

## Progress in the technology for manufacturing Bisphenol A

# Postęp w zakresie technologii produkcji bisfenolu A

DOI: 10.15199/62.2015.5.XX

The process for manufg. (p-OHC<sub>6</sub>HJ<sub>2</sub>CMe<sub>2</sub>) by ion exchange resin-catalyzed condensation PhOH with Me<sub>2</sub>CO under recycling the by-products of the reaction was improved to decrease the energy consumption. The improved technol. is transferred to Russia.

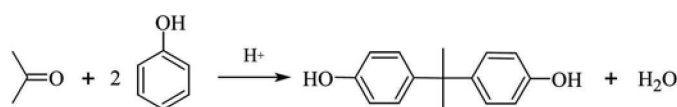


Fig. 1. Synthesis of Bisphenol A

Developments in the Polish process of technology to obtain Bisphenol A are described based on published information. This paper is part of an expertise, required for investment decisions relating to the transfer of the BPA production technology and modernization of a 70,000 t/y commercial plant according to a contract between Mexeo, Poland, and UPC, Russian Federation.

### BPA in the global market

The global BPA production volume was 4.5 mln t/y as early as a decade ago. A great majority of it is further processed in integrated processes to obtain polycarbonates or epoxy resins, rather than being used as intermediate products. According to forecasts for the global market, demand on BPA is going to be on a stable increase ranging 3-6%<sup>1)</sup>, which means that one or two new BPA plants are going to be built every year. In Poland, the demand on BPA is around 20,000 t/y. As the construction of a new polycarbonate complex is contemplated, the demand on BPA in Poland is going to reach 100,000 t/y, according to forecasts.

Bisphenol A (BPA) is an important intermediate product in the contemporary chemical processing industry. With its high production volume and numerous applications, it is obtained according to highly advanced and constantly improved production technology. Products manufactured from BPA have high and growing qualitative requirements. BPA is used mainly in the manufacturing of advanced plastics, including polycarbonates and epoxy resins (75% and 20% of consumption, respectively) for use in the construction and automobile industries as well as in electronic and optical materials. In those areas, the consumption of polymeric materials based on BPA in those industries has been growing dramatically for some time<sup>1)</sup>.

BPA is obtained by condensing phenol and acetone in the presence of acid catalysts (Fig. 1)<sup>2)</sup>. Ion-exchange resins are the main type of catalysts used in the synthesis of BPA nowadays. After being promoted, such catalysts are able to significantly improve the reaction in terms of rate and selectivity<sup>3-7)</sup>.

### The Polish technology to obtain BPA

The Polish process of technology to obtain BPA was developed in the 1970's in the "Blachownia" Institute of Heavy Organic Synthesis (ICSO) in Kędzierzyn-Koźle. There, Dr Maciej Kiedik was head of the BPA team which developed an advanced, innovative process of technology to obtain BPA. It was one of the three processes in the world, in which ion exchange resins were used as catalysts. The BPA process was successfully implemented in the "Blachownia" Chemical Works (BChW) in 1978. Thereafter, the technology was gradually improved and perfected, based on the experience in operating the commercial plant gained by the BPA team year after year.



Dr Maciej KIEDIK (Ph.D., M.Sc.Eng.) graduated (1971) from the Silesian University of Technology, Faculty of Chemical Technology and Engineering, in Gliwice. In the years 1971-2004 he worked in the "Blachownia" Institute of Heavy Chemical Synthesis (ICSO) in Kędzierzyn-Koźle, including the posts of head of the BPA Section and General Manager of ICSO. At present in MEXEO, he is responsible for R&D and implementation of the new technology ADVANCE BPA. Specialization: organic technology.



