to heat up the raw materials.

The process gas leaving the reformer is collected in the collector pipe from which it is directed to specific units using heat to produce vapour. Vapour is produced in three boilers supplied with demineralised water, chemically pre-treated by adding appropriate agents for treating boiler water to protect the boiler systems from corrosion. The process gas, after passing heat exchangers at appropriate temperature, is directed to the high-temperature CO conversion reactor. The reactor is filled with Fe-Cr catalyst. The exothermic reaction of CO conversion reduces the carbon oxide concentration and increases gas temperature. The heat of the converted gas is used in subsequent exchangers until the gas temperature reaches the level appropriate for entering the gas into the final purification system in the PSA unit.

The PSA (pressure swing adsorption) hydrogen purification unit employs the adsorption process to produce highly purified hydrogen. The impure hydrogen is purified by adsorption during the flow through the adsorber which is filled by the adsorbent. Adsorbent is a granular material capturing (adsorbing) impurities from raw hydrogen. The hydrogen purification system uses aluminium oxide, activated carbon and molecular sieve for selective adsorption of all impurities in hydrogen-rich gas.

The system comprises five identical adsorbers, each containing three beds. The first bed (lower) contains aluminium oxide which absorbs water; the second bed (middle) contains activated carbon which absorbs carbon dioxide and methane; the third bed (upper) contains a molecular sieve for eliminating carbon oxide and improving gas purity.

Pure hydrogen after the PSA system is available at two pressure levels. The low-pressure stream is available at approx. 1.3 MPa for the needs of the caprolactam process line, while the high-pressure stream (at approx. 2.70 MPa) is used in the ammonia process line. During the gas purification process, the stage of pressure reduction and blowdown of adsorbers produces gas which is then stored in the residual gas tank. This gas is the main fuel for the reformer.

The Hydrogen Production Plant has also been designed to utilise the hydrogen-rich syngas from V Methane Decomposition Plant (V MDP) for supplying the PSA unit and producing pure hydrogen.

Investment implementation – stages of construction

Under the Decision of the Management Board of the Company, in 2010 the design works of the new hydrogen production plant were commenced. The technological solutions of the plant were aimed at obtaining specific volumes of pure product on the basis of alternative natural gas supply sources where the dedicated gas was mainly the nitrided gas supplied to the Nitrogen Works from local deposits in the vicinity of Tarnów.

The objective of the investment project was to construct a hydrogen production plant with the production capacity of 8,000 Nm^3/h of 100% H_2, based on the Technical Design prepared by ZAT-BIPROZAT Design Office. The produced hydrogen is used in Phenol Hydrogenation System and Benzol Hydrogenation System in the Plastics Centre, and in the Ammonia Synthesis System in the Fertiliser Centre.

Photo 1. Hydrogen Production Plant. Capacity: 8,000 Nm^3/h of H_2

Photo 2. Hydrogen Production Plant reformer

The Hydrogen Production Plant was supplied by Hydro-Chem, affiliated company of Selas Fluid Processing Corporation – Linde Engineering Division USA. The Plant is located on the premises of the Fertiliser Centre at Azoty Tarnów, near the existing Natural Gas Conversion V (NGC V) system. For the needs of the Hydrogen Production Plant a natural gas compressor by the French company Howden was constructed. The compressor was built in the existing F-67 Compressor Hall, on the adapted foundation of the previous compressor by Škoda. Under the same task, the technological connections of utilities required for the operation of the plant were made, including the natural gas pipeline to supply gas from Rajsko-Rylowa deposits, with a pressure reduction/measuring unit, and a hydrogen pipeline to the Plastics Centre system.

The investment task was divided into four stages:

- The works of stage I included adjusting the V Methane Decomposition Plant (V MDP) to work with the new hydrogen production plant as the additional source of hydrogen for the needs of ammonia synthesis
- The works of stage II included making external connections to the new system and the construction of the natural gas pressure reduction/measurement unit
- The works of stage III included the construction of the new gas compressor to supply the hydrogen production plant
- Stage IV included the construction of the hydrogen production plant.

