

Process for the separation of phenol from phenol-containing streams from the preparation of bisphenol A

Bisphenols as condensation products of phenols and carbonyl compounds are starting materials or intermediates for the production of a large number of commercial products. The condensation product from the reaction of phenol and acetone, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA), is of particular industrial importance. BPA is used as the starting material for the production of various polymeric materials, such as, for example, polyarylates, polyether imides, polysulfones and modified phenol-formaldehyde resins. Preferred fields of application are the production of epoxy resins and polycarbonates.

The industrially relevant preparation methods for BPA are based on the acid-catalysed reaction of phenol with acetone, a phenol-acetone ratio of > 5:1 preferably being established in the reaction. As acidic catalysts there may be used both homogeneous and heterogeneous Brönstedt or Lewis acids, for example strong mineral acids such as hydrochloric or sulfuric acid. Gel-like or macroporous sulfonated crosslinked polystyrene resins (acidic ion exchangers) are preferably used. The embodiments hereinbelow relate to a process using acidic ion exchangers as catalysts. These may be mono- or hetero-disperse.

In order to achieve high selectivities, the reaction of phenol with acetone is carried out in the presence of suitable mercapto compounds as co-catalysts. These can either be homogeneously dissolved in the reaction solution or fixed to the sulfonated polystyrene matrix via ionic or covalent bonds. The reaction unit is a stratified bed or fluidised bed, through which the solution flows upwards or

downwards, or a column such as a reactive distillation column.

5 The selectivity of the reaction, as well as the long-term storage stability of the catalyst, are affected in a decisive manner by the quality of the raw materials phenol and acetone that are used. For the preparation in particular of BPA as a raw material for high-quality plastics such as, for example, BPA, very high demands
10 are therefore made of the purity of the basic materials phenol and acetone that are used. Typically, purities of > 99.95 wt.% for phenol and > 99.90 wt.% for acetone, with at the same time low contents of impurities (S < 0.5 ppm, Fe < 1 ppm), are regarded as being positive for the
15 achievement of high product purities and for minimising catalyst deactivation. For example, EP-A-876 319 describes freeing commercial phenol of troublesome impurities by treatment with molecular sieve and thus ensuring better usability in a process for BPA preparation.

20

EP-A-680 913 describes the use of modified acidic ion exchangers to remove hydroxyacetone from phenol for BPA synthesis.

25

The reaction of phenol with acetone in the presence of acidic catalysts and mercapto compounds as co-catalysts yields a product mixture that, as well as containing unreacted phenol and optionally acetone, primarily contains BPA and water. In addition, small amounts of typical
30 secondary products of the condensation reaction are formed, for example 2-(4-hydroxyphenyl)-2-(2-hydroxyphenyl)propane (o,p-BPA), substituted indanes, hydroxyphenylindanols, hydroxyphenyl-chromanes, substituted xanthenes and more highly condensed compounds having three or more phenyl
35 rings in the molecular framework.

The mentioned secondary products, as well as water, phenol and acetone, impair the suitability of BPA for the production of polymers and must be separated off by
5 suitable processes. For the production of polycarbonate in particular, high demands are made of the purity of the raw material BPA.

The working up and purification of BPA is carried out by a
10 multi-stage cascade of suitable purification processes such as, for example, suspension crystallisation, melt crystallisation, distillation and/or desorption. In an industrially preferred form, BPA is separated from the reaction mixture in the form of an approximately equimolar
15 crystalline adduct with phenol by cooling the reaction mixture with crystallisation of the BPA/phenol adduct. The crystallisation is preferably carried out in the form of suspension crystallisation. The BPA/phenol adduct crystals are subsequently separated from the liquid phase by means
20 of a suitable apparatus for solid/liquid separation, such as rotary filters or centrifuges, and fed to further purification. Adduct crystals so obtained typically have a purity of > 99 wt.% BPA, based on BPA and the secondary components with a phenol content of about 40 wt.%, based on
25 the total amount of adduct crystals. By washing with suitable solutions, which typically contain one or more components from the group acetone, water, phenol, BPA and secondary components, the adduct crystals can be freed of impurities adhering to the surface. The BPA/phenol adduct
30 crystals obtained following the above-described suspension crystallisation of the reaction solution and solid/liquid separation are fed to more extensive purification steps, wherein phenol is separated off and, optionally, a reduction in the concentration of secondary components is
35 achieved by the use of suitable purification operations

(suspension crystallisation, layer crystallisation, extraction, distillation).

