1,076,085

PATENT SPECIFICATION

NO DRAWINGS

1,076,085

Date of Application and filing Complete Specification September 24, 1965.
No. 40865/65.
Application made in France (*No.* 991741) *on October* 16, 1964.
Application made in France (*No.* 1010) *on January* 6, 1965.
Complete Specification Published July 19, 1967.

Index at Acceptance: Class B1, E3C5; **C2,** C(2A2:2A14:2R15:3A13A 3A4:3A13A3B1:3A13A3H1: 3A13A3L).
Int. Cl.: B 01 j

Process for continuously carrying out hydrogenation reactions in liquid phase.

COMPLETE SPECIFICATION

We, Les Usines De Melle, a French Body Corporate, of (Deux-Sevres), Melle, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method my which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for continuously carrying out a hydrogenation reaction in the liquid phase.

The manufacture of certain organic products by the conventional process of catalytic hydrogenation in the liquid phase is frequently faced with difficulties due to fragility of the starting material or the final product or both. Such fragility results in yield decrease and the formation of condensation products and of resins, which clog the catalyst, with consequent rapid decrease of the activity thereof.

The process of the present invention enables these difficulties to be substantially avoided.

In accordance with the present invention there is provided a process for continuously carrying out a hydrogenation reaction in the liquid phase, which comprises maintaining at a temperature suitable for the hydrogenation reaction, a bath comprising a suspension of a hydrogenation catalyst in a liquid diluent, which has a boiling point above the reaction temperature and which is chemically inert towards the reactants and reaction products, continuously feeding to the said bath the substance to be hydrogenated while introducing into the bath a sufficient excess of hydrogen for the reaction product or products to be entrained as vapour by the excess hydrogen, the hydrogen feed rate being above 0.3 cubic metres per hour per litre of bath, separating from the entrained products the amount of hydrogenated product corresponding to the feed and refluxing the remainder, in liquid condition, into the bath.

By introducing into the bath a suitable excess of hydrogen so that the reaction product or products are entrained as vapours by the excess hydrogen, the content of substance to be hydrogenated and of desired reaction products remain very low at any time in the bath, with the consequence that the risk of destruction of reactants or reaction products and of clogging of the catalyst is considerably diminished or even completely avoided.

In addition, the excess hydrogen ensures perfect dispersion of the catalyst and the substance to be hydrogenated. Under such circumstances the optimum temperature of the bath can be easily controlled within very narrow limits, which is a further advantage of this process. In actual practice the hydrogen feed rate is above 0.3 cubic metres per hour per litre of bath..

The liquid diluent through which the catalyst is dispersed preferably has a boiling point at least 50°C. above the reaction temperature and is stable under the operating conditions. Experience has shown that a diluent having a boiling point above 200°C is generally satisfactory. Examples of suitable liquid diluents are a hydrocarbon, an alchohol or an ester, or a mixture thereof. A preferred diluent is the 2-ethyl hexyl ester of 2-ethyl hexanoic acid.

The reaction conditions, such as temperature, hydrogen feed rate and volume of the bath, are chosen according to the nature of the substance to be hydrogenated

The apparatus may comprise a reactor provided with a heating device and pipes for introducing the hydrogen and the substance to be hydrogenated, the reactor being for example surmounted by a column fitted with a condenser and the pipes required to withdraw the desired product and reflux the excess condensate to the top of the column.

Preferably the hydrogen delivery pipe opens into the bottom of the reactor, where uniform dispersion of the hydrogen throughout the bath may be ensured by a suitable device, such as an agitator, or a perforated or porous plate. Preferably the pipe for introducing the substance to be hydrogenated opens as near as possible the hydrogen feed point, at the bottom of the reactor, so that the said substance may be automatically and immediately dispersed throughout the bath by the hydrogen stream.

It is within the scope of the invention to operate at a pressure other than atmospheric.

The following Examples illustrate the invention and clearly show the suitability of the process for the hydrogenation of furfural to furfuryl alcohol (Example 1), of aniline to cyclohexylamine (Example 2) and of furfuryl alcohol to tetrahydrofurfuryl alcohol (Example 3).

Prior to the present invention the manufacture of cyclohexylamine from aniline was carried out either in the vapour phase at atmospheric pressure or in the liquid phase at a superatmospheric pressure. In the first case there was obtained besides cyclohexylamine, dicyclohexylamine in high proportion and phenyl cyclohexylamine. In the liquid phase process, for reaching a satisfactory reaction rate the operation was to be conducted under a hydrogen pressure of between 100 and 400 atmospheres; but on the other hand a high cyclohexylamine yield, of the order of 80% is obtained.

It has now been found, as indicated in Example 2, that by applying to this reaction the process of the present invention it is possible both to carry out the reaction in the liquid phase at atmospheric pressure and to obtain a high cyclohexylamine yield.

This results from the fact that dicyclohexylamine formation takes place only from the cyclohexylamine and in contact with the catalyst. Bearing in mind that, in accordance with the process of the present invention, the cyclohexylamine formed is removed by the hydrogen stream as fast as it is produced, the concentration of cyclohexylamine in the bath is always very low and consequently the dicyclohexylamine formation is considerably diminished.

EXAMPLE 1

Into a cylindrical reactor of 55 millimetres diameter and 4 metres height there was placed a bath consisting of 3 litres of the 2-ethyl hexyl ester of 2-ethyl hexanoic acid containing 300 grams of finely divided copper catalyst in suspension. The bath was maintained at a temperature of 178°C., and there was continuously introduced thereinto, per hour, 300 grams of liquid furfural and 3.5 cubic metres of hydrogen.

