

PROCESS FOR THE PRODUCTION OF N-METHYL PYRROLIDONE
USING GAMMA BUTYROLACTONE AND MIXED METHYLAMINES AS
STARTING MATERIALS

BACKGROUND

The present invention relates to the production of N-methyl pyrrolidone (NMP). In particular, it relates to the use of gamma-butyrolactone (GBL) and mixed methylamines as starting materials, in such a way that the product is obtained by a continuous process in optimal purity and yields.

It is known from the prior art that there exist several processes for the synthesis of N-methyl pyrrolidone, using GBL and one methylamine, monomethylamine (MMA), as starting materials.

In J. Am. Chem. Soc., March 1949, pag. 897, Elvain and Vozza described a synthetic strategy aimed at the production of NMP with GBL and MMA as starting materials that exploited a discontinuous process, and with a double amount of the latter in comparison with his stoichiometric value.

After 4 hours of reaction at 280°C, NMP was recovered by distillation with a 90-93% yield.

In 1936 Spath and Lunder (Berichte 69, pag. 2727) described a similar process wherein a large excess of methylamine (4 mols per mol of GBL) was fed to a discontinuous reactor, with an approximately 90%

conversion after 3 hours.

NMP product purification involved complex dissolution processes, to be carried out in the ether from the effluent of the reaction and the ensuing distillations. In several patents (JP 7 221 420; JP 7400259; JP 7 420 585; JP 7 642 107) Mitsubishi Chemical Industries Co. Ltd. of Japan described continuous processes for the synthesis of NMP using GBL and MMA as starting materials. These are characterised by reactions with high molar ratios between water and GBL (typically ranging between 3 and 4 mols of water for each mol of GBL) and by the presence of great amounts of MMA (typically with molar ratios ranging between 1.4 and 3 mols of MMA per mol of GBL).

The processes designed by Mitsubishi result to be disadvantageous in terms of the high costs involved with the separation of unreacted MMA and its recovery and with the separation of the water forwarded to the reaction to which synthesis water adds up (one mol of water for each mol of reacted GBL).

To avoid the drawbacks associated with the discontinuous reaction in the presence of excess MMA and water, alternative methodologies have been proposed and these are based on the employment of catalysts.

In German Patent n. 2,159,858 owned by Mobil Oil a synthesis with GBL, MMA in the presence of 13X type zeolites is described.

In German Patent 4,203,527 owned by AKZO, a synthesis involving GBL, MMA and steam in the gas phase and at temperature of 275°C, on an NaX type zeolite is



described.

The above processes did not succeed in being applied industrially, as the employment of a catalyst subject to regenerations is disadvantageous in terms of the economic balance of the process as compared with non catalytic processes.

The aim of the present invention is that of proposing a process taking place in a continuous fashion wherein no catalysts are employed and where the feedstocks are, besides GBL, a mixture of methylamines.

The above feature gives way to the production of NMP at low investment costs, using cheaper raw materials and inferior utility consumptions, compared with the technologies of the previous art.

DESCRIPTION OF THE INVENTION

As known in the art, ammonia and methanol, reacting over an amination catalyst, produce a mixture of mono, di and trimethylamines (MMA, DMA, TMA).

The separation of the methylamines involves a complex sequence of 4 to 5 fractionators requiring significant investment and high energy consumptions.

The design of a methylamine plant can be driven toward the production of one methylamine only by recycling to the amination reactor the remaining unwanted methylamines.

This practice, however, requires additional investments and more heavy energy consumptions. Due to the above



constraints a producer of NMP using GBL and MMA as feedstocks would produce MMA only in case he can economically dispose the coproducts DMA and TMA.

The major innovation of the process of this invention is the possibility of using mixtures of methylamines in place of MMA in the production of NMP, making possible to establish a direct link between a NMP plant and a methylamines plant of cheaper design.

The synthesis of NMP from GBL and mixed amines follows basically the same principles of the synthesis from GBL and MMA.