5 The stream of liquid obtained in the solid/liquid separation (mother liquor) contains phenol, BPA, water formed in the reaction, unreacted acetone, and is rich in the secondary components typically formed in the preparation of BPA. In a preferred form, this stream of mother liquor is fed back into the reaction unit. In order
10 to maintain the catalytic activity of the acidic ion exchanger, all or some of the water that has formed is removed beforehand by distillation, any acetone that is still present also being removed wholly or partially from the mother liquor. The dewatered reaction stream so
15 obtained is supplemented with phenol and acetone and fed back into the reaction unit. Alternatively, it is possible to remove water and acetone wholly or partially by distillation before the suspension crystallisation of the BPA/phenol adduct is carried out. In the mentioned
20 distillation steps, a portion of the phenol present in the reaction solution can also be separated off by distillation.

25 Such a closed-circuit procedure has the problem that secondary products of the BPA preparation become concentrated in the circulating stream; these secondary products adversely affect the purity of BPA in the suspension crystallisation and can lead to deactivation of the catalyst system. In order to avoid excessive
30 concentration of secondary components in the circulating stream, a portion of the mother liquor mixture must be discharged from the system. The amount of secondary components removed from the process in this manner must correspond in the equilibrium state to the amount of
35 secondary components formed in the reaction. The discharge

is typically effected by removing a portion of the mother liquor from the circulating stream, it being possible for water of reaction that has formed, unreacted acetone and portions of phenol optionally to be removed by distillation
5 beforehand. The composition of the mother liquor at this point, and accordingly also the composition of the discharged portion, typically consists of from 70 to 90 wt.% phenol, from 3 to 15 wt.% BPA and from 3 to 15 wt.% other secondary components and isomers formed in the
10 reaction. Because ultimately only the last-mentioned portion of secondary components has to be removed from the process, the discharged amount is subjected to further working-up steps in order to minimise losses of material.

15 In a simple form, phenol is distilled off to a residual content of < 10 wt.%, so that a residual resin having a content of < 10 wt.% phenol, from 15 to 85 wt.% BPA and from 15 to 85 wt.% secondary components is obtained, which resin is removed from the process and disposed of, for
20 example, by burning or dumping.

In another form, a portion of the BPA contained in the discharged amount is recovered by distilling off a portion of the phenol from the discharged portion and feeding the
25 concentrated solution so obtained to suspension crystallisation and subsequent solid/liquid separation. It has proved advantageous here to pass the discharged amount, before or after the partial separation of phenol, over a rearrangement unit filled with acidic ion exchanger. This
30 unit is generally operated at higher temperatures than the reaction unit. In this rearrangement unit, under the conditions prevailing therein, some of the secondary components of the BPA preparation present in the circulating stream are isomerised to BPA, so that the total
35 yield of BPA can be increased. In the solid/liquid

separation, a portion of the BPA that is present is obtained in the form of a BPA/phenol adduct crystal and can be fed to further purification steps. A filtrate typically consisting of from 60 to 90 wt.% phenol, from 3 to 12 wt.% BPA and from 3 to 18 wt.% secondary components is additionally obtained. The phenol contained in this filtrate is distilled off to a residual content of typically < 10 wt.% and the resulting residual resin, containing < 10 wt.% phenol, from 14 to 80 wt.% BPA, from 20 to 86 wt.% secondary components, is fed to disposal.

The described processes for the working up of the discharged stream have the disadvantage that relatively large amounts of phenol, either in undissolved form or bonded in BPA or the secondary components, are still present in the residual resin that is finally disposed of. Disposal of the residual resin accordingly leads to a loss of raw materials.

The object of the present invention was therefore to find a process for the working up of discharged streams from a BPA production process, with which process phenol is obtained in high purity and in high yields.

