CYCLOPOL and CYCLOPOL-bis, technology for cyclohexanone in India

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Cyclohexanone is the main semi-finished product used to produce caprolactam - the raw material for producing polyamide fibres and materials (nylon). The installed global production capacities of caprolactam are estimated to achieve ca. 5.2 million t/year. These capacities are used to a degree at which the real production is obtained at the level of ca. 4.5 million t/year (data for 2012). 80% of the global production of caprolactam and simultaneously of cyclohexanone is based on the technology using benzene of petrochemical or carbochemical origin as the raw material. Zakłady Azotowe in Tarnów-Mościce also uses benzene - the raw material for the CYCLOPOL process - to produce caprolactam.

CYCLOPOL process

The process in Tarnów based on hydrogenating benzene to cyclohexane, then oxidising cyclohexane with atmospheric oxygen to cyclohexanol and cyclohexanone, dehydrogenating cyclohexanol to cyclohexanone and purifying the latter one was developed in the 1960s as the result of very close collaboration between Zakłady Azotowe in Tarnów-Mościce and the Institute of General Chemistry, currently the Industrial Chemistry Research Institute in Warsaw. At first, the process was implemented into the industrial practice in Tarnów on a pilot plant scale achieving at the end of the 1960s the production capacity of ca. 2000 t/year. Then, in 1974, it was implemented on a technical scale in the installation with the production capacity of 25 thousand tons of cyclohexanone per year.

Later, in 1976, the installation of cyclohexanone with the production capacity of 50 thousand t/yr was put to use in the Nitrogen Plant in Puławy as part of the Caprolactam Plant which was being built at that time. After all the start-ups, the process of producing cyclohexanone from benzene, known commonly under the registered name CYCLOPOL®, began its export career.

The technology for CYCLOPOL turned out to be one of the safest and economically the most attractive methods which are commonly applied for producing cyclohexanone from benzene, which affected the number of contracts on selling the licence and *know-how* to such countries as Slovakia (1977 and 2000), Spain (1981 and 1997), Taiwan (1987), Belarus (1986 and 1994), Russia (1986), Italy (1989), South Korea (1990), and India (1986, 1988, 1997 and 2009).

As it has been previously mentioned, the process of cyclohexanone production – CYCLOPOL – consists of the following stages:

- hydrogenation of benzene to cyclohexane
- oxidation of cyclohexane to the mixture of cyclohexanol and cyclohexanone
- distillation of the cyclohexanol-cyclohexanone mixture
- dehydrogenation of cyclohexanol to cyclohexanone.

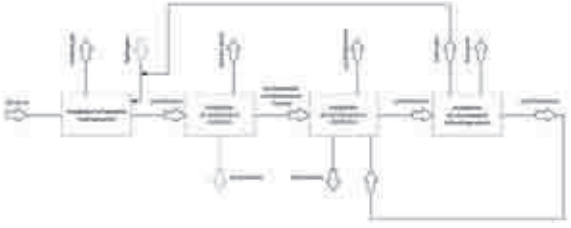

Fig. 1. Block diagram of installation for producing cyclohexanone from benzene

The process of benzene hydrogenation to cyclohexane is run in the counter-current two-stage system under the pressure of 0.15 -1.0 MPa.

Hydrogen or its mixture with nitrogen, e.g. synthesis gas containing ca. 75% of hydrogen and 25% of nitrogen, is used as gas for hydrogenation. The process is conducted on a stable catalytic bed with nickel present on Al_2O_3 as a catalyst.

Oxidation of cyclohexane to the mixture of cyclohexanol and cyclohexanone is the most important stage and simultaneously it has the deciding impact on the effectiveness of the whole production process (selectivity). Process fluids and parameters applied in the process may create fire hazard and explosive conditions; however, considerable knowledge of the process and the application of suitable, verified design solutions and safety measures entirely eliminate such potential hazard.

This process consists of the following stages and operations:

- oxidation of cyclohexane (with simultaneous decomposition of cyclohexyl hydroperoxides) to the mixture of cyclohexanol and cyclohexanone
- non-diaphragm cooling of post-reaction gases combined with the removal of formed water and the purification of these gases to allow their emission to the atmosphere
- distillation of unreacted cyclohexane
- acidolysis of cyclohexyl esters
- alkaline hydrolysis
- dehydration of the cyclohexanol-cyclohexanone mixture.

