Next Generation of Polish Technology to Obtain Bisphenol A – ADVANCE BPA process

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Introduction

Bisfenol A (BPA) is one of the most important intermediates in chemical processing nowadays. Its main applications include advanced plastics, such as polycarbonates (75% of consumption) and epoxy resins (20% of consumption), which are intended for use in the electronic, construction and automotive industries. The consumption of BPA-based polymeric materials in those industries has been observed to grow dynamically for some time. Given the high technological advancement of the product's final applications, the manufacture of Bisphenol A is one of the most complex and demanding processes of technology in the chemical industry. BPA plant is composed of 11 process units, comprising roughly 250 pieces of equipment, precisely designed and selected in accordance with the best engineering practices. A critical point of the plant, its synthesis unit is based on heterogenic catalysis - a highly advanced process in respect of technology and engineering. The effects of the industrial use of the technology are the synthesis, recovery, and purification of the product with purity above 99.9% on a scale of many thousand tons per year.

The consumption of BPA in Poland is now approx. 20,000 t/y. The construction of a new complex manufacturing polycarbonates is planned in the near future. The demand on Bisphenol A will thus increase by 50,000-100,000 t/y. According to forecasts, the increase in the global market demand on BPA will be stable, at a rate of 3% to 6% per year [1], which means that several new BPA plants will be required in the nearest 5 years.

Bisphenol A is obtained by condensing phenol and acetone in the presence of catalysts (Fig. 1) [2].

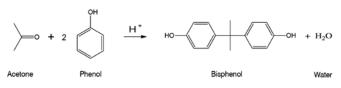


Fig. I. Scheme of synthesis of bisphenol A (BPA)

The catalysts used nowadays for the synthesis are mainly ionexchange resins $[3 \div 6]$. Promoters are also required in the synthesis process in addition to the catalysts themselves. Their function is to boost the reaction efficiency and selectivity [7].

This paper presents information about a new process to obtain Bisphenol A, which is a developed and much enhanced version of the earlier Polish BPA process [8].

A history of the development of the Polish BPA production technology

The history of the development and enhancement of the Polish BPA production technology was described earlier $[8 \div 10]$. The essential steps in the development of the Polish BPA production technology are presented in Figure 2.

Commercial production based on the BPA technology was launched at the Blachownia Chemical Works in Kędzierzyn-Koźle in 1978 (Photo 1.) [8]. It was one of the first BPA process technologies in the world, using an ion-exchange resin catalyst. The process technology was developed by Dr. M. Kiedik with his team, under the direction of Prof. E. Grzywa [11] at ICSO Blachownia in Kędzierzyn-Koźle [11 \div 39]. At the seventies of the last century Prof. Grzywa initiated research on applications of ion exchange resins as catalysts in chemical syntheses and later supported the coauthors in further development of bisphenol A and nonyphenol technologies, worked out at the ICSO institute.

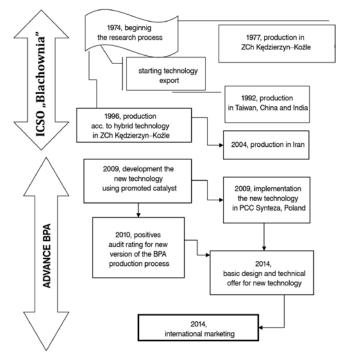


Fig. 2. The essential steps in the development of the Polish BPA production technology



Photo I. Bisphenol A (BPA) Plant in PCC Synteza in Kędziezrzyn Koźle

The ionite BPA process was regularly improved using many years of experience in the operation of commercial facilities. At the turn of the 21st century, the BPA process was licensed 8 times to foreign licensees: in Taiwan, China, Korea, India and Iran (Photos 2 and 3).



Photo 2. BPA Plant launched in China



Photo 3. Chinese Prime Minister Li Peng congratulates the Polish engineer (J. Kołt)

Regular R&D works, intended to boost the efficiency of the BPA synthesis process, led to the implementation, in 1996, of a first version of the hybrid technology, in which two types of catalysts were used: a sulfonated styrene-divinylbenzene copolymer catalyst was used in the step where contaminated process streams were reacted, and an ion exchange resin catalyst with a chemically bound were promoter was used in the step reaction of pure phenol streams with acetone [25]. 2,2- dimethyl-1,3-tiazolidyne was used as the reaction promoter, which was chemically bounded to the ion exchange resin. Their lifetimes in the process conditions were $10 \div 15$ years and $2 \div 3$ years for the copolymer type and the promoted catalyst, respectively.