While one mole of GBL reacting with one mole of MMA forms one mole of NMP and one mole of water, the reaction of one mole of GBL with one mole of DMA or with one mole of TMA forms, besides one mole of NMP, respectively one or two moles of methanol.

Consequently the product of the reaction will contain, besides NMP, non converted amines, water, methanol plus light and heavy by products.

Methanol and non converted amines, separated from the effluent of reaction, will be recycled to the amination reactor where, in presence of ammonia and of additional methanol, will be converted into mixed methylamines.

The production of NMP from GBL and mixed methylamines in the process of this invention is characterized in that the synthesis is carried out by a continuous non catalytic process in the liquid phase, via distinct reaction stages, preferably, but not limited to, three

connected in series.

According to the present invention three stages of the reaction leading to the production of NMP are characterised by what follows:

I stage of reaction

Amines: GBL molar ratio = between 1.05 and 1.5
Temperature (reactor outlet) = between 150 and 220°C
Residence time = between 10 and 40
minutes

II stage of reaction

Temperature = between 220 and 270°C
Residence time = between 1 and 3 hours

III stage of reaction

Temperature = between 250 and 310°C
Residence time = between 0.5 and 2.0
hours

In the three reactors the pressure ranges between 40 and 100 ATE, so as to keep the reactants in their liquid phase.

All reactors are of the adiabatic type and preferably tubular in shape.

Adequate reactors are also vessels subdivided into compartments by means of separation septs that avoid the reaction products to mix again as the reaction



progresses.

In the first reactor GBL exothermally reacts with the amines to afford production of hydroxybutyramide (NMH). In the following reactor NMH cyclisation reaction is triggered with formation of water, methanol and NMP. In the final stage, the NMP formation reaction goes to completion at high temperature.

The succession of the subsequent reaction stages as they are described in the present process leads to a reduction in GBL and NMH contents in the reaction effluents, which is a necessary condition for producing high purity NMP (99.5% minimum weight).

GBL, whose boiling point is very close to that of MMP (202°C) would not be separated from NMP by distillation.

During distillation, NMH would tend to go off again yielding MMA and GBL that would contaminate the product because not separable.

DESCRIPTION OF THE PROCESS

The features of the process of this invention will be more readily apparent from the following description of the preferred embodiments of the invention with reference to the accompanying drawings in which the process schemes are shown. In the drawings:

FIG. 1 shows a schematic representation of a process object of this invention for producing NMP from GBL and mixed methylamines.

FIG. 2 shows a schematic representation of a process for producing mixed methylamines integrated with the NMP process object of this invention.

With reference to Fig.1, mixed amines (line 1) mix with water (line 2) and with GBL (line 3) in static mixer 4 with a molar ratio of about 1.2:1 between methylamines and GBL.

The mixing activates the addition reaction with formation of NMH.

This reaction is exothermal and once gone to completion takes the mass temperature up to about 190°C.

The addition reactions go to completion in reactor 5 within about 20 minutes.

The liquid stream from the reactor (line 6) is heated up further in exchanger 7, by means of hot oil, and its temperature is taken up to 250°C.

After preheating, the liquid (line 8) feeds reactors 9 where NMH starts to cyclise, while water and methanol are formed at the same time.

Residence time in reactor 9 is approximately 2 hrs.

The reactor is of the tubular type, otherwise it is a vessel subdivided into compartments by separation septs that have the function of keeping the reaction products from mixing again.

The effluents from reactor 9 (line 10) feed heater 11 where temperature is raised to 280°C by thermal exchange with hot oil.

After the second preheating, the liquid (line 12) feeds reactor 13 where conversion of NMH to NMP goes to

completion with an approx. 1.5 hr. of residence time. Through valve 15, the effluent pressure is reduced producing a liquid phase in separator 16 (line 17), and a vapour phase (line 18) which both feed fractionation column 19 where non converted methylamines and methanol separate overheads and are recycled to the amination reactor in the methylamine plant (line 100).

The bottom product of column 19 feeds (line 20) subsequent column 21, wherein at the top reaction water separates (line 22) while light organic byproducts are obtained too (line 23).

