Jan. 9, 1968 S. C. SCHUMAN ETAL **3,363,009**

CONTINUOUS PROCESS FOR PRODUCING DETERGENT GRADE ALCOHOLS AND GLYCERINE

Filed June 8, 1964

3 Sheets-Sheet 1

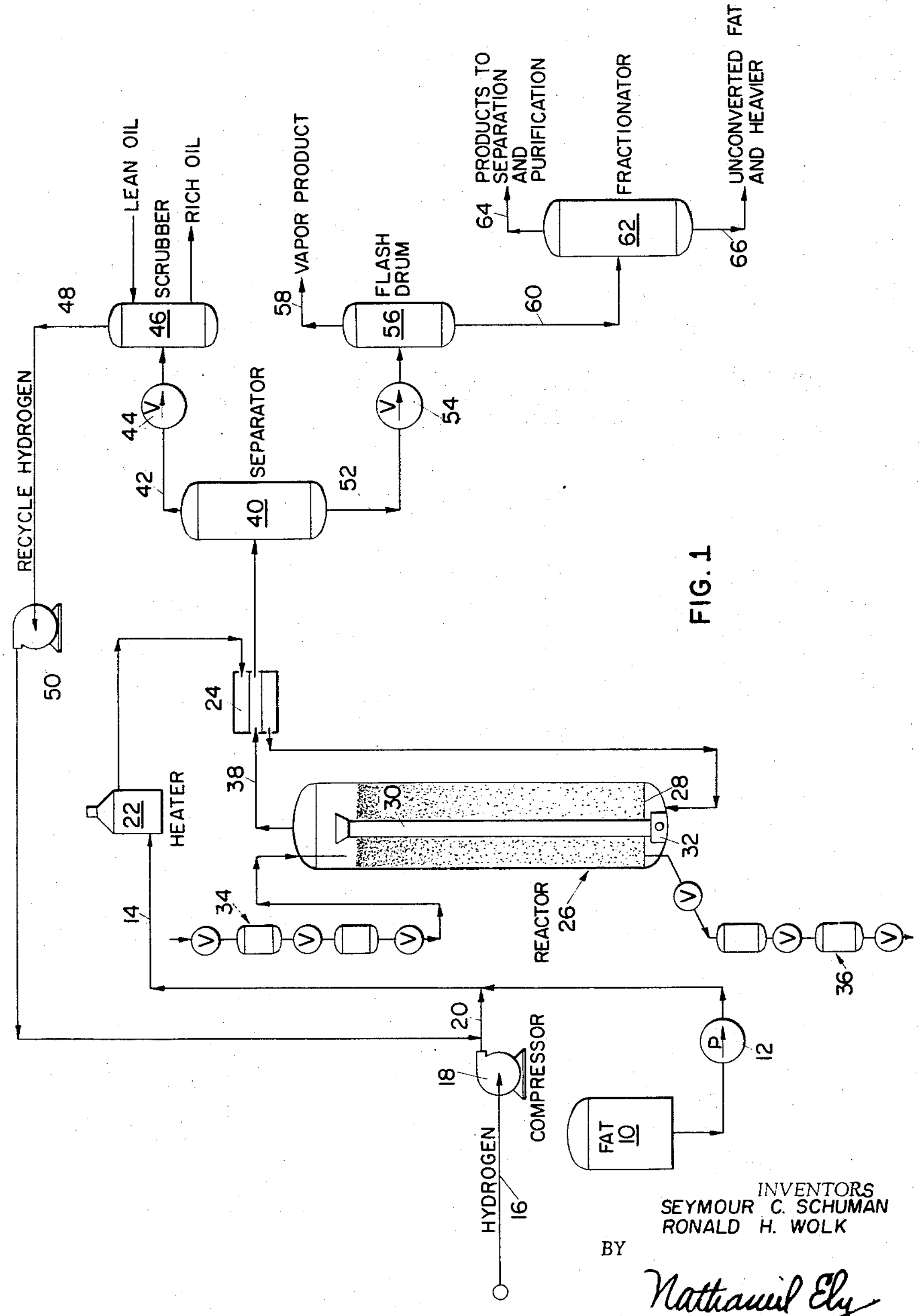

FIG. 1

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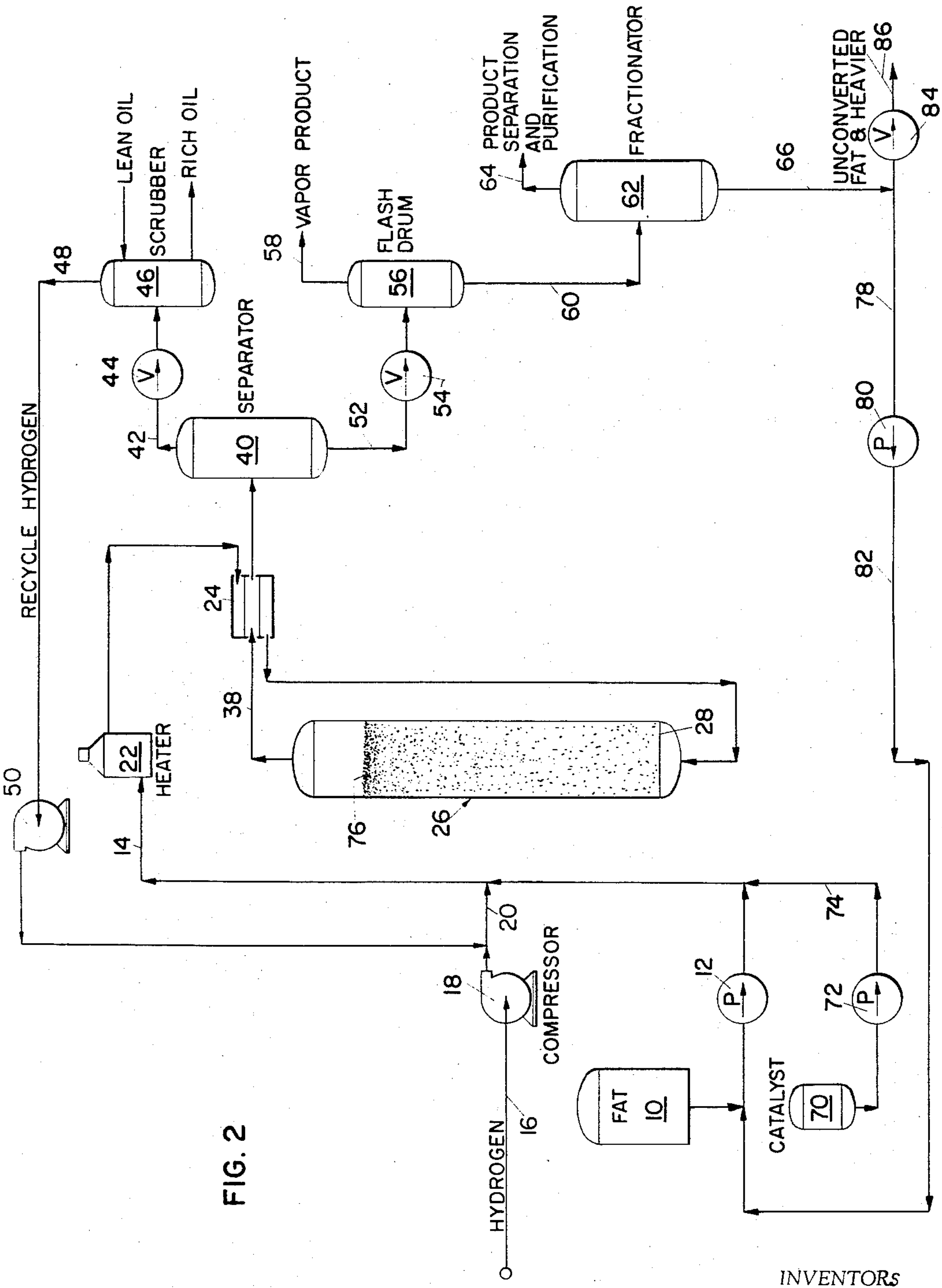

