**Title:** PROCESS FOR THE PRODUCTION OF FATTY ALCOHOLS

A continuous process for the production of a fatty alcohol from a fatty acid comprises: (a) providing an esterification zone maintained under esterification conditions; (b) supplying to the esterification zone (i) a fatty acid feed comprising at least one fatty acid and (ii) a fatty alcohol feed comprising at least one fatty alcohol; (c) reacting fatty acid and fatty alcohol in the esterification zone to form at least one high boiling ester of a fatty acid and of a fatty alcohol and to provide an esterification product mixture that is substantially free from fatty acid; (d) providing at least one hydrogenation zone containing a fixed bed of an ester hydrogenation catalyst and maintained under ester hydrogenation conditions; (e) subjecting said at least one high boiling ester of said esterification product mixture to liquid phase hydrogenation in said at least one hydrogenation zone thereby to form an exit stream comprising fatty alcohol; (f) recycling a part of the fatty alcohol of the exit stream from the hydrogenation zone to the esterification zone to form further high boiling ester; and (g) recovering another part of the exit stream as a product stream comprising fatty alcohol.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th>AT</th>
<th>Austria</th>
<th>FR</th>
<th>France</th>
</tr>
</thead>
<tbody>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GA</td>
<td>Gabon</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GN</td>
<td>Guinea</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GR</td>
<td>Greece</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IE</td>
<td>Ireland</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>NE</td>
<td>Niger</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>NO</td>
<td>Norway</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>PL</td>
<td>Poland</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>RO</td>
<td>Romania</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>SD</td>
<td>Sudan</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>SI</td>
<td>Slovenia</td>
<td>SK</td>
<td>Slovak Republic</td>
</tr>
<tr>
<td>SN</td>
<td>Senegal</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>TG</td>
<td>Togo</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>VN</td>
<td>Viet Nam</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These codes are used to identify the countries and territories that are party to the Patent Co-operation Treaty (PCT).
Process for the production of fatty alcohols

This invention relates to a process for the production of fatty alcohols.

Fatty alcohols are produced in large volumes annually by hydrogenation of esters of fatty acids. Those alcohols which are produced by hydrogenation of esters of naturally occurring long chain fatty acids are often called natural detergent alcohols since their primary commercial use is for the production of synthetic detergents. Such fatty alcohols typically contain from about 8 to about 22 carbon atoms.

In a typical known method of producing a natural detergent alcohol a natural oil or fat is hydrolysed to liberate the fatty acid component or components thereof from the triglycerides of the oil or fat, as well as glycerine. The free acid or mixture of free acids is then esterified with a lower alkanol, usually methanol, and hydrogenated, typically in the presence of a copper chromite hydrogenation catalyst, to yield a fatty alcohol or mixture of fatty alcohols whose chain length corresponds to the chain length of the fatty acid or acids used as feedstock. Methanol is a co-product of the hydrogenation reaction and is normally recycled to produce more methyl ester for hydrogenation. For example, hydrolysis of coconut oil yields a mixture of fatty acids containing lauric acid which is then converted to methyl laurate and other methyl fatty acid esters and hydrogenated to yield a mixture of alcohols containing lauryl alcohol. As examples of other natural oils and fats that can be used as the ultimate raw material, there can be mentioned palm kernel oil, sunflower oil, tallow, and lard.

Further teaching regarding the production of fatty alcohols by hydrogenation of methyl esters of fatty alcohols can be found in WO-A-90/08121.

Useful review articles providing further background
information to the prior art have appeared as follows:
(a) "Manufacture of fatty alcohols based on natural fats and oils" by Udo R. Kreutzer, JAOCSS, Vol. 61, No. 2 (February 1984), at pages 343 to 348;
(b) "Fatty alcohols" by J.A. Monick, J. Am. Oil Chemists' Soc., November 1979 (Vol. 56), at pages 853A to 860A;
(c) "Methyl esters in the fatty acid industry", by R.D. Farris, J. Am. Oil Chemists' Soc., November 1979 (Vol. 56), at pages 770A to 773A; and

A problem arises during recovery of the product alcohol from the hydrogenation product when a methyl ester of the fatty acid is used as the hydrogenation feedstock because the boiling point of the methyl ester and of the product alcohol normally lie within a few degrees centigrade one from another. Hence it is difficult to separate traces of unconverted methyl ester from the product alcohol. Further discussion of this problem and of a practical solution to this problem will be found in WO-A-90/08123. Although WO-A-90/08123 provides a solution to this problem, it involves additional processing steps which add to the plant construction costs and also to the operating costs of the plant, both of which increase the cost of production.

An alternative process for production of fatty alcohols which also starts from the free fatty acid comprises direct hydrogenation of the fatty acid or fatty acid mixture in the absence of an alcohol component for pre-esterification. This uses a slurry of a copper chromite catalyst. Because of the use of an acid feedstock such a process requires that most of the equipment has to be made of corrosion-resistant material. Moreover the hydrogenation
reaction requires use of a higher temperature and pressure than is required for hydrogenation of the corresponding methyl ester. The need for such high pressures adds considerably to the costs of constructing and operating such a plant. Moreover the use of a slurry process leads to a complicated procedure for separating catalyst from the hydrogenation product stream and for recycling the catalyst. In practice the rate of catalyst deactivation is appreciable so that the cost of catalyst make up is quite significant. In addition there is the problem of catalyst disposal; as this contains chromium it has to be disposed of in an environmentally acceptable way. Another drawback is that the catalyst activity is far from optimal because fresh catalyst is mixed with recycled catalyst containing catalyst particles that have been recycled many times and hence are relatively inactive as well as those that have been recycled fewer times and hence are of average activity.

The higher operating temperature, e.g. about 300°C, is about 50°C to 100°C higher than the temperature necessary for hydrogenation of the corresponding methyl ester with the result that these more rigorous hydrogenation conditions lead to some hydrogenation of the product fatty alcohol itself, yielding a corresponding amount of by-product hydrocarbon. Hence lower yields are generally obtained by this route than when using a methyl ester of a fatty acid as hydrogenation feedstock.