Pic. 1. Cyclohexane oxidation installation in Azoty Tarnów

The process of cyclohexane oxidation in the liquid phase with the air or with the air enriched with oxygen is run at a temperature from 155°C to 165°C, under a pressure from 0.8 MPa to 1.05 MPa,

in a multi-sectional bubble reactor in the presence of catalyst mixture (cobalt catalyst as the catalyst for cyclohexane oxidation and chromium catalyst for hydroperoxide decomposition). The total concentration of the catalysts is lower than 3 ppm. The post-reaction gases are passed to the installation of catalytic combustion of gases through the scrubber, wherein the non-diaphragm cooling of gases takes place in combination with the condensation of cyclohexane and water formed in the process and its removal, and through the absorption column, wherein cyclohexane residues are eluted from these gases.

The crude product containing ca. 0.6% wt. of hydroperoxides is introduced from the reactor for cyclohexane oxidation into two reactors for decomposition of cyclohexyl hydroperoxides which are working simultaneously. The process of hydroperoxide decomposition is conducted at a temperature from 155°C to 165°C and under a pressure from 0.7 MPa to 1.0 MPa, thus practically under the same conditions as the oxidation reaction, which does not provide high selectivity. The oxidation product from the reactors for decomposition of hydroperoxides is passed to an expander – an extractor wherein it is decompressed to the pressure of 0.02 MPa, rinsed with water to leach acids, and passed to the distillation column, wherein unreacted cyclohexane is separated from the by-products of its oxidation under the atmospheric pressure and at a temperature from 116°C to 123°C.

Liquid from the bottom part of the distillation column is fed to the hydrolyser, wherein cyclohexyl esters are subjected to hydrolysis, the so called acidolysis, at a temperature from 155°C to 170°C and under a pressure from 0.5 MPa to 0.7 MPa. The solution of acids, mainly dicarboxylic acids, obtained by washing the crude product from the expander – extractor, is also fed to the hydrolyser. Liquid from the bottom part of the hydrolyser, which is a mixture of acids and esters, so called MEK, after its dehydration can be combusted as an alternative fuel or used as the raw material for other types of synthesis.

Vapours from the hydrolyser are introduced into the saponification column, wherein the remaining part of cyclohexyl esters are subjected to alkaline hydrolysis using 45% solution of soda lye under a pressure from 0.4 MPa to 0.6 MPa and acids are neutralised. Liquid from the bottom part of the saponification column is passed to the reactor, wherein sodium salts of organic acids are decomposed using sulphuric acid and the mixture of monocarboxylic acids is isolated and, after being mixed with MEK, is aimed for the combustion or sale as the raw material for other types of synthesis. The separated solution of sodium sulphate is the process waste. The distillate from the saponification column, after cooling and water separation, is passed to the column of final dehydration from which the obtained depleted liquid is used as the main product of cyclohexane oxidation.

The product of cyclohexane oxidation, the so called cyclohexanol-cyclohexanone mixture containing also ca. 2 - 3% wt. of C_3 - C_6 alcohols, is subjected to the distillation process aimed for separating main constituents and their purification with isolating the main product – cyclohexanone. The process is conducted in a multiple column arrangement. In the preliminary column, the so called alcohol column, alcohol fraction is stripped from the oxidation product; this fraction is aimed for the combustion or sale. The purified low boiling oxidation product is passed to the cyclohexanone stripping column, from where the distillate is drained to cyclohexanone fractionating column where high purity cyclohexanone is obtained and used as the raw material for caprolactam synthesis, and its residue – cyclohexanol, also after the rectification, is passed to the installation of dehydrogenation. The depleted liquid is the process waste utilised by combustion.

