The main reactions occurring during production of BPA
Główne reakcje zachodzące w procesie produkcji bisfenolu A

Bisphenol A (BPA) is one of the key bulk intermediate products in the organic synthesis industry. Even though the principal reaction – condensation of phenol and acetone in the presence of an acidic catalyst – is very simple, the chemistry of the process executed in the large commercial plants is very complex. Several dozen chemical reactions have been identified as occurring in the execution of the BPA technology and actually affecting the process in terms of quality and competitiveness. Out of that large number, only the essential reactions have been presented in this paper. This is the material on which the 100,000 tpa of BPA technology being offered in the international market by the MEXEO Institute of Technology, Kędzierzyn-Koźle, was based.

BPA (BPA) is one of the key bulk intermediate products in the organic synthesis industry. The technology to manufacture BPA, which is an important starting material in the production of plastics, such as polycarbonates, epoxy resins, is of long standing in Poland. This is evidenced by the number of contracts to sell the Polish BPA technology to many foreign contractors (including Taiwan, China, India, Korea, Iran, Russia) as well as by BPA production in the “Blachownia” Chemical Works S.A. (later PCC Synteza) in Kędzierzyn-Koźle in the years 1978-2010. The development of the BPA technology has been detailed described in detail before [3]. Despite the relative simplicity of the principal reaction – condensation of phenol and acetone in the presence of an acidic catalyst, which is the decisive reaction for the formation of the final BPA product – the process execution in large commercial plants, taking into consideration stringent economic and environmental requirements, is highly complex in the chemical and technical aspect and highly advanced in the engineering aspect. Out of the several dozen chemical reactions taking place in the process, the most essential are described in this paper.

The BPA manufacturing plant requires the implementation of most of unit operations known in chemical engineering, including: distillation, crystallization, phase separation in multi-component liquid-liquid or liquid-solid systems, and complex heat transfer operations. This is connected with the physico-chemical properties of the material streams, the path of side processes and stringent requirements regarding purity in the case of the polycarbonate grade product, as well as because of numerous non-physical aspects of the manufacturing process, such as waste and waste water management, process economics and safety.

The process to manufacture BPA according to state-of-the-art technological solutions, is executed in 9 process units, including the respective steps of manufacturing: synthesis, product separation and recrystallization, forming (prilling or flaking) and weighing/packing, purification of process streams and waste treatment, recovery and recycling of raw materials. The above operations are executed in more than 400 apparatuses connected by means of nearly 2000 pipelines (Fig. 1).

Even though the BPA technology is ranked highly in the chemical industry globally (more than 5 mln tpa) and has been used for several decades, the process of technology itself has not been described in detail in the literature so far. More than 30 years of experience in the operation of the commercial BPA plant has enabled a systematization of the facts of the BPA process [4,5]. Many of these reactions, intermediates and products have for years been regarded as separate technological issues that need to be explained, described and solved by improving the...
technology, its figures for raw materials and utilities, to ultimately arrive at the maximum obtainable efficiency and purity of the final product. Figure 2 shows the bench scale system which is operated at MEXEO for studies on BPA synthesis.

It was the objective of this paper to present a review of the most essential chemical reactions taking place in the BPA production process, and affecting it in terms of quality and competitiveness. The material presented in this paper is the basis of the BPA technology being offered on the international market by MEXEO Institute of Technology, Kędzierzyn-Koźle, as the ADVANCE BPA technology in the scale of 70,000 tpa and 100,000 tpa. An international presentation of the BPA technology has taken place in Vienna recently. The latest license to manufacture 70,000 tpa of BPA based on the ADVANCE BPA process was granted in 2014 and has been the greatest transfer in organic technology in the history of Poland.

