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(54) Title: PROCESS

(57) Abstract: Process for converting 1-phenylethanol into styrene, which process comprises: (1) contacting a feed comprising 1-phenylethanol, organic acid and 2-phenylethanol with a catalyst to obtain a product comprising styrene, and (2) removing ester compounds based on 2-phenylethanol and organic acid from the product of step (1), in which process the feed of step (1) has a molar ratio o organic acid to 2-phenylethanol of at least 1:10.

PROCESS FOR CONVERTING 1-PHENYLETHANOL INTO STYRENE

The present invention relates to a process in which feed comprising 1-phenylethanol (also known as α-phenylethanol or methyl phenyl carbinol) is contacted with catalyst.

Background of the invention

A commonly known process comprises the manufacture of styrene and propylene oxide starting from ethylbenzene and propene. In general such process involves the steps of (i) reacting ethylbenzene with oxygen or air to form ethylbenzene hydroperoxide, (ii) reacting the ethylbenzene hydroperoxide thus obtained with propene in the presence of an epoxidation catalyst to yield propylene oxide and 1-phenylethanol, and (iii) converting the 1-phenylethanol into styrene by dehydration using a suitable dehydration catalyst.

As described in US-A-4,400,558, oxidation of ethylbenzene gives by-products such as 1-phenylethanol and acetophenone, and in minor amounts 2-phenylethanol and its precursors, such as 2-phenylethyl hydroperoxide. In step (ii) ethylbenzene hydroperoxide is itself converted to 1-phenylethanol, while more acetophenone and 2-phenylethanol are formed as by-products. Propene, ethylbenzene and propylene oxide are usually removed from the reaction mixture of step (ii) by distillation. The residue comprises 1-phenylethanol, acetophenone and a variety of by-products including 2-phenylethanol. This residue is subjected to step (iii). Styrene and acetophenone are usually removed from the reaction mixture obtained in step (iii), and the reaction mixture obtained can be recycled and sent again to the dehydration unit. The acetophenone rich fraction is

generally hydrogenated to convert acetophenone to 1-phenylethanol, which can also be sent to the dehydration unit.

A problem of 2-phenylethanol is that it is less easily converted into styrene while it cannot easily be separated from 1-phenylethanol by distillation. This means that 2-phenylethanol tends to build up in the dehydration unit.

Summary of the invention

It has now been found that 2-phenylethanol can be removed in a simple and effective way. It was found that 2-phenylethanol reacts more readily with organic acids such as benzoic acid than 1-phenylethanol in the dehydration unit. Organic acids can be added to the reaction mixture comprising 1-phenylethanol and 2-phenylethanol. However, generally organic acids are produced in the preparation of ethylbenzene hydroperoxide and/or propylene oxide. Therefore, the propylene oxide manufacturing process can be simplified in a further aspect in that organic acids do not need to be removed or need to be removed to a lesser extent in the process preceding the dehydration unit.

Therefore, the present invention now relates to a process for converting 1-phenylethanol into styrene, which process comprises:

(1) contacting a feed comprising 1-phenylethanol, organic acid and 2-phenylethanol with a catalyst to obtain a product comprising styrene, and

(2) removing ester compounds based on 2-phenylethanol and organic acid from the product of step (1),

in which process the feed of step (1) has a molar ratio of organic acid to 2-phenylethanol of at least 1:10.

Detailed description of the invention

In the present invention, ethylbenzene, 1-phenylethanol, 2-phenylethanol and styrene can contain substituents. The substituents can be either on the phenyl ring or on the ethyl or ethanol or ethylene chain. Most specifically, the compounds are unsubstituted ethylbenzene, 1-phenylethanol, 2-phenylethanol and styrene.

The feed comprising for 1-phenylethanol, organic acid and 2-phenylethanol for use in the present process will generally have been obtained by a process comprising:
(a) oxidation of ethylbenzene to obtain reaction product containing ethylbenzene hydroperoxide,
(b) optionally washing the reaction product of step (a),
(c) reacting at least part of the reaction product containing ethylbenzene hydroperoxide with propene to yield propylene oxide and aryl alcohol, and
(d) removing propylene oxide from the product obtained in step (c).