The technical documentation was drawn up by ZAT-BIPROZAT Design Office. The construction and assembly works were carried out by: ZWRI, ELZAT, AUTOMATYKA, INSAP, WIEZAT and JRCh.

Photo 3. PSA unit of the Hydrogen Production Plant

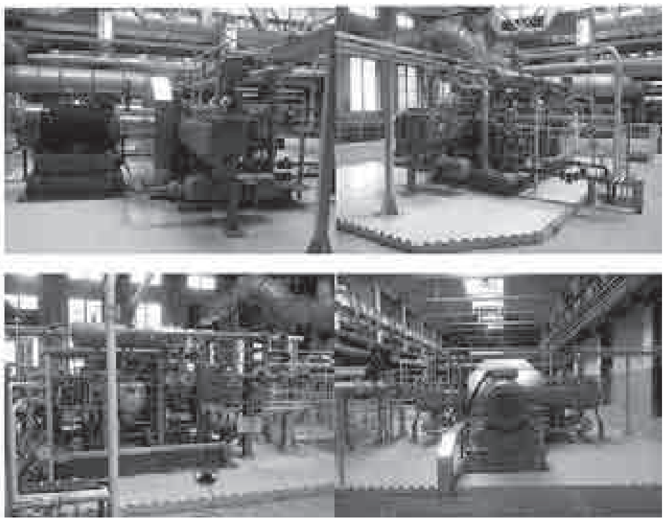

Photo 4. Methane compressor by Howden

In April this year the Technical Safety Committee approved the system for system trials and process line start-up. In May and June this year the mechanical, electric and measurement, and technological trials were carried out to verify the correctness of the assembly and construction of the system. As of the beginning of July the system was prepared for trial runs for the final acceptance and the completion of the investment task.

Summary

Natural gas from local sources used by Azoty Tarnów is undoubtedly the distinguishing characteristics of the company compared to other chemical industry plants in Poland. It has been confirmed that properly carried out modernisations and strategies implemented by the Nitrogen Works deliver the expected results. Implementing the idea of using natural gas from Tarnów's local deposits allows for building the competitive advantage in terms of the production costs of hydrogen and ammonia. Furthermore, this improves Azoty Tarnów's position in the event of potential problems of supply of natural gas from the East by reducing the volume of system gas acquired from third parties as compared to other plants in the petrochemical industry.

Artur KOPEĆ - M.Sc., is a graduate of the Faculty of Chemistry at the Wrocław University of Technology (2002), a manager school organized by the Rudzka Agencja Rozwoju and Training Partners (2008), as well of postgraduate studies in the field of entrepreneurship run by the Cracow University of Economics and the Cracow School of Business (2008). In 2010, he finished a course for members of supervisory boards of State Treasury companies. He has worked at Zakłady Azotowe in Tarnów-Mościce S.A. since 2003. As the start-up manager, he actively participated in starting up new installations in Tarnów, such as mechanical granulation of fertilisers and hydrogen production installations. He is co-author of a patent on the technology of producing ammonium sulphate nitrate. Currently, he is the head of the Department of Ammonia and a member of the board of the Azoty Tarnów Capital Group.

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Wiesław KOZIOŁ – M.Sc., is a graduate of Faculty of Chemistry at Krakow University of Technology (Politechnika Krakowska). He also completed post graduate studies in Department of Management in the Economy at Warsaw School of Economics (Szkoła Główna Handlowa w Warszawie).

His professional career started in Zakłady Azotowe w Tarnowie Mościcach S.A. in 1985. Until 1994 he worked in Engineering Department, where he started as a process engineer assistant and gradually promoted to a senior process engineer. In the said period he was involved mainly in the projects of Polysilicon Plant, POM Plant and PA-6 Plant. In 1994 he started working in Development Department holding a number of positions, currently the position of Department Director. Since then he has worked on the strategy of Company's development, development plans and the most important investment projects such as the revamping of PA-6 Plant, Concentrated Nitric Acid Plant, Engineering Plastics Compounding Plant, Fertilizers Mechanical Granulation Plant, the bottlenecking of Caprolactam Plant as well as Hydrogen Plant.

He is co-author of several patents.

Current position: Director of Corporate Department of Strategy and Development.