

Production of bisphenol A with reduced isomer formation

The present application relates to a process for the production of bisphenol A, wherein the mixture containing phenol and acetone is brought to a temperature of 48 to
5 54°C.

Bisphenols as condensation products of phenols and carbonyl compounds are starting substances or intermediates for the production of a large number of commercial products. Of particular industrial significance is the condensation
10 product of the reaction between phenol and acetone, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA). BPA is used as a starting substance for the production of various types of polymer materials, such as e.g. polyarylates, polyether imides, polysulfones and modified phenol-formaldehyde
15 resins. Preferred areas of application lie in the production of epoxy resins and polycarbonates.

Industrially relevant production methods for BPA are known and are based on the acid-catalysed reaction of phenol with acetone, wherein a phenol-acetone ratio of more than 5 : 1
20 is preferably established in the reaction. This reaction conventionally takes place continuously, and generally at temperatures of 45 to 110°C, preferably at 50 to 80°C, as described in DE-A-99 57 602. Both homogeneous and heterogeneous Bronsted or Lewis acids can be used as acid
25 catalysts, such as, for example, strong mineral acids, e.g. hydrochloric or sulfuric acid. Gel-like or macroporous sulfonated crosslinked polystyrene resins (acid ion exchangers) are preferably used. Divinylbenzene is normally used as the crosslinking agent, but others, such as
30 divinylbiphenyl, can also be employed. In addition to the catalyst, a co-catalyst can be used. These are usually

thiols, which carry at least one SH function. The co-catalyst can be both homogeneously dissolved in the reaction solution and, in the case of the acid ion exchangers, fixed on the catalyst itself. Homogeneous
5 co-catalysts are e.g. mercaptopropionic acid, hydrogen sulfide, alkyl sulfides, such as e.g. ethyl sulfide, and similar compounds. Fixed co-catalysts are aminoalkyl thiols and pyridylalkyl thiols which are ionically bonded to the catalyst, it being possible for the SH function to be
10 protected and only released during or after fixing to the catalyst. The co-catalyst can also be covalently bonded to the catalyst as alkyl or aryl thiol.

When phenol is reacted with acetone in the presence of acid catalysts, a product mixture is formed which, in addition
15 to unreacted phenol and possibly acetone, primarily contains BPA and water. In addition, small quantities of typical by-products of the condensation reaction occur, such as e.g. 2-(4-hydroxyphenyl)-2-(2-hydroxyphenyl)propane (o,p-BPA), substituted indanes, hydroxyphenylindanols,
20 hydroxyphenylchromanes, spirobisindanes, substituted indenols, substituted xanthenes and more highly condensed compounds with three or more phenyl rings in the molecular backbone. In addition, other secondary components, such as anisole, mesityl oxide, mesitylene and diacetone alcohol,
25 can form by self-condensation of the acetone and reaction with impurities in the raw materials.

For economic and technical reasons, the reaction is usually performed in such a way that a hundred per cent conversion of the acetone is not achieved and 0.1 - 0.6 wt.% acetone
30 is still contained in the reactor discharge.

The above-mentioned by-products, such as water, but also the unreacted feedstocks, such as phenol and acetone, impair the suitability of BPA for the production of polymers and have to be separated off by suitable processes. High demands are made of the purity of the raw material BPA, particularly for the production of polycarbonate.

One processing and purification method for BPA takes place by separating BPA out of the reaction mixture in the form of an approximately equimolar crystalline adduct with phenol by cooling the reaction mixture, allowing the BPA-phenol adduct to crystallise out in a suspension crystallisation. The BPA-phenol adduct crystals are then separated from the liquid phase by suitable apparatus for solid-liquid separation, such as rotary filters or centrifuges, and passed on for further purification.

Adduct crystals obtained in this way typically exhibit a purity of >99 wt.% BPA, based on the sum of BPA and the secondary components, with a phenol proportion of approx. 40 wt.%. By washing with suitable solutions, which typically contain one or more components from the group consisting of acetone, water, phenol, BPA and secondary components, the adduct crystals can be freed of impurities adhering to the surface.