Farid AKHMETOV (M.Sc.Eng.), graduated (2002) from the University of Technology, Faculty of Chemical Technology, in Kazan. He worked (2004-2011) in Kazanorgsintez Open Joint-Stock Company; one of his posts was that of Chief Process Engineer in the BPA complex (based on the Idemitsu Kosan technology). In the years 2011-2013, he was the Engineering Department Manager in the SIBUR Process Center. In 2013 he was appointed the head of the BPA and cumene facility modernization project, acting on behalf of JSC United Petrochemical Company (Unipec) in Moscow. Specialization: organic technology.

\* Corresponding author:

MEXEO Wiesław Hreczuch, ul. Energetyków 9, 47-225 Kędzierzyn-Koźle, Tel. (77) 487-38-10, Fax: (77) 487-38-11, E-mail: maciej.kiedik@mexeo.pl

The core of the BPA team at that time was made by scientists and design engineers in ICSO and process engineers in BChW. The team work led to a process in which the solutions used were as good as those offered by leading companies globally. In consequence, the Polish process of technology was licensed as many as eight times to companies abroad<sup>8-26</sup>.

Over the course of time, the Polish process of technology was becoming less and less competitive because of its high consumption of energy. Given the growing importance of energy consumption figures in the evaluation of manufacturing processes, this affected the competitiveness of the solution. Therefore, in 2004, ICSO undertook basic research intending to develop a new, alternative process of technology to obtain BPA<sup>27-29</sup>. The effort was based on two Polish and international patents<sup>27, 29</sup>.

Regardless of those efforts, studies intended to improve the old ICSO process<sup>30-41</sup> were undertaken by the Institute for Engineering of Polymer Materials and Dyes (IIMPIB) in Toruń, cooperating with Mexeo, an innovation-implementation company located in Kędzierzyn-Koźle. The improved process of technology is offered internationally by Mexeo and is covered by international patents<sup>36, 41</sup>. In 2014, Mexeo signed its first contract to license the technology abroad and deliver a documentation package and technical services for a 70,000 t/y BPA production unit.

This paper is intended to demonstrate the advantages of the new process of technology to obtain BPA. Comparison of the two new Polish processes to obtain BPA was based on available data and materials, except that the competitive ICSO process was analyzed only on the basis of published patent specifications<sup>27, 29</sup>, comprising a detailed description of the technology with complete compositions of the main process streams. The comparative analysis is a fragment of an expert's opinion, used by the Russian chemical company Unipec (UPC) for its investment decisions regarding the transfer of the BPA production technology. Among other things, UPC is a manufacturer of BPA, using an obsolete technology based on the homogeneous acid catalyst (HCl) in its old 60,000 t/y plant. The technology has the primary disadvantage of not being able to provide a top purity product. Moreover, its consumption of raw materials and energy per unit of production is too high. In consequence, the production process is not cost-effective.

In 2013, UPC started to investigate opportunities for modernization, by implementing available advanced processes of technology in its plant. The two Polish processes of technology were contemplated as potential solutions, and a comparative analysis was made using available information (patents, papers).

### The Mexeo technology

The unit for BPA synthesis and rearrangement of byproducts to the desirable isomer (p,p'-BPA) is the essential unit in the Mexeo technology. Its operation has a major impact on the consumption of raw materials (selectivity) and energy (increase in BPA concentration in the post-reaction mixture) per unit of production and is important to the purity and color of product. Some engineering and process modifications were implemented in the synthesis unit as well as a catalyst containing a chemically combined promoter (2,2-dimethyl-1,3-thiazolidin) was used.

This led to a much higher increase in BPA concentration in the synthesis unit (by more than 15%) and enabled a much lower energy consumption for the separation and purification of final product<sup>36, 41</sup>. The improvements have resulted in suitable conditions for reducing energy consumption per unit of production by a minimum of 40%. Consequently, the Mexeo process of technology to obtain BPA is comparable to the most advanced competitive processes.