Such a process preferably meets the following demands:

1. minimisation of phenol in the residual resin,
2. minimisation of BPA in the residual resin,
3. minimisation of the amount of residual resin,
4. provision of phenol of high purity (> 99.8 %) and having low contents of impurities (S, Fe, Cl) from the working-up process with high yields,

5. continuous procedure with minimal use of apparatus and energy.

5 The invention relates to a process for the continuous separation of phenol from a partial stream, produced in the preparation of bisphenol A and containing from 40 to 90 wt.% phenol, from 5 to 40 wt.% bisphenol A and from 5 to 40 wt.% secondary components formed in the reaction of
10 phenol and acetone to give bisphenol A,

in which process

- 15 a) the partial stream is fed to a distillation column containing at least 5 theoretical separation stages, and
- b) in the distillation column, phenol is distilled off at the top, and
- 20 c) a first portion of the bottom product is discharged from the process, and
- 25 d) a second portion of the bottom product is transferred continuously into a dwell-time container in which the secondary components contained in the bottom product are at least partially isomerised at temperatures of > 190°C and with a hydrodynamic dwell time of at least 120 minutes, in the presence of an acidic catalyst, and then fed back into the distillation column, the mass flow rate of the portion of the bottom product fed into the dwell-time container being more than 30 % of the mass flow rate of the partial stream introduced into the distillation column in step a).
- 30
- 35

The phenol distilled off in step b) preferably has a purity of > 99.8 wt.%.

5 The technical object is achieved by acid-catalysed cleavage of the discharged stream in a dwell-time container and continuous separation of the phenol over a vacuum column having a high separating capacity.

10 Figure 1 shows a preferred embodiment of the process according to the invention.

A partial stream 1 discharged from a process for the preparation of bisphenol A is fed into a distillation column 2 having a high separating efficiency. The high
15 separating efficiency is achieved by the theoretical separating stages, of which there are at least 5. In this distillation column, phenol vapours 3 are separated off at the top and are condensed in a condenser 4 to liquid phenol 5. The bottom product or discharge 6 from the
20 column 2 is circulated via a heat exchanger 7 so that the energy required for the vaporisation of phenol is thus introduced into the system. The condenser 4 and the vaporiser 7 may be independent parts of the installation or they may be integrated into the structure of the
25 distillation columns. A partial stream 9 of the bottom product is fed to disposal in the form of residual resin, optionally after storage in a buffer tank 10. Another partial stream 8 of the bottom product is fed to a dwell-time tank 11. In this dwell-time tank, the acid-catalysed
30 isomerisation and cleavage of BPA and secondary components take place, with the formation of phenol. The cleavage is accelerated by the addition of suitable acids (stream 12) by means of a metering unit 13. The phenol-containing discharge 14 from the dwell-time container 11 is combined

with the discharged partial stream 1 and thus fed back into the distillation unit 2 for the recovery of phenol.

5 The process is operated continuously and reaches an equilibrium state after a short time. The partial stream 1 discharged from the process for the preparation of bisphenol A may in principle be any product stream from a process for the preparation of BPA that contains the following components: from 40 to 90 wt.% phenol, from 5 to 10 40 wt.% bisphenol A and from 5 to 40 wt.% secondary components formed in the reaction of phenol and acetone to give bisphenol A.

15 Partial stream 1 is preferably a discharged partial stream from a BPA preparation process with suspension crystallisation and solid/liquid separation, a partial stream of the filtrate of the solid/liquid separation for the discharge of secondary products being fed off in the direction of the process according to the invention for the 20 separation of phenol. Before being fed into the distillation column 2, the mentioned partial stream 1 is optionally fed through an additional rearrangement unit, wherein a portion of the BPA contained in the filtrate is recovered by treatment with an acidic ion exchanger, 25 subsequent partial distillation of phenol, crystallisation and solid/liquid separation, and fed to the main process. In this case, the filtrate of the solid/liquid separation in the rearrangement unit is used as the feed stream 1 of the distillation column 2.

