

Process for preparing formic acid by reacting carbon dioxide with hydrogen (Reversible catalyst inhibition in the case of thermal cleavage)

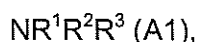
Abstract

5

The invention relates to a process for preparing formic acid, which comprises the steps

- (a) homogeneously catalyzed reaction of a reaction mixture (Rg) comprising carbon dioxide, hydrogen, at least one polar solvent selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and water and also at least one tertiary amine of the general formula (A1)

10



15

where

R^1 , R^2 , R^3 are each, independently of one another, an unbranched or branched, acyclic or cyclic, aliphatic, araliphatic or aromatic radical having in each case from 1 to 16 carbon atoms, where individual carbon atoms may, independently of one another, also be replaced by a heterogroup selected from among the groups -O- and >N- and two or all three radicals can also be joined to one another to form a chain comprising at least four atoms,

20

in the presence of at least one complex catalyst comprising at least one element selected from groups 8, 9 and 10 of the Periodic Table,

25

in a hydrogenation reactor

to give, optionally after addition of water, a two-phase hydrogenation mixture (H) comprising

30

an upper phase (U1), which comprises the at least one complex catalyst and the at least one tertiary amine (A1) and

a lower phase (L1) which comprises the at least one polar solvent, residues of the at least one complex catalyst and also at least one formic acid-amine adduct of the general formula (A2),

35



40

where

x_i is in the range from 0.4 to 5 and
 R^1, R^2, R^3 are as defined above,

- 5 (b) work-up of the hydrogenation mixture (H) obtained in step (a) according to one of the following steps
- (b1) phase separation of the hydrogenation mixture (H) obtained in step (a) into the upper phase (U1) and the lower phase (L1) in a first phase separation
10 apparatus
- or
- (b2) extraction of the at least one complex catalyst from the hydrogenation mixture (H) obtained in step (a) by means of an extractant comprising the at
15 least one tertiary amine (A1) in an extraction unit to give
- a raffinate (R1) comprising the at least one formic acid-amine adduct (A2) and the at least one polar solvent and
- 20 an extract (E1) comprising the at least one tertiary amine (A1) and the at least one complex catalyst
- or
- 25 (b3) phase separation of the hydrogenation mixture (H) obtained in step (a) into the upper phase (U1) and the lower phase (L1) in a first phase separation apparatus and extraction of the residues of the at least one complex catalyst from the lower phase (L1) by means of an extractant comprising the at
30 least one tertiary amine (A1) in an extraction unit to give
- a raffinate (R2) comprising the at least one formic acid-amine adduct (A2) and the at least one polar solvent and
- 35 an extract (E2) comprising the at least one tertiary amine (A1) and the residues of the at least one complex catalyst,
- (c) separation of the at least one polar solvent from the lower phase (L1), from the raffinate (R1) or from the raffinate (R2) in a first distillation apparatus to give
40

a distillate (D1) comprising the at least one polar solvent, which is recirculated to the hydrogenation reactor in step (a), and

a two-phase bottoms mixture (S1) comprising

5

an upper phase (U2) which comprises the at least one tertiary amine (A1) and a lower phase (L2) which comprises the at least one formic acid-amine adduct (A2),

10 (d) optionally work-up of the bottoms mixture (S1) obtained in step (c) by phase separation in a second phase separation apparatus to give the upper phase (U2) and the lower phase (L2),

15 (e) dissociation of the at least one formic acid-amine adduct (A2) comprised in the bottoms mixture (S1) or optionally in the lower phase (L2) in a thermal dissociation unit to give the at least one tertiary amine (A1), which is recirculated to the hydrogenation reactor in step (a), and formic acid, which is discharged from the thermal dissociation unit,

20 wherein carbon monoxide is added to the lower phase (L1), the raffinate (R1) or the raffinate (R2) directly before and/or during step (c)

and/or

25 carbon monoxide is added to the bottoms mixture (S1) or optionally to the lower phase (L2) directly before and/or during step (e).

Figure 1