It has also been proposed in a variation of this last mentioned process, to use a fatty acid as feedstock for hydrogenation and to recirculate product fatty alcohol to the inlet to the hydrogenation reactor. In this way an in situ esterification occurs in the hydrogenation reactor by which the fatty acid reacts with the product fatty alcohol to form wax ester. This process is also operated as a slurry process with finely divided copper chromite as the
hydrogenation catalyst. A further description can be found in an article "Natural fats and oils route to fatty alcohols" by Henning Buchold, Chemical Engineering, February 21, 1983, pages 42 and 43. The hydrogenation conditions include use of a process of about 4500 psia (about 310 bar) and a temperature of 590°F (310°C). The drawbacks to this process are similar to those for the fatty acid hydrogenation process and include high capital and operating costs due to the high pressure of operation. There are also the complications associated with use of a slurry process and dispersal of spent catalyst. In addition there is loss of potential product alcohol due to formation of by-product hydrocarbon at the high operating temperatures used.

It would accordingly be desirable to provide a process for the production of fatty alcohols, particularly natural detergent alcohols, which obviates the difficulties associated with use of the methyl ester of the fatty acid as the hydrogenation feedstock. It would further be advantageous to provide a process which requires a simpler plant and offers reduced operating costs compared with the known method involving use of the methyl ester of the fatty acid. It would further be desirable to provide a process for the production of fatty alcohols from fatty acids that uses recycle of product alcohol to produce a wax ester but that obviates the use of high operating pressures and of a catalyst slurry system.

The present invention accordingly seeks to provide a process for the production of fatty alcohols from fatty acids by a route in which recovery of product alcohol is simplified. It further seeks to provide a process for the production of fatty alcohols from fatty acids which avoids use of a methyl ester of the fatty acid as hydrogenation feedstock. It also seeks to provide a process wherein the use of an expensive gas recycle compressor is obviated,
thereby enabling considerable savings in capital and operating costs to be achieved in comparison to conventional processes for producing natural detergent alcohols. It also seeks to provide a process for the production of fatty alcohols from fatty acids that enables use of a wax ester as an intermediate but which obviates the use of extremely high hydrogenation pressures and avoids the disadvantages of using a recirculating catalyst slurry system.

According to the present invention there is provided a process for the production of a fatty alcohol from a fatty acid which comprises:

(a) providing an esterification zone maintained under esterification conditions;
(b) supplying to the esterification zone (i) a fatty acid feed comprising at least one fatty acid and (ii) a fatty alcohol feed comprising at least one fatty alcohol;
(c) reacting fatty acid and fatty alcohol in the esterification zone to form at least one high boiling ester of a fatty acid and of a fatty alcohol and to provide an esterification product mixture that is substantially free from fatty acid;
(d) providing at least one hydrogenation zone containing a fixed bed of an ester hydrogenation catalyst and maintained under ester hydrogenation conditions;
(e) subjecting said at least one high boiling ester of said esterification product mixture to liquid phase hydrogenation in said at least one hydrogenation zone thereby to form an exit stream comprising fatty alcohol;
(f) recycling a part of the fatty alcohol of the exit stream from the hydrogenation zone to the esterification zone to form further high boiling ester; and
(g) recovering another part of the exit stream as a product stream comprising fatty alcohol.

Preferably the fatty acid or fatty acids and the
fatty alcohol or fatty alcohols each contain from 6 to 20 carbon atoms.

The fatty acid or each of the fatty acids may be a saturated aliphatic acid or an unsaturated aliphatic acid containing one or more ethylenically unsaturated groups. Examples of fatty acids that can be used in the process of the invention include caproic acid, oleic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, heptadecanoic acid, stearic acid, elaidic acid, oleic acid, linoleic acid, nonadecanoic acid, arachidic acid, and the like, and mixtures of two or more thereof.

As examples of fatty alcohols produced by the process of the invention and used therein, there can be mentioned \( \eta \)-hexanol, \( \eta \)-heptanol, \( \eta \)-octanol, \( \eta \)-nonanol, \( \eta \)-decanol, \( \eta \)-undecanol, lauryl alcohol, \( \eta \)-tridecanol, myristyl alcohol, \( \eta \)-pentadecanol, \( \eta \)-hexadecanol, \( \eta \)-heptadecanol, \( \eta \)-octadecanol, \( \eta \)-nonadecanol, \( \eta \)-eicosanol, and the like, and mixtures of two or more thereof.

In step (b) of the process of the invention it is preferred to supply fatty acid and fatty alcohol in approximately stoichiometric amounts or with the fatty alcohol in excess. Hence in a particularly preferred process the fatty acid:fatty alcohol molar ratio of the reactants supplied to the esterification zone ranges from about 1:1 to about 1:3, more preferably from about 1:1 to about 1:2, e.g. from about 1:1 to about 1:1.5. Hence this molar ratio may be, for example, from about 1:1 to about 1:1.2.

In the process of the invention a fatty alcohol and a fatty acid are reacted in the esterification zone to form a high boiling ester. If a mixture of fatty acids is used as starting material, then a mixture of fatty alcohols will
be formed and hence a mixture of high boiling esters will also be formed. The high boiling esters have boiling points which are significantly higher than those of the fatty alcohol or the fatty acid from which they are derived. Typically the high boiling esters have boiling points of at least 240°C at atmospheric pressure. Thus \( \text{n-hexyl caproate} \) has a boiling point at atmospheric pressure of 246°C, while \( \text{n-hexyl alcohol} \) has a boiling point of 158°C and caproic acid a boiling point of 205°C at the same pressure. This difference in boiling points greatly facilitates recovery of fatty alcohol of a requisite grade. Examples of high boiling esters include \( \text{n-hexyl caproate} \), \( \text{n-heptyl oenanthate} \), \( \text{n-octyl caprylate} \), \( \text{n-nonyl pelargonate} \), \( \text{n-decyl caprate} \), \( \text{n-undecyl undecanoate} \), lauryl laurate, \( \text{n-tridecyl tridecanoate} \), myristyl myristate, \( \text{n-pentadecyl pentadecanoate} \), \( \text{n-hexadecyl palmitate} \), \( \text{n-hexadecyl palmitoleate} \), \( \text{n-heptadecyl heptadecanoate} \), \( \text{n-octadecyl stearate} \), \( \text{n-octadecyl elaidate} \), \( \text{n-octadecyl oleate} \), \( \text{n-octadecyl linoleate} \), \( \text{n-nonadecyl nonadecanoate} \), \( \text{n-eicosyl arachidate} \), and the like, and mixtures of two or more thereof.