30 In order to permit cleavage, separation and purification of the phenol-containing residual substances in a manner that is as efficient as possible, the following marginal conditions must be observed in the procedure according to 35 the invention: the distillation column 2 must have at least

5 theoretical separation stages, preferably at least 10 theoretical separation stages, in order to permit the separation of other low-boiling components such as, for example, isopropyl phenol and ensure concentration of the resulting phenol to a purity of > 99.8 wt.% at the top of the column. The distillation is preferably carried out with an absolute pressure at the top of the column of from 70 to 200 mbar, preferably from 90 to 120 mbar. The dwell-time tank 11 must be so constructed that a mean hydrodynamic dwell time of the circulating stream 8 of at least 2 hours, preferably at least 4 hours, is established, in order to achieve separation of BPA and secondary products that is effective and as complete as possible. The dwell-time reactor can be operated completely filled with upward or downward flow or in a level-controlled manner.

The isomerisation and the associated cleavage in the dwell-time container 11 in step d) is carried out in the presence of an acidic catalyst. As the acidic catalyst (stream 12) for the cleavage in step d) there may in principle be used a large number of strongly acidic, low or non-volatile Brönstedt acids, including phosphoric acid or the higher condensates thereof, sulfuric acid, alkanesulfonic acids having > 4 carbon atoms in the alkane chain, aromatic sulfonic acids, arylalkane-sulfonic acids or phosphonium acids. In addition to these homogeneously employed acids, it is also possible to use heterogeneous cleavage catalysts, such as, for example, strongly acidic aluminium oxide, supported Lewis acids, acidic zeolites or other aluminas, or polystyrene sulfonic acids. In this case, the metering unit 13 is not required and the heterogeneous catalyst is introduced into the dwell-time container 11 by means of a suitable retaining construction and exchanged as necessary. In a preferred embodiment of the invention, the isomerisation and cleavage in step d) are carried out in

the presence of sulfuric acid, phosphoric acid or p-toluenesulfonic acid, particularly preferably with sulfuric acid. The metering can be carried out, as shown in Figure 1, as a stream 12 via the metering unit 13 into the circulating stream of the bottom product of the distillation column 2. However, it is also possible for metering to be carried out into the intake stream 8 into the dwell-time container 11 or into the outlet stream 14 from the dwell-time container 11. Finally, metering can also be carried out into the partial stream 1 into the distillation column 2. Metering into the circulating stream of the bottom product of the distillation column 2 of the column is preferred.

The preferred concentration of the acidic cleavage catalyst is dependent on the amount of the cleavable secondary products in the intake stream and on the nature of the acid used and can readily be determined in simple experiments. For the preferred embodiment using sulfuric acid, the metered amount of acid is given as follows:

$$M(\text{sulfuric acid}) = c * (1 - X) * M(1)$$

where

M (sulfuric acid) represents the mass flow rate of sulfuric acid in kg/h, and
c represents the concentration factor, and
X represents the amount by weight of phenol in partial stream 1, and
M (1) represents the mass flow rate of partial stream 1 in kg/h.

For effective cleavage, c is from 0.001 % to 2 %, preferably from 0.005 to 1 %, particularly preferably from

0.01 to 0.2 %. For other acids, analogous equations with
0.001 % < c < 5 % apply.

For effective isomerisation and cleavage, the temperature
5 in the dwell-time container 11 must be > 190°C, preferably
> 200°C. In order to limit the use of additional
apparatuses, the supply of heat is effected in a preferred
embodiment directly by the vaporiser 7 of the distillation
column 2. This means that the intake stream 8 into the
10 dwell-time container 11 is not heated by a separate heat
exchanger and the bottom of the column 2 and the dwell-time
container 11 are operated at the same temperature.

In order to ensure efficient separation of the phenol from
15 the outlet stream 14 from the dwell-time container 11, it
is necessary that the circulating stream via the dwell-time
container should not be too small compared with the partial
stream 1. Otherwise, only incomplete cleavage of the
cleavable secondary products occurs and material that is
20 still cleavable is discharged via the discharged partial
stream 9, which is associated with a loss of material. The
mass flow rate introduced into the dwell-time container 11
is therefore > 30 %, preferably > 80 %, very particularly
preferably > 100 % of the mass flow rate of the partial
25 stream 1 coming from the process for the preparation of
bisphenol A.

