Title: PROCESS FOR REMOVING A KETONE AND/OR ALDEHYDE IMPURITY

Abstract: This invention relates to a process for producing an alkyl alkanate, said process comprising: introducing an olefin and a carboxylic acid into a reactor containing an acid catalyst, reacting said olefin with said carboxylic acid in the presence of an acid catalyst, so as to produce a product stream comprising an alkyl alkanate and an aldehyde and/or ketone impurity, contacting said product stream with hydrogen in the presence of a selective hydrogenation catalyst, so as to selectively reduce the aldehyde and/or ketone impurity to its corresponding alcohol, and separating the corresponding alcohol from the remainder of the product stream.
PROCESS FOR REMOVING A KETONE AND/OR ALDEHYDE IMPURITY

This invention relates to process for removing a ketone and/or aldehyde impurity from a product stream comprising an alkyl alkanoate.

Alkyl alkanoates may be produced by reacting an olefin with a carboxylic acid in the presence of an acidic catalyst. For example, ethyl acetate may be produced by contacting ethylene with acetic acid in the presence of an acidic heteropolyacid catalyst. The reaction produces a product stream comprising ethyl acetate, unreacted starting materials and aldehyde and ketone impurities, such as acetaldehyde, methyl i-propyl ketone, butyraldehyde, methyl propyl ketone, methyl i-butyl ketone, methyl - s-butyl ketone, methyl i-pentyl ketone, methyl ethyl ketone (MEK), as well as variety of C₈, branched and higher alkenes, such as methyl heptene and dimethyl hexene. The unreacted starting materials are recovered from the product stream, and recycled to the reactor. The ethyl acetate may be recovered from the remainder of the product stream, for example, by distillation. Unfortunately, however, it is difficult to reduce or maintain the MEK concentrations of the final product to below 50 ppm using this method, as the boiling points of these compounds are very similar to the boiling point of ethyl acetate.

Various attempts have been made to reduce the concentration of such aldehyde and/or ketone impurities further. As aldehydes and ketones may form azeotropes with alkyl alkanoates, attempts have been made to separate the impurities using azeotropic distillation (see for example EP 0 151 886).

EP 0 992 484 describes a process in which aldehyde and/or ketone impurities are removed from an alkyl alkanoate product stream by contacting the impure alkyl alkanoate product stream with a selective hydrogenation catalyst of, for example,
ruthenium in the presence of hydrogen. The hydrogenation reaction is preferably carried out at elevated pressures of 25 to 50 bar. Under the reaction conditions, the aldehyde and/or ketone impurities are selectively hydrogenated to the corresponding alcohols, leaving the alkyl alkanoate substantially unreacted. As alcohols tend to boil at a very different temperature to alkyl alkanoates, the former can be separated by simple distillation.

The alkyl alkanoate stream treated in EP 0 992 484, however, is produced by converting an alcohol feedstock by i) dehydrogenation, ii) oxidation, iii) reaction with an aldehyde or iv) oxidation to the corresponding aldehyde followed by the Tischenko reaction. There is nothing in EP 0 992 484 to suggest that alkyl alkanoate product streams which are produced by other methods may be purified using the same method.

The product stream from the reaction of an olefin with a carboxylic acid will comprise an alkyl alkanoate, aldehyde and/or ketone impurities, and also olefins. Under the conditions for selective hydrogenation of aldehydes and/or ketones, as disclosed in EP 0 992 484, most olefins present in the product stream will also be hydrogenated to produce the corresponding alkanes. This will include unreacted feed olefin. Hydrogenation of this olefin will lead to a loss of recyclable feedstock and an increased consumption of hydrogen. Hence it is not desirable to hydrogenate the product stream as directly formed from the reaction of an olefin with a carboxylic acid.

Our own EP 0 952 141 discloses a process for the production and purification of ethyl acetate from the reaction of ethylene with acetic acid. After removal of the majority of the unreacted ethylene and removal of the acetic acid, the ethyl acetate product stream comprising aldehyde and/or ketone impurities is fed to a distillation column. Volatile components and light ends, including some unreacted ethylene, are removed as an overhead stream, whereas heavier components are removed in the bottoms stream. A side draw comprising ethanol is taken and a fraction of this ethanol is separated from this stream prior to recycle of this stream back to the distillation column. The bottoms stream from the distillation column comprises the desired ethyl acetate product and also aldehyde and/or ketone impurities, which it is still required to remove.