FIG. 2

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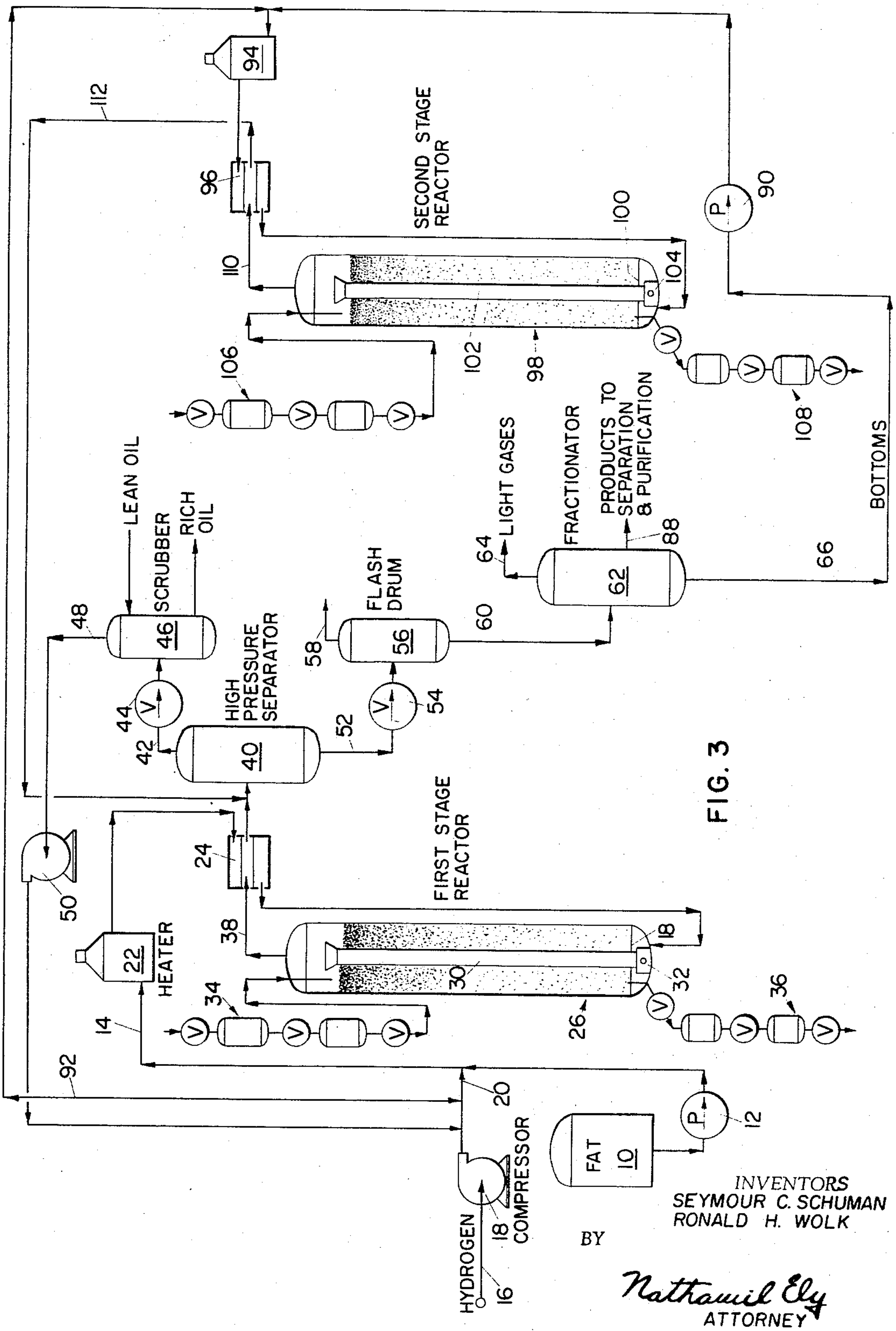

