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Process for Producing Pyrrolidone
and N-Alkyl Pyrrolidones

Akzo nv, Arnhem

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Description:

The application relates to a process for producing pyrrolidone and N-alkyl pyrrolidones from saturated or unsaturated 1,4-dicarboxylic acids and their anhydrides; hydrogen; and a primary amine or ammonia.

N-alkyl pyrrolidones, particularly N-methylpyrrolidone, are technically very important solvents in industrial petrochemistry and are also used as starting substances for various syntheses.

N-methylpyrrolidone is generally produced industrially using the Reppe process (Chem. Ing. Technik (22) 17, 1950, pp. 361 ff.), in which monomethylamine and gamma-butyrolac-

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tone are maintained with a suitable diluent for a certain period of time at temperatures exceeding 250°C via a dehydrating catalyst. Due to the freely occurring dimerization of N-methylpyrrolidone as a result of the reaction, the yield is only 85-90%, however.

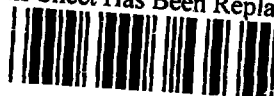
In US 4 885 371, a process for producing N-methylpyrrolidone is described in which monomethylamine and gamma-butyrolactone are reacted with each other via a borohydride catalyst.

A number of other publications (JP 01190667, JP 01186864, JP 01186863) also describe the synthesis of N-alkyl pyrrolidones, starting from gamma-butyrolactone, with primary, secondary, or tertiary amines. The mean reaction time is 3 h at 250°C.

According to the Soviet application no. 1558903, N-methylpyrrolidone is produced by reaction of gamma-butyrolactone and an excess of monomethylamine at 250°C via a Y zeolite as a catalyst. According to K. Hatada et al. (Bull. Chem. Soc. Japan 50(10), 1977, pp. 2517-2521), a copper-exchanged Y zeolite is used as a catalyst for the same reaction.

In the process of JP 49020585, N-methylpyrrolidone is obtained by reaction of monomethylamine, diluted with a large amount of water, and gamma-butyrolactone at 250°C and 2 hours reaction time.

The process of JP 51042107 uses gamma-butyrolactone, methylamine, and water in the ratio of 1:1.4:4 to produce N-





methyldpyrrolidone as the end product at a temperature of 250°C and a pressure of 45-50 kg/cm². The excess water serves as a carrier for the reuse of unreacted methylamine.

In accordance with JP 49000259, N-methyldpyrrolidone is obtained by heating a mixture of gamma-butyrolactone, alkylamine, and hydrogen for 3 hours at 270°C. A mixture of copper and a metallic oxide (Cu plus SiO₂, Al₂O₃, SiO₂-Al₂O₃, TiO₂, ZrO₂, or Cr₂O₃) is used as a catalyst. The reaction takes place in the gaseous phase, and the yield is only about 60%.

According to JP 47021420, N-methyldpyrrolidone is obtained with a yield of 99% when monomethylamine and gamma-butyrolactone are allowed to react with each other in the aqueous phase for a sufficient length of time.

JP 49020582 describes a process in which monomethylamine is first allowed to react with gamma-butyrolactone, followed by a cyclization, such as via an aluminum oxide catalyst.

Finally, DE 2200600 describes a process for producing N-methyldpyrrolidone from maleic anhydride, hydrogen, and an amine compound, in which a palladium-carbon catalyst is used. A yield of only at most 78.4% is obtained at a reaction temperature of 275°C and a pressure of 119 atm. The reaction occurs in an excess of water.

Furthermore, very long reaction times are prescribed and the reaction occurs under very high pressure, so that expensive process-related measures are needed.





All the aforementioned processes have the disadvantage either that the yield is low or that the product is unsatisfactorily impure and must undergo expensive purification following the process. With the exception of the process described in DE 2200600, the synthesis always starts from gamma-butyrolactone, which must be previously produced from 1,4-butanediol, maleic anhydride, or other educts, and isolated.

The object of the invention, therefore, is to provide a process in which N-alkyl pyrrolidones or pyrrolidone itself can be produced directly from the corresponding dicarboxylic acids or their anhydrides, without the otherwise common isolation of an intermediate product, and in which a high product yield is achieved while at the same time fulfilling the high purity requirements imposed on the product.

This object is met in accordance with the invention by allowing the dicarboxylic acids or their anhydrides to react with hydrogen in a suitable reactor via a first catalyst bed and subsequently reacting the unisolated intermediate product with a primary amine or ammonia via a second catalyst bed downstream from the first.

In the process according to the invention, the corresponding intermediate product is first obtained downstream from or above the first catalyst bed, with a yield and purity up to 98% or more, and, during its production and still in the gaseous phase state, is then reacted with the primary amine or ammonia above the second, downstream catalyst bed to





form N-alkylpyrrolidone or pyrrolidone. In this second step as well, the purity and yield are each on the average up to 98% or more.

Use of a catalyst containing copper for the first catalyst bed has proven advantageous for the process.

Likewise, use of a catalyst containing silicon or an aluminum-phosphate catalyst for the second, downstream catalyst bed has proven advantageous for the process.

In particular, catalysts with a zeolitic structure are preferred. The best results, however, are obtained using a copper chromite catalyst for the first catalyst bed and a cation-exchanged zeolite of type X or Y for the second catalyst bed. With this combination, a conversion of the reactants of up to 98% or more is possible.

