

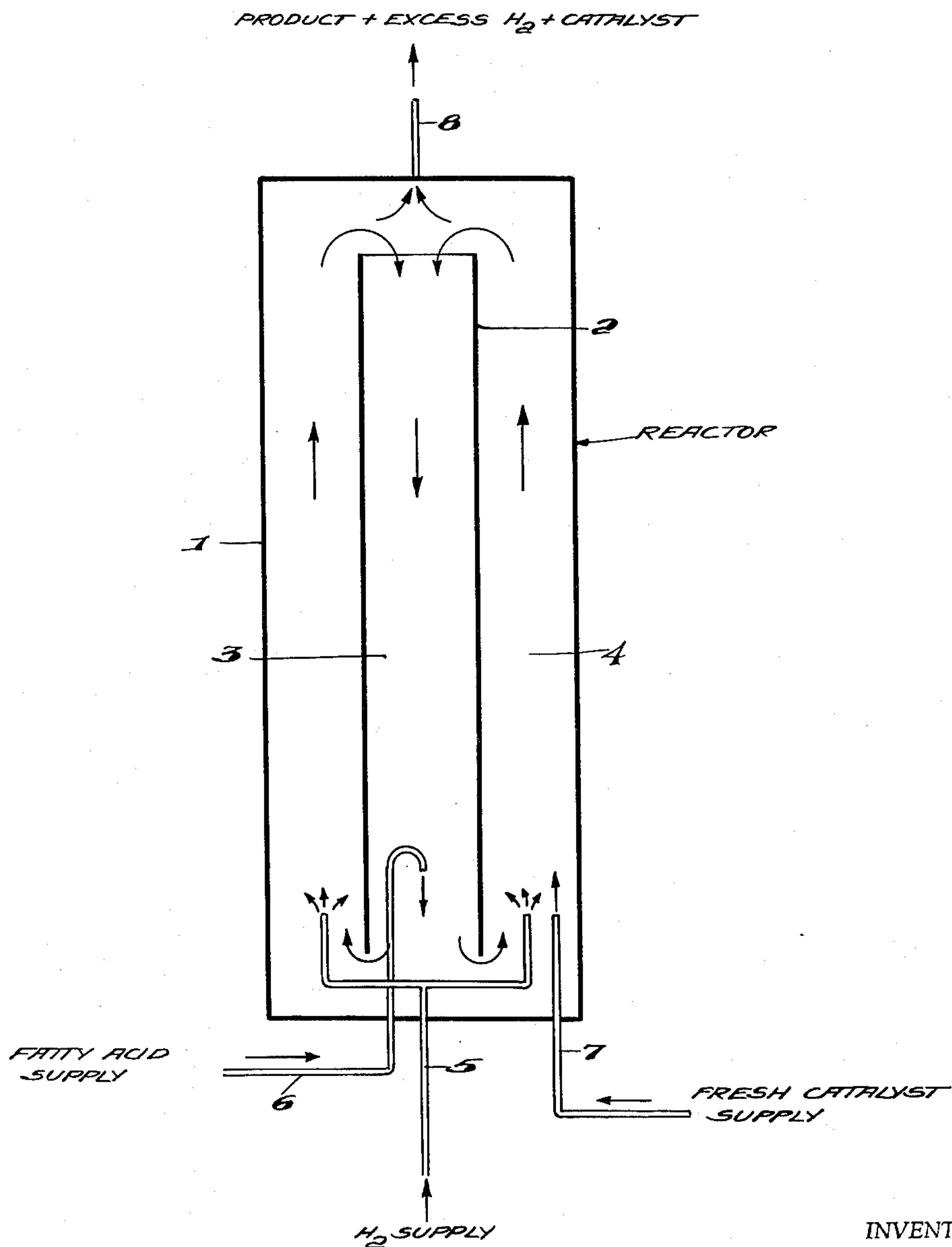
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PROCESS FOR THE PRODUCTION OF FATTY ALCOHOLS BY CATALYTIC  
HYDROGENATION OF FATTY ACIDS AND THEIR DERIVATIVES

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## PROCESS FOR THE PRODUCTION OF FATTY ALCOHOLS BY CATALYTIC HYDROGENATION OF FATTY ACIDS AND THEIR DERIVATIVES

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3 Claims. (Cl. 260-638)

The present invention relates to an improved process for the catalytic liquid phase hydrogenation of fatty acids and the derivatives of fatty acids to form fatty alcohols under superatmospheric pressures and raised temperatures in the presence of copper-chromium oxide catalysts. The hydrogenation of fatty acids with copper chromium oxide catalysts which can also be activated by additional components has already been known for some time.