No more licensing contracts were entered into after the year 2001, as the BPA process technology ceased to be cost-efficient, becoming obsolete and not competitive any more. The essential disadvantage of the former versions of the Polish BPA processes (the ion exchanger and hybrid one, respectively) was their high energy consumption. Efforts made at ICSO to improve the former BPA process which, even though not competitive in terms of its cost-efficiency, but still quite valuable in a very important area of industrial practice were stopped after the year 2003. Since the year 2005 ICSO initiated developing of an alternative technology, though based on laboratory scale results only [48,49], appart of the existing industrial practice.

Regardless of the above directions of activity, Dr Kiedik made an attempt to enhance, in collaboration with PCC Synteza SA, the Bisphenol A technology which had been successful for many years as an industrial reference. Starting from the year 2006, the works were continued in the Gliwice department of Institute for Engineering of Polymer Materials and Dyes in Toruń (IIMPiB) and, in the years 2007÷2009, were funded from a R&D grant awarded by the Ministry of Science and Higher Education [41]. An outcome of the project was to develop a mathematical model of the reactor [9], brief foredesign for the synthesis unit concept, and assumptions for the technology export offer relating to the upgraded version of low-energy consuming hybrid process to obtain 100,000 t/y of BPA. The co-authors of the new hybrid process include those specialists from ICSO and the Blachownia Chemical Works (PCC Synteza), who contributed the most to the development and improvement of the earlier versions of the BPA technology: Maciej Kiedik, Józef Kołt, Antoni Marek Korek, Jerzy Mróz, Anna Rzodeczko, Małgorzata Kałędkowska, Jan Muszyński and Jarosław Strzelczyk.

Dr Kiedik's team's intense research effort to enhance the BPA technology resulted in the development of a next generation BPA process, based solely on the use of the promoted catalyst, which was the subject of Polish and international patents $[42 \div 44]$ and was industrially proven in a 15,000 t/y facility at PCC Synteza in Kędzierzyn-Koźle [45, 46]. Contrary to the earlier process, the new technology applies entirely the promoted catalyst.

The new Polish technology to obtain Bisphenol A using a promoted catalyst

The "Advance BPA" Scientific and Industrial Consortium was established in 2011 to implement the new BPA production technology in the commercial practice. MEXEO innovative company has became the Consortium leader. The essential goals of the Consortium include the preparation of a design documentation package for the new BPA technology of 100,000 t/y capacity, which has internationally competitive parameters or economic indicators and guarantees much better ones, compared with those achievable in the earlier Polish BPA technology. The issued basic design and technical offer for the ADVANCE BPA technology will include the new way of synthesis with a promoted catalyst [44, 51]. After some modification, mainly in the synthesis process, and after shifting to the new catalyst having the chemically bound promoter (2,2-dimethyl-1,3-tiazolidyne) in it, the increase in BPA concentration in the postreaction mixture is much higher (a shift from 10% up to 15%), thereby much less energy is used for the final separation and purification of the end product. The improvements have enabled a reduction in unit energy consumption by as much as 40%. This makes the process competitive, compared with most instances of advanced BPA technology, offered by competitors. A schematic diagram of the BPA production plant based on the new BPA process is shown in Figure 3.

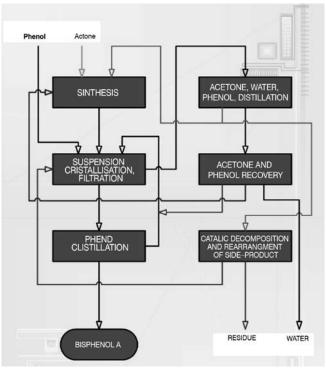


Fig. 3. Schematic diagram of BPA production plant based on new BPA process

As the result of R&D works combined with industrial tests at PCC Synteza, Dr Kiedik's team has managed to enhance and also to implement in the industrial facility further improvements located in the units of synthesis, isomerisation and rearrangement of side-products, dehydration of mother liquers and recovery of phenol from waste streams, which have led, by the end of 2009, to considerable reduction in the consumption of raw materials and energy, and significantly enhanced efficiency of the process to obtain BPA [47].

Owing to the economic crisis in 2010, specifically, owing to the low, inefficient production scale (15,000 t/y), judging by the currently applicable standards, combined with the lack of direct links with industrial processors of BPA into plastics, the BPA plant at PCC Synteza was shut-down after 31 years of uninterrupted operation. In spite of the above, unfavorable events, resulting from powerful macroeconomic conditions, the achieved level of advancement of the improved BPA technology has provided it with a competitive advantage in the international market. The key features of the improved technology served as a basis to apply for covering the process with patent protection globally.

Before the shut-down of the BPA plant at PCC Synteza, visualization of the major apparatus and equipment in the plant was prepared in order to document the course of the real process to obtain Bisphenol A in the reference plant. Moreover, multimedia presentations of the technology and the reference plant in the form of a film and graphic animation were prepared. The presentations were produced in the Polish, English, and Chinese language versions as part of the Patent Plus project of the Ministry of Science and Higher Education covering support for patenting inventions, and are available in the form of CD's (Fig. 4).