We have now found that aldehyde and/or ketone impurities present in product streams produced by the reaction between olefins and carboxylic acids may also be removed by selectively hydrogenating these impurities to their corresponding alcohols,
and separating these alcohols from the remainder of the product stream.

Accordingly, the present invention provides a process for producing alkyl
alkanoate, said process comprising:
introducing an olefin and a carboxylic acid into a reactor containing an acid
5 catalyst,
reacting said olefin with said carboxylic acid in the presence of an acid catalyst, so
as to produce a product stream comprising an alkyl alkanoate and an aldehyde and/or
ketone impurity,
contacting said product stream with hydrogen in the presence of a selective
10 hydrogenation catalyst, so as to selectively reduce the aldehyde and/or ketone impurity
to its corresponding alcohol, and
separating the corresponding alcohol from the remainder of the product stream.
A preferred embodiment of the present invention comprises:
taking the product stream from said reaction of olefin with carboxylic acid,
15 feeding said product stream to a distillation column,
taking from the distillation column a side draw comprising an alkyl alkanoate and
an aldehyde and/or ketone impurity, such that said side draw stream forms the product
stream comprising an alkyl alkanoate and an aldehyde and/or ketone to be hydrogenated.
Optionally this embodiment of the process may comprise the further steps of:
20 separating any unreacted hydrogen from the hydrogenated side draw, and
recycling the hydrogenated side draw back to the original distillation column.
It has been found that selection of the appropriate side draw stream comprising
alkyl alkanoate and an aldehyde and/or ketone impurity for hydrogenation, and
25 subsequent recycling of the hydrogenated stream back to the column is particularly
desirable due to the ability of the existing process to separate the impurities from the
hydrogenated stream. The alkyl alkanoate product is typically obtained by removing
from the base of the distillation column an alkyl alkanoate rich product stream also
comprising alcohol, and separating the corresponding alcohol from the remainder of the
product stream.

Another preferred embodiment of the present invention comprises:
taking the product stream from said reaction of olefin with carboxylic acid,
30 feeding said product stream to a distillation column,
taking from the distillation column a base stream draw comprising an alkyl
alkanoate and an aldehyde and/or ketone impurity, such that said base stream forms the
product stream comprising an alkyl alkanoate and an aldehyde and/or ketone to be
hydrogenated.

It has been found that this base stream is also suitable for hydrogenation, and is
particularly desirable due to the ability to use the existing process units to separate many
impurities from the rest of the product stream prior to hydrogenation. For example, light
ends, such as acetaldehyde, may be removed from the top of the distillation column. A
stream comprising water and alcohol may be removed from a side draw on the
distillation column, such that from the base of the distillation column is obtained a
substantially anhydrous alkyl alkanoate rich product stream comprising alkyl alkanoate
and an aldehyde and/or ketone impurity. This base stream comprises less impurities and
the total volume of the stream is smaller.

In this embodiment the hydrogenated base stream may optionally be passed to a
further column for separation of unreacted hydrogen, prior to the separation of the
corresponding alcohol formed from the remainder of the product stream.

The reaction conditions necessary for producing alkyl alkanoates from the reaction
between olefins and carboxylic acids are well-known in the art, and are described by
way of example in GB-A-1259390. Any suitable olefin may be used as a starting
material. Preferred examples include ethylene, propylene and butylene, with ethylene
being most preferred. Suitable carboxylic acid starting materials include C1-C4 mono-
carboxylic acids. Preferably, acetic acid is employed. The type of alkyl alkanoate
eventually produced depends on the type of olefin and carboxylic acid used. Typically,
the alkyl alkanoate is a C_{2+} alkyl C_{2+} alkanoate. Preferably, the alkyl alkanoate is
selected from the group consisting of ethyl acetate, i-propyl acetate, n-butyl acetate, s-
butyl acetate and t-butyl acetate. Most preferably, the alkyl alkanoate is ethyl acetate.

The mole ratio of olefin to the carboxylic acid may be 1:1 to 18:1, preferably
10:1 to 16:1.

In certain cases, it may be desirable for water to be present in the olefin/carboxylic
acid reaction mixture. For example, water may be added to the reaction mixture in the
form of steam in an amount of 1-10 mole %, preferably from 3 to 7 mole %, eg 5 to 6.5
mole %, based on the total amount of carboxylic acid, olefin and water in the reaction
mixture. Water is believed to enhance the stability of the catalyst.

