

A method for the esterification of a fatty acid

The invention relates to a method for the esterification of a fatty acid and a plant for the production of fatty acid ester by means of a heterogeneous catalysis using the method in accordance with the invention. In this method one of the C12-, C14-, C16, C18-, C18'- or C18''- fatty acids, namely lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid or linolenic acids can be used for esterification with one of the following alcohols: methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol or 2-ethyl-hexanol.

According to a customary method, a pre-determined amount of fatty acid is esterified in batches. In this the fatty acid is placed in a heatable container with a stirring mechanism and heated to approximately 100° to 250° C. A catalyst is added and the esterification is carried out at a temperature which is kept constant, and with a constant infeed of alcohol. A stream of vapour from the container is led into a separating column, in which water which is released during esterification is separated from the co-vaporised alcohol. The water can be thus removed from the process, by which means the conversion is improved. On completion of the esterification process the remainders of alcohol and water are removed by further heating. A continuous method for the esterification of fatty acids is described in US-A- 6 069 261, in which a "permanent" auxiliary gas is used for removing water continuously. An auxiliary gas of this kind, which is

hydrogen or nitrogen for example, does not enter into a chemical reaction with reactants of the esterification.

The object of the invention is to provide a further method for the esterification of fatty acids, which can be carried out continuously and in which no auxiliary gas such as hydrogen or nitrogen has to be used. This object is satisfied by the method defined in claim 1.

The method for the esterification of a fatty acid F is carried out in a column with a one or multi-part packing. In addition to its function as a reactor, the packing has the function of a stripping section. It is formed as a reaction zone, at least in an upper part, in which a heterogeneous catalysis of the fatty acid F is carried out with an alcohol A used in the same molar ratio or in excess. A gaseous alcohol-rich counter-flow is produced in the sump by vaporisation. Water is removed from the reaction zone by means of a counter-flow acting as a stripping gas. The loaded stripping gas is at least partially liquefied at the head of the column. The head product is separated into a water-rich fraction as well as an alcohol-rich fraction. The alcohol-rich fraction is returned to the process as a starting material for the esterification and for the production of the stripping gas.

The dependent claims 2 to 9 concern advantageous embodiments of the method in accordance with claim 1. A plant for the carrying out of this method is the subject of claim 10.

The invention will be explained in the following on the basis of the drawings, which show:

- Fig. 1 a plant with a column, in which a catalytic reaction zone is arranged, which is used for carrying out the method in accordance with the invention,
- Fig. 2 a section of the catalytic reaction zone,
- Fig. 3 a head region of a preferred embodiment of the column and
- Fig. 4 a part of a plant for cleaning the fatty acid ester, which has been produced.

The plant illustrated in Figure 1 comprises a column 1, out of whose sump an intermediate product, namely a mixture, which contains the fatty acid ester obtained in accordance with the invention, can be extracted via a line 51 and fed to a part of a plant 7 for cleaning and concentration. The present description applies to the manufacture of a fatty acid ester E, for example a fatty acid isopropyl ester, which boils more easily than the corresponding fatty acid F.

The starting products of the method in accordance with the invention are the alcohol A and a fatty acid F. The intermediate product obtained in the column 1 still contains remains of the starting products as well as impurities. The intermediate product is further treated in a separating column of the part of the plant 7, so that eventually a fatty acid ester E can be obtained, the purity of which is at least 99 % by weight. The cleaned product is extracted via the line 71. A remainder of fatty acid F separated in the separating column is returned to the method via a line 72.

The column 1 contains a packing part, which is formed as a catalytic reaction zone 3, in which an esterification takes place by means of a heterogeneous catalysis. A mixture containing an alcohol A and a fatty acid F is applied to the packing part 3 via a line 10 and a distributor 30. A second packing part 4 with a distributor 40 is arranged under the packing part 3. Additional alcohol A is fed into the process via a line 11 and the distributor 40.