In order to allow the acid-catalysed cleavage to proceed
successfully, it is additionally necessary to select a
30 hydrodynamic dwell time in the dwell-time container 11 of
at least 2 hours, preferably at least 4 hours.

Examples

The following Examples 1 to 7 are carried out in a test installation according to Figure 1.

5

An industrial installation for the preparation of bisphenol A yields, after reaction and separation of BPA, a discharged partial stream 1 which is fed to working up by distillation in the vacuum distillation column 2. The partial stream 1 is fed to the distillation column 2 with a mass flow rate $M(1)$ and contains phenol in an amount by weight of X and other components in an amount by weight of $(1-X)$, which other components substantially contain BPA and its isomers as well as various branched and higher condensation products of acetone and phenol, such as, for example, hydroxyphenyl-substituted indanes, chromanes, trisphenols and similar cleavable products. The composition (without the phenol component) in all the examples and comparison examples is: p,p-BPA 35-40 wt.%, o,p-BPA 9 to 12 wt.%, hydroxyphenyl-substituted indanes 15 to 19 wt.%, hydroxyphenyl-substituted chromanes 18 to 22 wt.%, trisphenol 3 to 5 wt.%, other constituents 9 to 12 wt.%. This corresponds to a typical composition of a discharged stream from a bisphenol A production installation.

25

Table 1 shows the purity $C(5)$ and the mass flow rate $M(5)$ of the resulting phenol stream 5 at the top of the column for the various conditions on which Examples 1 to 7 are based. The column 2 used has 20 theoretical plates and was operated with a reflux ratio of about 0.6 and with the pressures that become established with establishment of the temperature $T(11)$ at the bottom of the column 2 in thermodynamic equilibrium. The temperature in the dwell-time container 11 is the same as the temperature at the bottom of the column 2. The indicated values relate to

35

equilibrium conditions, which become established after a few hours with continuous operation of the column.

For optimum recovery of phenol from the partial stream 1 it is desirable to maximise the mass flow rate $M(5)$ and the purity $C(5)$ of the phenol stream 5 separated off, in order to obtain a maximum amount of highly pure phenol. At the same time, the mass flow rate $M(9)$ of unusable residual resin 9 is to be minimised. In Examples 1 and 2 according to the invention, the mass flow rate $M(5)$ of the phenol stream 5 separated off is increased by the cleavage of the cleavable constituents contained in the partial stream 1, so that, based on the amount by weight X of phenol in the partial stream 1, a phenol yield $Y = M(5) / (X * M(1))$ of > 1.20 is obtained and, at the same time, a phenol stream 5 of high purity $C(5)$ is obtained and the mass flow rate $M(9)$ of discharged residual resin 9 is minimised.

In Examples 1 to 3 and 5 to 7, cleavage in the dwell-time container 11 is assisted by the addition of sulfuric acid. The amounts of sulfuric acid $M(\text{sulfuric acid})$ used are given by the following equation:
$$M(\text{sulfuric acid}) = c * (1 - X) * M(1).$$

In Comparison Example 3, the temperature $T(11)$ in the dwell-time container 11 is lowered to 180°C . The phenol yield falls to 1.03 as a result, i.e. effective cleavage no longer takes place.

Comparison Example 4 shows the effect of the sulfuric acid concentration. Without the feeding in of additional acid ($c = 0$ in Example 4 means $M(\text{sulfuric acid}) = 0$) there is no effective cleavage and the phenol yield therefore falls to 0.97.

Comparison Example 5 shows the effect of the mass flow rate of the stream of bottom product fed through the dwell-time container 11. Effective cleavage and recovery of phenol is only obtained with an adequate mass flow rate $M(8)$ of the bottom product fed through the dwell-time container 11 and back into the column 2. For $M(8) < 0.3 * M(1)$, the phenol yield therefore falls to 1.05.

Comparison Example 6 is carried out with an otherwise identical construction using a column of lower separating efficiency (number of theoretical plates = 1). Although a high phenol yield $Y = 1.27$ is reached in this case, only moderate phenol purity ($C(5) = 96.2$ wt.%) is achieved at the top of the column.

Comparison Example 7 is carried out with the column 2 already used in Examples 1 to 5, but the dwell-time container 11 is avoided so that no dwell time for cleavage is available. As a result, a high phenol yield Y in the phenol stream 5 is not achieved despite the addition of sulfuric acid.