The liquid stream forming during the solid-liquid separation (mother liquor) contains phenol, BPA, water formed during the reaction and unreacted acetone, and is enriched in the secondary components typically forming during BPA production. This mother liquor stream is generally fed back into the reaction unit. To maintain the catalytic activity of the acid ion exchangers, water that

has formed previously is removed by distillation and any acetone still present is also removed from the mother liquor at the same time. The dehydrated reaction stream thus obtained is supplemented with phenol, acetone and optionally co-catalyst and is fed back into the reaction unit. However, the phenol can also be added, wholly or partly, before the dehydration. Alternatively, water and acetone can also be removed by distillation before carrying out the suspension crystallisation of the BPA-phenol adduct. In the distillation steps mentioned, a partial quantity of the phenol present in the reaction solution can also be removed by distillation at the same time.

In a circulating operation of this type, the problem occurs that by-products from BPA production become concentrated in the circulating stream and lead to the deactivation of the catalyst system and to poorer product qualities. To avoid excessive concentration of secondary components in the circulating stream, a partial quantity of the circulating stream - optionally after partial or complete recovery of phenol by distillation - is discharged from the process chain as so-called BPA resin.

Furthermore, part or all of the circulating stream can be passed through a rearrangement unit filled with acid ion exchanger after the solid-liquid separation and before or after the separation of water and residual acetone. This unit is generally operated at higher temperatures than the reaction unit. In this rearrangement unit, some of the secondary components from BPA production present in the circulating stream are isomerised to BPA under the prevailing conditions, so that the total yield of BPA can be increased.

For the further recovery of secondary components, the resin can also be subjected to thermal, acid- or base-catalysed cleavage. The phenol released in this case, and optionally also isopropenylphenol, can be separated off by
5 distillation and returned to the reaction.

The BPA-phenol adduct crystals obtained following the suspension crystallisation of the reaction solution and solid-liquid separation described above are fed into further purification steps, wherein the separation of
10 phenol and optionally the reduction of the concentration of secondary components are achieved.

Thus, the BPA-phenol adduct crystals can be recrystallised for further purification from phenol, organic solvents, water or mixtures of the above solvents, which can
15 optionally also contain BPA and its isomers, by a suspension crystallisation. By selecting suitable solvents, the phenol present in the adduct crystals can also be completely or partly removed at the same time. Any phenol remaining in the BPA after the recrystallisation is then
20 separated off completely by suitable distillation, desorption or extraction methods.

Alternatively, the phenol can also be removed from the BPA-phenol adduct crystals by melting-out processes.

After separating off the phenol, a bisphenol A melt is
25 obtained, which can be used for the production of polycarbonate by the transesterification process (melt polycarbonate) without previous solidification. However, the bisphenol A melt can also be solidified by known processes, e.g. by the prilling process or by flaking, for
30 sale or further use. The melt can also be dissolved in sodium hydroxide solution and used for the production of

polycarbonate by the interfacial polycondensation process. The bisphenol A that has been freed of phenol can optionally be subjected to another purification step, such as e.g. melt crystallisation, distillation and/or
5 recrystallisation from phenol, water or an organic solvent, such as e.g. toluene, or mixtures of these substances, before further processing.

In the context of the process described, the content of secondary components, the so-called isomers, plays a
10 decisive role in the quality of the bisphenol. These so-called isomers (indanes, chromanes, trisphenols, o,p-BPA etc.) influence the crystallisation of the bisphenol A from the reaction solution. As the content of them in the reaction solution increases, their influence also grows. To
15 achieve adequate quality in the crystallisation in spite of this, parts of the circulating stream, the so-called BPA resin, have to be discharged from the circulation, as already described above. For economic reasons, it is necessary to keep the quantity discharged as small as
20 possible since phenol and acetone are lost here as bisphenol A and isomers. While it is true that the processes known to the person skilled in the art, such as rearrangement and resin cleavage, make it possible to recover some of the raw materials, this is however
25 associated with energy input and additional investment costs.