The packing consisting of the two parts 3 and 4 has, in addition to its function as a reactor, the function of a stripping section. The alcohol A is used in the same molar ratio or in excess. Thus a gaseous alcohol-rich counter-flow 50 can be produced in the sump by vaporisation which, acting as a stripping gas 50', removes water W from the reaction zone 3. The heat needed for the vaporisation is supplied to an apparatus 5 by heating a branch flow 53 (heat supply Q_+). Water W and also alcohol A is already taken up by the stripping gas 50 in the lower part 4 of the stripping section out of the liquid mixture which emerges from the reaction zone 3.

The loaded stripping gas (arrow 60) is at least partially liquefied at the head of the column in an apparatus 6 (heat extraction Q_-) and separated into two fractions 62 and 63. The fraction 63 of the head product is water rich and has a proportion of water W of 80% by weight for example. The alcohol rich fraction 62 contains 95%-98% by weight of alcohol A for example. It is returned to the process as a starting material for the esterification and to produce the stripping gas 50. The separation of the head product into the alcohol-rich fraction 62 and the water-rich fraction 63 can be undertaken for example by means of a membrane process, per-

vaporation, by means of a phase separator or by means of a distillation column.

The alcohol A which is fed in via the lower distributor 40 is vaporised on the packing 4 and thus contributes to the stream of the stripping gas 50. The necessary heat of vaporisation is given up by the stripping gas 50, which is brought into an overheated state in the sump by vaporisation.

In the example shown, the catalytic reaction zone 3 is made up of vertical layers 31 and flow passages 32 for the stripping gas 50'. A mixture 10', which contains the starting materials A and F, flows into and onto the layers 31. Details of the reaction zone 3 are illustrated in the cut-out of Figure 2, namely a border region between a flow passage 32 with the stripping gas 50' and a layer 31, which contains a granulated material 310 of a catalyst. A fabric 311 from a durable material forms pockets in which the granulated material 310 is enclosed. The mixture 10' flows inside one pocket and on the exterior side of the fabric 311, inside the pocket with meandering flow paths and outside as a trickle film. Water W enters into the stream of the stripping gas 50' through the surface of the trickle film 10", because a relatively small partial pressure of the water W is present in this. Alcohol A is transported in both directions through the surface of the trickle film 10". Suitable packings for the reaction zone 3 are described in EP-A- 0 396 650 or in EP-A- 0 631 813.

The starting materials A and F are already partially reacted together to advantage in a pre-reactor 2, wherein 10 to 30% of the fatty acid F is converted to ester E. Thus a mixture of alcohol A, fatty acid F, ester E and

water W flows into the column 1 through the line 10. Then further 20% to 70% of the fatty acid F is converted in the reaction zone 3.

A further packing 8 and a distributor 80 - see Figure 3 - is advantageously built into the column 1 above the stripping section 3, 4. Fatty acid F, which carries with it the stripping gas 60, is caught in this packing 8 with a part 68 of the alcohol-rich and returned fraction 62.

Figure 4 shows the part of the plant 7 for cleaning the fatty acid which has been produced. One component of this part of the plant 7 is a relaxation vaporiser 9, in which the intermediate product of the line 52 liberates a greater part of the remaining alcohol A in vapour form. This alcohol-rich vapour is led away via a line 92. It can be used further for the esterification. The alcohol-low mixture is led into a separating column 70 through the line 91. The extraction of the cleaned ester E (line 71) takes place there. The head product which can be extracted from a condenser 75 through a line 76 contains alcohol A and volatile impurities, in particular air. Fatty acid F (line 72) and not easily volatised impurities (line 74) can be extracted from the sump to which heat is supplied using a heating circuit 73. The part of the plant 7 can however also be arranged as a distillation column.

In Figure 4 a separating process is described, which may be used when the fatty acid ester E boils at a lower temperature than the corresponding fatty acid F. In the case of fatty acids, which are esterified with higher alcohols (for example 2-ethyl-hexanol), inverse ratios apply with regard to the cleaning in the part of the plant 7. The fatty acid ester is received in the sump of the separating column 70 and has to be worked up further

(not illustrated). Fatty acid and remaining alcohol, which can be extracted in the head from the separating column 70, are returned to the process.