More modifications in the units for BPA synthesis, isomerization, rearrangement of byproducts, dewatering of post-crystallization liquor and phenol recovery from waste have also been developed and verified in commercial conditions. They further reduce the consumption of raw materials and energy and improve the process efficiency. The quality of development of the improved BPA process has given us an advantage over competitive companies offering BPA technology globally. Some of the key elements of the improved process of technology have been used as the substantiation in our application for an international patent covering the new technology. The Mexeo technology uses a commercially verified, innovative method to carry out the reaction in a single reactor packed with an ion-exchange resin with a chemically combined catalyst promoter<sup>36, 41</sup>. The BPA synthesis reactor is divided into reaction zones by means of filtration slot nozzles located at several levels in the ion exchange resin bed. The solution enables efficient recovery of the heat of the exothermal reaction running in the respective reaction zones as well as control over the phenol-to-acetone ratio by mole (Fig. 2). A better process efficiency is obtained by feeding the reactor with a recirculated phenolic stream<sup>36, 41, 42</sup> having a sufficiently high concentration of isomers and other byproducts after their rearrangement and isomerization. In order to improve the efficiency of operation of the synthesis unit, the feed stream must have a stable concentration of the o,p-BPA isomer (approx. 4%) and all byproducts (approx. 8%). This will lead to a highly stable selectivity of the catalytic process in spite of the inevitable, gradual decrease in the selectivity of the promoted catalyst as it becomes more and more deactivated in the operation.

In a tank-type reactor with a gravitational, unidirectional flow of the reaction mixture, which is packed with an ion-exchange resin and in which approx. 20% of functional groups (-SO<sub>3</sub>H) are neutralized by means of 2,2-dimethylthiazolidin or cysteamine, deactivation of the promoter in the catalyst bed proceeds layer by layer. The deactivation mechanism is such that the top layer contains a practically non-promoted cation exchanger in which the content of active acid groups is low, productivity is several times as low as in other layers and selectivity is below 90%. Therefore, the selectivity of the catalyst will go down, on average, from its initial 98% to less than 94% during operation. This loss is compensated by our new technological solution, which keeps stable process efficiency and stable selectivity.

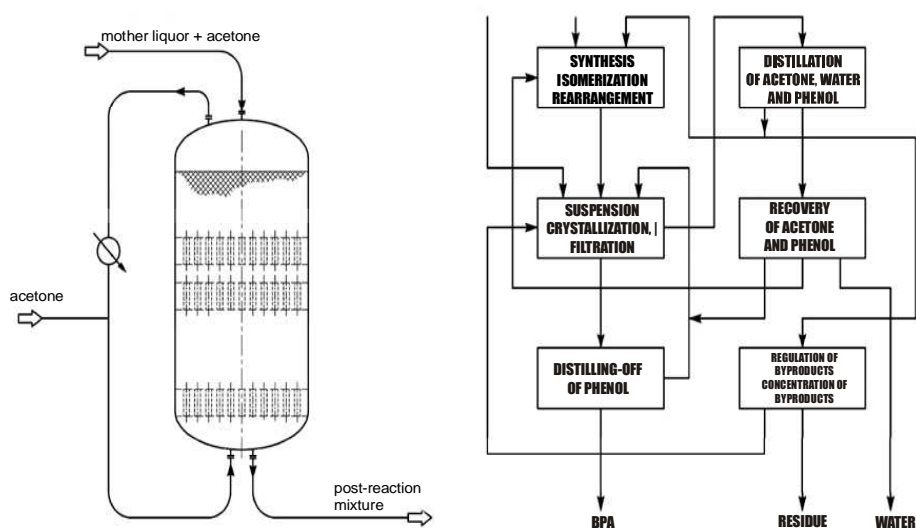
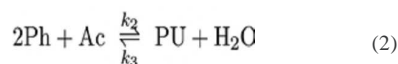