The object of the present invention was therefore to provide a process for the production of bisphenol A in which the isomer formation during the reaction is reduced
30 and a high purity of bisphenol A in the end product is achieved after the crystallisation and filtration, and thus

the quantity discharged from the circulating stream, the so-called BPA resin, can be kept low.

It has now been found that this object can be achieved by a special way of conducting the reaction.

- 5 The invention relates to a process for the production of bisphenol A, wherein
- a) phenol and acetone are mixed together, and
 - b) the mixture containing phenol and acetone is brought to a temperature in the range of 48 to 54°C, and then
 - 10 c) the mixture containing phenol and acetone is brought into contact with an acid ion exchanger as catalyst at this temperature, and
 - d) the mixture containing phenol and acetone is reacted to form bisphenol A.
- 15 It is an essential feature of the process according to the invention that the mixture containing phenol and acetone is brought to a temperature of 48 to 54°C, preferably 50-53°C, particularly preferably 51.5 to 52.5°C in step b) before the reaction.
- 20 The acid ion exchanger in step c) is preferably used in combination with a co-catalyst.

Other substances can also be contained in the mixture containing phenol and acetone. For example, in addition to p,p-bisphenol A itself, the so-called isomers, which are

25 contained in the recycled partial stream of the mother liquor, which originates from the crystallisation and filtration of the BPA-phenol adduct, can also be contained therein. These are the compounds known to the person

skilled in the art, such as e.g. o,p-bisphenol A, o,o-bisphenol A, trisphenols, (hydroxyphenyl)chromanes, (hydroxyphenyl)indanes, (substituted) indanes, (substituted) indenols, (substituted) spirobisindanes, 5 isopropenylphenol and its dimers and oligomers, (substituted) xanthenes, as well as other more highly condensed compounds with three or more phenyl rings in the molecular backbone. In addition, other substituted phenols, anisoles, methanol, mesityl oxide, mesitylene, diacetone 10 alcohol and water, degradation products of the catalyst and of the co-catalyst as well as impurities from the raw materials can also be contained in the recycled partial stream.

By cooling the mixture containing phenol and acetone from 15 the otherwise conventional 55 to 60°C to 48 to 54°C, the starting temperature of the reaction is ultimately reduced to a temperature in the range of 48 to 54°C. As a result, the isomer formation during the reaction on the acid ion exchanger becomes more selective with regard to p,p- 20 bisphenol A, the desired main product. At the same time, the quantity to be discharged from the recycled partial stream of the mother liquor, which originates from the crystallisation and filtration of the BPA-phenol adduct crystals, i.e. ultimately the quantity of BPA resin to be 25 discharged to keep the content of by-products, the so-called isomers, in the reactor constant at a level that is acceptable for the performance of the crystallisation and the purity of the end product, is reduced. Because of the smaller discharge, less bisphenol resin is formed as a 30 residual substance. Thus, the quantity of BPA resin is a direct indication of the isomer formation in the reaction. By reducing the reactor inlet temperature, the resin

formation can be reduced by up to 50%, which represents a large economic saving with constant product quality.

The reaction is preferably conducted in such a way that a reactor temperature of 77°C is not exceeded. It is
5 preferable to conduct this reaction adiabatically. In practice, this generally leads to the highest temperature occurring at the reactor outlet. The reactor outlet temperature is therefore the highest temperature occurring in the reactor. Conducting the reaction adiabatically here
10 also includes a method of conducting the reaction in which the reactor jacket is heated slightly from the outside to avoid crystallisation in wall areas.

