

PROCESS FOR THE PREPARATION OF ISOPROPANOL

present invention relates to a process for the hydrogenation of a benzene-contaminated feed of acetone to prepare isopropanol.

Isopropanol is a very useful intermediate in organic synthesis as well as a commercially important solvent.

Acetone is produced in large amounts as a by-product in the manufacture of phenol by the cumene process. In a cumene process benzene is alkylated with propene and/or isopropanol to synthesize cumene, cumene is oxidized into cumene hydroperoxide and cumene hydroperoxide is acid cleaved to generate phenol and acetone. The acetone produced by this cumene-process is contaminated by benzene. As indicated in for example EP-A-0434485, the production of acetone in the cumene process is considered a disadvantage because the demand for phenol increases much faster than the demand for acetone. Therefore it is suggested in EP-A-0434485 to hydrogenate acetone, obtained in the cumene process into isopropanol, and recycle the isopropanol into the cumene process.

EP-A-0434485 does not describe the presence of benzene in the acetone generated by the cumene process.

If the acetone generated by the cumene process of EP-A-0434485 does contain benzene, the presence of this benzene in the generated isopropanol recycle stream does not affect the process. Any benzene present in the recycle stream can be re-used in the formation of cumene. Accordingly, in the process as described by EP-A-0434485, it is advantageous to hydrogenate acetone only.

Moreover, if the acetone does contain benzene, one skilled in the art would expect only the acetone to react. The hydrogenation of benzene is much more

difficult than the hydrogenation of acetone. This is illustrated, for example, by the article by E. de Ruiter and J.C. Jungers, Bull. Soc. Chim. Belg., 58 page 230, 1949, where it is stated that when a mixture of acetone and benzene is hydrogenated the acetone reacts first.

Recently it has become desirable to convert acetone, obtained in the cumene process, into isopropanol which can be used for other purposes than the recycle into the cumene process. The presence of any amounts of benzene, however, makes it disadvantageous to use the isopropanol for any purpose other than recycling to the cumene process.

The removal of traces of benzene from acetone by distillation is very difficult. Removal of benzene from isopropanol after hydrogenation is even more difficult because of the close boiling points of benzene and isopropanol.

The object of the present invention is therefore to provide a process wherein benzene-contaminated acetone, such as acetone generated by the cumene process, can be converted in an economically attractive manner to isopropanol useful for other purposes than recycling.

Such an economically attractive process has been found by hydrogenating benzene present.

Accordingly this invention provides a process for the preparation of isopropanol, wherein a benzene-contaminated feed of acetone is hydrogenated to obtain isopropanol and hydrogenation products of benzene.

The process according to the invention can advantageously be used to prepare isopropanol containing a reduced amount of benzene or even essentially no benzene, which is suitable for various applications.

By isopropanol containing essentially no benzene is understood isopropanol that contains less than 2 ppm (2 mg/kg), suitably less than 1 ppm (1 mg/kg), preferably

F containing from 0.01 to 1 wt% of benzene
FF and wherein the hydrogenation of acetone and benzene is carried out simultaneously.

12 April 2006

less than 0.4 ppm (0.4 mg/kg), more preferably less than 0.1 ppm (0.1×10^{-6}), even more preferably less than 20 ppb (20 $\mu\text{g/kg}$), and most preferably no benzene.

5 In the process according to the invention benzene can, for example, be hydrogenated into cyclohexane, cyclohexene or cyclohexadiene.

Preferably more than 70%, more preferably more than 90%, even more preferably more than 95% and most preferably 99% to 100% of the benzene is hydrogenated.

10 Preferred factors to influence the hydrogenation of benzene include the type and amount of catalyst used; the temperature; the quantity of each of the reactants or the flow-rate at which each of the reactants are fed to the reactor. Preferably hydrogenation of benzene is
15 accomplished by using a specific type of catalyst, capable of hydrogenating benzene, whereas all other factors are preferably chosen such to obtain an optimal hydrogenation.