The following starting materials can be used as fatty acid F or alcohol A for the esterification. As F one of the C12-, C14-, C16-, C18-, C18'- or C18"- fatty acids, namely lauric acid, myristic acid, palmitic acid, stearic acid, oleic or linoleic acid); as A one of the alcohols methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol or 2-ethyl-hexanol.

An ion exchange resin or an inorganic catalyst can be used as a catalyst, wherein the catalysts are preferably present in a strongly acid form and the ion exchange resin is preferably made macroporous. If methanol, ethanol, n-propanol, isopropanol, n-butanol or isobutanol is the alcohol A, then the catalyst - in this case an ion exchange resin - must be able to be used at temperatures between 120° C and 140°C; it must only lose activity moderately in this temperature interval. If 2-ethyl-hexanol is the alcohol A, then the catalyst - in this case an inorganic catalyst - has to be usable at temperatures of 150-230° C.

In the following a few values of method parameters will be given for the esterification of palmitic acid (PA) with isopropanol (IPA).

For the starting materials A = IPA and F = PA a respective purity of 95% and 98% (% by weight) is preferred. However other values are also possible, namely, in the ranges 88% - 100% for IPA and 95%-100% for PA. The pre-reactor 2 is operated at 100° C and 2 bar. It can however also be operated at temperatures of up to 140° C and at correspondingly higher pressures of up to 4 bar. As a rule differing amounts of IPA are fed in

through the lines 21 and 11. The ratio of IPA (line 21) to IPA (line 11) is preferably 2.5, can however also be in the range of 1 to 4. The head pressure in the column 1 amounts to 2 to 5 bar and correspondingly the temperature in the reaction zone 3 amounts to 120° C to 140° C. The intermediate product (line 53) is heated up to a temperature of between 170°C and 200°C in the heating apparatus 5; it can however also be heated more to 250° C.

A stripping gas 60 (Fig. 1) is present in the head of the column above the packing 8 (Fig. 3), which has a temperature between 115° C and 140° C and which contains 5% to 12% water W. The intermediate product in the line 53 contains 50% to 80% ester and 2% to 10% IPA.

A relaxation vaporisation 9 is carried out at 1 bar and 160° to 210° C. In this the proportion of IPA is decreased to about 0.5%. The separating column 70 is operated at 15 to 40 mbar. The temperature in the condenser 75 is reduced to a value between 80° and 100° C and a temperature between 220°C and 240° C is produced in the heating circuit 73. The upper limit of this temperature can also be 250°C.

Two examples of esterification in accordance with the invention which were obtained in pilot experiments are given in the following.

Example 1: The esterification of palmitic acid with isopropanol was continually carried out in a column at atmospheric pressure under the following conditions:

Reaction column:

inner diameter: 50 mm.

Enrichment section and stripping section: Sulzer packing BX

Reaction zone: catapak-S/ filled with strongly acidic ion exchanger, which is stable at temperatures of up to 140° C.

Feed streams:

palmitic acid (feed 1): 2.16 kg/h - isopropanol (feed 2): 1.44 kg/h

Product streams:

head product: 1.2 kg/h - sump product: 2.4 kg/h

Operating conditions:

head pressure: 1013 mbar - return ratio: 0.2

temperature in the reaction zone: approximately 98° C - sump temperature: 157.9° C

Measured sump concentrations (in % by weight): isopropylpalmitate 14.04
isopropanol: 10.61 - palmitic acid: 74.5 - water; 0.83

Example 2: the same construction as in example 1 was realised in a pressure column. In this an already pre-activated feed was used, with which a pre-reactor could be simulated. By means of slight excess pressure a temperature in the range of the reaction zone of approximately 140° C was set in the reaction zone. The following operating conditions led to a significantly higher reaction conversion.