**Reactions in the BPA process**

BPA is obtained in the condensation reaction of phenol with acetone in the presence of a strongly acidic ion exchanger resin catalyst (1):

\[
\text{H}_3\text{C}-\text{OH} + \text{H}_3\text{C}-\text{C}^\text{+} \text{OH} \rightarrow \text{H}_3\text{C}-\text{C}-\text{H}_3 + \text{H}_2\text{O}
\]

The reaction mechanism is quite well known from the literature\(^{10}\). The process comprises 4 steps:

Step I is acetone molecule protonation leading to the formation of stable carbocation (2):

\[
\text{H}_3\text{C}=\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{C}^+\text{OH}
\]

Step II is the electrophilic substitution of carbocation leading to the formation of the intermediate 2-(4-hydroxyphenyl)-propan-2-ol (rate-determining step) (3):

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}^+\text{OH} & \rightarrow \text{H}_3\text{C}-\text{C}^+\text{OH} \\
\end{align*}
\]

It runs with the formation of the intermediate complex \(\sigma (1)\) and elimination of the hydrogen cation (regeneration of catalyst).

Step III is the protonation of the strongly electronegative oxygen atom in the hydroxy group leading to the formation of an unstable transition complex in the cationic form and elimination of the water molecule. This gives the stable carbocation, same as in Step IV (4):

\[
\text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_2\text{O}
\]

Finally, in Step IV, the carbocation attacks another phenol molecule whereby the BPA molecule is formed and the hydrogen cation is reconstructed (5):

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_3\text{C}-\text{OH} & \rightarrow \text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_2\text{O} \\
\end{align*}
\]

Other, parallel reactions also take place in the BPA synthesis, whereby numerous byproducts are formed.

The possibility of activation of the para position in the phenol molecule leads to the formation of 2\(^{2\pm4}\) isomers of BPA hydroxy groups: para-para, ortho-para, para-ortho and ortho-ortho. The actual number is 3 because the isomers ortho-para, para-ortho are symmetrically identical (6).

Another substitution of 2-(4-hydroxyphenyl)-2-propylium (4) carbocation in the BPA molecule leads to the formation of a group of trisphenol isomers:

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_3\text{C}-\text{OH} & \rightarrow \text{H}_3\text{C}-\text{C}^+\text{OH} + \text{H}_2\text{O} \\
\end{align*}
\]
and a homologous series having different degrees of condensation of hydroxycumyl substitutes.

The reaction (3) path indicates that it is possible to stop the reaction in the step of catalytic elimination of the water molecule with the formation of ortho- and para-isopropenylphenol and reconstruction of the catalytic hydrogen cation (8).

\[
\text{(8)}
\]

However, byproducts are formed not only in the synthesis unit but also in other process units operated at high temperatures, especially above 150°C. The processes are much accelerated in the presence in the reaction medium of acidic substances, such as sulfonic acids contained in the cation exchanger, or cation exchanger dust. This affects the overall process selectivity and product quality. The acidic substances may break through only in emergency situations. In a correctly run synthesis process, they ought to be efficiently removed by means of special mechanical filters and then neutralized in anion-exchanger packed reactors.

Selectivity of the BPA synthesis process may be improved by introducing the operation of isomerization and regrouping of byproducts. This is carried out by contacting them with a macroporous cation exchanger or gel-type cation exchanger comprising a suitable promoter (to be described later in the text) and, additionally, by way of catalytic decomposition of BPA and byproducts by means of basic catalysts.

In consequence of these catalytic processes, the BPA hydroxy group isomers are isomerized towards the obtaining of a kinetically privileged 4,4' isomer (9):

\[
\text{(9)}
\]

The catalytic decomposition is applied to handle a stream which contains concentrated byproducts and BPA, obtained after the separation of the BPA-phenol adduct, water, acetone, and excess of phenol from the reaction mixture. The operation is most preferably carried out in a continuous manner using a distillation tower with recycling part of the distillate as reflux. In reactions (10) – (12) phenol and 2-p-hydroxyphenylpropene are recovered:

\[
\text{(10)}
\]

\[
\text{(11)}
\]

Owing to this, additional amounts of BPA are obtained in Reaction (13):

\[
\text{(13)}
\]