The product of step (d) can suitably be used as feed for step (1) of the process according to the present invention.

Conventionally, the above process for manufacturing the feed comprising 1-phenylethanol would comprise washing the reaction product of step (a) with aqueous base in an amount sufficient to neutralize acidic components thereof and separating the resulting mixture into an aqueous stream and a deacidified organic stream. The base contaminated, deacidified hydroperoxide stream would subsequently be washed with water and the resulting mixture separated into an organics contaminated water phase and an organic phase having a reduced alkali metal content. Such process has been described in US-A-5,883,268. Recently, it has been found that it can be beneficial not to wash the reaction product containing

hydroperoxide with aqueous base. This has been described in co-pending European patent application 02250791.7 (our case TS 1212). However, the present process makes even the water wash obsolete. Therefore, in the present invention the reaction product containing ethylbenzene hydroperoxide is preferably used without having been washed with water or aqueous base.

The reaction product containing ethylbenzene hydroperoxide obtained by oxidation of an ethylbenzene compound, generally contains organic acids. These organic acids generally comprise a substantial amount of benzoic acid and smaller amounts of other acids. It has been found to be acceptable that these organic acids are present during the epoxidation step wherein ethylbenzene hydroperoxide is reacted with propene to yield propylene oxide and 1-phenylethanol. If the organic acids remain in the reaction mixture during epoxidation, they can be put to good use in the subsequent step where they can react with 2-phenylethanol.

Ethylbenzene hydroperoxide is reacted with propene to yield propylene oxide and 1-phenylethanol. In such epoxidation step a homogeneous catalyst or a heterogeneous catalyst can be applied. As homogeneous catalysts molybdenum compounds are frequently applied, while catalysts comprising titanium on a silica carrier are often used as heterogeneous catalysts. Conditions under which epoxidation is carried out are known in the art and include temperatures of 75 to 150 °C and pressures up to 80 bar. The reaction medium is preferably in the liquid phase.

The effluent from the epoxidation step is normally first subjected to a separation treatment such as distillation to remove the propylene oxide formed. From the residual stream, ethylbenzene is generally removed by distillation. The residual stream will generally contain

1-phenylethanol, acetophenone and 2-phenylethanol. This residual stream will further contain benzoic acid if the alky aryl hydroperoxide has not been washed or washed only to a limited extent.

This residual stream can be subjected to one or more further separation treatments. Such separation treatment can comprise separating compounds having a molecular weight of at least 195 from the aryl alcohol containing stream. Such process has been described in European patent application 02252618.0 (our TS 1112).

As mentioned above, the feed for use in the present invention will contain both 1-phenylethanol and 2-phenylethanol. Generally, a substantial amount of 1-phenylethanol will have been produced in the reaction of aryl hydroperoxide with propene, and a much smaller amount of 2-phenylethanol.

The feed for use in step (1) of the present invention will generally comprise of from 60 to 85 %wt of 1-phenylethanol, of from 0.3 to 10.0 %wt of 2-phenylethanol and of from 0.1 to 10.0 %wt of organic acid.

The molar ratio of 1-phenylethanol to 2-phenylethanol in step (1) will generally be of from 5:1 to 300:1, more specifically of from 20:1 to 200:1.

The molar ratio of organic acid to 2-phenylethanol is at least 1:10, more specifically of from 1:5 to 20:1, more specifically of from 1:5 to 10:1, more specifically of from 1:5 to 5:1, most specifically of from 1:2 to 2:1. Most preferably, the 2-phenylethanol and organic acid are present in about equimolar amounts.

The organic acids which can be present depend on the ethylbenzene compound subjected to oxidation. Generally, the majority of the organic acids present will be benzoic acid.

The ester compound formed will generally be 1-phenylethylbenzoate.

Additional organic acids can be added to the reaction mixture to remove 2-phenylethanol. However, it is preferred to produce the organic acids for use in the present invention in the manufacture of the feed by process steps (a)-(d), more preferably by steps (a), (c) and (d) only.

