The completeness of the conversion of the free carboxyl groups present in the carboxylic acid melt is determined with the acid number (mg KOH/g) measured after the reaction. Minus any acid added as a catalyst, it is 0.01 to 50, preferably 0.1 to 10. Not all carboxyl groups present in the system need be present as esters of the alcohols used, but a portion thereof may instead be present in the form of dimeric or oligomeric esters with the OH end of the hydroxycaproic acid.

The esterification mixture is fed into stage 4, ~~a membrane system or preferably~~ a distillation column. When a dissolved acid was used as the catalyst for the esterification reaction, the esterification mixture is appropriately neutralized with a base, in which case 1 to 1.5 base equivalents are added per acid equivalent of the catalyst. The bases used are generally alkali metal or alkaline earth metal oxides, carbonates, hydroxides or alkoxides, or amines in substance or dissolved in the esterification alcohol. It is likewise possible to use ion exchangers, which are preferably reusable time and again by regeneration.

When a column is used in stage 4, the feed to the column is preferably between the top stream and the bottom stream. The excess esterification alcohol ROH, water and corresponding esters of formic acid, acetic acid and propionic acid are drawn off via the top at pressures of 1 to 1500 mbar, preferably 20 to 1000 mbar, more preferably 40 to 800 mbar, and temperatures between 0 and 150°C, preferably 15 and 90°C and especially 25 and 75°C. This stream can either be combusted or preferably worked up further in stage 12.

The bottoms obtained are an ester mixture which consists predominantly of the esters of the alcohol ROH used with dicarboxylic acids such as adipic acid and glutaric acid, hydroxycarboxylic acids such as 6-hydroxycaproic acid and 5-hydroxyvaleric acid, and of oligomers and free or esterified 1,4–cyclohexanediols. It may be advisable to permit a residual content of water and/or alcohol ROH up to 4% by weight each in the ester mixture. The bottom temperatures are 70 to 250°C, preferably 80 to 220°C, more preferably 100 to 190°C.

The stream from stage 4, which has been substantially freed of water and esterification alcohol ROH, is fed into stage 5. This is a distillation column in which the feed is between the low-boiling components and the high-boiling components. The column is operated at temperatures of 10 to 300°C, preferably 20 to 270°C, more preferably 30 to 250°C, and pressures of 1 to 1000 mbar, preferably 5 to 500 mbar, more preferably 10 to 200 mbar.

The top fraction consists predominantly of residual water and residual alcohol ROH, esters of the alcohol ROH with monocarboxylic acids, predominantly C_3- to C_6-monocarboxylic esters with hydroxycarboxylic acids such as 6-hydroxycaproic acid,

The hydrogenation can be performed in one reactor or a plurality of reactors connected in series. The hydrogenation in the liquid phase over a fixed bed can be performed either in trickle mode or liquid phase mode. In a preferred embodiment, a plurality of reactors are used, in which case the predominant portion of the esters is hydrogenated in the first reactor and the first reactor is preferably operated with liquid circulation for heat removal and the downstream reactor(s) is/are preferably operated without circulation to complete the conversion. Cycle gas is unnecessary especially in trickle mode.

The hydrogenation can be performed batchwise, preferably continuously.

The hydrogenation output consists essentially of 1,6-hexanediol and the alcohol ROH. Further constituents are in particular, if the overall low-boiling stream of stage 5 was used, 1,5-pentanediol, 1,4-butanediol, 1,2-cyclohexanediols and small amounts of monoalcohols having 1 to 6 carbon atoms, optionally ethers and water.

The hydrogenation output is separated in stage 7, for example ~~a membrane system or preferably~~ a distillation column, into the alcohol ROH which additionally comprises the majority of the further low-boiling components and a stream which comprises predominantly 1,6-hexanediol in addition to 1,5-pentanediol and the 1,2-cyclohexanediols. Top temperatures of 0 to 120°C, preferably 20 to 100°C, more preferably 30 to 90°C, and bottom temperatures of 100 to 270°C, preferably 140 to 260°C, more preferably 160 to 250°C, are established at a pressure of 10 to 1500 mbar, preferably 30 to 1200 mbar, more preferably 50 to 1000 mbar. The low-boiling stream can either be returned directly into the esterification of stage 3 or pass into stage 9 or into stage 12.

The stream comprising 1,6-hexanediol is purified in a column in stage 8. In this purification, 1,5-pentanediol, the 1,2-cyclohexanediols and any further low boilers present are removed via the top. If the 1,2-cyclohexanediols and/or 1,5-pentanediol are to be obtained as additional products of value, they can be separated in a further column. Any high boilers present are discharged via the bottom. 1,6-Hexanediol with a purity of at least 99.5%, preferably at least 99.7%, more preferably more than 99.9%, is withdrawn from a sidestream of the column. Top temperatures of 50 to 200°C, preferably 60 to 150°C, and bottom temperatures of 130 to 270°C, preferably 150 to 250°C, are established at pressures of 1 to 1000 mbar, preferably 5 to 800 mbar, more preferably 20 to 500 mbar.

If only small amounts of 1,6-hexanediol are to be prepared, stages 7 and 8 can also be combined in a batchwise fractional distillation.

In order to operate the process according to the invention in a very economically viable