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(54) Titre : PROCESSUS DE SYNTHESE DE 3-METHYLE PYRIDINE
(54) Title: PROCESS FOR THE SYNTHESIS OF 3-METHYL-PYRIDINE

(57) Abrégé/Abstract:
The present invention discloses a process for the synthesis of 3-methyl-pyridine from formaldehyde, paracetaldehyde, ammonia and acetic acid, whereby said compounds are reacted and said process comprises the following parameters:

a) a reaction temperature of 260-300°C;
b) a molar ratio of formaldehyde and paracetaldehyde of 0.7-1-4 Mol/Mol:
c) an ammonia concentration of 10-20 weight-%
d) an acetic acid concentration of 4-20 weight-%
e) a paracetaldehyde concentration of 0.4-1.6 Mol/kg
f) a retention time of 10-30 minutes in case of a continuous reaction and 10- 90 minutes in case of a discontinuous reaction; and
g) a reaction pressure of 30-130 bar

Abstract

The present invention discloses a process for the synthesis of 3-methyl-pyridine from formaldehyde, paracetaldehyde, ammonia and acetic acid, whereby said compounds are reacted and said process comprises the following parameters:

a) a reaction temperature of 260-300°C;
b) a molar ratio of formaldehyde and paracetaldehyde of 0.7-1-4 Mol/Mol:
c) an ammonia concentration of 10-20 weight-%
d) an acetic acid concentration of 4-20 weight-%
e) a paracetaldehyde concentration of 0.4-1.6 Mol/kg
f) a retention time of 10-30 minutes in case of a continuous reaction and 10-90 minutes in case of a discontinuous reaction; and
g) a reaction pressure of 30-130 bar

PROCESS FOR THE SYNTHESIS OF 3-METHYL-PYRIDINE

FIELD OF THE INVENTION

The present invention concerns a process for the production of 3-methyl-pyridine (3-picoline) from formaldehyde, paracetaldehyde, ammonia and acetic acid.

BACKGROUND OF THE INVENTION

3-picoline is a colourless, flammable liquid which is used as a solvent, for the production of medicaments and insecticides as well as for the synthesis of nicotinic acid and nicotine amide.

Several synthetic routes for the production of 3-picoline are known in the art, which are generally based on an addition/cyclization reaction of aldehyde/keten mixtures with an ammonia compound. Said reactions can run in the gas phase or in the liquid phase as well as using a catalyst.

The process according to the present invention is based on the publication of Grayson, J. and Dinkel, R., "An improved Liquid-Phase Synthesis of Simply Alkylpyridines", *Helvetica Chimica Acta*, Vol. 67 (1984), p. 2100-2110.

The authors of this publication describe in table 2, p. 2108 inter alia the synthesis of 3-picoline from acetaldehyde and formaldehyde, whereby different ammonia sources are compared with regard to 3-picoline yield as well as to the presence of diverse, unwanted side products.

In particular, it is shown that the use of ammonia acetate results in a yield of 44%, whereby 3-ethylpyridine as the main side product is present in an amount of 18%.

Thus, the technical problem to be solved is to improve the process of Grayson and Dinkel with regard to 3-picoline yield, reduction of 3-ethylpyridine amount as main side product as well as an increase in the space/time yield.

SUMMARY OF THE INVENTION

Said problem is surprisingly solved by the process according to the present invention for the synthesis of 3-methyl-pyridine from formaldehyde, paracetaldehyde, ammonia and acetic acid, whereby said compounds are reacted and said process comprises the following parameters:

a) a reaction temperature of 260-300°C;
b) a molar ratio of formaldehyde and paracetaldehyde of 0.7-1.4 Mol/Mol:
c) an ammonia concentration of 10-20 weight-%;
d) an acetic acid concentration of 4-20 weight-%;
e) a paracetaldehyde concentration of 0.4-1.6 Mol/kg;
f) a retention time of 10-30 minutes in case of a continuous reaction and 10-90 minutes in case of a discontinuous reaction; and
g) a reaction pressure of 30-130 bar.