FIG. 3

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CONTINUOUS PROCESS FOR PRODUCING DETERGENT GRADE ALCOHOLS AND GLYCERINE

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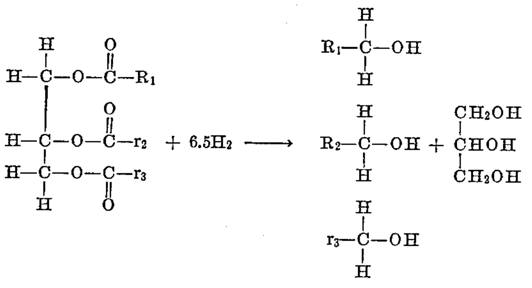
5 Claims. (Cl. 260—638)

This invention relates to improvements in the process for producing, continuously, detergent grade alcohols and glycerine.

It is known that straight chain aliphatic alcohols have considerable value for use as wetting agents and detergents. The use of these compounds (also called fatty alcohols) as household cleaners has long been recognized, either when used as the alcohol itself or as the sulfated alcohol. Detergents made from such fatty alcohols have excellent foam characteristics, good detergency, and are quite mild with respect to their effect on the skin. Importantly, in addition, these materials are biodegradable so that waste disposal problems caused by their use are substantially avoided.

However, in the past, the high cost of fatty alcohols and their sulfated derivatives has prevented their widespread use. At first glance, the high cost of such alcohols is surprising, since they may be produced from various fats and oils which are relatively inexpensive and in ample supply. However, study of present methods of manufacture of fatty alcohols from fats readily demonstrates the reason for their high cost. For example, in one method of manufacture, the fat is hydrolyzed or saponified to a mixture of glycerine and fatty acids. The fatty acids are then separated from the glycerine, esterified, reduced to the alcohols using sodium and de-esterified. Most or all of the operations in this multi-step process are carried out batchwise, substantially increasing the overall process cost. When sodium is used for reduction, special construction materials are required, but it is absolutely necessary to avoid any air leakage into the system. Even when catalysts other than sodium are employed for the hydrogenation step, conventional methods where the ester is contacted batchwise with finely divided catalyst, lead to many problems associated with elimination of catalyst from the final product wherein, in general, the catalyst must be filtered out and then reused for additional batches.

Theoretically, a typical triglyceride may be directly converted to glycerine and a mixture of fatty alcohols in a single step as follows:



In the example, the alkyl groups, R and *r* may be of varying chain length depending on the source of the triglyceride. The alkyl groups also may be unsaturated (*r*) or saturated (R). In the conversion, as represented theoretically above, the primary reaction is the hydrosplitting of a carbon-oxygen bond; collaterally unsaturated alkyl groups may be hydrogenated to yield saturated alcohols. From such a hydrosplitting reaction, saturated alcohols with carbon numbers of from about 10 to about 20 may be produced depending on the source and composition of the fat or triglyceride used as the feed material. Actually, alcohols with from about 10 to about 14 carbon numbers are more highly desired than those with from about 16 to about 20 carbon atoms because of generally better detergent properties. However, the more valuable alcohols are generally difficult to produce using an inexpensive raw material such as tallow which has a molecular structure such that by the simple reaction indicated above, alcohols of the higher chain length are substantially produced.

It is obvious that considerable effort would have been devoted to exploring the possibilities of the single step hydrogenation process for producing fatty alcohols, rather than the multi-step process involving hydrolysis and reduction of a carboxylic acid or its ester. However, such efforts on the single step process have not been conspicuously successful. It is apparent from the reaction as shown that to obtain the theoretical product distribution, the hydrosplitting reaction must be carefully controlled. Uncontrolled reactions will produce propylene glycol, propanol or even propane, rather than the more valuable glycerine, leading to excessive consumption of valuable hydrogen in addition to a decreased value of the overall product. Excess hydrogenation may even reduce the fatty alcohols produced to their corresponding hydrocarbons with a considerable diminution in product value.