A di-ether such as diethyl ether may also be present in the olefin/carboxylic acid reaction mixture. For example, di-ether may be co-fed to the reactor, together with the other reactants. The amount of di-ether employed is suitably in the range from 0.1 to 6 mole %, preferably in the range from 0.1 to 3 mole % based on the total amount of carboxylic acid, olefin, water and diethyl ether in the reaction mixture. The di-ether employed may correspond to the by-product di-ether derivable from the reactant olefin.

The olefin/carboxylic acid reaction mixture may also comprise alcohol. Alcohol may be produced as a by-product of the reactor: for example, ethanol may be formed by the hydration of ethylene. This ethanol may be introduced to the reactor as a by-product recycle, so as to suppress the formation of more ethanol in the reactor.

As mentioned above, the reaction between an olefin and a carboxylic acid is catalysed by an acid catalyst, preferably an acidic heteropolyacid catalyst. Heteropolyacids are well-known and are described extensively in, for example, EP 0757027. Suitable heteropolyacids include:

- 12-tungstophosphoric acid: $\text{H}_2[\text{PW}_{12}\text{O}_{40}]\cdot\text{xH}_2\text{O}$
- 12-molybdophosphoric acid: $\text{H}_2[\text{PMo}_{12}\text{O}_{40}]\cdot\text{xH}_2\text{O}$
- 12-tungstosilicic acid: $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]\cdot\text{xH}_2\text{O}$
- 12-molybdosilicic acid: $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]\cdot\text{xH}_2\text{O}$
- Cesium hydrogen tungstosilicate: $\text{Cs}_3\text{H}[\text{SiW}_{12}\text{O}_{40}]\cdot\text{xH}_2\text{O}$

The preferred heteropolyacids have high molecular weights of 700-8500. These catalysts may be employed in an unsupported or supported form. Where supported heteropolyacid catalysts are employed, they may be supported on siliceous supports. Suitable siliceous supports are well-known in the art and described, for example, in EP 0757027. Preferred siliceous supports are those derived from synthetic silica, for example, fumed silica. Supports may be produced by the flame hydrolysis of SiCl4. Specific examples of such supports include Support 350 made by pelleting of AEROSIL® 200 (both ex Degussa).

The olefin/carboxylic acid reaction is suitably carried out at a temperature in the range from 100 - 300°C, preferably, 150-200°C. The reaction pressure is suitably at least 400 KPa, preferably from 500-3000 KPa, and most preferably, 800 - 1000 KPa depending upon the relative mole ratios of olefin to acid reactant and the amount of
water used. The vapours of the reactant olefins and acids are passed over the catalyst suitably at a GHSV in the range from 100 to 5000 per hour, preferably from 300 to 2000 per hour.

The product stream thus formed may be treated to remove the majority of the unreacted olefin and carboxylic acid. For example, where the product stream is derived from the reaction of ethylene with acetic acid, the stream may be introduced to a flash drum where the majority of the ethylene may be removed, and subsequently the stream may be introduced to an acid removal column wherein acetic acid is removed.

As well as alkyl alkanoate, the product stream comprises aldehyde and/or ketone impurities. Examples of aldehyde impurities include acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde Examples of ketone impurities include acetone, methyl I-propyl ketone, methyl propyl ketone, methyl I-butyl ketone, methyl-s-butyl ketone, methyl,I-pentyl ketone and MEK. These impurities may form more than 5 ppm, preferably, 5 to 500 ppm, more preferably, 5 to 400 ppm, and more preferably, 5 to 200 ppm of the product stream, prior to treatment.

In the preferred embodiments the product stream is then introduced to a distillation column comprising a side draw. Preferably the column operates at less than 5 bar, preferably less than 3 bar and most preferably between 1 and 2 bar. The product stream is preferably introduced to the upper half of the distillation column, most preferably between one-eighth and three-eighths of the way from the top, and most preferably one quarter of the way from the top.