Dehydrogenation of cyclohexanol to cyclohexanone is an endothermic catalytic process conducted in the vapour phase. Cyclohexanol vapours overheated to the temperature of ca. 300°C are passed to the stable catalytic bed of the dehydrogenation reactor. Fe-Zn system is used as the catalyst which is additionally chemically prepared in order to develop the active surface. Heat for endothermic dehydrogenation reaction is delivered diaphragmatically by means of hot flue gases (with a temperature of 450°C - 500°C) from methane combustion which are circulating continuously. The process of cyclohexanol dehydrogenation to cyclohexanone (with 50-70% conversion) with hydrogen release takes place on the catalyst at a temperature from 330°C to 400°C and under the pressure of 0.05 MPa.

The condensed product of dehydrogenation, so called crude cyclohexanone, is passed to the distillation and rectification unit. Hydrogen purified from the residues of organic compounds, mainly from cyclohexene and cyclohexanone, after its compression, is delivered to the installation of benzene hydrogenation.

Figure 2 illustrates the diagram of the CYCLOPOL process.

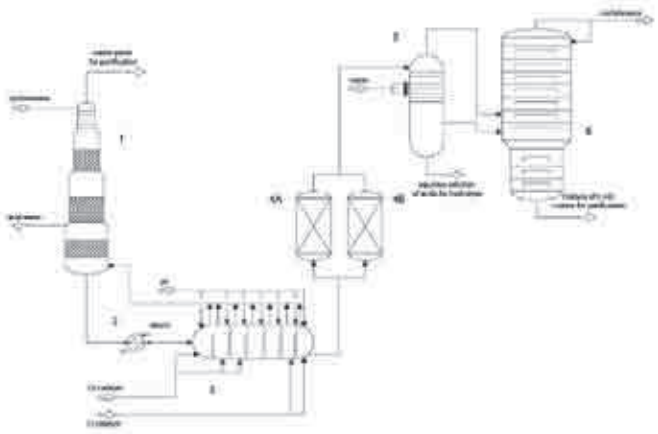

Fig. 2. Diagram of cyclohexane oxidation reaction unit based on the CYCLOPOL process: 1 – scrubber, 2 – preheater, 3 - reactor, 4A & 4B – reactors for hydroperoxide decomposition, 5 – expander – extractor, 6 – distillation column

CYCLOPOL-bis process

As the result of modernising and intensifying the installation of obtaining cyclohexanone from benzene, its safety quality was improved as well as it became more economically attractive by reducing the consumption of energy (e.g. by using a two-stage distillation process of unreacted cyclohexane). Its environmental noxiousness was significantly reduced (catalytic purification of post-reaction gases combined with energy recovery). The implementation of the modernised process of cyclohexane oxidation on an industrial scale in Tarnów in 2003 was the landmark in this technology. As a result, the selectivity of cyclohexane oxidation (the majority of by-products are formed at this stage of the process) was considerably improved in comparison to the CYCLOPOL process as well as the quality of anhydrous mixture (cyclohexanol-cyclohexanone mixture leaving the installation of oxidation) was significantly improved. The significant changes were introduced into cyclohexane oxidation unit while the main characteristic features of the CYCLOPOL process were kept, that is, the separation of unreacted cyclohexane under acidic conditions and the basic shape of the oxidation reactor. The implementation of the modernised oxidation process (it should be emphasised that the immediate transformation from the scale of laboratory research to the industrial scale was successful, which speaks for vast knowledge of the process and confirms high competencies of engineers) was the result of the collaboration among the specialists from Zakłady Azotowe in Tarnów-Mościce, the Institute of Organic Chemistry of the Polish Academy of Sciences and the Faculty of Chemical and Process Engineering at the Warsaw University of Technology which started on the initiative of the Nitrogen Plant in 1993. The collaboration was realised with the participation of the specialists from the Design Office at the Nitrogen Plant (BIPROZAT Tarnów), mainly in the field of engineering and designing. Research and development tasks realised in the first period as part of the targeted project co-financed by the Committee for Scientific Research (KBN – Komitet Badań Naukowych) included the

following areas: engineering of oxidation reactions (hydrodynamics, mass exchange, macrokinetics), mechanism of cyclohexane oxidation, catalysis and new process solutions. Owing to these works, deep knowledge of oxidation process was acquired and the mathematical model for the key stage of the process – the process of cyclohexane oxidation – was developed. It became a useful tool for modernising the process of cyclohexane oxidation.