As the catalysts are sensitive to free acids and water, it is usual not to employ a free fatty acid for the hydrogenation but rather a fatty acid ester, preferably the methyl ester. The fatty acid methyl esters can be easily produced by the interchange of ester radicals of neutral fats. It is, however, frequently not desirable to process the glycerin, which is necessarily produced in the process, separately. While it might be economically more advantageous in many cases to start out from cheap fatty acids or even from fatty acid distillates of certain composition, the esterification of the fatty acids with methyl alcohol, which becomes necessary, is complicated and expensive. In addition, the recovery of the methanol from the hydrogenated material and the concentration of the methanol before reuse requires additional apparatus and expense.

In order to obtain a usable starting product with an acid number below 0.5, distillation of the methyl ester is necessary. During the hydrogenation, a portion of the methyl ester and free methanol is split up and the carbon monoxide liberated thereby either damages the catalyst or is hydrated into methane.

In the high pressure hydrogenation process according to the invention it was found advisable to make use of esters of fatty acids with the corresponding alcohols. The esterification of the fatty acids to be hydrogenated with the alcohol or alcohol fractions produced during the hydrogenation can be carried out by heating the acid and the alcohol together in stoichiometrical quantities. The esterification takes place very quickly up to a residual acid number of about 10, but the remaining esterification to an acid number less than 0.5, such as is generally required for the hydrogenation, requires many times as long.

For the hydrogenation according to the invention a fatty acid or an incompletely esterified mixture of fatty acid with an alcohol formed therefrom or first-run alcohol is introduced into the high-pressure system for the hydrogenation. The remaining esterification then takes place in the hydrogenating apparatus. For this purpose it is necessary for the material to be hydrogenated to be brought momentarily into an excess of fatty alcohol under conditions which are favorable for the esterification with regard to temperature, thorough mixing and eventually also for removing the water of reaction. The hydrogenating apparatus therefore essentially is filled practically with completely reacted material which is saturated with hydrogen and maintained in intensive movement.

The high-pressure hydrogenation in the liquid phase which takes place under known conditions, that is, temperatures of 200 to 350° C. and pressures of 200 to 700 atms. in the presence of copper chromium oxide catalysts, is particularly advantageously, for example, carried out in a system which comprises two vertically arranged upper

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and lower interconnected high-pressure chambers in which a large quantity of reaction mixture circulates.

The hydrogen or the gas containing hydrogen employed for the hydrogenation is preferably introduced in finely distributed state at the lower end of one of the high-pressure chambers of the circulating system. The long, preferably very narrow high-pressure chamber is so constructed that the material to be hydrogenated is given a uniform velocity by the hydrogen bubbles and that the reversal at the upper end of the chamber takes place in such a manner that local eddy formation and slowing down of the flow are impossible. The finely dispersed rising hydrogen effects a reduction in the density of the material to be reacted in the rising portion of the system. Reacted material and excess hydrogen are preferably drawn off at the upper connecting piece. The intensive circulation is attained by the fact that the quantity of hydrogen conducted through is more than three times and preferably 10 to 50 times that necessary for the hydrogenation of the material fed into the system. The circulating velocities of the reaction mixture attained by the introduction of hydrogen amounts to at least 0.2 m./sec. and preferably 1 to 2 m./sec.

The excess hydrogen or gas containing hydrogen leaving the system is returned into the system after the reaction products and the catalyst have been removed. It is not necessary for this purpose to release the pressure on the hydrogen. It is rather to be recommended that only the pressure on the reacted material and the portion of the catalyst which are drawn off during continuous operation of the process be released.

Previously the continuous production of the fatty alcohols was usually effected in several autoclaves or extended reaction chambers through which the fats to be hydrogenated and the catalysts suspended therein flow consecutively and in which the fats are repeatedly brought into contact with hydrogen. The material to be hydrogenated is continuously passed through the reaction space but not fed into a chamber in which a large quantity of almost completely or completely reacted material is maintained in intensive thorough admixture with the catalyst and the hydrogen.