The esterification step may be effected autocatalytically or in the presence of an esterification catalyst. Alternatively a combination of autocatalytic reaction and catalytic esterification may be used.

The esterification zone may be an autocatalytic esterification zone. Alternatively the esterification zone may contain at least one charge of a solid esterification catalyst selected from ion exchange resins containing sulphonic acid and/or carboxylic acid groups. As an example of a suitable esterification catalyst there may be mentioned Amberlyst 16 ion exchange resin. ("Amberlyst" is a trade mark). However, numerous other commercially available ion exchange resins may alternatively be used, as will be
apparent to those skilled in the art.

In a preferred process the esterification zone or zones is or are operated at a temperature of from about 75°C to about 275°C, preferably about 100°C to about 250°C, and at a pressure of from about 0.001 bar up to about 6 bar. Esterification is a reversible reaction and results in production of a molecule of water and a molecule of high boiling ester for each molecule of fatty acid that reacts with a molecule of a fatty alcohol. The esterification conditions are desirably selected so that the temperature used is above the boiling point of water at the operating pressure in the relevant esterification zone so as to vaporise water of esterification and drive the esterification reaction as far as possible towards completion. If an ion exchange resin catalyst is used in the esterification step, then the temperature that is used in the relevant esterification zone may be limited by the thermal stability of the resin.

It is further possible to use a combination of a catalytic esterification zone and an autocatalytic esterification zone. For example, it may be preferred to mix the fatty acid feed and the fatty alcohol feed and to pass the mixture first through (i) a catalytic esterification zone containing a charge of a solid esterification catalyst maintained at a temperature of, for example, from about 100°C to about 140°C, e.g. 110°C, so as to convert at least about 70% of the fatty acid or acids, e.g. up to about 90% or more thereof, to the corresponding high boiling ester or esters, and then through (ii) an autocatalytic reaction zone operated at a higher temperature, for example in the range of from about 180°C to about 250°C, e.g. 240°C, in order to cause further esterification to occur. In the autocatalytic reaction zone the reaction temperature is desirably maintained at a
temperature significantly above the boiling point of water at the prevailing pressure so as to vaporise water of esterification and to drive the esterification reaction as far as possible towards 100% completion.

Alternatively there can be used an autocatalytic esterification zone followed by a catalytic esterification zone.

The hydrogenation zone or zones may be operated at a temperature of from about 100°C to about 250°C and at a pressure of from about 1 bar to about 60 bar. A single hydrogenation zone may be used with optional recycle of part of the exit stream therefrom to act as diluent for incoming material from the esterification zone. Alternatively two or more hydrogenation zones in series may be used; in this case the hydrogenation zones can be operated according to the teachings of WO-A-87/07598, WO-A-88/05767 or WO-A-89/05286. In the process described in these three documents the liquid feed to the or each hydrogenation zone is fed to an upper end thereof in co-current with a hydrogen-containing gas.

In a preferred arrangement according to the teachings of WO-A-88/05767 make up hydrogen gas is supplied to the final hydrogenation zone and the gaseous effluent therefrom is supplied to an earlier hydrogenation zone, i.e. the first hydrogenation zone if two zones only are used.

The hydrogen-containing gas supplied to said at least one hydrogenation zone preferably contains a major amount of hydrogen and at most a minor amount of one or more inert gases, such as nitrogen, methane, other low molecular weight hydrocarbons, such as ethane, propane, n-butane and iso-butane, carbon oxides, neon, argon or the like. Preferred hydrogen-containing gases are accordingly gases containing at least about 50 mole % up to about 95 mole % or more (e.g. about 99 mole %), of H₂ with the balance comprising one or more of N₂, CO, CO₂, Ar, Ne, CH₄ and other
low molecular weight saturated hydrocarbons. Such hydrogen-containing gases can be obtained in conventional manner from synthesis gas and other usual sources of hydrogen-containing gases, followed, if necessary, by appropriate pretreatment to remove impurities, such as sulphurous impurities (e.g. \( \text{H}_2\text{S}, \text{COS}, \text{CH}_3\text{SH}, \text{CH}_3\text{SCH}_3, \) and \( \text{CH}_3\text{SSCH}_3 \)) and halogen-containing impurities (e.g. \( \text{HCl} \) and \( \text{CH}_3\text{Cl} \)) which would exert a deleterious influence on catalytic activity, i.e. catalyst inhibition, poisoning or deactivation, as well as by the removal of the bulk of the carbon oxides. Preparation of suitable hydrogen-containing gases will accordingly be effected according to usual production techniques and forms no part of the present invention. Thus the hydrogen-containing gas supplied to the hydrogenation zone may be, for example, a 94 mole \% hydrogen stream produced by steam reforming of natural gas followed by the water gas shift reaction:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2,
\]

then by \( \text{CO}_2 \) removal to give a gas containing about 1 mole \% to about 2 mole \% carbon oxides, and finally by methanation to give a gas containing only a few ppm by volume of carbon oxides. Substantially pure hydrogen from an electrolysis plant may be used, as can also purified hydrogen streams obtained by the pressure swing adsorption treatment of hydrogen admixed with \( \text{CO}, \text{CO}_2 \) and light hydrocarbon gases, in each case with excellent results. For a discussion of production of hydrogen streams by pressure swing adsorption reference may be made to a paper entitled "Hydrogen Purification by Pressure Swing Adsorption" by H.A. Stewart and J.L. Heck, prepared for Symposium on Adsorption - Part III, 64th National Meeting of the American Institute of Chemical Engineers, New Orleans, Louisiana, U.S.A., March 16-20, 1969.