The interdisciplinary research and development activities in combination with the operations, investigations and tests conducted on the installation in Tarnów contributed to the further development and significant improvement in the CYCLOPOL technology.

The essence of change consisted in dividing the process into two stages by separating the process of cyclohexyl hydroperoxide synthesis from the process of their selective decomposition and choosing the optimum parameters of aeration, pressure and temperature for these separated, different phases of the oxidation process. At the first stage, covering cyclohexane oxidation at high temperature, under the increased pressure and in the presence of trace amounts of oxidation catalyst, the highest possible amount of hydroperoxides is formed. The process takes place in a multi-chamber bubble reactor for oxidation.

The second stage includes the catalytic decomposition of hydroperoxides at low temperature and under the low pressure, which ensures a high selectivity of this process. This stage of the process is conducted in an additional multi-chamber flow reactor (unlike the CYCLOPOL process in which hydroperoxides are mainly decomposed in the oxidation reactor and the remaining part is decomposed in two reactors for decomposition having far poorer parameters regarding the satisfactory selectivity).

Also the aqueous solution of acids obtained by washing the oxidation product prior to its hydrolysis was pre-treated.

The modernised technology was named CYCLOPOL-bis. Its implementation resulted in the significant reduction of raw material consumption indices and at the same the improved quality of obtained cyclohexanol-cyclohexanone mixture.

The process of cyclohexane oxidation based on the CYCLOPOL-bis technology is conducted in the liquid phase using the air under the pressure of ca. 0.95 MPa and at a temperature of ca. 165°C in the multi-sectional bubble column reactor in the presence of an almost trace amount of cobalt catalyst (catalyst concentration 0.05 ÷ 0.1 ppm in the reaction liquid). Heat of this exothermic reaction is recovered by cyclohexane vaporisation. Circulating cyclohexane with a temperature of ca. 60 - 70°C is introduced to the last sections of the reactor in order to prevent hydroperoxides from decomposition in the oxidation reactor. The post-reaction gases from the reactor are passed through the scrubber and the absorption column to the installation of catalytic gas combustion.

The product from the reactor for cyclohexane oxidation containing as the main components of the process, apart from cyclohexanol and cyclohexanone, ca. 2% wt. of cyclohexyl hydroperoxides, is introduced into the cyclohexanone stripping column after its decompression to the pressure of 0.02 MPa and washing with water in the expander - extractor in order to leach acids. In this column, it is subjected to pre-concentration achieving the concentration of hydroperoxides at the level of 4% wt.; then it is fed to the reactor for hydroperoxide decomposition. The selective decomposition of formed hydroperoxides takes place in the presence of catalyst mixture in the reactor at a temperature of ca. 85°C and under the pressure close to the atmospheric pressure. The catalyst of hydroperoxide decomposition consists mainly of chromium catalyst and a smaller amount of cobalt catalyst which are fed to the reactor as the solutions of chromium 2-ethylcaproate or cobalt 2-ethylcaproate in cyclohexane or cyclohexanone. Using exclusively cobalt catalyst is also possible. However, it requires a certain modification of the process parameters with practically no change in the process selectivity. The total concentration of catalysts in the reactor required to provide, along with adequately selected residence time and temperature, an almost complete decomposition of hydroperoxides is ca. 3 - 4 ppm.

The product leaving the reactor for decomposition is passed to the subsequent extractor, wherein acid residues are leached from it and their aqueous solution is delivered to the unit of hydrolysis. After washing with water, the product is passed to the distillation column wherein unreacted cyclohexane is separated from the products of its oxidation under the atmospheric pressure and at a temperature of ca. 115°C. Liquid from the bottom part of the distillation column is fed to the hydrolyser wherein cyclohexyl esters are subjected to acidolysis at a temperature from 155°C to 170°C and under a pressure of 0.5 – 0.7 MPa, similarly to the CYCLOPOL process.