20 Hydrogenation of acetone and benzene in the benzene-contaminated acetone feed can be carried out in one or more separate steps but is preferably carried out simultaneously. Therefore the catalyst is preferably a catalyst, capable of hydrogenating acetone and benzene simultaneously.

25 Preferably the hydrogenation of acetone and benzene is carried out in the presence of a catalyst containing a metal capable of hydrogenation.

Preferred metals for hydrogenation include copper, nickel, platinum, palladium, ruthenium, and rhodium. Only
30 one metal or a combination of metals can be used. Preferably the metal is supported on a carrier. Suitable carriers include carbon, alumina, silica, zirconia and titania supports. Silica supports are preferred because the use of a silica support results in a very high
35 selectivity with regard to the hydrogenation of acetone

into isopropanol. Preferred examples of silica supports include Kieselguhr, precipitated silica and silica gel.

5 An especially preferred catalyst is a hydrogenation catalyst comprising nickel, preferably supported on a carrier. A catalyst comprising nickel on a silica carrier is most preferred.

10 For practical reasons, currently, amounts in the range from 5 %w/w to 80 %w/w metal on a carrier can be used. If the hydrogenation metal is nickel, catalysts containing more than 25 %w/w nickel, preferably more than 50 %w/w nickel and more preferably in the range of 50 up to 70 %w/w nickel, are preferred.

15 A preferred way to achieve simultaneous hydrogenation of acetone and benzene is the use of a nickel catalyst having a dispersion and nickel content such that the nickel surface is at least 15 m² nickel per gram catalyst. More preferably the nickel surface is at least 20 m² nickel per gram catalyst, and most preferably the nickel surface is at least 30 m² nickel per gram catalyst. A suitable practical upper limit is formed by 50 m² nickel per gram catalyst.

20 The nickel surface can be determined by measurement of the monolayer capacity for chemisorption of hydrogen as described by J.W.E Coenen and B.C. Linsen, in 25 "Physical and Chemical Aspects of Adsorbents and Catalysts" B.C. Linsen, ed. Academic Press (1970) 471 or R.Z.C. van Meerten, A.H.G.M. Beaumont, P.F.M.T. van Nisselrooij and J.W.E. Coenen, Surface Si. 135 (1983) 30 565. For the determination of the nickel surface, the monolayer is defined as the amount of hydrogen adsorbed at 1 bar pressure of hydrogen and 293 K. The adsorption of hydrogen was determined after reduction at 725 K for 4 hours, subsequent evacuation during 2 hours at 675 K, and controlled hydrogen admission.

The catalyst has preferably a bulk density in the range from 800-1200 kg/m³, preferably a BET-surface area in the range of 100-250 m²/g, preferably a pore volume in the range of 0.20 to 0.50 cm³/g and preferably an extrudate diameter in the range from 1 to 6 mm.

Preferably the catalyst is present as a fixed bed. In an advantageous embodiment the process according to the invention is operated at trickle flow. That is, liquid acetone trickles along the surface of the catalyst, which is packed in an atmosphere full of hydrogen gas.

Preferably the molar ratio of hydrogen to acetone should be at least 1. More preferably the molar ratio of hydrogen to acetone lies in the range from 1:1 to 10:1, most preferably in the range from 1.5:1 to 5:1.

The hydrogenation process can be performed at a wide range of reaction temperatures, reaction pressures, superficial liquid and gas velocities used. Dependent on the type of catalyst used, each of those reaction conditions is optimized such as to obtain optimal hydrogenation of the benzene. For example, a less active catalyst will require a higher reaction temperature. Furthermore the use of higher superficial liquid and gas velocities requires higher temperatures, whereas the use of a lower reaction temperature can require lower superficial liquid and gas velocities. Preferably temperatures applied in the reactor lie in the range from 40 to 150 °C, more preferably in the range from 60 to 130 °C. As the catalyst ages, higher temperatures may be required. Reaction pressure preferably lies in the range from 1 to 100 barg, more preferably in the range from 10 to 40 barg. A higher pressure will result in increased costs for compressing the gas whereas a lower pressure can result in poor conversion rates.