In operation of the process of the invention, under
steady state conditions, the composition of the gas (whether dissolved in the liquid phase or present in the gaseous state) exhibits a significant variation between different parts of the hydrogenation zone or zones. Thus, for example, the partial pressure of hydrogen is highest in the, or in each, hydrogenation zone at the respective gas inlet end thereof and lowest at the exit end for gaseous effluent therefrom, whilst the combined partial pressures of any inert materials present is lowest at the respective gas inlet end to the, or to each, hydrogenation zone and highest at the exit end for gaseous effluent therefrom. It is thus possible to discharge from the hydrogenation zone or from one of the hydrogenation zones a purge gas containing about 50 mole % or more, typically at least about 75 mole %, of inert gases and less than about 50 mole % of hydrogen, typically less than about 25 mole % of hydrogen. This purge gas can be passed through the esterification zone or one of the esterification zones to strip water of esterification from a liquid esterification mixture. Under suitable operating conditions it is possible to operate the process of the invention so that the effluent gas stream or gas streams contain a relatively small concentration of hydrogen (e.g. 45 mole % or less) and consist predominantly of inert gases (e.g. N₂, Ar, CH₄ etc). In this case the effluent gas stream or streams from the plant is or are relatively small and consequently hydrogen losses are minimal. In general the composition and rate of withdrawal of the purge gas stream or streams from the hydrogenation zone will be dependent in large part upon the level of inert gases in the hydrogen containing gas. In the limit, when operating with very pure hydrogen, the solubility of inert gases in the reactor effluent is sufficient to purge such inert gases from the plant and it becomes unnecessary to purge an effluent gas stream from the hydrogenation zone or zones,
the inert gases being purged in the course of work up of the hydrogenation product. In this case a separate supply of stripping gas can be supplied to the esterification zone.

Because any inert gases present are automatically concentrated in any gaseous effluent stream or streams when operating according to the teachings of WO-A-87/07598 or WO-A-88/05767, it is not necessary on economic grounds in such circumstances to recycle the gaseous effluents from the hydrogenation zone or zones so as to obtain efficient usage of hydrogen. Recycle of gas is necessary in conventional vapour phase hydrogenation processes in order to achieve efficiency of operation. This is because a high molar ratio of hydrogen to ester has to be used to maintain the vapour phase conditions in the hydrogenation zone, even when the relatively volatile methyl esters are used. Because of the low volatility of the high boiling esters used in the process of the present invention the amount of hydrogen required to maintain them in the vapour phase would be impracticably large; therefore a liquid phase hydrogenation step is preferred. Moreover, as it is not necessary to recycle a gas stream which contains appreciable concentrations of inert gases so as to achieve satisfactory economy of hydrogen consumption, the total operating pressure of the plant can therefore be reduced although the maximum hydrogen partial pressure is maintained; hence the construction costs can be reduced as the plant not only operates at a lower pressure but also no gas recycle compressor is needed. The absence of a gas recycle compressor, which is in itself an expensive item of equipment, means also that the civil engineering work associated with its installation, such as provision of a mounting and a compressor house therefor, is obviated. In addition the ancillary items of equipment normally needed when a gas recycle compressor is installed, such as a drive
motor, power transformer, and instrumentation, are not required. There is also a saving in pipework for the plant as no provision for recycle of gas is needed. Although it is difficult to generalise, preliminary calculations suggest that the overall capital savings that can be achieved for the hydrogenation section of the plant by adopting the teachings of WO-A-87/07598, WO-A-88/05767 or WO-A-89/05286 for a fatty alcohol production plant with a throughput of 50,000 tonnes per year can be as much as about 20% compared with the cost of a conventionally designed vapour phase hydrogenation plant.

It will normally be preferred that the liquid exit stream from said at least one hydrogenation zone is subjected to evaporation under reduced pressure in an evaporation zone to vaporise fatty alcohol therefrom and to produce a liquid bottoms stream. In this case the evaporation zone may be operated at a temperature of from about 100°C to about 250°C and at a pressure of from about 0.001 bar up to about 0.8 bar. The dwell time in the evaporation zone may range from about 0.5 seconds up to about 60 seconds. Material of the liquid bottoms stream is recycled to the esterification zone in step (f). Part of the liquid bottoms stream can be treated to remove heavy by-products therefrom prior to recycle to the esterification zone.

In a preferred process the or each said at least one hydrogenation zone contains a fixed bed of a reduced copper chromite catalyst and is operated under liquid phase hydrogenation conditions. Such a reduced copper chromite catalyst is preferably prepared according to the teachings of EP-A-0301853.

The process is preferably operated so that, in step (c), the conversion of fatty acid to high boiling ester is substantially complete so that the esterification product
mixture is substantially free from fatty acid. Hence it is preferred that the conversion of fatty acid to high boiling ester in the esterification zone is preferably at least about 95% or more, more preferably at least about 98%, and even more preferably at least about 99%, up to 99.9% or higher. However, it is not necessary that in step (e) the high boiling ester or esters be completely hydrogenated in passage through the hydrogenation zone. It suffices if the conversion of high boiling ester to fatty alcohol is at least about 15% per pass, although it will normally be preferred to operate with conversions of at least about 35% per pass. However, the use of higher conversions per pass, e.g. 50% or more up to 75% or more as allowed by equilibrium considerations, is not excluded, nor is the operation of the process under conditions such that 90% or more conversion per pass is achieved, up to 95% or even higher, e.g. 99.9% per pass. Any unconverted high boiling ester in the exit stream from the hydrogenation zone can be recycled in step (f) of the process to the esterification zone.