The catalytic decomposition distillate comprises 2-p-hydroxyphenylpropene which tends to undergo dimerization very fast and without any catalyst, even at ambient temperatures; the process mechanism is typical of alkene dimerization with the formation of identifiable tautomers, denoted in the industrial practice by the symbols DL1 and DL2 (14):

\[
\text{(14a)} \quad \text{(14b)}
\]

It also undergoes oligomerization (15):

\[
\text{(15)}
\]

Next, linear dimers and oligomers of 2-p-hydroxyphenylpropene react in the presence of an acidic catalyst to BPA with a nearly 100% selectivity. The presence of a reactive double bond in the molecules of DL1 and DL2 (14) in the absence of the acidic catalyst may lead to cyclization and the formation of 3-(4-hydroxyphenyl)-1,1,3-trimethyl-2,3-dihydro-1H-inden-5-ol (DC compound) (16):

\[
\text{(16)}
\]
which, in basic catalysis conditions (during catalytic decomposition) may undergo the following reaction (17):

The reaction (17) takes place also if, in emergency conditions, acidic compounds are present in the process streams subjected to high temperatures above 150°C; this has an adverse effect on the process.

The possibility of the isomerism of the location of the OH group may result in the formation of more dimerization products (18):

followed by cyclization, which results in a chromene derivative, also known as the Dianin compound, or the codimer (19):

Codimer (Dianin compound)

In the presence of a basic catalyst (during catalytic decomposition), the codimer may decompose with cleavage of phenol and the formation of 2,2,4-trimethyl-2H-chromene in reaction (20):

Catalytic decomposition gives a distillate, composed mainly of phenol, 2-p-hydroxyphenylpropene, its linear dimers (DL-1 and DL-2) and oligomers as well as some amounts of byproducts, such as TMC and TMI, cyclic dimers (DC) and the codimer. After addition of phenol thereto, the distillate is contacted with the cation exchanger in a separate reactor at temperatures in the range 60-90°C, to recover BPA according to (21-23):
The mechanism of action of thiols as cocatalysts of BPA synthesis

The mechanism of action of thiols as cocatalysts (promoters) is that more reactive carbocations are formed. In the first step, the 2-hydroxy-2-propylium carbocation reacts with the thiol, whereby hemimercaptoketal is formed via an unstable transition complex (26):

\[
\begin{align*}
R & \quad \text{H} \\
\text{C} & \quad \text{H}_2 \text{C}-\text{CH}_2 \text{SH}^+ + \text{H}^+ + \text{C} & \quad \text{H}_2 \text{C}-\text{CH}_2 \text{OH} & \quad \text{H}_2 \text{C}-\text{CH}_2 \text{OH} + \text{H}_2 \text{O} \\
\text{C} & \quad \text{CH} & \quad \text{R} & \quad \text{C} & \quad \text{S} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]

In the next step, by protonation of the hemimercaptoketal hydroxy group with elimination of water leads to the formation of a new, more stable, 2-organylsulfanyl-2-propylium carbocation (27):

\[
\begin{align*}
\text{CH}_2 & \quad \text{H}_2 \text{C} \\
\text{C} & \quad \text{CH} & \quad \text{OH} \\
\text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\text{C} & \quad \text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\text{S} & \quad \text{C} & \quad \text{R} \\
\end{align*}
\]

The terminal step of the reaction between the sulfanylpropylium carbocation and phenol is similar to reaction (3) and leads to the formation of the afore-mentioned 2-(4-hydroxyphenyl)-propylium carbocation, with reconstruction of the thiol molecule (28).

\[
\begin{align*}
\text{C} & \quad \text{OH} \\
\text{S} & \quad \text{C} & \quad \text{R} \\
\text{C} & \quad \text{S} & \quad \text{C} & \quad \text{R} \\
\text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]

Therefore, the thiol group is an essential structural element of the promoter molecule.