The superficial gas velocity is preferably in the range of 0.01-10 m/s, and the superficial liquid velocity is preferably in the range of 0.0001-0.1 m/s.

5 The gas is preferably essentially pure hydrogen, though this hydrogen can contain minor amounts, for example in the range of 0 to 15 %w/w, of for example methane, ethane, nitrogen and other impurities.

10 The process according to the invention can advantageously be applied to feeds of acetone containing benzene in a wide range of concentrations. Possible benzene concentrations in a feed of acetone could lie in the range from 0.01 ^{ppmv} ~~ppm~~ to 1% ^{wt-%} benzene, and more likely in the range from 0.1 ^{ppmv} ~~ppm~~ to 100 ^{ppmv} ~~ppm~~ benzene. The process according to the invention is further especially
15 advantageous for feeds of acetone containing at least 0.5 ^{ppmv} ~~ppm~~ benzene, and its advantages become more pronounced as the benzene concentration increases to at least 1 ^{ppmv} ~~ppm~~. The advantages are most pronounced for acetone feeds containing at least 1.5 ^{ppmv} ~~ppm~~ benzene.

20 The process according to the invention can very advantageously be combined with a process for the preparation of phenol. The present invention therefore also provides a process for the preparation of phenol comprising:

- 25 a) alkylating benzene with isopropanol and/or propylene to synthesize cumene;
b) oxidizing the cumene of step (a) into cumene hydroperoxide;
c) acid cleaving the cumene hydroperoxide generating
30 phenol and benzene-contaminated acetone;
d) preferably concentrating the benzene-contaminated acetone, generated in step c);
e) hydrogenating of the benzene-contaminated acetone of step d) into isopropanol containing hydrogenation
35 products of benzene.

Steps a) to c) can conveniently be carried out as described in for example EP-A-0371738 and EP-A-0434485. Step d) can conveniently be carried out by distillation. Step e) is preferably carried out as described herein before. Isopropanol generated in step e) can be used as a solvent in various applications. If desired isopropanol generated in step e) can also be recycled to step a). Such a recycle can conveniently be carried out as described in for example EP-A-0371738 and EP-A-0434485.

To further improve the quality of the isopropanol the process according to the invention is preferably combined with a series of separation steps.

The invention therefore also provides a process for the hydrogenation of a benzene-contaminated feed of acetone as described herein before comprising the steps of:

- i) ^{simultaneous} ^{both components of} hydrogenation of ~~a benzene-contaminated~~ feed of acetone in the presence of hydrogen, yielding a reaction product containing isopropanol;
- ii) separation of gaseous products from the reaction product of i); yielding a liquid reaction product;
- iii) separation of light by-products and unreacted acetone from the liquid reaction product of ii), yielding a crude isopropanol product;
- iv) separation of heavy by-products from the crude isopropanol product of iii), yielding a purified isopropanol product;
- v) recycling unreacted acetone and/or part of the light by-products obtained in step iii) and/or part of the heavy by-products in step iv) to the hydrogenation in step i).

Such a process comprising a train of separation steps results in a very high quality of isopropanol. Furthermore the recycling of the by-products as listed in step v) improves the selectivity of the process.

*F containing from 0.01 ppmw to 1 wt% of benzene
FF and hydrogenation products of benzene*

12 April 2006

The process can be carried out batch-wise, semi batch-wise or continuously. Suitably, the process is performed in a continuous manner. In such a continuous process a, preferably preheated, preferably pre-mixed, feed of benzene-contaminated acetone and hydrogen is fed to step i) for start-up. Subsequently the acetone and benzene are, preferably simultaneously, hydrogenated. The effluent of step i) can contain isopropanol, by-products such as di-isopropylether and/or hexyleneglycol, optionally hydrogenation products of benzene, such as for example cyclohexane, and, if any, unreacted hydrogen and/or acetone.