In step (g) of the process a part of the exit stream is recovered as a product stream comprising fatty alcohol. Any remaining fatty alcohol in the exit stream can be recycled to the esterification zone in step (f) of the process. Because of this recycle feature it is not crucial to success to aim for maximum recovery of fatty alcohol from the exit stream from the hydrogenation zone. For example, it is perfectly feasible to recover only, for example, about 30% to about 40% of the product alcohol present in the exit stream from the hydrogenation zone and to recycle the rest thereof to the esterification zone. Indeed it is beneficial to recycle at least 50% of the fatty alcohol in the exit stream from the hydrogenation zone in step (f) so that this can provide the fatty alcohol feed (ii) of step (b) of the process of the invention. In a particularly preferred
process the rate of fatty alcohol recycle is at least, and
even more preferably more than, stoichiometric with respect
to the feed rate of the fatty acid (i) of step (b). In this
way the feed mixture to the hydrogenation zone can contain a
mixture of high boiling ester and excess fatty alcohol, the
excess fatty alcohol acting as an inert diluent in the
hydrogenation reaction of step (e). The use of an inert
diluent in this step is beneficial since it can act as a
heat sink to absorb the exothermic heat of reaction released
in the hydrogenation step.

In order that the invention may be clearly
understood and readily carried into effect a preferred
process in accordance with the invention will now be
described, by way of example only, with reference to the
accompanying drawings in which:

Figure 1 is a flow diagram of a plant for the
production of detergent alcohols from a fatty acid
feedstock; and

Figure 2 is a laboratory scale apparatus for
studying the liquid phase hydrogenation of lauril laurate
and other esters.

It will be understood by those skilled in the art
that, as the drawing is diagrammatic, a number of ancillary
items of equipment which would be necessary for operation of
the plant, such as heat exchangers, coolers, pressure
regulators, pressure relief valves, flow control valves,
storage tanks, vacuum pumps, pumps, and the like have been
omitted for the sake of clarity. The provision of such
ancillary items of equipment forms no part of the present
invention and will be in accordance with conventional
chemical engineering practice.

Referring to the drawing, a hot lauric acid
feedstock is supplied to the plant in line 1 and is admixed
with a hot mixture, supplied in line 2, of recycled lauril
alcohol, high boiling esters (i.e. lauryl laurate), and
dilauryl ether. The resulting mixture flows on in line 3 at
a temperature of 110°C to the top of an esterification
reactor 4 containing a number of trays 5. Each tray 5 may
be empty or may have trapped thereon a pre-determined
quantity of a solid esterification catalyst, such as an ion
exchange resin. An example of a suitable ion exchange resin
is one containing sulphonylic acid groups or carboxylic acid
groups or both, such as Amberlyst 16. (The word Amberlyst
is a trade mark). A series of downcomers (not shown) is
provided for allowing liquid to pass down reactor 4 from one
tray 5 to the next lower tray, whilst one or more upcomers
are provided for each tray 5 to allow gas to pass up the
reactor 4 from tray to tray and to agitate the liquid, or
the mixture of catalyst and liquid, on each tray 5. A
fuller description of a reactor which can be readily
modified to form reactor 4 can be found in WO-A-90/08127. A
gas stream is passed upwardly through reactor 4 from line 6.
The pressure in reactor 4 is slightly in excess of
atmospheric pressure. In passage down reactor 4 from each
tray 5 to the next lower tray lauryl alcohol undergoes
esterification with lauryl alcohol to form lauryl laurate,
this reaction occurring autocatalytically, if the trays 5
contain no ion exchange resin, or catalytically, if the
trays 5 contain an esterification catalyst. The upflowing
gas from line 6 serves to effect mixing of the liquid on
each tray and to carry away, as vapour, water of
esterification. The gas and water vapour mixture exits
reactor 4 in line 7.

A liquid phase comprising high boiling ester,
lauryl alcohol and dilauryl ether is withdrawn from reactor
4 in line 8 and is pumped by pump 9 into line 10 where it
encounters and is mixed with a hydrogen feed gas in line 11.
The resulting mixture in line 12 passes on in line 13,
optionally after admixture with recycled liquid in line 14, to a hydrogenation reactor 15 which contains a charge of a reduced copper chromite hydrogenation catalyst and is operated under liquid phase hydrogenation conditions. Hydrogenation reactor 15 is operated at a pressure of 36.3 bar (512 psig) and a temperature of 196°C.

A liquid/gas mixture comprising mainly lauryl alcohol, but also containing some high boiling ester and dilauryl ether, together with unreacted hydrogen and inert gases, is recovered from the bottom of hydrogenation reactor 15 in line 16 and passed through a gas-liquid separator 17. The gas phase passes via line 18 and pressure reduction valve 19 to line 6.

The liquid phase from gas-liquid separator 17 passes in line 20 and is pumped by means of pump 21 via lines 22 and 23 and pressure reduction valve 24 to an evaporator 25 operated under vacuum. Part of this liquid phase can be recycled through cooler 26 to line 14. Cooler 26 is typically supplied with a liquid heat exchange medium at an elevated temperature, for example 180°C or thereabouts. In the event of an interruption of feedstock supply the cooler 26 can be used to maintain the liquid circulating through reactor 15 at the requisite temperature.

The heated mixture of liquid and vapour flows on from evaporator 25 in line 27 to a gas-liquid separator 28. The vapour phase passes in line 29 to condenser 30 and thence by line 31 into collection vessel 32. Product fatty alcohol passes on in line 33 to storage. Line 34 is connected to a vacuum pump (not shown).

The liquid recovered from the bottom of gas-liquid separator 28 is a mixture consisting mainly of lauryl alcohol but admixed with high boiling ester and dilauryl ether. This passes in line 35 to pump 36 and is recycled to form the stream in line 2 through lines 37 and 38, valve 39
and line 40.