Fig. 2. Reactor and flow sheet of the process for manufacturing Bisphenol

The effect is justified by the process kinetics. Assuming that the BPA synthesis process comprises reactions (formation of BPA and formation of byproducts) which run in parallel, it is possible to describe the conversions by Equations (1) and (2):



wherein Ph denotes phenol, Ac denotes acetone, PU denotes byproducts, and  $k_1$ ,  $k_2$ ,  $k_3$  denote the respective reaction rate constants,  $s^{-1}$ . The general equations defining the reaction rate, (1) and (2), in conditions of considerable excess of phenol over acetone can be described by Equations (3) and (4):

$$r_1 = k_1 x_{Ac} \quad (3)$$

$$r_2 = k_2 x_{Ac} - k_3 x_{PU} \quad (4)$$

wherein  $r_1$  denotes the rate of reaction (1),  $r_2$  denotes the rate of reaction (2),  $x_{Ac}$  denotes a molar fraction of acetone in the reaction mixture, kmol/kmol, and  $x_{PU}$  denotes a molar fraction of byproducts in the reaction mixture, kmol/kmol. Assuming that instantaneous selectivity of the process of formation of product  $P$  is expressed by the defining equation (5)<sup>43</sup>:

$$S_P = \frac{r_P / \nu_P}{-r_A / \nu_A} \quad (5)$$

wherein  $r_P$  denotes the rate of conversion of reactant  $A$  to product  $P$ ,  $r_A$  denotes the rate of general conversion of reactant  $A$ ,  $\nu_P$  and  $\nu_A$  denote the respective stoichiometric coefficients, we obtain the following Equation (6) describing the selectivity of formation of BPA in the process by means of reactions (1) and (2):

$$S_{BPA} = \frac{r_1}{r_1 + r_2} = \frac{k_1}{k_1 + k_2 - k_3 \frac{x_{PU}}{x_{Ac}}} \quad (6)$$

An analysis of the right-hand side of Equation (6) indicates that an increase in the byproduct content of the reaction mixture will lead to increased selectivities of the BPA formation process. In operating a commercial reactor, the effect is seen by the compensation of unfavorable consequences of a natural decrease in the catalyst's selectivity, which leads to a desirable, stable high selectivity of the catalytic process. Therefore, in the Mexeo process as well as in other known technological solutions<sup>42</sup>, the reactor is fed with a phenolic stream containing nearly-equilibrium concentrations of isomers and other byproducts in order to stabilize selectivity at a sufficiently high level.

Consequently, the synthesis and rearrangement solutions in the Mexeo technology enable us to obtain a more than 15% increase in BPA concentration in the reaction and a stable, high selectivity of approx. 98%; therefore, the outgoing stream at the reactor outlet contains up to 27% of BPA. Moreover, based on our long-standing experience in operating commercial plants, the mixture outgoing from the BPA synthesis reactor is made to flow through a system of mechanical filters in order to protect it from small dust particles and/or fragmented cation exchanger grains that may penetrate into the high-temperature zone. The stream is then made to flow through an anion-exchanger filter in order to eliminate any acidic compounds originating from the cation exchanger that may cause decomposition processes in the high-temperature zone, thus leading to the formation of harmful contaminants deteriorating the color of the final product.

The reaction unit is composed of several reactors. One of them is a standby reactor: it is used in rotation for preparing a fresh portion of the promoted catalyst before one of the other reactors is switched off for replacing its spent catalyst packing. This enables the production process to be continued without stoppage for catalyst replacement and the plant is operated with its assumed capacity all the time.