The reaction mixture employed according to the invention preferably consists of already reacted fatty alcohol saturated with hydrogen. Into this, the fatty acid or preferably ester obtained from and of the same kind as this acid is introduced and, owing to the intensive movement, immediately distributed so uniformly in a large excess of fatty alcohol that the remaining esterification takes place almost instantaneously. One of the advantages of the process according to the invention is that the hydrogen dissolves far better in fatty alcohol than in fatty acid or fatty acid esters. Under the conditions of high-pressure hydrogenation a certain quantity of fatty alcohol dissolves about 25% more hydrogen than the same quantity of fatty acid. In the process according to the invention this dissolved hydrogen which consequently is in homogeneous phase, serves for the hydrogenation. As the contents of the reactor are always saturated with hydrogen, the free fatty acids introduced into the material to be hydrogenated no longer have a deleterious effect on the catalyst. Moreover, free fatty acid is again removed very quickly by the already described, practically instantaneous esterification with a large excess of fatty alcohol. In addition, the fatty alcohols which form the greatest portion of the reaction mixture dissolve larger quantities of water than the corresponding fatty acids or esters. As a consequence the relatively small quantity of water liberated by the esterification of the relatively small quantity of fatty acid introduced is dissolved in the



fatty alcohol medium and the deleterious effects of water on the catalyst are avoided.

Similarly catalyst poisons which get into the reaction chamber with the initial material to be hydrogenated are immediately absorbed by a relatively large quantity of circulating catalyst which has already been used and thus rendered harmless. Freshly fed catalyst therefore can enter a practically detoxified medium and therefore can exert a greater catalytic efficiency.

For this reason it is advisable to separate the addition of the material to be hydrogenated and of the catalyst spacially so that contact of a highly active fresh catalyst directly with the fresh material containing fatty acid does not take place. The catalyst is preferably made into a paste with fatty alcohol or is suspended therein for introduction into the high-pressure system.

As the freshly fed catalyst retains its high activity in view of the hydrogen being in homogeneous phase, that is dissolved in fatty alcohol, and because of the practically instantaneous removal of all substances injurious to the fresh catalyst by the rapid circulation, the total result is an extremely rapid and effective hydrogenation.

It is known that fatty alcohols under the conditions of high-pressure hydrogenation tend to split off water to form olefines which then in turn are again hydrogenated into saturated hydrocarbons. This secondary reaction can be avoided if the reaction temperature is kept as low as possible during the hydrogenation. The reaction water liberated during the esterification reaction which is in the dissolved or in the gas phase but not present as a separate liquid phase, exerts a retarding effect on the formation of the hydrocarbons as such presence of water shifts the chemical equilibrium. The conditions of the process according to the invention substantially completely avoid the above mentioned secondary reaction with the formation of hydrocarbons. The hydrogenation temperature is dependent upon the activity and the quantity of catalyst and preferably amounts to 250 to 350° C.

A particularly suitable apparatus for carrying out the process according to the invention is one in which an upright elongated vessel is provided with an interior upright tube having open ends terminating above the bottom and below the top of such vessel or otherwise provided with an upright partition to divide the space within the vessel into at least two upright spaces communicating at the top and bottom. The upper end of such interior tube or partition is constructed as a sieve. Such vessel during operation of the process is essentially filled with substantially fully hydrogenated product saturated with hydrogen and containing the hydrogenation catalyst suspended therein which is recycled through the upright spaces provided by the interior tube or partition. The recycling flow is effected by the introduction of the hydrogen or hydrogen containing gas at the lower end of one of such spaces so as to cause the liquid and hydrogen admixed therewith to flow upwardly in said space. The sieve like portion at the upper end of the interior tube or partition serves to separate the excess gaseous hydrogen from the liquid and catalyst mixture and permit the bath to flow downwardly through the other space as the flow is not retarded by too great a content in hydrogen bubbles. Preferably, the fresh catalyst is supplied to the liquid cycle just after the introduction of the hydrogen. On the other hand, the fresh material to be hydrogenated is preferably added to the liquid cycle at a point in the liquid cycle substantially after the point where the new catalyst is supplied. For example, the fresh catalyst may also be supplied to that space to which the hydrogen is supplied just above the point where the hydrogen is introduced, whereas the fresh material to be hydrogenated may be supplied to the other space in which the substantially completely hydrogenated material maintained in the cycle flows downwardly so that it only contacts the catalyst suspended therein at a point remote from where the fresh catalyst is produced. Hydrogenated

material is withdrawn from the top of recycling liquid.

The quantity of essentially completed hydrogenated material, which is saturated with hydrogen and contains hydrogenation catalyst dispersed therein, which is recycled per unit of time is at least ten times, preferably 100 to 1000 times, the quantity of fresh fatty acid product to be hydrogenated which is introduced per unit of time.