A side stream is taken in line 41 from line 37 for treatment in a heavy by-product control module indicated at 42. After passing through a pressure reduction valve 43 the side stream is heated in evaporator 44. The mixture of vapour and liquid passes on in line 45 to a further gas-liquid separator 46. A liquid bottom stream comprising mainly a mixture of high boiling ester and dilauryl ether is purged from the plant in line 47 and pumped by pump 48 to storage or disposal in line 49. The vapour in line 50 is mainly lauryl alcohol. It is condensed in condenser 51, collects in vessel 52, and is recycled to line 2 by means of line 53, pump 54 and line 55. Reference numeral 56 indicates a connection to a vacuum pump (not shown).

A liquid level controller 57 connected to a liquid level sensor in gas-liquid separator 17 is used to control valve 24. A further liquid level controller 58 connected to a liquid level sensor in gas-liquid separator 28 is connected to a throttle valve 59 in line 34 whereby the pressure in separator 28 can be varied. In this way the rate of evaporation of fatty alcohol and its rate of offtake in line 33 can be controlled. Line 60 can be used for in-bleed of N₂ in case it is desired to raise the pressure in separator 28.

The flow rates in kg moles per hour are indicated in the following Table 1, as well as pressures and temperatures.
Table 1

<table>
<thead>
<tr>
<th>Line No.</th>
<th>1</th>
<th>2</th>
<th>7</th>
<th>8</th>
<th>11</th>
<th>20</th>
<th>33</th>
<th>35</th>
<th>41</th>
<th>49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lauryl alcohol</td>
<td>-</td>
<td>110</td>
<td>-</td>
<td>10</td>
<td>206</td>
<td>96</td>
<td>110</td>
<td>-</td>
<td>3.143</td>
<td>-</td>
</tr>
<tr>
<td>Lauryl laurate</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>134</td>
<td>-</td>
<td>35</td>
<td>-</td>
<td>35</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Diisauryl ether</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>35</td>
<td>-</td>
<td>35</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>210</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

| Pressure (bar) | 1.1 | 1.1 | 0.1 | 0.18 | 37 | 36 | 0.1 | 0.3 | 1.1 | 1.1 |
| Temperature (°C) | 120 | 120 | 120 | 120 | 100 | 195 | 50 | 230 | 230 | 100 |

The invention is further illustrated in the following Examples.

**Example 1**

1 kg of technical grade lauric acid and 2 kg of lauryl alcohol were heated together in a distillation apparatus. Water of esterification was distilled from the reaction flask as the reaction progressed. When less than 0.5% of the lauric acid remained the excess lauryl alcohol was removed by distillation at atmospheric pressure to give a product comprising 88% lauryl laurate, 7.5% lauryl alcohol and the balance a mixture of by-products, the principal one of which was C\(_{12}\) olefin (1%) produced by dehydration of lauryl alcohol and the others being high boiling materials.

Upon repeating the procedure of this Example with distillation of the reaction product mixture under reduced pressure, the amount of olefinic by-products is reduced due to the use of a lower distillation temperature during product recovery.
Example 2

The procedure of Example 1 is repeated with the following acids and alcohols to give similar yields of esters:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Alcohol</th>
<th>Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylic acid</td>
<td>n-octanol</td>
<td>n-octyl caprylate</td>
</tr>
<tr>
<td>Capric acid</td>
<td>n-decanol</td>
<td>n-decyl caprate</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>Myristyl alcohol</td>
<td>Myristyl myristate</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>n-hexadecanol</td>
<td>n-hexadecyl palmitate</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>n-hexadecanol</td>
<td>n-hexadecyl palmitoleate</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>n-octadecanol</td>
<td>n-octadecyl stearate</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>n-eicosanol</td>
<td>n-eicosanyl arachidate</td>
</tr>
</tbody>
</table>

Example 3

The product from Example 1 was subjected to hydrogenation in the apparatus illustrated in Figure 2 of the accompanying drawings. The crude lauryl laurate produced in Example 1 was supplied in line 101 to a heated feed tank 102 under a blanket of nitrogen from line 103. Line 101 and all other liquid feed lines were wrapped with insulation and thermostatically controlled electrical heating tape so that the material therein could be kept molten so as to prevent blockage of any liquid line. Reference numeral 104 indicates a vent line from tank 102. From tank 102 the ester was pumped through line 105 and valve 106 and then through one of filters 107 and 108 by means of a piston operated pump 109. The flow rate through pump 109 could be checked by closing valve 106 and supplying the crude lauryl laurate feed via line 110 from a feed rate check burette 111.

The ester feed passed through a further valve 112 from pump 109 to line 113 and was then mixed with hydrogen from line 114. The hydrogen flow rate was controlled by valve 115 under the influence of pressure indicator controller recorder 116 and was measured by flow indicator recorder 117. The mixed liquid-gas feed was supplied in line
118 to the top of a jacketed hydrogenation reactor 119. This contained a charge 120 of 240 cm$^3$ of a copper chromite hydrogenation catalyst, which had been carefully pre-reduced according to EP-A-0301853 surmounted by a layer of glass beads 121. The internal diameter of reactor 119 was 2.5 cm and its length was 1 metre. Hot oil could be passed through the jacket 122 of the reactor; reference numerals 123 and 124 indicate the oil inlet and outlet ports respectively. A thermocouple 125 positioned in bed 120 was connected to a temperature indicator recorder 126.

The bottom end of reactor 119 had an outlet pipe 127 acting as an overflow from a pool of liquid 128 in the bottom of the reactor 119. Liquid could be drawn from pool 128 through line 129 and valve 130 by means of a gear pump 131. Reference numerals 132 and 133 indicate pump suction filters. From pump 131 the liquid could be recycled to the inlet end of reactor 119 through valve 134 by means of line 135.

The liquid recovered in line 127 represents the "make" of product alcohol plus a corresponding amount of any unconverted lauryl laurate. This passed in admixture with effluent gas to secondary reactor 136. This secondary reactor also contained a charge 137 of 240 cm$^3$ of copper chromite catalyst (also pre-reduced according to EP-A-0301853) surmounted by a layer of glass beads 138. The internal diameter of reactor 136 was also 2.5 cm and its length was 1 metre. Hot oil could also be passed through the jacket 139; reference numerals 140 and 141 indicate the oil inlet and outlet ports respectively. A thermocouple 142 positioned in catalyst bed 137 was connected to a temperature indicator recorder 143.