### The reference technology

In the competitive BPA process, the synthesis is carried out in a three-step cascade-type reaction system with an ion-exchange resin catalyst in which 20.2% of its sulfonic groups were modified with 2,2-dimethylthiazolidin<sup>27, 29</sup>. In the first step of the synthesis, a phenolic solution of acetone (2.72%) is contacted with the ion-exchanger catalyst. The post-reaction mixture is then cooled down (in a heat exchanger with indirect cooling) and acetone is added to obtain its concentration at approx. 2.54%<sup>27</sup>. In the second step of the synthesis, the solution of acetone, phenol and their condensation products is contacted again with the ion exchanger catalyst to increase the p,p'-BPA isomer content to 12.5%. The mixture resulting from the synthesis step II is then combined with the crystallization liquor resulting from the solvent crystallization of the BPA-phenol adduct (1.0:1.3). A homogeneous solution of the post-crystallization liquor and the solution formed in the synthesis step II is cooled down to 57°C and then enough acetone is added to obtain its concentration of 2.7%. The stream is then contacted with the ion exchange catalyst in the synthesis step III. Condensation of acetone with phenol in the synthesis step III gives, at the reactor outlet, a solution containing 17% p,p'-BPA and 0.93% o,p-BPA as well as other components. The outgoing solution from the multi-step reaction system is made to flow through a 100 mesh screen filter. Then, it is concentrated by evaporating water, acetone and a portion of phenol at temperatures in the range 125-130°C and a pressure of 50 mm Hg to obtain a residue which contains 21.19% p,p'-BPA and 1.18 o,p-BPA.

A flow sheet for this process of technology to obtain BPA<sup>29</sup> is shown in Fig. 3.

### The advantages of the Mexeo technology

Basic information about the consumption of materials and energy in various BPA processes is provided in Table 1. In advanced processes of technology, product purity is much better than in earlier ones because of the use of fractional crystallization. However, the solution accounts for higher investments costs and higher consumption of energy. On the other hand, purity 99.93% is a generally accepted purity standard for BPA, and can be obtained by means of suspension crystallization. The solution is offered, as an option, in the Mexeo technology. Moreover, the two technologies guarantee an identical color of the product – 5 APHA (American Public Health Association). Moreover, in both technologies, the consumption of acetone is lower (0.265 t/t BPA), in comparison with the earlier technology.

As regards raw materials, the consumption of phenol is the essential indicator of cost-effectiveness of the process. Of the two processes of technology, the one offered by Mexeo is superior (0.836 t/t BPA, compared with 0.847 t/t BPA).

After improving the selectivity of condensation by recycling the phenolic stream containing byproducts in nearly-equilibrium concentrations to the reactors in the synthesis unit and in the isomerization and rearrangement unit, the outgoing stream from the reactor in the Mexeo process contains as much as 27% BPA, compared with 17% in the reference process. This reduces the consumption of energy in the subsequent steps (product separation and purification) because the volume of circulating phenolic solutions (also called mother liquor) is smaller. This, in turn, reduces the consumption of steam, cooling water, as well as electric energy, mainly in the liquor dewatering unit and phenol regeneration unit. Also less energy is consumed in the crystallization unit. The results of parametric simulation of changes in the values of energy indicators vs. BPA concentration and total BPA concentration in product streams are shown in Table 2.