In step ii) a subsequent separation of gaseous products from the reaction product in step i) is carried out. Preferably a gas-liquid separator is used for this purpose. The gaseous products can comprise amongst others vapourized by-products and unreacted hydrogen. Preferably part of the gaseous product is purged and the remainder is preferably recycled to step i). Step ii) yields a liquid reaction product. Subsequently light by-products and unreacted acetone are separated from this liquid reaction product in step iii). Preferably this separation is accomplished by distillation. This separation yields a crude isopropanol product from which the heavy by-products are separated in step iv). This separation is also preferably accomplished by distillation. The separation yields a purified isopropanol product. In a preferred embodiment this purified isopropanol product is even further processed to yield a finalized isopropanol product. Preferably such a further processing into finalized isopropanol product is carried out by additional steps of:

vi) separation of an azeotrope of isopropanol, water and cyclohexane from the purified isopropanol obtained in step iv) yielding a finalized isopropanol product;

vii) separation of the azeotrope of isopropanol, water and cyclohexane obtained in step vi) in water and an azeotrope of isopropanol and cyclohexane; and
viii) optionally recycling the azeotrope of isopropanol and cyclohexane obtained in step vii) to step vi).

The separations in step vi) and vii) are preferably carried out by distillation.

Unreacted acetone and part of the light by-products obtained in step iii) and part of the heavy by-products in step iv) are recycled to the hydrogenation in step i). In a preferred embodiment the recycle stream from step iii) to step i) comprises mainly acetone and di-isopropyl ether. Preferably the recycle stream from step iv) to step i) comprises mainly hexylene glycol. By recycling these by-products the selectivity of the process is improved resulting in an improved overall yield of isopropanol.

An illustration of a process according to the invention is now described by reference to figure 1.

A feed of benzene-contaminated acetone (101) is mixed with a feed of fresh hydrogen (103), preheated in a heat exchanger (105) and fed into a reactor (107), containing a 55-62 %w/w nickel on silica catalyst, having a nickel surface of 34 m²/g, in a fixed catalyst bed. A stream of reaction effluent (109) is withdrawn from the reactor (107) and cooled in a heat exchanger (111). After cooling, the gaseous compounds in the reaction effluent are separated from the liquid compounds in a gas-liquid separator (113). At the top of the gas-liquid separator (113) a stream of gas (115) is withdrawn. Part of this stream (115) is purged (117), whereas the other part is recycled to the reactor (119). At the bottom of the gas-liquid separator a stream of liquid (121) is withdrawn and fed into a distillation column (123). At the top of this distillation column (123) a stream of

light products (125) is withdrawn. The stream (125) comprises mainly unreacted acetone and the by-product diisopropyl ether. Part of this stream of light products (125) is purged (127), whereas the other part is recycled to the reactor (129). At the bottom of this distillation column (123) a stream of crude isopropanol (131) is withdrawn and fed into a second distillation column (133). At the bottom of this second distillation column (133) a stream of heavy products (135) is withdrawn. The stream (135) comprises mainly the by-product hexylene glycol. Part of this stream of heavy products (135) is purged (137), whereas the other part is recycled to the reactor (139). At the top of this second distillation column (133) a stream of purified isopropanol (141) is withdrawn and fed into a third distillation column (143). From the bottom of this third distillation column (143) a stream of finalized isopropanol is obtained (145). From the top of this third distillation column (143) a stream of azeotrope of cyclohexane, water and isopropanol (147) is obtained which is fed into a fourth distillation column (149). From the bottom of this fourth distillation column (149) a stream of water is obtained (151), which is discarded. From the top of the fourth distillation column (149) a stream of azeotrope of cyclohexane and isopropanol (153) is obtained that is recycled to the third distillation column (143).

The invention is further illustrated by the following examples.

Examples

A reactor tube having a length of 35 cm, an internal diameter of 10 mm was provided with a fixed bed containing 5 grams of a catalyst as specified in table 1. An acetone feed containing 50 ppmw (50 mg/kg) benzene was fed to the reactor at a weight hourly space volume (WHSV)

as indicated in table 1. The acetone feed was hydrogenated in the presence of hydrogen and a catalyst and under a pressure and temperature as stated in table 1. The benzene conversion and acetone conversion are given in table 1. The selectivity towards isopropanol, based on total conversion products of acetone was >99%. Benzene content of the effluent isopropanol product was determined by gas-chromatography/mass spectrometry at a single ion mode mass 78. The benzene content of the effluent isopropanol is given in table 1.

