

THE POLISH BISPHENOL A TECHNOLOGY – GENERAL INFORMATION

Bisphenol A (BPA) belongs to the group of key, large-volume intermediates of industrial organic synthesis. The development of production technology of this raw material of significant importance for the plastics industry (polycarbonates, epoxy resins) has a long tradition in Poland. The leader in this field is Dr. Eng. Maciej Kiedik. A measurable effect of its scientific and development activities are numerous licenses for the sale of the Polish bisphenol A manufacturing technology, concluded with contractors in Taiwan, China, India, Korea, Iran and Russia, as well as over 30 years of BPA production in Zakłady Chemiczne "Blachownia" (later PCC Synteza S.A.) in Poland. The development issues of the discussed BPA technology are described extensively in several articles published in recent years^{1,2,3,4,5,6}.

Implementation of bisphenol A production technology on a large scale, taking into account high economic and environmental requirements, shows a significant degree of technical complexity as well as a high level of engineering advancement. Due to the physicochemical properties of material streams, a number of side processes, whether high requirements for the purity of the product dedicated to the production of polycarbonates, as well as due to numerous non-physical aspects of the manufacturing process (issues of sewage and waste management, process economics, process safety etc.) the BPA production plant requires the implementation of the majority of known chemical engineering of unit operations, including: distillation, crystallization, phase separation in multicomponent liquid-liquid systems, liquid-solid systems, complex heat exchange operations, etc.

The process of BPA production in the plant constructed based on the current state of technical knowledge is carried out in 9 technological units, including particular stages of the manufacturing process, such as: synthesis, separation and recrystallization of the product, forming (prilling or flaking) and confectioning of the product, purification of process streams and wastewater, regeneration and recirculation of raw materials and others.

Despite the significant position of BPA production in the global chemical industry (over 5 million tonnes of product per year) and its exploitation for several decades, this technology has not been comprehensively described in the scientific literature from the process engineering side. The experience of the authors in the area of the BPA manufacturing process on an industrial scale being the effect of among others over 30 years of experience in the operation of an industrial installation constructed according to its own technology, allowed to systematize knowledge in this field.

¹ Kiedik M., Grzywa E., Chruściel A., *Przem. Chem.* 86/1:29-32 (2007)

² Kiedik M., Chruściel A., Sokołowski A., *Przem. Chem.* 87/9:969-974 (2008)

³ Kiedik M., Kubica S., Hreczuch W., Basta A., *Przem. Chem.* 91/8:1000-1004 (2012)

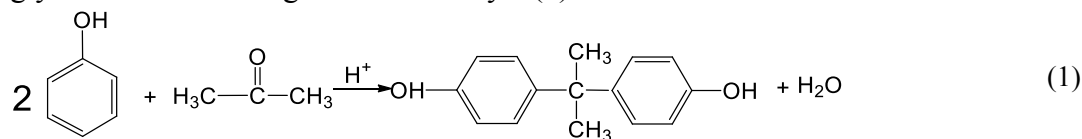
⁴ Kiedik M., Kubica S., Chruściel A., Hreczuch W., *Chemik*, 67: 1097-1104 (2013)

⁵ Kiedik M., Akhmetov F., *Przem. Chem.*, 94: 677-681 (2015)

⁶ Kiedik, M., Chruściel, A., Hreczuch, H. *Przem. Chem.* 95,9,1000-1006 (2016)

THE IMPORTANT CHEMICAL REACTIONS IN BISPENOL A TECHNOLOGY

Bisphenol A is formed by the condensation reaction of phenol with acetone in the presence of a strongly acidic ion exchange resin as catalyst (1):

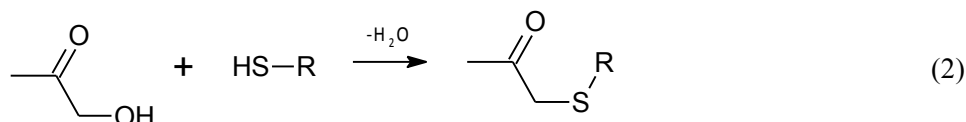


The mechanism of the synthesis has been comprehensively described in the literature^{2,7}. In the BPA synthesis node there are also parallel reactions, as a result of which a number of by-products are formed. The possibility of activating the para position in the phenol molecule leads both to the formation of 3 isomers of the hydroxy groups of bisphenol A, as well as a series of homologues differing in the degree of condensation of the hydroxykumyl substituents.

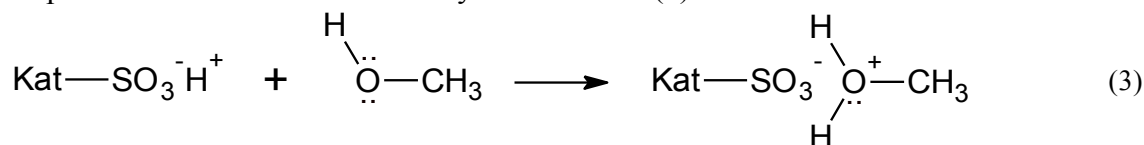
The use of thiol promoters (cocatalysts) plays an important role in the catalytic synthesis of BPA.