Some of the more volatile components of the stream, such as, for example, acetaldehyde will be removed in the overhead stream from this column. In a preferred embodiment the stream to be passed to the hydrogenation unit is withdrawn from this column via the side draw. The side draw position is selected so that the impurities which it is desired to hydrogenate are contained in the draw stream, but also to fit in with the existing process steps, for example, for ethanol separation. In selection of the side draw position it is also preferable to avoid significant quantities of species detrimental to the selective hydrogenation of the impurities. “Detrimental” as defined herein, includes any species which may reduce the efficiency of the hydrogenation process, and includes, for example, catalyst inhibitors or species which compete to be hydrogenated but which it is not desirable to hydrogenate, such as unreacted feed olefin. The side draw may also
comprise alcohol, water and alkyl alkanoate. Preferably this side draw is taken from
below the point at which the product stream from the reaction of an olefin with a
carboxylic acid is introduced to the distillation column, to avoid any of the light ends
entering the hydrogenation unit. More preferably the side draw is taken from a point
above that at which the stream comprising the alcohols produced in the hydrogenation is
returned to the column. It will be apparent that the optimum position for the side draw in
this embodiment will depend on a number of factors, including, but not limited to, the
size of the column and number of stages, the exact feed composition initially fed to the
column, and the conditions under which the column is operated. The side draw is
preferably taken from between one-quarter and three-quarters of the way down the
column, preferably from half-way down the column. In another preferred embodiment,
the side draw is taken from the point at which the ethanol concentration is at its highest.

The aldehyde and/or ketone impurities are selectively hydrogenated when the
product stream (which is preferably a side draw or base stream as defined above) is
contacted with hydrogen in the presence of a selective hydrogenation catalyst. The
selective hydrogenation catalyst is selected to be relatively active with respect to the
hydrogenation of aldehyde and/or ketone carbonyl groups, but relatively inactive with
respect to the hydrogenation of alkyl alkanoate carbonyl groups. Suitable catalysts
comprise transition metals such as nickel, palladium, platinum, ruthenium, rhodium and
rhenium. Such catalysts may be supported, for example, on alumina, silica or carbon.
The metal loadings on such supported catalysts may range from 0.1 to 50 wt %,
preferably, 0.5 to 10 wt %. Examples of specific catalysts include Ni on alumina or
silica, Ru on carbon or silica, Pd on carbon, Rh on carbon and Pt on carbon. In a
preferred embodiment, a 3-5wt% Ru catalyst supported on carbon or silica is employed.

The selective hydrogenation step may be carried out in the presence of any
suitable solvent, for example, acetic acid, water, and/or alkyl alkanoate. For example,
the presence of water is believed to enhance the activity of the preferred Ru-based
hydrogenation catalysts.

The hydrogen employed in the selective hydrogenation step may be employed in
pure or impure form. Optionally, an inert gas such as nitrogen may be co-fed to the
reaction.

The selective hydrogenation step may be carried out at 40 to 200°C, preferably, 40
to 120°C, preferably 60 to 120 °C, and more preferably 60 to 90 °C or, more preferably, 80 to 100 °C. The combined partial pressure of the product stream and hydrogen employed in the hydrogenation step ranges from 1 to 80 bar, preferably, 1 to 50 bar, more preferably, 1 to 40 bar, and more preferably 1 to 25 bar. In certain embodiments of the invention, relatively low pressures of 1 to 10 bar, preferably, 1 to 5 bar, for example 2 to 3 bar may also be employed.

The mole ratio of the product stream to hydrogen employed may be 1000:1 to 5:1, preferably from 100:1 to 10:1, for example, 20:1, preferably 70:1 to 50:1, for example 60:1.

The product stream may be passed over the selective hydrogenation catalyst at a liquid hourly space velocity (LHSV) of 0.1 hr⁻¹ to 20 hr⁻¹, preferably 0.2 to 1.5 hr⁻¹. Alternatively the LHSV is preferably 1 hr⁻¹ to 15 hr⁻¹, and most preferably 5 to 10 hr⁻¹.

Under the selective hydrogenation conditions of the present invention, the aldehyde and/or ketone impurities in the product stream are selectively hydrogenated to their corresponding alcohols. Such alcohols may be separated from the alkyl alkanoate product by any suitable method, including distillation. Thus, where MEK is present as a ketone impurity in an ethyl acetate product stream, it may be reduced by the reducing agent to produce sec-butanol. The sec-butanol can then be separated from the desired ethyl acetate. As sec-butanol boils at a very different boiling point to ethyl acetate, it can, for example, be separated using distillation techniques.

As well as separating the alcohols produced by the selective hydrogenation step from the product stream, it may also be desirable to separate any unreacted hydrogen from the product stream after the selective hydrogenation step. This may be achieved by using a flash tank, whereby the recovered hydrogen may be disposed of, for example, by purging or to a flare. Alternatively, the hydrogen may be recovered for re-use.

Preferably, the hydrogenated stream is introduced to a separation column whereby the hydrogen is removed from the top of the column, and the stream comprising the alkyl alkanoate and alcohol is removed from the bottom.