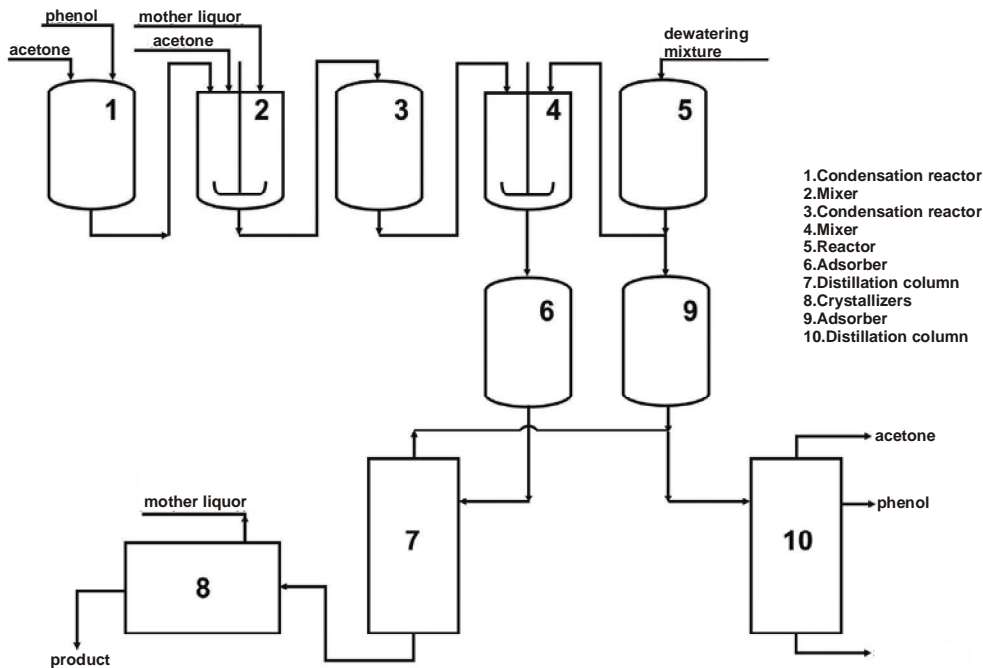


Fig. 3. Flow sheet of the process according to<sup>29</sup>

Table 1. Comparison of various processes for manufacturing Bisphenol A

Parameter	Purity, %	Acetone consumption, max. t/t	Phenol consumption, max. t/t	Increase in BPA conc., %	Energy consumption max. GJ/t
Old Polish technology	99,9	0,275	0,860	10	12,5
Mexeo technology	99,98	0,265	0,836	17	7
Reference technology <sup>27, 29)</sup>	99,99	0,265	0,847	10	n/a

n/a – not available

Carrying out a BPA synthesis in the presence of a stream of isomers and other byproducts which are present in a rather high, stable concentration, resulting from the kinetics of a continuous stationary process enables both control of the formation of byproducts and maintenance of high selectivity of the reaction at approx. 98% over the catalyst's entire lifetime (nearly 99% if isomerization and rearrangement are taken into account). In the reference process according to the patent referred to above<sup>27)</sup>, the feeds to the synthesis steps I, II and III contain 0; 0.32 and 1.31% of byproducts, respectively. Therefore, one of the patents<sup>29)</sup> proposes additional isomerization and rearrangement of byproducts to p,p'-BPA in order to obtain higher selectivities of the process. However, the material balance indicates that the feed to that unit contains 2.21% o,p-BPA and 2.92% of all byproducts.

If the expected concentration of BPA in the final post-reaction mixture outgoing from the reactor in step III is 17%, this corresponds to an increase in concentration by approx. 10%, as indicated by the material balance. Separation of BPA from a lean mixture like this requires high consumption of energy in the process. A comparison of the balances of the two processes for a capacity 70,000 t/y indicates that the increase in BPA concentration in the reaction is 17% in the Mexeo process and approx. 10% in the reference process; it follows that the reaction mixture flow rates are 51.5 t/hr and 87.5 t/hr, respectively.

This indicates that the amount of thermal energy used for the heating, dewatering by distillation, and regeneration of phenol will be 70% higher in the reference process. The same result (an increase by 70%) is observed in the reference case for the consumption of cooling water for the transfer of heat and electric energy (pumps).

Table 2. Parametric simulation of the energy indicators of BPA synthesis vs. product concentration in the post-reaction stream, production capacity 70 Gg/year (8,75 Mg/hr)

Parameter	Unit	Mexeo technology (Advance BPA) <sup>30-41)</sup>	Reference technology <sup>27, 29)</sup>
Increase in BPA concentration in synthesis unit	%	17%	0%
Amount of post-reaction mixture	Mg/hr	51.5	87.5
Thermal energy for drying mother liquor	MJ/hr	1310	2230
Thermal energy for regeneration of phenol	MJ/hr	2080	3540
Total consumption of heat for drying and regeneration	MJ/hr	3400	5770
Total consumption of heat as 10 bar steam	kg/g	2900	2900
Consumption of water for collecting such heat	m <sup>3</sup> /hr	100	170
Difference in consumption of energy	%	100	170

Product concentration in the outgoing stream is one of the essential criteria in the assessment of various BPA processes of technology in terms of energy consumption. In the process of technology offered by Mexeo, the parameter is as high as 27%, which is an explicit advantage, differentiating it from synthesis units in competitive processes as regards energy consumption. In severe price competition conditions, the parameter has an effect on the cost-effectiveness of production.