Feed streams:

feed 1: 2.3 kg/h with the following composition (in % by weight):

isopropylpalmitate: 24.3 - isopropanol: 21.6 - palmitic acid: 52.1 - water:
2.0

feed 2: isopropanol: 1.84 kg/h

Product streams:

head product: 1-43 kg/h - sump product: 2.71 kg/h

Operating conditions:

head pressure: 5100 mbar - return ratio: 0.2

temperature in the reaction zone: approximately 140° C - sump temperature: 192°C

Measure sump concentration (in % by weight): isopropylpalmitate 64.0 -
isopropanol: 7.7 - palmitic acid: 28.3 - water: 0.06.

Patent claims

1. A method for the esterification of a fatty acid F in a column (1) with a one or multi-part packing (3, 4), which, in addition to a function as reactor, has the function of a stripping section and which is formed as a reaction zone (3), at least in an upper part with catalysts fixed in the packing, in which method a heterogeneous catalysis of the fatty acid F is carried out with an alcohol A used in the same molar ratio or in excess, a gaseous alcohol-rich counter-flow (50) is produced in the sump by vaporisation, water is removed from the reaction zone by means of the counter-flow acting as a stripping gas, the loaded stripping gas (60) is at least partially liquefied at the head of the column, the head product is separated into a water-rich fraction (63) as well as an alcohol-rich fraction (62) and the alcohol-rich fraction is returned to the process as a starting material for the esterification and for the production of the stripping gas.
2. A method in accordance with claim 1, characterised in that, in a lower part (4) of the stripping section (3,4), water and alcohol is separated with the stripping gas (50) out of the liquid mixture which leaves the reaction zone (3).
3. A method in accordance with claim 1, characterised in that a further packing (8) is incorporated above the stripping section (3,4), in

which fatty acid, which the stripping gas (6) carries with it, is caught with a part (68) of the alcohol-rich and returned fraction (62).

4. A method in accordance with one of the claims 1 to 3, characterised in that alcohol is fed into the reaction zone (3) or below it, which contributes to the flow of the stripping gas (50, 50') in vaporised form.
5. A method in accordance with one of the claims 1 to 4, characterised in that the separation of the head product into the water-rich fraction (62) and the alcohol-rich fraction (63) is carried out by means of pervaporation, in a phase separator or a distilling column.
6. A method in accordance with one of the claims 1 to 5, characterised in that a partial esterification is carried out with the starting materials A and F in a pre-reactor (2) and the so-formed mixture of fatty acid F, alcohol A, ester E and water W is applied into the reaction zone (3) of the column (1) or above it.
7. A method in accordance with one of the claims 1 to 6, characterised in that a part (52) of the liquid sump mixture (52) is prepared further by means of a relaxation vaporiser (9) or a distillation column and in a separation column (70), so that finally a fatty acid ester E is obtained, the purity of which is at least 99 % by weight.
8. A method in accordance with one of the claims 1 to 7, characterised in that, for the esterification, the following starting materials are used as fatty acid F and/or alcohol A: one of the C12-, C14-, C16-,

C18-, C18'- or C18"- fatty acids, namely lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid or linolenic acid and one of the alcohols methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol or 2-ethyl-hexanol.

9. A method in accordance with one of the claims 1 to 8, characterised in that an inorganic catalyst is used as a catalyst, which can preferably be used at temperatures of 150 to 230° C, or an ion exchange resin is used, which only loses activity moderately when carrying out the method at temperatures above 120° C and up to 140°C, wherein the catalysts are preferably present in a strongly acidic form and the ion exchange resin is preferably made macroporous.
10. A plant for the production of the ester E by means of a heterogeneous catalysis with a method in accordance with one of the claims 1 to 10, characterised by a column (1) with a part (3) of a packing (3, 4) for carrying out the heterogeneous catalysis, the packing including porous catalyst supports (31) and flow channels (32) for the stripping gas (50') between the catalyst supports, wherein, on carrying out the method in the pores of the catalyst supports, the mixture to be treated forms a downwardly directed flow of liquid (10'), the stripping gas forms an upwardly directed flow and the liquid phase is in direct contact to the gaseous phase, so that a material exchange can take place.