Harmful effect of contamination of raw materials

Contaminants that may be present in raw materials, such as hydroxyacetone in phenol or methanol in acetone, tend to react with the cation exchanger catalyst promoter. These are an important group of undesirable chemical reactions which greatly reduce the catalyst’s activity as well as selectivity of the BPA synthesis process. Reactions have been identified which result in the deactivation of the catalyst’s promoters by hydroxyacetone found in phenol as contaminant in amounts of several dozen or less ppm. The phenomenon is undesirable and has a measurable effect on catalyst efficiency. Hydroxyacetone reacts with the cation exchanger promoter and reduces its concentration in reaction medium by blocking the thiol groups. The main reactions taking place between hydroxyacetone and the thiols, used as promoters for acidic ion exchanger catalysts, are:

reaction of 3-mercaptoproponic acid with hydroxyacetone (29), (30)

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} \\
\text{C} & \quad \text{CH}_2 \text{SH} \\
\text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\text{C} & \quad \text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]

or

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} \\
\text{C} & \quad \text{CH}_2 \text{SH} \\
\text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]

Based on these reactions between hydroxyacetone and mercaptane promoters, a mechanism of deactivation of the cation exchanger with sulfonic groups neutralized with cysteamine was proposed. It is based on the following reactions (33):

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} \\
\text{C} & \quad \text{CH}_2 \text{SH} \\
\text{S} & \quad \text{C} & \quad \text{R} & \quad \text{H}_2 \text{O} \\
\end{align*}
\]
In the case of 2,2-dimethylthiazolidine as promoter, the path of the thiol-blocking reaction is virtually the same as in the case of cysteamine, assuming that the “forming” of the promoted catalyst by means of 2,2-dimethylthiazolidine is based on its acidic hydrolysis according to equation (34) resulting in the formation of cysteamine and release of acetone molecule (35):

\[
(34) \quad \begin{array}{c}
\text{H}_2\text{C} \\
\text{S} \\
\text{NH}
\end{array}
\xrightarrow{\text{H}^+} \begin{array}{c}
\text{HS} \\
\text{CH}_3
\end{array} + \begin{array}{c}
\text{O} \\
\text{C} \text{H}_3
\end{array}
\]

According to the best knowledge of the subject and the authors’ experience in industrial operation of production plants, the safe level of the content of hydroxyacetone in phenol for use in the production of BPA in the presence of catalysts promoted by means of thiols is a maximum of 2 ppm. If phenol with a higher content of hydroxyacetone is used in the BPA synthesis, it is necessary to provide a special reactor for preliminary purification of phenol before sending it downstream.

As in the case of phenol contamination with hydroxyacetone, quick deactivation of the promoter takes place as it comes into contact with methanol that may be present in acetone as a contaminant in amounts ranging from 200 to 300 ppm. In a regenerated acetone, methanol tends to accumulate and its content may be much higher, leading to deactivation of the promoted catalyst, which is indicated by a noticeable loss of its activity and reaction selectivity, even to below 85%.

This is attributable to the reaction path of S,S-dimethylation of the thiol promoter with methanol on the surface of the strongly acidic sulfonic catalyst, where the first step is the methyloxonium ion stabilization (35):

\[
(35) \quad \text{KatSO}_3\text{H}^+ + \begin{array}{c}
\text{H} \\
\text{O} \\
\text{CH}_3
\end{array} \xrightarrow{\text{H}^+} \text{KatSO}_3\text{O}^+\text{CH}_3
\]

This rather stable transition ion, known for its reactivity and susceptibility to the nucleophilic attack (11), may further react with the thiol (competitive reaction to (26)), which results in the thiol group susceptibility to the nucleophilic attack [11], may further react with the thiol promoter with methanol on the surface of the strongly acidic sulfonic catalyst, where the first step is the methyloxonium ion stabilization (36):

\[
(36) \quad \begin{array}{c}
\text{Kat} \\
\text{SO}_3\text{H}^+
\end{array} + \begin{array}{c}
\text{HS} \\
\text{CH}_3
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\text{Kat} \\
\text{SO}_3\text{H}
\end{array} + \begin{array}{c}
\text{HS} \\
\text{CH}_3
\end{array} + \begin{array}{c}
\text{NH}_2
\end{array} + \text{H}_2\text{O}
\]

In the effect of the subsequent step of S-methylation and protonation of the amine group, the resulting double-positive ion may effectively neutralize the catalyst’s active sites (37).

\[
(37) \quad \text{KatSO}_3\text{H}^+ + \begin{array}{c}
\text{CH}_3
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\text{S} \\
\text{Kat}
\end{array}
\]

Moreover, the resulting molecule of a dimethylsulfonium cysteamine derivative, having lost its nucleophilic properties, loses also its ability to participate in reaction (26) which is decisive for the BPA synthesis reaction path.