It may be preferred that the reaction takes place in a reactor. More preferably, said reactor is a system with a high efficiency of mixing like stirring devices as well as continuous flow-through stirrer vessels and discontinuous stirrer vessels. Most preferably, said reactor is a loop-reactor or jet-loop-reactor.

Loop- and jet-loop-reactors according to the invention are characterized by the fact that the respective reactants are brought to reaction with the catalyst-solution in a continuous manner. One major advantage of jet-loop-reactors compared to stirrer vessels for the production of 3-picoline is the more intensive and faster mixing of fluids when operating under a high circulation stream, resulting in an increased passage of heat and material. Preferably, the process according to the invention is operated in a loop reactor with stream zones. Another advantage of stream-powered loop reactors is a finer dispersion of the added phases and thus a bigger specific interphase.

Furthermore, it may be preferred that side products are removed in the process of re-cycling the catalyst. Generally, all technical means known in the art can be employed, like e.g. extraction and rectification. Especially preferred is distillation.

The process according to the invention contemplates the addition of ammonia and formaldehyde both in molecular form as well as in form of their addition product hexamethylene-tetratimne (Urotropine).

The process according to the invention is distinguished from the prior art inter alia by combining a higher selectivity with regard to the formation of 3-methylpyridine with an increased space/time yield. This results in a major technical advantage, since normally an increased space/time yield results in a decrease in selectivity.

The process according to the present invention is further explained by the following, non-limiting example.

Example 1

The reaction takes place continuously in a 100 Litre reactor with a very high degree of mixing. Pumps are used to add the catalyst solution (a mixture of water, ammonia and acetic acid) and the educts (paracetaldehyde and formalin).

261 kg/h of catalyst solution (75 weight-% water, 15 weight-% ammonia and 10 weight-% acetic acid) are brought into the reactor via high-pressure pumps. Simultaneously, 13 kg/h paracetaldehyde and 26.8 kg/h formalin solution (37.4 weight-%) are added continuously via high-pressure pumps. The reactor temperature is kept at 278°C and the reactor pressure at 100 bar. A retention time of 20 minutes results in a crude solution containing 10.02 kg/h 3-picoline and 0.37 kg/h 3-ethylpyridine. Under these condition, a 3-picoline yield of 64.6% (based on formaldehyde) and a 3-ethylpyridine yield of 3.5% (based on acetaldehyde) is achieved. All pyridine bases were analyzed via gas chromatography.

The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the synthesis of 3-methyl-pyridine from formaldehyde, paracetaldehyde, ammonia and acetic acid, wherein said compounds are reacted and said process comprises the following parameters:

a) a reaction temperature of 260-300°C;

b) a molar ratio of formaldehyde and paracetaldehyde of 0.7-1.4 Mol/Mol:

c) an ammonia concentration of 10-20 weight-%;

d) an acetic acid concentration of 4-20 weight-%;

e) a paracetaldehyde concentration of 0.4-1.6 Mol/kg;

f) a retention time of 10-30 minutes in case of a continuous reaction and 10-90 minutes in case of a discontinuous reaction; and

g) a reaction pressure of 30-130 bar.

2. The process according to claim 1, wherein said process takes place in a reactor system with a high efficiency of mixing.

3. The process according to claim 2, wherein said reactor system is a continuous or discontinuous flow-through stirrer vessel.

4. The process according to claim 2, wherein said reactor system is a loop-reactor.

5. The process according to any one of claims 1 to 4, wherein side products are removed in the process of re-cycling the catalyst.

6. The process according to claim 5, wherein said side products are removed via rectification or extraction.

7. The process according to any one of claims 1 to 6, wherein the space/time yield of 3-methylpyridine is more than 50 kg/m^3*h.

8. The process according to any one of claims 1 to 6, wherein the space/time yield of 3-methylpyridine is more than 80 kg/m^3*h.

9. The process according to any one of claims 1 to 6, wherein the space/time yield of 3-methylpyridine is more than 100 kg/m^3*h.

10. The process according to any one of claims 1 to 9, wherein the 3-methylpyridine yield is at least 64% (based on formaldehyde) and the 3-ethylpyridine yield is at most 4% (based on paracetaldehyde).