Step (1) of the present invention comprises dehydration of 1-phenylethanol. This process is well known in the art. It can be carried out both in the gas phase and in the liquid phase. Suitable dehydration catalysts include for instance acidic materials like alumina, aluminium silicates, H-type synthetic zeolites, mineral acids, organo-sulphonic acids and carboxylic acids. Dehydration conditions are also well known and usually include reaction temperatures of 100-260 °C for liquid phase dehydration and 210-320 °C, typically 280-310 °C, for gas phase dehydration. Pressures usually range from 0.1 to 10 bar. In principle any known dehydration process can be applied in the process according to the present invention. For the purpose of the present invention liquid phase dehydration is preferred. It was observed that the 2-phenylethanol and organic acid reacted well at the liquid phase reaction conditions. In a preferred embodiment the liquid phase dehydration is carried out at a temperature in the range of from 100 to 260 °C and a pressure of from 0.1 to 1.0 bar using a homogeneous acid dehydration catalyst, preferably an organo-sulphonic acid catalyst. A preferred catalyst is para toluene sulphonic acid.

Liquid phase dehydration is well known to someone skilled in the art, for example from US-A-3,526,674.

A well known phenomenon in the liquid phase dehydration of phenylethanol is the formation of

substantial amounts of by-products, such as heavy condensation products. The production of these undesirable products lessens the economics and efficiency of the process. In order to reduce the formation of undesirable heavy by-products, an agent such as nitro or nitrosubstituted aromatics can be added. This has been described in more detail in US-A-5,639,928.

The reaction mixture obtained in step (1) of the present invention will contain styrene. The ester compounds based on 2-phenylethanol and organic acid can be removed from the product of step (1) before removing styrene, or the styrene is removed from the product of step (2).

The ester compounds can be removed from other compounds relatively easily. A suitable method comprises subjecting at least part of the product of step (1) to distillation.

Preferably, at least part of the product of step (2) is recycled to step (1) as discussed in more detail hereinafter.

Independent from the removal of the ester compounds, the reaction mixture obtained in step (1) will generally be separated into a styrene rich fraction and a styrene lean fraction. The separation of the styrene rich fraction and the styrene lean fraction can be effected in several ways, but most suitably is achieved by flashing or distillation. In such separation, the styrene rich fraction will generally be removed as the top fraction.

The styrene lean fraction contains compounds such as unconverted 1-phenylethanol and acetophenone. The 1-phenylethanol can be recycled to the dehydration step (1).

An acetophenone rich fraction usually is separated off from the reaction mixture of step (1). This fraction

can be hydrogenated to convert acetophenone to 1-phenylethanol, which can be used as feed for step (1).

The styrene rich fraction obtained by the process according to the present invention can be purified further in any way known to someone skilled in the art.

The invention is further illustrated by the following examples without restricting its scope to these particular embodiments.

Example 1

In a reactor, air was blown through ethylbenzene. The product contained ethylbenzene hydroperoxide.

The product obtained was reacted with propene in the presence of a titanium on silica catalyst as described in the Example according to the teaching of EP-A-345856. Unconverted ethylbenzene and propylene oxide were removed from the product, and a crude 1-phenylethanol feed was obtained. This feed was subjected to a dehydration reaction. Styrene product was removed, and unconverted 1-phenylethanol and 2-phenylethanol were recycled to the dehydration reactor feed. Acetophenone from the dehydration reaction product was partially hydrogenated to 1-phenylethanol and also recycled to the dehydration reactor feed. The combined feed stream to the dehydration reactor (referred to below as "Feed A") contained the following compounds:

1-phenylethanol	76.7 %wt
2-phenylethanol	2.5 %wt
benzoic acid	0.13 %wt
acetophenone	13.1 %wt

The remainder of the feed consisted of a wide range of further compounds. No substantial amount of further acids was present.

Benzoic acid was added to this feed so that the total benzoic acid concentration was 1.1 %w.