Although cysteamine is the thiol group carrier in equations (36) and (37), the promoter blocking mechanism occurs also with the use of 2,2-dimethylthiazolidine, as in reaction (33). The accumulation of methanol in acetone may be prevented by removing it in a special column.

The oxidation of thiol promoters is a related question, connected with side reactions involving the promoter and accounting for loss of catalytic activity. Although the well known thiol oxidation reaction series are complex and lead to the formation of sulfonic groups via sulfinic and sulfenic acids and sulfones, the most probable reaction is a gentle catalytic oxidation to disulfides, of which the inactive molecules may combine two sulfonic groups of the catalyst (38).

\[
(38) \quad \text{H}_2\text{N}-\text{S} \xrightarrow{\frac{1}{2} \text{O}_2} \text{H}_2\text{N}-\text{S}-\text{S}-\text{NH}_2 + \text{H}_2\text{O}
\]

The negative effect of contact with the air on the promoted catalyst’s activity was confirmed in industrial practice.

Table 1. Summary of by-products occurring in the production process of BPA.

<table>
<thead>
<tr>
<th>Chemical name (symbol)</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(prop-1-en-2-yl)phenol, (PIPH)l</td>
<td>![Image]</td>
</tr>
<tr>
<td>4-(propan-2-yl)phenol</td>
<td>![Image]</td>
</tr>
<tr>
<td>2-[2-(4-hydroxyphenyl)propan-2-yl]phenol (2,4-isomer of BPA)</td>
<td>![Image]</td>
</tr>
<tr>
<td>4-tert-butylphenol</td>
<td>![Image]</td>
</tr>
<tr>
<td>2,2'-propano-2,2'-dihydridophenol</td>
<td>![Image]</td>
</tr>
<tr>
<td>1,1,3-trimethyl-1H-inden-5-ol</td>
<td>![Image]</td>
</tr>
<tr>
<td>4,4'-(4-methylpent-2-eno-2,4-diyl)diphenol (linear dimer of PIPH, DL-1)</td>
<td>![Image]</td>
</tr>
<tr>
<td>4,4'-(4-methylpent-1-eno-2,4-diyl)diphenol (linear dimer of PIPH, DL-2)</td>
<td>![Image]</td>
</tr>
<tr>
<td>3-(4-hydroxyphenyl)-1,1,3-trimethyl-2,3-dihydro-1H-inden-5-ol (cyclic dimer of PIPH, DC)</td>
<td>![Image]</td>
</tr>
</tbody>
</table>
A number of reactions which are essential for the process of commercial production of BPA have been presented in which numerous byproducts are found that may be involved in the production of BPA (Table). The byproducts are present in the reaction mixture at different concentrations ranging from trace amounts to several percent (e.g., 2,4-isomer of BPA). The knowledge and understanding of the essential chemical reactions taking place in the production of BPA, any transient products that may be formed in the process, and the role of contaminants that are introduced into the process resulting in the formation of byproducts enable the suitable choice and sequence of unit operations in the process of technology, thus leading to advantageous solutions in comparison with those offered by competition.

**Literature**


**Captions to Figures**

Fig. 1. Fragment of 3D visualization of BPA production plant, of 100 t/y capacity, according to the MEXEO technology from Kędzierzyn-Koźle - plant overview (designed by FLUOR S.A., Gliwice, 2016).

Fig. 2. Laboratory stand and reactors for studying kinetics of the BPA synthesis and for testing the solid catalysts in the MEXEO Institute of Technology in Kędzierzyn-Koźle.

Table 1. Summary of by-products occurring in the production process of BPA.