In the preferred process of the present invention wherein a side draw stream from a distillation column has been hydrogenated, the unreacted hydrogen may be separated from the hydrogenated stream prior to returning the stream comprising the alkyl alkanoate and alcohol back to the original distillation column. The hydrogenated stream
is introduced to a separation column whereby the hydrogen is removed from the top of the column, and the stream comprising the alkyl alkanoate and alcohol is removed from the bottom. Most preferably this hydrogen stream is recovered and recycled for re-use. The alkyl alkanoate stream from the hydrogen separation unit may also be treated to remove any aqueous phases. This can be done using, for example, a settling unit. Most preferably this separation is done using a decanter. In a preferred embodiment the alkyl alkanoate stream passes to a mixer, where water is admixed, and then a decanter, where water is allowed to separate and thus remove a proportion of the ethanol. The oil-rich phase comprising a major proportion of alkyl alkanoate, and small amounts of alcohol and water, including substantially all of the alcohol formed in the hydrogenation reaction, is then fed back to the original distillation column. Preferably this feed is introduced just below the position of the side draw removal.

It should be noted that any alkene impurities present in the product stream may also be hydrogenated under the conditions of the selective hydrogenation step to produce alkanes.

These and other aspects of the present invention will now be described with reference to Figure 1, which is a schematic diagram of an apparatus suitable for carrying out a process according to an embodiment of the present invention.

The apparatus comprises a distillation column 10, which is fed with an ethyl acetate product stream via line 12. This ethyl acetate product stream is produced by the reaction between ethylene and acetic acid in the presence of a heteropolyacid catalyst. The apparatus further comprises a hydrogenator 14, a knock-out pot or separation column 16, a settling unit (e.g. a decanter) 18 and a second distillation column 20.

In operation, a product stream comprising ethyl acetate, water, ethanol, methyl ethyl ketone, acetaldehyde and volatile components such as hydrogen, diethyl ether, butanes, butenes, methyl pentanes and methyl pentenes is introduced to the distillation column 10 via line 12. The column 10 has 40 theoretical trays and the feed containing the impurity is preferably introduced into the column at 10 stages from the top. The column 10 is operated at between 72 and 115°C and at 1.5 barg pressure. Under these conditions, acetaldehyde, a proportion of the more volatile components of the product stream, and a small amount of any water/ethanol/ethyl acetate azeotropes present may be removed as an overhead stream 22. This stream 22 is purified using distillation column
20, which specifically removes acetaldehyde from a recycling diethyl ether stream which is returned back to the front end of the process.

A significant proportion of the less volatile components, such as ethyl acetate, is collected from the base of the column 10. This stream 28 may be recovered for further purification (not shown).

A side draw 30 comprising MEK, water, ethanol and ethyl acetate is removed from the column 10 at point P, which is a chimney tray 20 theoretical stages below the top of the column and 10 stages below the feed. The temperature in the column at the side draw is 99.9 deg C. The side draw is the point at which the ethanol concentration is at its highest. This side draw 30 is introduced to the hydrogenator 14 at a LHSV of between 0.1 and 20 hr⁻¹. Hydrogen is also introduced to the hydrogenator 14 via line 32. The flow through the hydrogenator, although shown in figure 1 in an up-flow configuration, may be up-flow or down-flow. The hydrogenator 14 contains a 3-5% Ru catalyst supported on C, and is maintained at between 40 and 120 °C and 1 to 50 barg.

Under these conditions, the MEK impurity in the side draw 30 is selectively hydrogenated to its corresponding alcohol, sec-butanol.

Once treated in the hydrogenator 14 the product stream is introduced into a separating column or knock-out pot 16 via line 34. In the separating column (knock-out pot) 16, the treated product stream is allowed to degas, causing any unreacted hydrogen to separate from the remainder of the product stream as an overhead stream 36. This stream 36 may be flared, purged or recycled for re-use. The remainder of the product stream is removed from the separating column (knock-out pot) 16 via line 38, mixed with water using an online mixer and introduced into a decanter or settling unit 18.

The decanter (settling unit) is maintained at 40°C. Here, the product stream separates into an oil rich phase 40 and an aqueous phase 42. The oil rich phase 40 comprises a major proportion of ethyl acetate, and small amounts of ethanol, water and substantially all of the sec-butanol resulting from the hydrogenation of the MEK. The aqueous phase 42 comprises water, and can be separated for further purification via line 44.