The accompanying drawing diagrammatically shows an apparatus suitable for carrying out the process according to the invention.

In such drawing the interior of reactor 1 is divided by upright tube 2 into two upright spaces 3 and 4 communicating at the top and bottom. Hydrogen is supplied to the lower end of space 4 through supply conduit 5. Fresh fatty acid material to be hydrogenated is supplied to the lower end of space 3 through supply conduit 6. Fresh catalyst is supplied to the lower end of space 4 through conduit 7. A mixture of the product, catalyst and excess hydrogen are withdrawn from reactor 1 through conduit 8.

The term "fatty acids" is used herein to designate straight or branch chained saturated or unsaturated aliphatic carboxylic acids containing 6 to 24 carbon atoms.

The following examples will serve to illustrate several embodiments of the process according to the invention.

#### Example 1

The hydrogenation was carried out in a 2 liter autoclave provided with a reciprocating magnetic stirrer. Separate lines extending to the bottom of the reaction chamber in the autoclave were provided for the introduction of hydrogen and the fatty acid starting material. A third feed conduit extending to about the middle of the reaction chamber height was provided for the introduction of fresh catalyst suspension. Another tube extending downwardly about 60 mm. from the top of the autoclave was provided for the common withdrawal of hydrogen, reaction product and catalyst so as to maintain a certain reaction mixture content in the autoclave. The remaining usable space within the autoclave was about 1 liter.

The feed used for the hydrogenation was a distilled cocoanut fatty acid product having an acid number of 257, a saponification number of 260, an iodine number of 12 and a hydrocarbon content of 0.5%.

The autoclave was filled with the fatty alcohol product resulting from the hydrogenation of the cocoanut oil fatty acid product containing 4% of a copper-chromium oxide catalyst, barium promoted copper chromite. Thereafter the autoclave was heated and maintained at a temperature of 300° C. and 300 cc. per hour of fresh cocoanut oil fatty acid and 12 g. per hour of the catalyst (as a 25% suspension in fatty alcohol product) supplied thereto. The hydrogen supply line was connected to a hydrogen supply container maintained at a gauge pressure of 320 atmospheres. A mixture of hydrogen, the hydrogenation product and catalyst were continuously withdrawn from the top of the autoclave so as to maintain a constant liquid level in the autoclave. The quantity of hydrogen thus withdrawn was 3 Nm<sup>3</sup>h (normal cubic meters per hour, normal cubic meter—a unit of measure for gases measured at 760 mm. Hg. and 0° C.). The mixture was passed through a high pressure separator and a low pressure separator while releasing the pressure thereon. The decompressed gas from which the hydrogenation product and the catalyst had been separated was recompressed and recycled.

The fatty alcohol hydrogenation product after separation from the catalyst had an acid number of 0 and an OH number of 270, and an iodine number of 0 and contained 0.75% of hydrocarbons.

After the catalyst had been used 20 times its activity had been so reduced that the hydrogenation temperature had to be increased 18° C. to obtain the same results.



## Example 2

The hydrogenation was carried out in a recycling apparatus constructed of a 6 meter long upright outer tube 70 mm. in diameter and a 5.50 meter inner tube 30 mm. in diameter, the lower end of which is 10 cm. above the bottom of the outer tube and the upper end of which is extended 30 cm. by a wire mesh ring of the same diameter. The mesh width of such wire mesh was about 6 mm. The hydrogen was supplied in finely divided state in the lower end of the recycling apparatus in the annular space between the inner and outer tube. Fresh catalyst was also supplied to the space between the inner and outer tubes near the hydrogen inlet and the fatty acid product to be hydrogenated was introduced into the inner tube above its lower end so as to be somewhat ahead of the fresh catalyst inlet in the liquid recycling in the apparatus. The highest point of the recycling apparatus was connected to a high pressure separator, the gas chamber of which was connected to the hydrogen inlet over a mist collector pump and preheater. The lower end of the high pressure separator was connected to a low pressure separator over a decompression valve. The upper portion of the low pressure separator was connected to a gasometer for withdrawal of the decompressed gas. The hydrogenation was carried out at a gauge pressure of 300 atmospheres. In order to maintain such pressure fresh hydrogen was injected into the hydrogen cycle ahead of the pump serving to recycle the hydrogen to the hydrogenation apparatus.