The reaction takes place preferably in the gaseous phase, in order to achieve optimum conversion of the reactants.

To enable better control of the reaction and sufficiently exact dosing of the reactants, diluents such as gases, water, or aprotic solvents can be present. It has proven advantageous for the reactants of the first step, especially for hydrogen, to be introduced to the reaction system after diluting with nitrogen. Likewise, the primary amine is easier to dose in a diluted, aqueous solution. Overall, by using the previously mentioned diluents a reaction is achieved that proceeds continuously.





The temperature inside the reactor is 225 to 350°C above the first catalyst bed and 225 to 400°C above the second catalyst bed, whereby 250 to 300°C is preferred for the first catalyst bed and 260 to 340°C for the second catalyst bed. Maximum space-time yields are obtained in this case.

The molar ratio of 1,4-dicarboxylic acid or its anhydride to hydrogen is from 1 to 20 to 1 to 250, whereas the molar ratio of hydrogen to the primary amine or ammonia is from 15 to 1 to 250 to 1.

The reaction is further characterized by short to very short retention times of the applicable reaction mixture above the respective associated catalyst bed. These times are 0.01 to 15 seconds in each case and can be reduced to times under 3 seconds by employing appropriate flow rates and reactant ratios.

The reaction can also be conducted advantageously when the reaction pressure is only within the range from 0.1 to 10 bar and when, in most cases, the general ambient pressure is not exceeded, so that the reaction can be conducted using simple apparatus or reactors suitable for slight overpressure.

The product according to the invention can be obtained with a yield and purity of up to 98% or more and contains as by-products only some gamma-butyrolactone and possibly propionic acid, both of which can be eliminated easily. Particularly when producing N-methylpyrrolidone from maleic acid, methylamine, and water, the unconverted gamma-butyro-





lactone is easily separated, since it is converted during the distillation to gamma-hydroxy N-methyl butylamide, which, together with possibly other by-products, remains behind in the distillation residue.

The present invention is explained in more detail by the following example.

Example 1

A conventional glass reactor was fitted with a feed opening at a suitable location between the first and second catalyst beds.

The catalyst for the first catalyst bed comprised 21.95 g Cu chromite catalyst (manufacturer: Alfa) and the catalyst for the second catalyst bed 15.9 g NaX zeolite.

1.584 mol/h hydrogen and 0.016 mol/h maleic anhydride were fed over the first catalyst bed and additionally 0.017 mol/h monomethylamine and 0.096 mol/h water through the reactor feed opening.

The temperature was 275°C above the first catalyst bed and 275° above the second catalyst bed.

After a total reaction time of 4 hours, 6.09 g N-methylpyrrolidone was obtained. The yield was 96%.





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Patent Claims:

1. Process for producing pyrrolidone and N-alkyl pyrrolidones from saturated or unsaturated 1,4-dicarboxylic acids and their anhydrides; hydrogen; and a primary amine or ammonia, characterized in that the dicarboxylic acid or its anhydride is allowed to react in an appropriate reactor with hydrogen or ammonia via a first catalyst bed and the unisolated intermediate product is subsequently reacted with the primary amine or ammonia directly via a second, downstream catalyst bed.

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2. Process in accordance with Claim 1, characterized by the use of a catalyst containing copper for the first catalyst bed.
3. Process in accordance with Claim 1, characterized by the use of a catalyst containing silicon or an aluminum-phosphate catalyst for the second catalyst bed.
4. Process in accordance with Claim 3, characterized in that the catalyst has a zeolitic structure.
5. Process in accordance with one or more of Claims 1 to 4, characterized by the use of a copper chromite catalyst for the first catalyst bed and a cation-exchanged zeolite of type X or Y for the second catalyst bed.
6. Process in accordance with one or more of Claims 1 to 5, characterized in that the reaction occurs in the gaseous phase.
7. Process in accordance with one or more of Claims 1 to 6, characterized by the presence of diluents.
8. Process in accordance with Claim 7, characterized in that the diluent comprises gases, water, or aprotic solvents.
9. Process in accordance with one or more of Claims 1 to 8, characterized in that the temperature inside the reactor above the first catalyst bed is 225 to 350°C.

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10. Process in accordance with one or more of Claims 1 to 9, characterized in that the temperature inside the reactor above the second catalyst bed is 225 to 400°C.
11. Process in accordance with one or more of Claims 1 to 10, characterized in that the temperature is 250 to 300°C above the first catalyst bed and 260 to 340°C above the second catalyst bed.
12. Process in accordance with one or more of Claims 1 to 11, characterized in that the molar ratio of 1,4-dicarboxylic acid or its anhydride to hydrogen is from 1 to 20 to 1 to 250.
13. Process in accordance with one or more of Claims 1 to 12, characterized in that the molar ratio of hydrogen to the primary amine or ammonia is from 15 to 1 to 250 to 1.
14. Process in accordance with one or more of Claims 1 to 13, characterized in that the retention time of the reactants above the respective catalyst bed is 0.01 to 15 seconds.
15. Process in accordance with one or more of Claims 1 to 14, characterized in that the pressure inside the reactor is 0.1 to 10 bar (0.01 to 1.0 MPa).