The bottom product in column 21 feeds (line 24) fractionation column 25 where at the bottom heavy by-products are disposed (line 26) whereas at the top (line 27) purified NMP separates.

After GC analysis NMP results to be no less pure than 99.5% by weight, with a water content lower than 0.05% by weight.

FIG. 2 shows a schematic representation of a process for producing mixed methylamines integrated with the NMP process object of this invention.

Non converted amines and methanol stream from the NMP plant (line 100) join make up ammonia (line 101), make up methanol (line 102) and a recycling ammonia rich stream (line 116).

The mixture (line 104) after preheating (105) flows (line 106) to the amination reactor 107.

The reactor effluent (line 108) preheats the reactor feed in 105 and, following the preheater, (line 109) is

condensed in cooler 110.

The condensate flows (line 111) to separator 112, where gases containing carbon monoxide and hydrogen are separated (line 113).

The condensate flows (line 114) to column 115 which separates overheads (line 116) an ammonia-trimethylamine stream, which is recycled (line 116).

Bottoms of column 115 flow (line 117) to column 118 which separates at bottoms water to be disposed (line 119) and overheads a stream of mixed methylamines which flows to the NMP plant (line 1).



CLAIMS

1. A process for the production of N-methylpyrrolidone obtained by reaction of gamma butyrolactone and mixed methylamines, consisting of a mixture of mono, di and trimethylamine or any combination of the abovementioned methylamines, characterised in that the synthesis is carried out by a continuous non catalytic process in the liquid phase, via stages of reaction connected in series.
2. A process according to claim 1 characterised in that the stages of reaction are three with the following characteristics:
 - a) the first stage of the reaction operates at a temperature ranging between 150°C and 220°C at the reactor outlet, with a residence time ranging between 10 and 40 minutes;
 - b) the second stage of the reaction operates at a temperature ranging between 220°C and 270°C at the reactor inlet, with a residence time ranging between 1 and 3 hrs;
 - c) the third stage of the reaction operates at a temperature ranging between 250°C and 310°C at the reactor inlet, with a residence time ranging between 0,5 and 2 hrs.
3. A process according to claims 1 and 2 characterised in that the first stage of the reaction operates at temperature ranging between 170°C and 200°C at the reactor outlet.





4. A process according to claims 1 and 2, characterised in that the first stage of the reaction operates with residence time ranging between 15 and 25 minutes.

5. A process according to claims 1 and 2 characterised in that at the second stage of the reaction the residence time ranges between 1.5 and 2.5 hrs.

6. A process according to claims 1 and 2, characterised in that at the third stage of the reaction the residence time ranges between 1.0 and 1.5 hours.

7. A process according to claims 1 and 2 characterised in that in the reaction system the molar ratio between mixed methylamines and gammabutyrolactone ranges between 1.05 and 1.5.

8. A process according to claim 7 characterised in that in the reaction system the molar ratio between mixed methylamines and gammabutyrolactone ranges between 1.1 and 1.3.

9. A process according to claims 1, 2, 3 and 7 characterised in that the reactants are kept in the liquid phase by operating the reaction system at pressure ranging between 40 and 100 ATE.





10. A process according to claim 9, characterised in that the reaction system is operated at pressure ranging between 60 and 80 ATE.

11. A process according to any of preceding claims wherein the reactors of each of the reaction stages consist of vessels characterised by the presence of septa with the function of creating a piston type reactant flow through separate reaction compartments which keep the products from remixing.

12. A process according to claim 11 wherein the reactors of each of the reaction stages consist of vessels characterised by being of the tubular type.

13. A process for the production of N-methyl-pyrrolidone according to all the preceding claims wherein said process is integrated with a process for the production of methylamines, the integration being characterized by the fact that the non converted methylamines and methanol, recovered from the effluent of the synthesis of N-methyl-pyrrolidone is recycled to the amination reactor where, in presence of ammonia and of additional methanol, will be converted into mixed methylamines.