The reactor was surmounted by a column having a height of 2 metres filled with packing and fitted with a condenser at its head. The product was withdrawn from the condenser in amount corresponding to the amount of furfural feed and the remainder of the condensate was refluxed to the head of the column to allow the high boiling ester to remain in the reactor and to maintain constant the volume of the reaction bath.

There was produced per hour 305 grams of a mixture consisting of 15 grams of furfural, 287 grams of furfuryl alcohol and 3 grams of high boiling by-products, i.e., a total conversion of the furfural of 95% and a furfuryl alcohol yield of 99% reckoned with respect to the furfural converted.

After 300 hours' running under the same operating conditions, exactly the same conversion and the same yield were obtained, which is a proof that the activity of the catalyst remained unaltered.

EXAMPLE 2

A cylindrical reactor of 55 millimeters diameter and 4 meters in height was charged with a reaction bath consisting of 3 litres of the 2-ethyl hexyl ester of 2-ethyl hexanoic acid containing 300 grams of finely divided nickel catalyst suspended therein.

The bath was maintained at 175°C, and there was introduced thereinto 230 grams per hour of liquid aniline and, through the bottom of the reactor, 4.2 cubic metres per hour of hydrogen. The reactor was surmounted with a distillation column of 2 metres in height, filled with a packing and provided at its head with a water-cooled condenser followed by a brine-cooled condenser. The cyclohexylamine produced was, after distillation in the column, continuously withdrawn in amount corresponding to the amount of aniline feed.

This withdrawal of cyclohexylamine was from the top of the column, to which the excess condensate was refluxed. This reflux caused the unconverted aniline and the dicyclohexylamine formed to be driven back to the foot of the column, from which they were removed.

86.5% of the aniline was converted into cyclohexylamine, and only 7% into dicyclohexylamine. The percentage of unconverted aniline amounted to 4.7%.

EXAMPLE 3

Into a cylindrical reactor identical to that used in Example 1 there is introduced a reaction bath consisting of 320 g. of finely divided nickel catalyst suspended in

3 litres of a hydro-carbon fraction containing about 80% by weight of pentadecane, about 10% by weight of tetradecane and about 10% by weight of hexadecane. This hydrocarbon fraction, at atmospheric pressure, distils off from 255° to 285°C. The catalytic bath is brought to and maintained at a temperature of 160°C, and 196 g/hr. liquid furfuryl alcohol and 4.5 cubic metres/hr. impure hydrogen containing 5% by volume of inert gases (nitrogen and methane) are continuously introduced into the reactor.

The reactor, like that in Example 1, is surmounted by a 2-metre-high packed column fitted with a condenser at the head of the column. An amount of reaction product corresponding to the amount of furfuryl alcohol fed is withdrawn from the condenser and the remainder of the condensate is refluxed to the top of the column to maintain the high-boiling diluent mixture in the reactor and to maintain a constant reaction bath volume.

All the apparatus is maintained under an excess pressure of 0.5 kg/cm².

Under these operating conditions there is obtained 202 g/hr. of a reaction product consisting of 1.76 mole of tetrahydrofurfuryl alcohol and 22 g. of a mixture of aliphatic alcohols and diols (resulting from the cleavage of the furfuryl nucleus), methylfurane and furfuryl alcohol. The amount of unconverted furfuryl alcohol is about one gram.

The terahydrofurfuryl alcohol yield amounts to 88% based on the amount of furfuryl alcohol converted.

WHAT WE CLAIM IS:—

1. A process for continuously carrying out a hydrogenation reaction in the liquid phase, which comprises maintaining at a temperature suitable for the hydrogenation reaction, a bath comprising a suspension of a hydrogenation catalyst in a liquid diluent, which has a boiling point above the reaction temperature and which is chemically inert towards the reactants and reaction products, continuously feeding to the said bath the substance to be hydrogenated while introducing into the bath a sufficient excess of hydrogen for the reaction product of products to be entrained as vapour by the excess hydrogen, the hydrogen feed rate being above 0.3 cubic metres per hour per litre of bath, separating from the entrained products the amount of hydrogenated product corresponding to the feed and refluxing the remainder, in liquid condition, into the bath.

2. A process according to claim 1, wherein the liquid diluent has a boiling point at least 50°C. above the reaction temperature.

3. A process according to either one of claims 1 or 2, wherein the liquid diluent has a boiling point above 200°C.

4. A process according to any one of claims 1 to 3, wherein the liquid diluent is a hydrocarbon, an alcohol, an ester, or a mixture thereof.

5. A process according to any of the preceding claims, wherein the substance to be hydrogenated is furfural and the reaction product is furfuryl alcohol.

6. A process according to any one of claims 1 to 4, wherein the substance to be hydrogenated is aniline and the reaction product is cyclohexylamine.

7. A process according to any one of claims 1 to 4, wherein the substance to be hydrogenated is furfuryl alcohol and the reaction product is tetrahydrofurfuryl alcohol.

8. A process according to either one of claims 5 or 6, wherein the liquid diluent is the 2-ethyl hexyl ester of 2-ethyl hexanoic acid.

9. A process according to claim 7, wherein the liquid diluent is a hydrocarbon fraction containing about 80% by weight of pentadecane, about 10% by weight of tetradecane and about 10% by weight of hexadecane.

10. A process for continuously carrying out a hydrogenation reaction in the liquid phase, substantially as hereinbefore described with reference to the Examples.

STEVENS, LANGNER, PARRY &
ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

Sheerness: Printed for Her Majesty's Stationery Office by Smiths Printers and Duplicators.—1967.
Published at the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.