The aqueous solution of acids, mainly dicarboxylic acids, obtained by washing the product from the oxidation reactor is also fed to the hydrolyser after its blowing with superheated steam in the stripping column, wherein cyclohexanol and cyclohexanone are stripped and the remaining low amounts of cyclohexyl hydroperoxides (not decomposed in the decomposition reactor) are decomposed to cyclohexanol and cyclohexanone under the conditions with the low content of desirable products of oxidation. It is an additional improvement of the process selectivity in comparison to the standard method based on CYCLOPOL. The distillate from this column is used as liquid for leaching acid residues from the oxidation product obtained from the reactor for cyclohexyl hydroperoxide decomposition. The concentration of acid solutions with washing the product obtained from the oxidation reactor is a well known method used in Tarnów which can replace the stripping column and achieve practically the same result regarding the process selectivity. Then, such a solution can be used as the commercial product - the valuable raw material for other processes of chemical synthesis.

Vapours from the hydrolyser are drained to the saponification column like in the CYCLOPOL process. The distillate from the saponification column is drained to the column of final dehydration. Liquid from the bottom part of the dehydration column is the main product of cyclohexane oxidation. The course of other process operations is the same as in the CYCLOPOL process.

The production capacity of the installation operating in Tarnów based on the CYCLOPOL-bis technology is 32.6 thousand tons of c-none per year. The process is continuously being improved to minimise the unit costs of producing cyclohexanone, to improve its quality and to reduce the environmental noxiousness. Regarding the selectivity and quality of cyclohexanone, it has achieved the level of the most successful processes of the global companies. The modernised solutions for the CYCLOPOL-bis process are protected by patent. Figure 3 illustrates the diagram of the modernised reaction unit based on CYCLOPOL-bis.

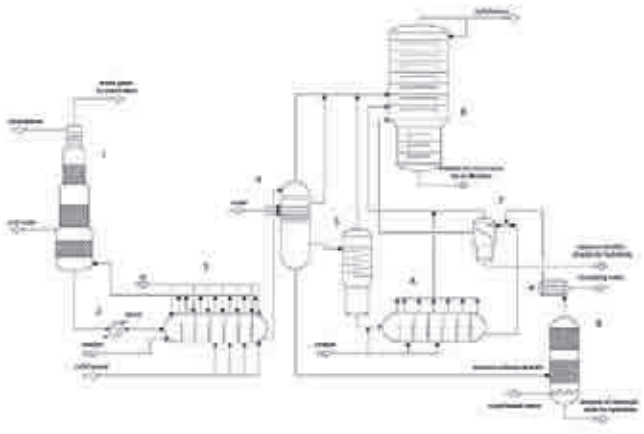

Fig. 3. Diagram of cyclohexane oxidation reaction unit based on CYCLOPOL-bis process: 1 – scrubber; 2 – preheater; 3 – reactor; 4 – expander extractor; 5 – distillation column; 6 – reactor for hydroperoxide decomposition; 7 – separator; 8 – distillation column of cyclohexane; 9 – stripping column

Technology for cyclohexanone in India

As it has been mentioned at the beginning, after the successful implementation of the CYCLOPOL process in Zakłady Azotowe in Tarnów and Puławy, its international "career" started. The installation in the company PROQUIMED in Castellon della Plana, Spain, operating under the licence of the Swiss company INVENTA was modernised on the basis of some elements from this process. It was the second contract in the history on making the CYCLOPOL technology available to a foreign partner (the first contract had been signed on making the whole technology available to the company CHEMKO in Strážske, Slovakia). The modernisation was based on replacing the whole interior of the cyclohexane oxidation reactor and performing the new one using the original concepts introduced in the reactors in Tarnów and Puławy as well as on resigning from the circulation of the post-reaction gases used to dilute the air introduced into the reaction system.

Introducing these innovations improved the process selectivity measured in the reduced consumption of the main raw material – benzene – for producing cyclohexanone and stabilised the operation of the installation as a consequence of avoiding the formation of deposits in the reactor for cyclohexane oxidation. The formation of deposits seriously reduces safety of the process and moreover it forces the stoppage of the installation operation for the period of their mechanical removal. As part of the contract, the Polish party gave a year's warranty on the operation of the reaction system without the need to stop it in order to remove deposits.