The feed used for the hydrogenation was a mixture of the fatty acids and palm kernel oil and coconut oil having an acid number of 265, a saponification number of 267, an iodine number of 12 and a hydrocarbon content of 0.5%.

To start out the tubular recycling apparatus was filled with the fatty alcohols obtained in the hydrogenation of a palm kernel and coconut oil fatty acid mixture. Such fatty alcohols had about 6% of copper-chromium oxide catalyst suspended therein. The charge was then heated and maintained at 300° C. while 8.5 liters per hour of fresh fatty acid feed and fresh catalyst in a quantity of 6% based upon the weight of the fresh fatty acid supplied were introduced through the inlets indicated above while a substantial excess of hydrogen was being recycled through the apparatus. The fresh catalyst was introduced as a 25% suspension in the fatty alcohol hydrogenation product. The hydrogenation product recovered had an acid number of 0, a saponification number of 2.5, an OH number of 278 and a hydrocarbon content of 1%.

After continued use the activity of the catalyst will drop but this can be compensated for by increasing the temperature used for the hydrogenation.

## Example 3

The procedure of Example 1 was repeated using the same apparatus except that 900 cc. per hour of coconut oil fatty acid esterified to an acid number of 15 with coconut oil fatty alcohols and 18 g. per hour of copper chromite were supplied to the autoclave instead of the 700 cc. per hour of coconut fatty acids and 12 g. per hour of catalyst. The temperature and pressure employed were the same as in Example 1. The hydrogenation product after being freed of catalyst had an acid number of 0, a saponification number of 10, an OH number of 254 and a hydrocarbon content of 0.9%.

In order to obtain a product having a lower saponifica-

tion number the hydrogen, fatty alcohol and catalyst mixtures leaving the top of the autoclave were supplied to an autoclave of the same type as the first autoclave which was operated at the same temperature and pressure. The hydrogenation product leaving the top of the second autoclave after separation from the catalyst had an acid number of 0, a saponification number of 2.7, an OH number of 267.5 and a hydrocarbon content of 1.1%.

A portion of the fatty alcohol hydrogenation product was employed for the partial esterification of further quantities of coconut oil fatty acids in preparation for hydrogenation.

Sperm oil can be hydrogenated in a manner analogous to the hydrogenation of the coconut oil fatty acid coconut oil fatty alcohol partial ester in the present example.

We claim:

1. In a process for the continuous hydrogenation of fatty acid containing material selected from the group consisting of fatty acids, fatty acid esters and mixtures of such fatty acids and esters to produce the corresponding fatty alcohol by making such fatty acid containing material with the corresponding fatty alcohol which is to be produced containing a copper chromium oxide catalyst suspended therein and treating such mixture of fatty acid containing material and fatty alcohol with an excess of hydrogen at temperatures between about 200 and 350° C. and pressures of about 200 to 700 atmospheres, separating off the excess hydrogen, the fatty alcohol and water produced in the hydrogenation and a portion of the catalyst and recycling such excess hydrogen and the remaining fatty alcohol and catalyst suspended therein, the steps of recirculating the fatty alcohol containing the catalyst suspended therein sequentially through at least two elongated upright spaces in a reactor having their top and bottom ends communicating, supplying hydrogen to the lower end of one of such spaces to effect such recirculation, introducing the fatty acid containing material to be hydrogenated through a separate inlet into another of such spaces, supplying fresh catalyst to the cycle near the location where the hydrogen is supplied but downstream from where the fatty acid material is introduced and withdrawing the fatty alcohol and water produced, excess hydrogen and catalyst from the cycle at the upper end of the reactor, the quantity of the fatty alcohol circulated in the reactor per unit of time being 10 to 1000 times that of the fatty acid containing material introduced per unit of time.

2. The process of claim 1 in which the quantity of the fatty alcohol circulated in the reactor per unit of time is 100 to 1000 times that of the fatty acid containing material introduced per unit of time.

3. The process of claim 1 in which the quantity of hydrogen introduced into the reactor is 3 to 50 times the quantity required to hydrogenate the fatty acid containing material introduced.

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LEON ZITVER, Primary Examiner.



**UNITED STATES PATENT OFFICE**  
**CERTIFICATE OF CORRECTION**

Patent No. 3,180,898

April 27, 1965

Karl-Heinz Eisenlohr et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 21, for "making" read -- mixing --.

Signed and sealed this 1st day of February 1966.

(SEAL)

Attest:

**ERNEST W. SWIDER**  
Attesting Officer

**EDWARD J. BRENNER**  
Commissioner of Patents