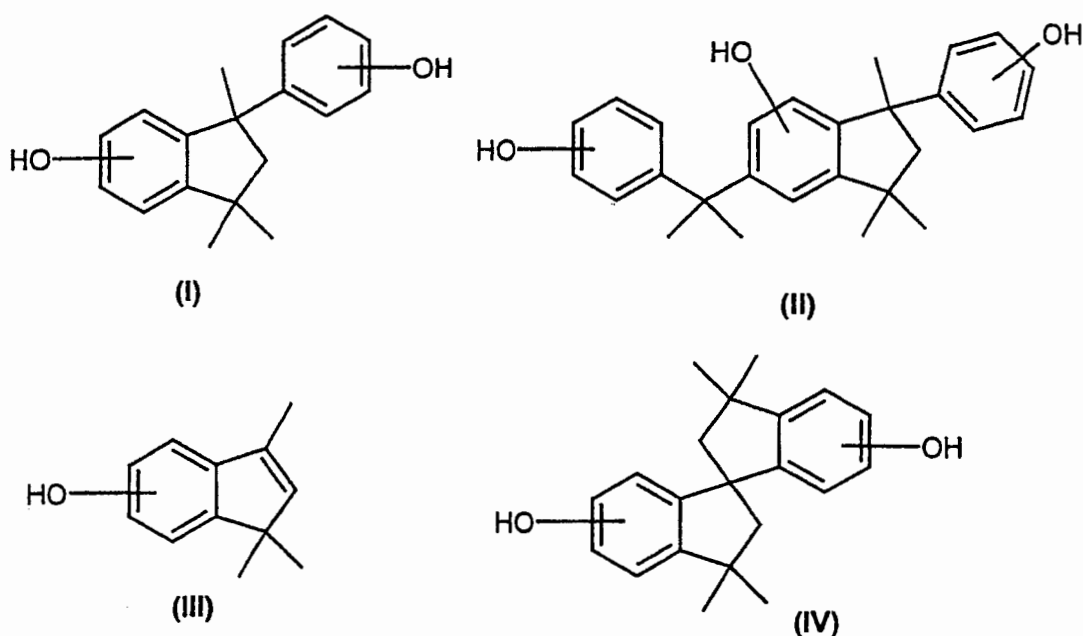
As a result of the low temperature at the beginning of the reaction, at which a high concentration of acetone is still
15 present, in particular the self-condensation of acetone as well as the formation of chromanes, indanes and other by-products of bisphenol A production known to the person skilled in the art are reduced.

To obtain a bisphenol of sufficient quality and to be able
20 to perform the crystallisation and filtration of the bisphenol A-phenol adduct crystals without any problems, a content of 100 g/l of the so-called isomers in the reaction mixture after the reaction should, if possible, not be exceeded. A content of 60 to 100 g/l of the so-called
25 isomers in the reaction mixture at the reactor outlet is preferably established. As a result of the process according to the invention, the discharge of the partial stream of the recycled mother liquor originating from the crystallisation and filtration of the BPA-phenol adduct
30 crystals can be quantitatively reduced without exceeding the limit of 100 g/l of the so-called isomers in the

product mixture at the reactor outlet. A process is therefore preferred in which a product mixture is obtained in step d) from which a bisphenol A-phenol adduct is then crystallised out and filtered off and bisphenol A produced therefrom, and wherein the mother liquor forming during the crystallisation and filtration is partly recycled into the mixing of phenol and acetone in step a), wherein a partial stream is discharged from the recycled mother liquor and wherein this partial stream makes up quantitatively less than 6 wt.%, based on the quantity of bisphenol A produced, ignoring any phenol present. The discharged partial stream of the mother liquor therefore amounts to less than 6 wt.%, quantitatively, based on the quantity of bisphenol A produced, taking into account all the components contained in the partial stream except phenol. The content of phenol in the partial stream of the mother liquor to be discharged can readily be determined by the person skilled in the art using common analytical methods.

The quantity of BPA resin ultimately formed can also be further reduced in the process according to the invention by methods known to the person skilled in the art, such as e.g. rearrangement and resin cleavage.