The success in implementing the elements of the CYCLOPOL process in Spain resulting in the significant modernisation of the competitive technology (INVENTA) opened the door to India. There, the installation of cyclohexane oxidation identical to the one in PROQUIMED was operating under the licence from INVENTA in the company GUJARAT STATE FERTILIZERS COMPANY LIMITED which was then transformed and changed its name into GUJARAT STATE FERTILIZERS & CHEMICALS Ltd.

GUJARAT STATE FERTILIZERS & CHEMICALS Ltd (GSFC) is currently one of the largest chemical complexes in India located in the city Fertilizernagar, Vadodara (Baroda) district, GUJARAT state. It was established on 15 February 1962 as a fertiliser company fitting in the Hindu programme of green revolution - the programme of agriculture development and food consumption. In the years 1974÷1982, at the so called Stage III of the company development, the fertiliser complex was expanded by the segment of organic chemistry through building and putting to use the installation of caprolactam, polyamide 6, methyl ethyl ketone oxime and melamine I. In the years 1989-2000, during Stage V of the company development, the second installation of caprolactam and melamine II started up. Nowadays, GSFC is producing: caprolactam – ca. 80 tt/yr, fertilisers (urea, NPK, ammonium sulphate, APS, DAP) – ca. 1.6 mt/yr, melamine (the only manufacturer in India) – ca. 15 tt/yr, liquid fertilisers, polyamide-6 – ca. 10 tt/yr, methyl ethyl ketone oxime – ca. 3 tt/yr, biofertilisers (the first manufacturer in India). According to the data from the Annual Report for the period from 04.2010 to 03.2010, GSFC sales revenues were – Rs. 4755 crores (ca. 850 million USD), EBIDTA – Rs. 1273 crores (ca. 230 million USD), net profit (PAT) – Rs. 749 crores (ca. 130 million USD). The company employs 4180 people. The development project for the coming years (Stage VII) includes the construction of an integrated fertiliser and petrochemical complex in the city Dahej which will include: the installation of urea with the production capacity of 1 mt/yr, the installation of caprolactam with the production capacity of ca. 100 tt/yr and the installation of melamine with the production capacity of 40 tt/yr.

This is the history and the present day of the company. However, let us come back to the 1980s. At that time, GSFC Board of Directors decided to introduce the scope of changes into their installation (operating from 1974 in the line cyclohexanone – caprolactam – polyamide 6) that was analogous to the changes in PROQUIMED. Additionally, its production capacity of 20 tt/yr was to be increased as part of the modernisation.

The Swiss company CORA Engineering in Chur was helpful in contacting and then concluding a contract (in 1986) on releasing the licence, *know-how* and technical assistance. This company was established by the specialists previously working in INVENTA who knew the Hindu world and GSFC environment well (they took part in designing, building and putting to use the first installation of caprolactam) and it was a certain continuation of INVENTA.

The contract realisation, with the involvement of the technology co-creator - the Industrial Chemistry Research Institute in Warsaw - ended in the real success.

In the second half of the 1980s, the Hindus planned to build a new Caprolactam Production Plant with the capacity of 50 tt/yr. After the success achieved during the modernisation of cyclohexane oxidation installation operating in GSFC, the company decided to perform the installation for producing cyclohexanone on the basis of the Polish technology (which at that time was co-owned by Zakłady Azotowe in Tarnów, Zakłady Azotowe „Puławy" and the Industrial Chemistry Research Institute in Warsaw).

Pic. 2. Installation of cyclohexanone in Baroda (a part)

The Polish party was again cooperating with the company CORA (which was later transformed and operating under the name ENCO). The production of caprolactam from cyclohexanone was based on the BASF technology. The whole project, known in GSFC under the common name Capro Expansion Project (CEP), was performed by the contractor UHDE GmbH – Dortmund and the subcontractor – ENCO. On 23 February 1988, GSFC signed the contract with UHDE GmbH on building and putting to use the production plant of caprolactam from benzene.

However, POLSERVICE, representing the business of the Polish party and ENCO, signed a contract on cooperation which was the base for granting the licence on using the CYCLOPOL process and *know-how* transfer. As part of the concluded contract, the Polish party also prepared the technical documentation and delivered the most important equipment for the installation. The Polish specialists were also offering all forms of the technical service as provided in the contract.