In 2012, two more improvements<sup>29)</sup> were implemented in the reference process: passing the entire post-reaction mixture onto the "stabilizer" bed (anion exchanger), and periodic "dewatered" of the ion-exchanger. Introduction into the process of contacting the post-reaction mixture with the anion exchanger bed (referred to by the authors as "stabilizer") before the high temperature zone is justified. The concept has been known and used for over two decades in earlier reference plants based on the "old" Polish technology. The periodic washing of the operated ion exchanger catalyst bed with phenolic streams was also known and used for many years. In fact, the operation is intended to remove from the bed the excess heavy byproduct content which affects the reactor's efficiency in the reference plant, rather than dewater the ion exchanger bed.

If serially connected reactors are operated in a cascade system, then it is necessary to shut down the whole plant every 1.5 year and replace the deactivated catalyst bed. This is a lengthy procedure, which has a measurable negative effect on the capacity and cost-effectiveness of a commercial plant. The construction and maintenance in operation of a parallel, rotation synthesis unit in a cascade system does not seem economically reasonable, either: the costs of both the investment and the operation are simply too high. In the concept where reactors are operated in parallel according to the Mexeo technology, the catalyst bed in the reactors is replaced periodically, one by one, because an extra reactor is used as a rotation reserve. This does not interfere with the process. Moreover, being able to phase the filling of the successive reactors is also desirable for a stable, interrupted operation of the whole synthesis unit. As an extra advantage, this is a safety measure in the case of an emergency stoppage of a reactor, enabling it to be repaired without shutting down the whole plant.

## Summary

The synthesis unit is the main area of innovation in the R&D work of the authors of the BPA production technology. A number of key equipment for the other process units, including product separation methods, being acquired from specialist outsourced vendors are subject to selection as options. Their most desirable combination, again, is the competence of the authors of the technology and has an effect on the general characterization of economic indicators and the expected quality of product. Therefore, it is advised that design issues concerning the complex, advanced technology should be tackled in cooperation with those specialists who have the practical knowledge in operating, development and implementation of improvements of commercial plants.

For developing its technology and preparing technical documentation, Mexeo has employed most of the key specialists (process engineers, design engineers, analysts, and supervisory personnel for the production plant) who have gained their experience in the commissioning and operation of commercial BPA plants in Poland and abroad.

Received: 30-03-2015

## LITERATURE

1. anonymous. Bisphenol A. World market outlook and forecast. Merchant Research & Consulting Ltd., May 2009.
2. P. Dianin, Zh. Russ. Fiz.-Khim. Obsh. 1891, 23, 492.
3. V.H. Sirjolev, H. Vanda, Chem. Prum. 1956, 6, 201.
4. J. De Jong, F.D.H. Dethmers, Recl. Trav. Chim. Pays-Bas. Belg. 1965, 84, 460.
5. P.K. Ghosh, T. Guha, A.N. Saha, J. Appl. Chem. 1967, 17, 239.
6. M. Kiedik, Doctoral dissertation: Badania nad otrzymywaniem p,p-dwufenylopropanu przy użyciu wymiennicy jonowych jako katalizatorów [Studies on the obtaining of p,p-diphenylolpropane using ion exchanger catalysts], Warsaw University of Technology, Warsaw 1978.
7. D.B. Luten, S. Ballard, C.G. Schwarzem, US Patent No. 2602821 (1953); Canadian Patent No. CA 47, 7544 (1953).
8. M. Kiedik et al., Polish Patent No. 107840 (1977).
9. M. Kiedik, E. Grzywa et al., Polish Patent No. 113641 (1977).
10. M. Kiedik, E. Grzywa et al., Polish Patent No. 115709 (1977).