The oil rich phase 40 is returned to the distillation column 10 via line 46 just below the location of the total side draw. Under the operating conditions of column 10 most of the ethyl acetate and the sec-butanol in the oil rich phase 40 concentrates at the
base of the column 10 and can be separated as a base stream 28. This base stream may
be introduced into a further distillation column (not shown), where it can be separated
into a substantially pure ethyl acetate stream, and a sec-butanol stream. The latter can
be purged.

5 Example 1

In this example, 30g of an ethyl acetate product comprising approximately 200
ppm MEK was contacted with a 5% Ru/C catalyst from Engelhard. The reaction
mixture was magnetically stirred, and pressurised to 2.5 barg with hydrogen. The
system was then heated to 70°C and left for 16hrs. After this period the heating and
stirring was turned off and the reactor left to cool to room temperature. Analysis by GC
demonstrated that the MEK was absent (detection limit <10ppm) and no ethanol due to
hydrogenation of ethyl acetate was detected.

Example 2

A test system comprised of the following:

15 Ethyl Acetate 84.3%
Ethanol 9.6%
Water 6.1%
MEK 180ppm
Acetaldehyde 50ppm

20 Olefin 200ppm (2,4,4, Trimethylpent-2-ene)
sec-Butyl acetate 160ppm
sec-Butanol 40ppm.

The above components were premixed and saturated with hydrogen before being passed
through a liquid full catalyst bed, operating in an up-flow direction, containing a surface
impregnated 3% Ru on carbon catalyst (supplied by Johnson Matthey) at 100 deg C, 40
barg hydrogen pressure and an LHSV of 8.5 hr⁻¹. Under these conditions a steady 80%
conversion of MEK was observed.
Claims

1. A process for producing alkyl alkanoate, said process comprising:
   (a) introducing an olefin and a carboxylic acid into a reactor containing an acid catalyst,
   (b) reacting said olefin with said carboxylic acid in the presence of an acid catalyst, so as to produce a product stream comprising an alkyl alkanoate and an aldehyde and/or ketone impurity,
   (c) contacting said product stream with hydrogen in the presence of a selective hydrogenation catalyst, so as to selectively reduce the aldehyde and/or ketone impurity to its corresponding alcohol, and
   (d) separating the corresponding alcohol from the remainder of the of the product stream.

2. A process according to claim 1 wherein the product stream from the reaction between the olefin and the carboxylic acid is fed to a distillation column prior to hydrogenation, and a side draw stream comprising an alkyl alkanoate and an aldehyde and/or ketone impurity is removed from said distillation column, such that said side draw stream forms the stream comprising an alkyl alkanoate and an aldehyde and/or ketone to be hydrogenated.

3. A process according to claim 2 wherein water is separated from the hydrogenated product stream.

4. A process according to claim 2 or 3 wherein the hydrogenated product stream is returned to the distillation column.

5. A process according to claim 1 wherein the product stream from the reaction
between the olefin and the carboxylic acid is fed to a distillation column prior to hydrogenation, and a base stream comprising an alkyl alkanoate and an aldehyde and/or ketone impurity is removed from said distillation column, such that said base stream forms the stream comprising an alkyl alkanoate and an aldehyde and/or ketone to be hydrogenated.

6. A process according to any preceding claim wherein unreacted starting materials are removed from the product stream of the reaction between the olefin and the carboxylic acid prior to hydrogenation.

7. A process according to any preceding claim wherein unreacted hydrogen is removed from the hydrogenated product stream.

8. A process according to any preceding claim wherein the selective hydrogenation catalyst comprises nickel, palladium, platinum, ruthenium, rhodium or rhenium.

9. A process according to claim 8 wherein the selective hydrogenation catalyst is supported.

10. A process according to any preceding claim wherein the acid catalyst is a heteropolyacid catalyst.

11. A process according to any preceding claim wherein the olefin is ethylene, propylene or butylene.

12. A process according to claim 11 wherein the olefin is ethylene.

13. A process according to any preceding claim wherein the carboxylic acid is a C₁-C₄ monocarboxylic acid.

14. A process according to claim 13 wherein the carboxylic acid is acetic acid.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

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According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>EP 0 992 484 A (KVAERNER PROCESS TECHNOLOGY) 12 April 2000 (2000-04-12) cited in the application examples 6-9</td>
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<td>Y</td>
<td>US 2 525 829 A (L. W. ROYER) 17 October 1950 (1950-10-17) column 3, line 10 - line 50; claims</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

### Date of the actual completion of the international search

26 October 2001

### Date of mailing of the international search report

06/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk, Tel: (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Wright, M
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Form PCT/GB2010 (patent family annex) (July 2002)