The bottom end of secondary reactor 136 had an outlet pipe 144 through which liquid product and gas passed to separation vessel 145. A purge gas stream was taken from vessel 145 in line 146 and then through pressure let down
valve 147 to purge gas line 148. The liquid product stream, containing lauryl alcohol in admixture with unconverted lauryl laurate, was recovered in line 149 after passage through valve 150 which was under the control of level sensor 151.

The product in line 127 was sampled using sample point 152 and analysed for comparison with the product in line 149. Reference numeral 153 indicates a flow meter.

The analysis results are set out below in Table 2.

The following operating conditions were used:

<table>
<thead>
<tr>
<th>Operating Pressure</th>
<th>36.4 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of reactor 119</td>
<td>197°C</td>
</tr>
<tr>
<td>Temperature of reactor 136</td>
<td>190°C</td>
</tr>
<tr>
<td>Liquid recycle rate (line 135)</td>
<td>2400 cm³/hr</td>
</tr>
<tr>
<td>Liquid feed rate (line 101)</td>
<td>60 cm³/hr</td>
</tr>
<tr>
<td>Hydrogen purge rate</td>
<td>5 l/hr at 1 bar and 0°C</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Feed and Product Analysis</th>
<th>w/w %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>line 101</td>
</tr>
<tr>
<td>Lauryl alcohol</td>
<td>7.5</td>
</tr>
<tr>
<td>Lauryl laurate</td>
<td>88.0</td>
</tr>
<tr>
<td>C₁₂ olefin</td>
<td>1.0</td>
</tr>
<tr>
<td>C₁₂ alkane</td>
<td>-</td>
</tr>
<tr>
<td>Di lauryl ether</td>
<td>-</td>
</tr>
<tr>
<td>Heavies/Unknowns</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The analysis of the intermediate reaction product in line 127 shows that a substantial conversion of the lauryl laurate is effected in the first reactor 119. A further stage of hydrogenation requiring a second reactor,
thereby effectively doubling the catalyst volume, only effects a moderate increase in the conversion of lauryl laurate to lauryl alcohol.

The results set out in Table 2 were obtained by gas chromatography. The gas chromatographic conditions were:
initial temperature 130°C for 4 minutes followed by 8°C/minute temperature increase to 275°C, holding at 275°C for 10 minutes. The column comprised 25 metres of 0.32 mm capillary tube coated with OV 101 silicone. The carrier gas was helium, and the inlet pressure was 1.7 bar. The retention time for lauryl alcohol was 9 minutes, and that for lauryl laurate was 24 minutes.

**Comparative Example A.**

This Example is provided to demonstrate the presence of an alcohol/high boiling ester equilibrium in the hydrogenation step. In this Comparative Example lauryl alcohol was contacted with hydrogen over the hydrogenation catalyst at a relatively low hydrogenation pressure so as to demonstrate that the hydrogenation step is reversible:

\[ 2C_{12}H_{25}OH \rightleftharpoons C_{11}H_{23}COOC_{12}H_{25} + 2H_2. \]

The procedure of Example 3 was used except that lauryl alcohol was fed to the equipment in line 101 and a substantially lower operating pressure was used.

<table>
<thead>
<tr>
<th>Operating pressure</th>
<th>3.25 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of reactor 119</td>
<td>195°C</td>
</tr>
<tr>
<td>Temperature of reactor 136</td>
<td>189°C</td>
</tr>
<tr>
<td>Lauryl alcohol feed (97% technical grade)</td>
<td>60 cm³/hr</td>
</tr>
<tr>
<td>Liquid recycle (line 135)</td>
<td>2400 cm³/hr</td>
</tr>
<tr>
<td>Hydrogen purge rate</td>
<td>6 l/hr (measured at 1 bar and 0°C)</td>
</tr>
</tbody>
</table>

The results obtained are summarised in Table 3.
Table 3

<table>
<thead>
<tr>
<th>Product Distribution wt %</th>
<th>line 128</th>
<th>line 149</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauryl alcohol</td>
<td>54.5</td>
<td>41.3</td>
</tr>
<tr>
<td>Lauryl laurate</td>
<td>41.6</td>
<td>54.4</td>
</tr>
</tbody>
</table>

A further experiment where the product in line 149 was used as the feed in line 105 established that the equilibrium wt % ratio of lauryl alcohol to lauryl laurate was about 11.4:1 at 191°C and 36.4 bar operating pressure. The hydrogen purge rate was 2 l/hr (measured at 1 bar and 0°C).

Example 4

The procedure of Example 3 was repeated except that the hydrogen purge rate was 2 l/hr (at 0°C and 1 bar) and the temperatures of reactor 119 and reactor 136 were 195°C and 189°C respectively. The effect of liquid recycle around reactor 119 was investigated using a feed containing 69.5% lauryl laurate and 25.1% lauryl alcohol. The results are shown below in Table 4; pump 131 was switched off and valves 130 and 134 were closed in the zero recycle experiments.

Table 4

<table>
<thead>
<tr>
<th>line 135 rate (cm³/hr)</th>
<th>lauryl alcohol % w/w</th>
<th>lauryl laurate % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>line 127</td>
<td>2400</td>
<td>62.4</td>
</tr>
<tr>
<td>line 149</td>
<td>2400</td>
<td>76.3</td>
</tr>
<tr>
<td>line 127</td>
<td>0</td>
<td>63.5</td>
</tr>
<tr>
<td>line 149</td>
<td>0</td>
<td>73.5</td>
</tr>
</tbody>
</table>
The effect of the liquid recycle is an improvement in overall conversion for the complete system and an improvement in overall selectivity for each reactor.