Example	Catalyst	T (°C)	P (barg)	mol H ₂ /mol acetone	WHSV (kg feed/kg cat/hr)	Acetone conv. (%w/w)	Benzene conv. (%w/w)	Benzene left in end product
1	Leuna 6564 tl 1.2	90	20	2	1.5	> 99.9	> 99.9	< 20 ppb
2	Leuna 6512 AS	130	20	2	1.5	99.9	> 99.9	< 20 ppb
3	Leuna 6512 AS	70	20	2	0.5	> 99.9	> 99.9	26 ppb
4	Leuna 6512 AS	90	20	2	0.5	> 99.9	> 99.9	< 20 ppb
5	Leuna 6512 AS	110	20	2	0.5	> 99.9	> 99.9	< 20 ppb

- Leuna 6512 AS is a 55-62 %w/w nickel on silica catalyst, having a nickel surface of 34 m²/gram catalyst, a bulk density of 850-1150 kg/m³, a BET surface are of 180-240 m²/gram catalyst and a Pore volume of 0.25-0.45 cm³/gram catalyst (Leuna-Catalyst 6512 AS obtained from CRI KataLeuna).
- Leuna 6564 tl 1.2 is a 28 %w/w nickel on alumina catalyst, having a nickel surface of 43 m²/gram catalyst, a bulk density of 810-910 kg/m³, a BET surface are of 100-120 m²/gram catalyst and a Pore volume of 0.38-0.46 cm³/gram catalyst (Leuna-Catalyst 6564 tl 1.2 obtained from CRI KataLeuna).

A M E N D E D C L A I M S

1. Process for the preparation of isopropanol, wherein a feed of acetone containing from 0.01 ppmw to 1 wt% of benzene is hydrogenated to obtain isopropanol and hydrogenation products of benzene, and wherein the hydrogenation of acetone and benzene in the feed is carried out simultaneously.

2. Process as claimed in claim 1, wherein hydrogenation is carried out in the presence of a catalyst, comprising nickel.

3. Process as claimed in claim 2, wherein hydrogenation is carried out in the presence of a nickel catalyst having a nickel surface of at least 15 m² nickel per gram catalyst.

4. Process as claimed in claim 2 or 3, wherein the catalyst is present as a fixed bed.

5. Process as claimed in any one of claims 2-4, wherein the process is operated at trickle flow.

6. Process as claimed in any one of claims 1-5, wherein the feed of acetone contains from 0.1 ppmw to 100 ppmw of benzene.

7. Process for the preparation of phenol comprising:

a) alkylating benzene with isopropanol and/or propylene to synthesize cumene;

b) oxidizing the cumene of step (a) into cumene hydroperoxide;

c) acid cleaving the cumene hydroperoxide generating phenol and benzene-contaminated acetone;

d) preferably concentrating the benzene-contaminated acetone, generated in step c);

e) hydrogenating the benzene-contaminated acetone of step d) into isopropanol containing hydrogenation products of benzene.

8. Process as claimed in claim 7, wherein step e) is carried out according to any one of claims 1-7.

9. Process for the hydrogenation of a benzene-contaminated feed of acetone as claimed in any one of claims 1-8 comprising the steps of:

i) simultaneous hydrogenation of both components of a feed of acetone containing from 0.01 ppmw to 1 wt% of benzene in the presence of hydrogen, yielding a reaction product containing isopropanol and hydrogenation products of benzene;

ii) separation of gaseous products from the reaction product of i); yielding a liquid reaction product;

iii) separation of light by-products and unreacted acetone from the liquid reaction product of ii), yielding a crude isopropanol product;

iv) separation of heavy by-products from the crude isopropanol product of iii), yielding a purified isopropanol product;

v) recycling unreacted acetone and/or part of the light by-products obtained in step iii) and/or part of the heavy by-products in step iv) to the hydrogenation in step i).