From the moment of signing the contract and its coming into force, began an intensive period of preparing, adjusting and accepting the design documentation, numerous meetings and discussions with the investor, contractor and subcontractor. GSFC started to realise

the investment. During the assembly, the groups of Polish specialists, designers, process engineers and the industry specialists were repeatedly visiting the site in order to supervise the progress of works and make essential adjustments on the spot.

The training courses on theory and practice were conducted for GSFC technicians in Tarnów, Puławy and IChP-Warszawa (the Industrial Chemistry Research Institute in Warsaw).

The new cyclohexanone production plant with the capacity of 45.25 tt/yr was built as the second one since 1984, that is, since the start-up of the production plant in CHEMKO in Strážske, Slovakia which had the capacity of 80 tt/yr and was constructed on the basis of the Polish technology. The process and the installation offered for GSFC were considerably modernised in comparison to the installations operating in Tarnów, Puławy and Strážske, particularly in the field of engineering solutions that resulted in reduced consumption of the energy, the incineration of alkaline waste in combination with the recycle of formed soda to neutralise (saponification) volatile acid products of cyclohexane oxidation (which reduced the consumption of soda lye) and in improved quality of cyclohexanone. The experience gained during the operation of continuously improved process in Tarnów, Puławy and Strážske was used for that purpose.

Also the experience and solutions were applied which had been adopted in some installations previously designed for foreign customers (from Taiwan and South Korea) as the subject matter of the contract and never realised for the reasons beyond the control of the licensor. Some of the adopted solutions were the prototypes, the others were considerably modified in comparison to the operating installations. The new engineering and construction solutions were used as well. The assembly of the installation ended with the so called pre-commissioning supervised by the licensor's specialists; then the installation start-up began from the so called complex tests, that is, from conducting the process on equivalent fluids (water, nitrogen).

After the successfully completed complex tests, the particular technological units of cyclohexanone installation were gradually set working already using the process fluids. The start-up was supervised by a group of 20 people – each including five specialists from Zakłady Azotowe in Tarnów, the Design Office and ENCO, three specialists from IChP and two specialists from the Nitrogen Plant in Puławy. The process parameters were stabilised and the construction and assembly defects were repaired while the technological operation was running.

It was also a period of the intensive training of the personnel in practical operation of the installation and of adapting for the purpose of the cooperation of the European and Hindu team whose participants many times expressed significantly different approaches to solve arising problems.

Finally, on 20 August 1993, all the installations constituting the cyclohexanone production plant were put to use and after six days of a non-stop and stable operation, they met the conditions for 96-hour Guarantee Test Run.

During the test, the installation achieved the capacity at the level of 101.4% of the design capacity and lower parameters than the ones guaranteed in the contract.

On 6 September 1993, GSFC signed the Acceptance Certificate of taking over the installation to operate as it met all the conditions agreed in the contract. The licensor's representatives and all the parties involved in realising this complex project attained the success. It was another project which was the specific milestone in the development path and expansion of the Polish technology for obtaining cyclohexanone from benzene.

At that time, the installation in Tarnów was subjected to research on improving the CYCLOPOL process. In the second half of the 1990s, the research was aimed at enhancing the production capacities of cyclohexanone installations, which was necessitated by the increased production capacity of the installation of caprolactam.

The last stage of these works consisted in implementing the safe process of cyclohexane oxidation with the air enriched with oxygen. As a result of such a solution, the production capacity of the operating installation increased by 25% without making any considerable expenditures. Again, the new solution attracted the Hindu partner who for the third time decided to implement the solution from Tarnów into their installation. Similarly as in the previous contract, the new one was signed on 7 May 1997 with the participation of POLSERVICE and ENCO. This contract included the transfer of licence, *know-how*, technical documentation and supervision service for the modernisation of the installation operating in GSFC and for the improvement of its production capacity *(debottlenecking*) by 25%. Enriching the air with oxygen was the main element of this project.