**Example 5**

A feed solution was prepared containing 54.4 wt% lauryl laurate, 41.3 wt% lauryl alcohol and the balance impurities including C₁₂ hydrocarbons and di-lauryl ether. This was subjected to hydrogenation by the procedure of Example 3 except that the feed solution feed rate was 40 cm³/hr and the inlet temperature to reactor 119 was 195°C, while the hydrogen effluent flow rate, measured at 0°C and 1 bar, was 6 litres/hr. The product distribution in line 127 was 74.11 wt% lauryl alcohol and 20.1 wt% lauryl laurate and that in line 149 was 82.9 wt% lauryl alcohol and 10.9 wt% lauryl laurate.

**Example 6**

When the procedure of Example 5 was repeated with a feed rate of feed solution of 80 cm³/hr the analysis of the product in line 127 was 65.0 wt% lauryl alcohol and 29.3 wt% lauryl laurate and the analysis of the material in line 149 was 77.7 wt% lauryl alcohol and 17.5 wt% lauryl laurate.

**Example 7**

The procedure of Example 3 or Example 4 is repeated in turn with each of the esters of Example 2 with similarly good results.

**Example 8**

The product of any one of Examples 3 to 7 is successfully distilled, under pressure conditions chosen so that the boiling point of the alcohol did not exceed 170°C, to yield the corresponding alcohol in good yield.
CLAIMS

1. A continuous process for the production of a fatty alcohol from a fatty acid which comprises:
   (a) providing an esterification zone maintained under esterification conditions;
   (b) supplying to the esterification zone (i) a fatty acid feed comprising at least one fatty acid and (ii) a fatty alcohol feed comprising at least one fatty alcohol;
   (c) reacting fatty acid and fatty alcohol in the esterification zone to form at least one high boiling ester of a fatty acid and of a fatty alcohol and to provide an esterification product mixture that is substantially free from fatty acid;
   (d) providing at least one hydrogenation zone containing a fixed bed of an ester hydrogenation catalyst and maintained under ester hydrogenation conditions;
   (e) subjecting said at least one high boiling ester of said esterification product mixture to liquid phase hydrogenation in said at least one hydrogenation zone thereby to form an exit stream comprising fatty alcohol;
   (f) recycling a part of the fatty alcohol of the exit stream from the hydrogenation zone to the esterification zone to form further high boiling ester; and
   (g) recovering another part of the exit stream as a product stream comprising fatty alcohol.

2. A process according to claim 1, in which the fatty acid and the fatty alcohol each contain from 6 to 26 carbon atoms.

3. A process according to claim 1 or claim 2, in which the esterification zone is an autocatalytic esterification zone.
4. A process according to claim 1 or claim 2, in which the esterification zone contains at least one charge of a solid esterification catalyst selected from ion exchange resins containing sulphonic acid and/or carboxylic acid groups.

5. A process according to any one of claims 1 to 4, in which the esterification zone is operated at a temperature of from about 100°C to about 250°C and at a pressure of from about 0.001 bar up to about 6 bar.

6. A process according to any one of claims 1 to 5, in which the hydrogenation zone is operated at a temperature of from about 100°C to about 250°C and at a temperature of from about 1 bar to about 60 bar.

7. A process according to any one of claims 1 to 6, in which the exit stream from the hydrogenation zone is subjected to evaporation under reduced pressure in an evaporation zone to vaporise fatty alcohol therefrom and to produce a liquid bottoms stream.

8. A process according to claim 7, in which material of said liquid bottoms stream is recycled to the esterification zone in step (f).

9. A process according to claim 7 or claim 8, in which at least a part of said liquid bottoms stream is treated to remove heavy by-products therefrom prior to recycle to the esterification zone.

10. A process according to any one of claims 7 to 9, in which the evaporation zone is operated at a temperature of from about 100°C to about 250°C and at a pressure of from
about 0.001 bar up to about 0.8 bar.

11. A process according to any one of claims 7 to 10, in which the dwell time in the evaporation zone is from about 0.5 seconds up to about 60 seconds.

12. A process according to any one of claims 1 to 11, in which the rate of recycle of fatty alcohol in step (f) is sufficient to provide at least a stoichiometric amount of fatty alcohol for reaction with the fatty acid or acids of the fatty acid feed.

13. A process according to claim 12, in which the fatty acid:fatty alcohol molar ratio lies in the range of from about 1:1 to about 1:2.

14. A process according to any one of claims 1 to 13, in which the hydrogenation zone contains a fixed bed of a reduced copper chromite catalyst and is operated under liquid phase hydrogenation conditions.

15. A process according to any one of claims 1 to 14, in which a purge gas stream is recovered from said at least one hydrogenation zone and is used as stripping gas in the esterification zone for stripping water of esterification from a liquid esterification mixture.

16. A process according to any one of claims 1 to 15, in which in step (e) the conversion of high boiling ester to fatty alcohol is from about 15% to about 50% in passage through said at least one hydrogenation zone.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07C29/149 C07C31/125

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)

IPC 5 C07C

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

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>FR,A,1 154 907 (CALIFORNIA RESEARCH CORPORATION) 18 April 1958 see page 1, right column, paragraph 3 - page 3, left column, paragraph 4 see page 3 - page 4; claims see figure</td>
<td>1,2</td>
</tr>
<tr>
<td>Y</td>
<td>WO,A,90 08123 (DAVY MCKEE LTD) 26 July 1990 cited in the application see page 30 - page 33; claims see figures 1,2</td>
<td>1,2</td>
</tr>
</tbody>
</table>

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

24 January 1994

Date of mailing of the international search report

01.02.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HJ Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016

Authorized officer

Kinzinger, J

Form PCT/ISA/210 (second sheet) (July 1992)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-A-1154907</td>
<td></td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>WO-A-9008123</td>
<td>26-07-90</td>
<td>AU-B- 637998</td>
<td>17-06-93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU-A- 4946690</td>
<td>13-08-90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-T- 4504411</td>
<td>06-08-92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OA-A- 9381</td>
<td>15-09-92</td>
</tr>
</tbody>
</table>