Fig.4. Multimedia presentation of the technology and the reference plant in the form of film and graphic animation

The new BPA process technology discussed herein, of which the history of development spans all the stages of a research cycle which is indispensable for reaching a degree of maturity which enables implementation, has been proven industrially and fully documented, as required for further design works. The industrial exploitation have confirmed that the economic and quality indicators featured by the new BPA process technology may well compete against the chemical giants, such as Bayer, General Electric, DOW or Mitsubishi [40]. Given the fact that those major global manufacturers of BPA, rather, are not interested in selling their own licenses, chances are that the export of the new Polish technology may be resumed and the technology may serve as an implementation basis for the construction of a Bisphenol A plant in Poland in future, as part of a complex of plants manufacturing polycarbonates and/or epoxy resins. The use in the new Polish BPA process of valuable and unique technological solutions, specifically, the use in the Bisphenol A synthesis of solely the promoted catalyst in an innovative reaction system, has enabled a measurable reduction in the consumption of energy and raw materials per product unit (Tab. 1.).

The ADVANCE BPA technology allows for optional replacement of the adduct's second suspension crystallization step by the fractionated crystallization of bisphenol A, which leads to its finest purity and thermal stability standards [43, 44]. science • technique

Comparison of the offered parameters and unit consumption figures for energy and raw materials in the Polish processes to obtain BPA (data from proprietary offer materials and from the literature [48, 49]).

Parameter	BPA purity, %, minimum	Color, APHA, max	Consump- tion of acetone, t/t, max	Consump- tion of phenol t/t, max	Increase of BPA concen- tration in the reaction, Δ BPA %	Consump- tion of energy, GJ/t, max
Earlier Polish BPA process	99.9	5	0.275	0.860	10	12.5
Declared ICSO BPA technology "ISOBIS" [48, 49]	99.99	5	0265	0.847	10	
New ADVANCE BPA process	99.93 / 99.98*)	5	0.265	0.836	15	7

*) For the option with fractionated crystallization

In economical terms, reduction of phenol consumption by 0.01 t/t of BPA (Tab.1.), at the production scale of 100,000 t/y, brings about effect of 1.5 million Euros. Assuming an average price 2.5 Euros per I GJ, the difference in energy consumption of 5 GJ/t BPA gives an additional quote of 1.2 million Euros per year. It is worth to mention, that any lower increase of BPA concentration in the reaction mixture, directly implies relevant increase of energetic demand (GJ/t), to separate a unit of the final product. Taking into account the indicated differences and including all the other related exploitation costs, the expected economical effect can be estimated as no less than 3 million Euros per year (30 Euros/t. of BPA). This means a significant advantage of the offered ADVANCE BPA process over the other technologies of worse material and energetic indicators.

Summary

The technology offer of the new ADVANCE BPA process features a proprietary, industrially proven, new technology to manufacture Bisphenol A, which is competitive in the aspect of product quality as well as technological parameters and economic indicators, compared with related state-of-the-art solutions, as well as patent protection covered in three international invention proposals which enable the technology to be licensed in the global market. In the neighboring countries (Central and East Europe), practically the total demand on BPA is satisfied from imports, in the absence of own major production capacities. Given the lower production costs, according to the parameters of the new ADVANCE BPA process of technology, and/or lower costs of transport, compared with other manufacturers, the product made in the region will have a competitive advantage.

Market studies indicate that 5 to 8 more new BPA plants will be required in the world in the near future to cover the globally increasing demand on BPA as a chemical raw material. This creates conditions for the export of licenses for this competitive technology offer, including basic design package, design supervision, and delivery of key apparatus and equipment.

This article is based on the paper presented at the VII Chemical Technology Congress, held in Krakow on July 2012 [50].