The works related to the project performance (detailed design documentation and construction) on the basis of the documentation prepared by BIPROZAT Tarnów were carried out by GSFC. On 10-27 October 1999, a team of eight people (four representatives from BIPROZAT, one representative from the Nitrogen Plant, one representative from IChP and two representatives from ENCO) conducted the technological start-up of the modernised installation unit for oxidising cyclohexane. While working in GSFC, the team evaluated whether the quality of the modernised installation conforms to the technical documentation and supervised the installation start-up after the standstill required for performing the project. On 17 October 1999, the design (balanced) load of the installation was reached and the guarantee test run began. The test completed on 22 October 1999 met all the contract obligations; on 25 October 1999, GSFC signed a proper certificate of accepting and taking over the modernised installation to operate.

The third contract with the same partner, the first such case in the history of exporting scientific and technological achievements of the Polish chemical industry and a very rare case on a global scale, passed into history and strengthened the brand quality of the CYCLOPOL process as well the position of its owners on the Hindu market.

As it has been previously mentioned, the modernised process known as CYCLOPOL-bis was implemented into the installation of cyclohexane oxidation in Azoty Tarnów in 2003. The information about this process was disseminated in the professional literature. Moreover, the interest was developed among the companies which could apply the process. GSFC company soon expressed its interest. Similarly as in the previous project, on 20 July 2009, the Nitrogen Plant signed a contract on transferring the licence to GSFC for using the CYCLOPOL-bis process in their installation. At the same time, a similar contract was concluded with the Nitrogen Plant in Puławy and the Industrial Chemistry Research Institute in Warsaw. This was the contract on releasing the modernised technology for cyclohexanone and cyclohexanol rectification. The modernisation of the distillation technology developed by these two parties consisted in removing boiling compounds accumulated between the cyclohexanone and cyclohexanol stage in recirculating stream that was supplying the process of cyclohexanol dehydrogenation.

Similarly as in the previous contracts with GSFC, the Polish party collaborated with ENCO on concluding and executing the contract.

Apart from the licence and *know-how* transfer, the signed contract included the task of elaborating technical documentation and performing the service while modernising the Installation of Cyclohexanone in the CAPRO-2 Production Plant. Simultaneously, BIPROZAT concluded a separate contract on delivering important and key proprietary equipment of the licensor, that is, the interiors of reactors used for cyclohexane oxidation and hydroperoxide decomposition. The equipment designed by BIPROZAT was manufactured by the Chemical Equipment Construction Company (ZBACH - Zakład Budowy Aparatury Chemicznej). It has been already sent to GSFC.

The stage of preparing the documentation is completed. The detailed design documentation has been prepared by GSFC and verified by the licensor. In accordance with the contract provisions, GSFC is currently conducting the works on completing the equipment as well as constructing and assembling the modernised installation. The modernised installation of cyclohexanone and cyclohexanol has already been modernised. The performed modernisation was based on the licence and *know-how* transferred to the Hindu party by the Nitrogen Plant in Puławy and IChP.

In autumn of this year, the start-up and guarantee test run are planned to be conducted.

The Plant is continuing its research and works on the CYCLOPOL-bis process in the field of technology and engineering solutions. This modernisation of the installation in Tarnów is supposed not to be the final one. The probability of the 5th transfer of technology to GSFC can be predicted. A very good opinion of GSFC and trust built during a long-term and productive cooperation may result in its continuation not only in the field of cyclohexanone, but also, for example, in the field of caprolactam. CYCLOPOL-bis is supposed to be applied in other installations which are currently working on the basis of the CYCLOPOL technology.

This briefly described long-term cooperation of Azoty Tarnów with the Hindu company GSFC shows that the release of the company's technologies (licence transfer and *know-how* sale) does not have to influence negatively the company's competitiveness providing that the licensor is active in the field of process research, development and modernisation. This cooperation, in turn, brings measurable advantages. It is an incentive for the development of the engineers and establishes the Plant reputation. The licensor acquires new areas for the potential expansion of their business.

Taking into account the specialists, the participation in developing the technology, in implementing new solutions and in actions related to the licence transfer and the cooperation with the foreign partners is a remarkable engineering experience and fulfilment of their professional activities. It is great satisfaction to participate in a creative project realised in collaboration with a big interdisciplinary team.

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International Symposium on Preparative and Industrial Chromatography and Allied Techniques (SPICA '2012)

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