In particular the formation of indanes, indenols and spirobisindanes is favoured by high temperatures. Formulae (I) and (II) show examples of indanes, formula (III) an example of an indenol and formula (IV) an example of a spirobisindane.



It is known that isomers such as o,p-BPA can still be rearranged during the reaction, whereas indanes, spirobisindanes and indenols cannot. Their formation in the
 5 reaction must therefore be especially avoided as far as possible and their concentration in the reaction mixture kept low.

It has been shown that the content of these indanes, spirobisindanes and indenols in the product mixture at the
 10 reactor outlet can be reduced by the process according to the invention to less than 15 g/l.

The process according to the invention enables a BPA to be produced in a purity of more than 99.5 wt.% of p,p-bisphenol A after crystallisation and filtration of the
 15 BPA-phenol adduct, subsequent washing with phenol and separation of the phenol by distillation and/or desorption, without additional purification by recrystallisation being necessary.

The bisphenol A produced by the process according to the
 20 invention can be reacted with phosgene by the interfacial

polycondensation process or with diaryl carbonates, preferably diphenyl carbonate, by the melt process to form polycarbonate.

Example 1 (according to the invention)

5 A reaction solution consisting of 4 wt.% acetone, 6 wt.% isomers, 7 wt.% bisphenol A, 0.05 wt.% water, 300 ppm mercaptopropionic acid and the remainder being phenol (approx. 83 wt.%) is passed from top to bottom through a reactor charged with 100 m³ of phenol-moist, acid ion
10 exchanger Lewatit SC104 at a throughput of 30 t/h. This corresponds to a bisphenol A production of 4.2 t/h. The reactor inlet temperature is regulated at 52°C. The reactor outlet temperature is 75°C. At this setting, the partial stream of mother liquor discharged amounts to 5.1 wt.%,
15 quantitatively, based on the quantity of bisphenol A produced, taking into account all the components contained in the partial stream except phenol. The content of indanes, spirobisindanes and indenols is 12 g/l in total in the reactor discharge using this method of operation.

20 **Example 2 (comparative example)**

The test is performed as in Example 1, but the reactor inlet temperature is now 56°C and the reactor outlet temperature 79°C. At this setting, the partial stream of mother liquor discharged amounts to 8 wt.%, quantitatively,
25 based on the quantity of bisphenol A produced, taking into account all the components contained in the partial stream except phenol. The content of indanes, spirobisindanes and indenols is 19 g/l in total in the reactor discharge using this method of operation.

Claims

1. Process for the production of bisphenol A, wherein
 - a) phenol and acetone are mixed together and
 - b) the mixture containing phenol and acetone is brought to a temperature in the range of 48 to 54°C, and then
 - c) the mixture containing phenol and acetone is brought into contact with an acid ion exchanger as catalyst at this temperature, and
 - d) the mixture containing phenol and acetone is reacted to form bisphenol A,wherein the ion exchanger in step c) is used in combination with a cocatalyst.
2. Process according to claim 1, wherein the temperature of the reaction in step d) does not exceed 77°C.
3. Process according to one of claims 1 or 2, wherein the reaction in step d) is conducted adiabatically.
4. Process according to one of claims 1 to 3, wherein a product mixture is obtained in step d) from which a bisphenol A-phenol adduct is then crystallised out and filtered off and bisphenol A produced therefrom, and wherein the mother liquor forming during the crystallisation and filtration is partly recycled into the mixing of phenol and acetone in step a), a partial stream being discharged from the recycled mother liquor and this partial stream making up quantitatively less than 6 wt.%, based on the quantity of bisphenol A produced, ignoring any phenol present.

5. Process according to one of claims 1 to 4, wherein the content of the indanes, spirobisindanes and indenols in the product mixture obtained in step d) is less than 15 g/l, based on the product mixture.
6. Process for the production of polycarbonate, wherein bisphenol A is produced according to one of claims 1 to 6 and then reacted with phosgene by the interfacial polycondensation process or with diphenyl carbonate by the melt process to form polycarbonate.