The feed containing 1.1 %w benzoic acid was subjected to a dehydration reaction in the liquid phase, as follows: para toluene sulphonic acid was added to the feed at a level of 200 ppmw. The feed containing catalyst was fed at a rate of 30 grams/hour to a reactor containing 64 g of heavy liquid formed in a previous dehydration reaction. The reactor was operated at 220 °C and 0.2 bar in once through mode. Vapour products were allowed to exit the reactor via a distillation column comprising 5 trays, to which reflux was applied. Overhead products were condensed into an organic layer and an aqueous layer. The organic layer was analysed using gas chromatography to determine styrene, 1-pheynlethanol and 2-phenylethanol concentrations. Heavy components formed were allowed to accumulate in the reactor. The reactor was operated continuously for 48 hours. At the end of the run the amount of heavy components formed was determined by weighing. The heavy liquid was also analysed by gas chromatography to determine the concentrations of the ester of 2-phenylethanol with benzoic acid, and the ester of 1-phenylethanol with benzoic acid.

During the run a total of 35 g of 2-phenylethanol was fed to the reactor. Of these 16 g (45%) was recovered in overhead product. Therefore, 19 grams (55%) of the 2-phenylethanol remained in the reactor or reacted to other compounds in the reactor, and would not lead to build-up of 2-phenylethanol in a recycle. Of these, 12 grams was found to have reacted to form the ester of 2-phenylethanol and benzoic acid which was present in the reactor (23 grams of ester present). The ester of 1-phenylethanol and benzoic acid could not be detected in the heavy liquid.

Comparative Example

The above example was repeated with the exception that no additional benzoic acid was added to "Feed A". The reaction was continued for a total of 67 h. During the run a total of 50 g of 2-phenylethanol was fed to the reactor. Of these, 36 g (72%) was recovered in overhead product. Therefore, only 14 grams (28%) of the 2-phenylethanol remained in the reactor or reacted to other compounds in the reactor and would not lead to build-up of 2-phenylethanol in a recycle. Of these, 3 grams was found to have reacted to form the ester of 2-phenylethanol and benzoic acid which was present in the reactor (6 grams of ester present). The ester of 1-phenylethanol and benzoic acid could not be detected in the heavy liquid.

C L A I M S

1. Process for converting 1-phenylethanol into styrene, which process comprises:
(1) contacting a feed comprising 1-phenylethanol, organic acid and 2-phenylethanol with a catalyst to obtain a product comprising styrene, and
(2) removing ester compounds based on 2-phenylethanol and organic acid from the product of step (1),
in which process the feed of step (1) has a molar ratio of organic acid to 2-phenylethanol of at least 1:10.

2. Process according to claim 1, in which process step (1) is carried out in the liquid phase.

3. Process according to claim 1 and/or 2, in which process the feed of step (1) has a molar ratio of organic acid to 2-phenylethanol of from 1:5 to 20:1.

4. Process according to any one of the preceding claims, in which process the ester compounds based on 2-phenylethanol and organic acid are removed by subjecting at least part of the product of step (1) to distillation.

5. Process according to any one of the preceding claims, in which process at least part of the product of step (2) is recycled to step (1).

6. Process according to any one of claims 1 to 5, in which process ester compounds based on 2-phenylethanol and organic acid are removed from the product of step (1) before removing styrene.

7. Process according to any one of claims 1 to 5, in which process styrene is removed from the product of step (2).

8. Process according to any one of the preceding claims, wherein the feed comprising 1-phenylethanol, organic acid and 2-phenylethanol is obtained by a process comprising:

(a) oxidation of ethylbenzene to obtain reaction product containing ethylbenzene hydroperoxide,

(b) optionally washing the reaction product of step (a),

(c) reacting at least part of the product of step (b) with propene to yield propylene oxide and 1-phenylethanol, and

(d) removing propylene oxide from the product obtained in step (c).

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/08703

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C1/24 C07C15/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00 05186 A (SHELL INT RESEARCH ;SLUIS JACOBUS JOHANNES V D (NL)) 3 February 2000 (2000-02-03) claims; examples	1-8
Y	US 3 526 674 A (BECKER MITCHELL ET AL) 1 September 1970 (1970-09-01) cited in the application column 6, line 35 - line 52; table III	1-8
Y	GB 1 583 091 A (EXXON RESEARCH ENGINEERING CO) 21 January 1981 (1981-01-21) page 4, line 38 -page 5, line 6	1-8
A	US 4 400 558 A (NEMET-MAVRODIN MARGARET I ET AL) 23 August 1983 (1983-08-23) cited in the application *the whole document*	1-8

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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