The examples and comparison examples show that it is possible in the process according to the invention, using a distillation column 2 and a dwell-time container 11, with addition of an acidic cleavage catalyst, to obtain phenol of high purity in an increased yield at the top of the column and at the same time to minimise the amount of residual resin.

30

35

Table 1

	M(1)	X	c	T(11)	C(5)	M(5)	Y	M(9)	M(8)	$\tau(11)$
	[t/h]	[-]	[%]	[°C]	[wt.%]	[t/h]	[-]	[t/h]	[t/h]	[h]
Ex. 1 1) 2)	2.75	0.65	0.06	205	99.88	2.19	1.22	0.56	3.10	19.4
Ex. 2 1) 2)	2.40	0.50	0.06	210	99.91	1.72	1.43	0.68	2.95	20.3
Comp. Ex. 3 1) 2)	2.65	0.62	0.06	180	99.75	1.69	1.03	0.96	2.80	21.4
Comp. Ex. 4 1) 2)	2.80	0.59	0.0	205	99.87	1.60	0.97	1.20	3.05	19.7
Comp. Ex. 5 1) 2)	2.75	0.63	0.05	200	99.89	1.82	1.05	0.93	0.5	120.0
Comp. Ex. 6 3) 2)	2.90	0.62	0.06	205	96.25	2.28	1.27	0.62	3.2	18.8
Comp. Ex. 7 1) 4)	2.90	0.58	0.05	205	99.58	1.70	1.01	1.20	3.2	0

5 where

M(1) = mass flow rate of partial stream 1,

X = phenol content in partial stream 1,

C = concentration factor for sulfuric acid addition

10 $M(H_2SO_4) = c * (1 - X) * M(1)$; 96 % sulfuric acid was added,

T(11) = temperature in the dwell-time container 11,

C(5) = purity/gel content of phenol in the phenol stream 5,

M(5) = mass flow rate of the phenol stream 5,

15 Y = phenol yield based on the content of phenol in partial stream

$$1: Y = M(5) / (X * M(1)),$$

M(9) = mass flow rate of discharged residual resin 9 for disposal,

20 M(8) = mass flow rate of bottom product through the dwell-time container 11,

$\tau(11)$ = hydrodynamic dwell time in the dwell-time container 11.

Footnotes:

- 5 1) a vacuum column having 20 theoretical plates
 is used
- 2) a dwell-time container having a volume of 60
 m3 is used
- 3) a vacuum column having 1 theoretical plate
10 is used
- 4) the dwell-time container 11 is avoided

Patent claims

1. Process for the continuous separation of phenol from a partial stream produced in the preparation of bisphenol A and containing from 40 to 90 wt.% phenol, from 5 to 40 wt.% bisphenol A and from 5 to 40 wt.% secondary components formed in the reaction of phenol and acetone to give bisphenol A,
- in which process
- a) the partial stream is fed to a distillation column containing at least 5 theoretical separation stages, and
 - b) in the distillation column, phenol is distilled off at the top, and
 - c) a first portion of the bottom product is discharged from the process, and
 - d) a second portion of the bottom product is transferred continuously into a dwell-time container in which the secondary components contained in the bottom product are at least partially isomerised at temperatures of $> 190^{\circ}\text{C}$ and with a hydrodynamic dwell time of at least 120 minutes, in the presence of an acidic catalyst, and then fed back into the distillation column, the mass flow rate of the portion of the bottom product fed into the dwell-time container being more than 30 % of the mass flow rate of the partial stream introduced into the distillation column in step a).

2. Process according to claim 1, in which sulfuric acid is used as the acidic catalyst in step d).
3. Process according to either claim 1 or claim 2, in
5 which the isomerisation in step d) is carried out at temperatures of $> 200^{\circ}\text{C}$.
4. Process according to any one of claims 1 to 3, in
10 which the isomerisation in step d) is carried out with a hydrodynamic dwell time of at least 4 hours.
5. Process according to any one of claims 1 to 4, characterised in that phenol having a purity of > 99.8 wt.% is obtained in step b).