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Literature

- Bisphenol A, World market outlook and forecast, Merchant Research & Consulting Ltd., may 2009.
- 2. Dianin P., Zh. Russ. Fiz.-Khim. Obsh. 1891, 23, 492.
- 3. Vladimir H. Sirjolev., Vanda H., Chem. Prum. 1956, 6, 201.
- 4. De Jong J., Dethmers F.D.H., Recl. Trav. Chim. Pays-Bas. Belg. 1965, 84, 460.
- 5. Ghosh P.K., Guha T., Saha A.N., J. Appl. Chem. 1967, 17, 239.
- 6. Kiedik M., Ph.D. dissertation, Politechnika Warszawska, Warsaw 1978.
- Luten D.B., Ballad S., Schwarzem C.G., US Pat. 2602821; CA 47, 7544, 1953.
- 8. Kiedik M., Grzywa E., Chruściel A., Przem. Chem. 2007, 86, nr 1, 29.
- Kiedik M., Chruściel A., Sokołowski A., Przem. Chem. 2008, 87, nr 9, 969.
 Kiedik M., Kubica S., Hreczuch W., Basta A., Przem. Chem. 2012, 91,
- nr 8, 1558. 11. Kiedik M. et al., *Polish Patent* 107840 (1977).
- 12. Kiedik M., Grzywa E. et al., Polish Patent 113641 (1977).
- Kiedik M., Grzywa E. et al., Polish Patent 115709 (1977).
- 14. Kiedik M. et al. Polish Patent 124542 (1978).
- 15. Kiedik M. et al., Polish Patent 123971 (1979).
- 16. Kiedik M. et al., Polish Patent 130206 (1980).
- 17. Kiedik M. et al., Polish Patent 153148 (1987).
- 18. Kiedik M. et al., Polish Patent 153149 (1987).
- 19. Kiedik M., Grzywa E. et al., Polish Patent 153396 (1987).
- 20. Kiedik M. et al. Polish Patent 164289 (1990).
- 21. Kołt J., Kiedik M. et al., Polish Patent 168654 (1992).
- 22. Kiedik M. et al., Polish Patent 169996 (1993).
- 23. Kiedik M. et al., Polish Patent 181992 (1995).
- 24. Kiedik M. et al. Polish Patent 182008 (1995).
- 25. Kiedik M., Grzywa E. et al., Polish Patent 183597 (1996).
- 26. Kiedik M. et al., Polish Patent Application P-323110 (1997).
- 27. Kołt J., Kiedik M. et al., Polish Patent Application P-328836 (1998).
- 28. Kiedik M. et al., Polish Patent 189401 (1998).
- 29. Kiedik M. et al., Polish Patent 189400 (1998).
- 30. Kiedik M. et al., Polish Patent Application P-332879 (1999).
- 31. Kiedik M. et al., Polish Patent Application P 337475 (1999).
- 32. Kiedik M., Grzywa E. et al. Polish Patent 183597 (1997).
- 33. Kiedik M. et al., Polish Patent 107987 (1977).
- 34. Kiedik M., et al., Polish Patent Application P-332879 (1997).
- 35. Kiedik M., Opracowanie optymalnego katalizatora dla procesu otrzymywania bisfenolu A o czystości poliwęglanowej [Development of an optimum catalyst for the process to obtain a carbonate-grade Bisphenol A]. Projekt EUREKA E ! 2503 CAT-BPA, 2000–2003.
- 36. Kiedik M. et al., Polish Patent Application P-347705 (2001).
- 37. Kiedik M. et al., Polish Patent Application P-354905 (2002).
- 38. Kiedik M. et al., Polish Patent Application P-355703 (2002).
- 39. Kiedik M. et al., Polish Patent Application P- 349079 (2001).
- 40. Information about the Dow/Kellog process of technology (not published)
- Kiedik, M., Badania i opracowanie energooszczędnego procesu otrzymywania Bisfenolu A [Studies on and the development of an energy-efficient process to obtain Bisphenol A] A R&D Project No. R05 007 02, 2007–2009
- 42. Kiedik M. et al., European Patent EP1809589 (2005).
- 43. Kiedik M. et al., European Patent Application EP 2090562 AI (2008).
- 44. Kiedik M. et al., Patent Application PCT/PL2011/000010 (2011).
- 45. Kiedik, M., Chruściel, A., Sokołowski, A., Opis procesu technologicznego "Program kompleksowych udoskonaleń procesu technologicznego wytwarzania Bisfenolu A w PCC Synteza S.A" [A process of technology description: A program of complex improvements for the process of technology to manufacture Bisphenol A at PCC Synteza SA], not published, 2008.
- 46. Kiedik, M 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 SA"] not published, 2009.

- 47. Kiedik, M., Chruściel, A., Sokołowski, A., monografia Nowe inicjatywy organizacyjne i technologiczne w zakresie chemii przemysłowej. "Innowacja techniczna zamiast inwestycji. Bezinwestycyjne wdrożenie nowego energooszczędnego procesu otrzymywania bisfenolu A w PCC Synteza" [monograph 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"], Politechnika Opolska, 2009.
- 48. Krueger A. et al., Polish Patent Application P- 369166 (2007).
- 49. Krueger A., Tkacz B., Przem. Chem. 2013, 92, nr 2, 148,
- 50. Kiedik M., Kubica S., Hreczuch W., Chruściel A., Projekt nowego procesu otrzymywania bisfenolu A, referat wygłoszony na VII Kongresie Technologii Chemicznej w Krakowie w lipcu 2012 roku, [A project for the new process to obtain bisphenol A], section referate presented during the VII Congress of Chemical Technology, Krakow, July 2012, published abstract.
- 51. Kiedik M. et al., Polish Patent Application P349079 (2013).

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