11. M. Kiedik et al., Polish Patent No. 124542 (1978).
12. M. Kiedik et al., Polish Patent No. 123971 (1979).
13. M. Kiedik et al., Polish Patent No. 130206 (1980).
14. M. Kiedik et al., Polish Patent No. 153148 (1987).
15. M. Kiedik et al., Polish Patent No. 153149 (1987).
16. M. Kiedik, E. Grzywa et al., Polish Patent No. 153396 (1987).
17. M. Kiedik et al., Polish Patent No. 164289 (1990).
18. J. Kołt, M. Kiedik et al., Polish Patent No. 168654 (1992).
19. M. Kiedik et al., Polish Patent No. 169996 (1993).
20. M. Kiedik et al., Polish Patent No. 181992 (1995).
21. M. Kiedik et al., Polish Patent No. 182008 (1995).
22. M. Kiedik, E. Grzywa et al., Polish Patent No. 183597 (1996).
23. M. Kiedik et al., Patent Application No. P-323110 (1997).
24. J. Kołt, M. Kiedik et al., Patent Application No. P-328836 (1998).
25. M. Kiedik et al., Polish Patent No. 189401 (1998).
26. M. Kiedik et al., Polish Patent No. 189400 (1998).
27. B. Tkacz et al., Polish Patent No. 210812 (2007).
28. A. Krueger, B. Tkacz, Przem. Chem. 2013, 92, No. 2, 148.
29. T. Rdesińska-Ćwik et al., Polish Patent No. 217484 (2012).
30. M. Kiedik, E. Grzywa, A. Chruściel, Przem. Chem. 2007, 86, No. 1, 29.
31. M. Kiedik, A. Chruściel, A. Sokołowski, Przem. Chem. 2008, 87, No. 9, 969.
32. M. Kiedik, S. Kubica, W. Hreczuch, A. Basta, Przem. Chem. 2012, 91, No. 8, 1558.
33. M. Kiedik, Badania i opracowanie energooszczędnego procesu otrzymywania Bisfenolu A [R&D work on a low-energy process to obtain Bisphenol A]. R&D Project No. R05 007 02, 2007-2009..
34. M. Kiedik et al., European Patent EP 1809589 (2005).
35. M. Kiedik et al., European Patent Application. EP 2090562 A1 (2008).
36. M. Kiedik et al., Patent Application No. PCT/PL2011/000010 (2011).
37. M. Kiedik, A. Chruściel, A. Sokołowski, Program kompleksowych udoskonaleń procesu technologicznego wytwarzania bisfenolu A w PCC Synteza SA, [A program of complex improvements for the process of technology to manufacture Bisphenol A at PCC Synteza S.A.], not published, 2008.
38. M. Kiedik et al., Sprawozdanie z przebiegu nadzoru autorskiego pt. Wdrożenie programu kompleksowych udoskonaleń procesu technologicznego wytwarzania bisfenolu A w PCC Synteza SA, [A report on the course of authors' supervision "Implementation of a complex program of improvement for the process of technology to manufacture Bisphenol A at PCC Synteza S.A."], not published, 2009.
39. M. Kiedik, A. Chruściel, A. Sokołowski, Nowe inicjatywy organizacyjne i technologiczne w zakresie chemii przemysłowej. "Innowacja techniczna zamiast inwestycji. Bezinwestycyjne wdrożenie nowego energooszczędnego procesu otrzymywania bisfenolu A w PCC Synteza", [New organizational and technological initiatives in industrial chemistry. „Technological innovation in place of investment projects. The implementation of a new, energy-efficient process to obtain Bisphenol A at PCC Synteza without investing"], Opole University of Technology, 2009.
40. M. Kiedik, S. Kubica, W. Hreczuch, A. Chruściel, 7th Chemical Technology Congress in Cracow, July 2012
41. M. Kiedik et al., Patent Application No. P.349079 (2013).
42. Information and offer relating to the Dow/Kellogg process [not published].
43. F. Helfferich, Kinetics of multistep reactions, Elsevier, Amsterdam 2004