Proposals for clarifying the mechanism of action of thiols performing as cocatalysts of BPA synthesis, connected with the ionic cation exchanger, have been presented by several authors^{7,8,9,10,11}. These explanations are based on the concept of the privileged formation of sulfanylpropion carbocations obtained as a result of the protonation of the acetone molecule. The element of the promoter molecule structure that determines its properties is the thiol group, which due to its reactivity under the conditions of the process is exposed to poisoning by certain impurities present in applied raw materials, such as hydroxyacetone in phenol and methanol in acetone, and oxidation by oxygen from the air.

Reactions resulting in deactivation of catalyst promoters by hydroxyacetone present as phenol contamination in an amount up to several tens of ppm are described in the literature^{6,11}. In general, hydroxyacetone reacts with a promoter bounded to cation exchanger, reducing its concentration in the reaction medium by binding to thiol groups (2).



Deactivation of the promoter also occurs intensive by contact with methanol, which is a contaminant present in the acetone feed, present in an amount of 200 to 300 ppm. The reason for the above phenomenon may be the course of the S, S-dimethylation process of the thiol promoter with methanol, on the surface of a strongly acidic sulphonic catalyst, which first step is the stabilization of the methyloxonium ion (3):



⁷ H. Schnell and H. Krimm, *Angew. Chem.* **75**, 662 (1963)

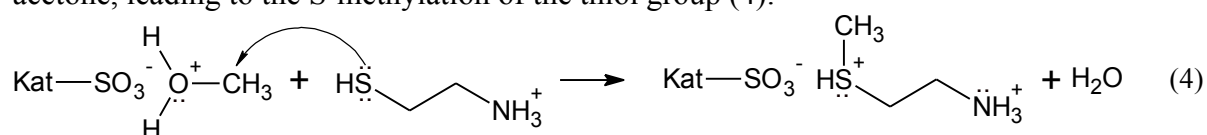
⁸ Zeidan R K, Dufaud V, Davis M E. *J. Catal.*, 2006, 239(2): 299–306

⁹ Chen C C, Cheng S, Jang L Y. *Micropor. Mesopor. Mat.*, **2008**, 109, 258–270

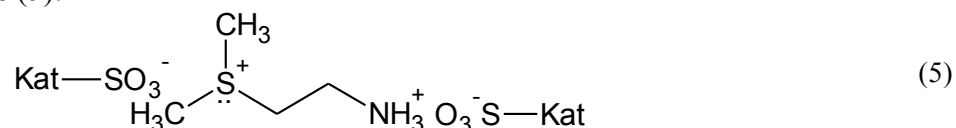
¹⁰ Shimizu K, Kontani S, Yamada S, Takahashi G, Nishiyama T, Satsuma A. *Applied Catalysis A, Gen.*, **2010**, 380, 33–39

¹¹ Kiedik, M. *at al.* Internal Report from realization of R&D topic 10-21/Ex/I/97. Institute of Heavy Organic Synthesis (ICSO), Kędzierzyn-Koźle, Poland. Dec. 1997. Not published.

This relatively stable transition ion, known for its reactivity and susceptibility to nucleophilic attack¹², may further react with thiol, competitive to the catalytic reaction with acetone, leading to the S-methylation of the thiol group (4):

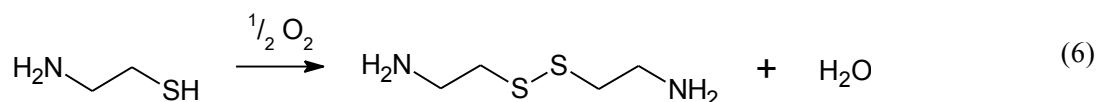


As a result of the further stage of S-methylation and the protonation of the amino group (in this case 2-aminoethane thiol), the obtained dipositive ion can effectively neutralize the catalyst active sites (5):



As follows from the practice of operating the BPA industrial plant, the content of accumulated methanol in regenerated acetone increases in the operation cycle and over time becomes many times higher than the initial level of its occurrence in the raw material.

A similar issue related to promoter side reactions that lead to a decrease in catalyst activity is the oxidation of thiol promoters. However the commonly known series of thiol oxidation reactions is complex and leads to the formation of sulpho groups, through the formation of sulfinic, sulfenic or sulfone acids, the most likely reaction of the promoter deactivation in the analyzed case is a delicate catalytic oxidation to disulfides, which inactive molecules can bind to two sulfone groups of the catalyst (6).



The above-mentioned side processes, implying the irreversible binding of thiol promoters to stable compounds lead to gradual, layeric reduction of the catalyst activity as well as its selectivity.

One of the important elements of the presented technology is the construction and operating method of the BPA synthesis reactor that allows controlled elimination of the inactive catalyst bed zones from the process, that allows to increase the selectivity of the BPA synthesis process comparing to the traditional single-zone reactor.

¹² Olah, G.A., White, A.M., O'Brien, D.H. *Chem. Rev.* **1970**, 70, 561