In addition to the decreased value of the products produced and excessive consumption of hydrogen, uncontrolled hydrogenation, by producing many different kinds of products, drastically increases separation problems and ultimate recovery of the products. Because of these inherent difficulties in controlling the single step hydrogenation of fats, efforts in this direction have utilized batch or semi-batch procedures; as is well known, the economics of such batch processes is greatly inferior to continuous processes. In addition, efforts on the single step process have utilized high hydrogen pressures (from about 100 to 300 atmospheres of hydrogen), highly active catalysts which are readily poisoned, and relatively low temperatures from about 530° F. to about 660° F.

The high pressures require heavily constructed autoclaves which must be sealed and unsealed between reaction batches with all of the difficulties thereof. The highly active catalysts which have been employed (generally of the copper chromite, or zinc chromite types) are expensive and easily poisoned, particularly by sulfur. When they are used as a slurry with the reaction mixture, it is necessary to devote considerable attention to their subsequent removal, both from the standpoint of catalyst recovery, and from the standpoint of obtaining ultimate products free of trace amounts of catalysts.

When tallow is used as a raw material, considerable attention must be given to preparing the tallow so that it will contain a minimum amount of sulfur providing minimum sulfur poisoning of the catalyst. As mentioned previously, when tallow is used as raw material, large amounts of the less valuable fatty alcohols are produced. For all of these reasons, alcohols produced by single step hydrogenation of an inexpensive feed such as tallow are very expensive and for this reason, have not found wide application as detergents or surface active materials.

It is an object of this invention to provide a continuous process for the production of detergent grade alcohols and glycerine.

A further object of this invention is to produce such detergent grade alcohols and glycerine from an inexpensive fat source such as tallow or tallow greases with minimum pretreatment of the fat source.

A further object of this invention is to produce maximum yields of detergent grade alcohols and glycerine, with low hydrogen consumption, minimum production of hydrocarbons, and minimum downstream separation difficulties.

A secondary object of the invention is to accomplish this optimization of yields, hydrogen consumption and separation problems, by careful control of the hydrogenation environment under continuous reaction conditions.

A further object of this invention is to use inexpensive, sulfur-resistant catalysts of the type conventionally employed in petroleum refining practice, and to remove the fatty alcohol and glycerine products substantially uncontaminated with catalyst so that only trace amounts, if any, must be ultimately separated from the products. Using inexpensive catalysts, the relatively small amount of carryover of catalyst into the product makes it unnecessary to reuse the trace amounts which may be carried over.

Finally, a further primary object of this invention is to increase the yield of the more valuable alcohols with carbon numbers of from about 10 to about 14, and decrease the yields of the less valuable alcohols with carbon numbers from 16 to 20, even when the fatty raw material has a composition which tends, a priori, to produce the less valuable higher alcohols.

Further objects and advantages of our invention will appear from the following description of preferred forms of embodiment thereof when taken with the attached drawings, FIGURES 1, 2, and 3 of which are schematic flow diagrams of fat conversion systems.

With particular reference to FIG. 1 which is a representation of the simplest form of embodiment of our invention, the melted fat is withdrawn from heated storage tank **10** by pump **12** and pumped through line **14**. Hydrogen in line **16**, compressed to operating pressure by compressor **18**, is introduced into line **14** through line **20**. The mixture is passed serially through preheat furnace **22**, and heat exchanger **24** and is then introduced into reactor **26**.

Reactor **26** is a pressure vessel of uniform cross section with grid **28** for distributing the fat and hydrogen mixture and is suitably filled with catalyst in such a manner that the liquid fat and hydrogen passing upwardly through the catalyst mass expand the mass at least 10% above its settled state and place the catalyst in random motion in the reactor liquid. The liquid effluent is separated at the upper part of the reactor into a product stream and a recycle stream. The recycle stream is maintained by withdrawing liquid into a tube **30** through the center of the reaction zone and by means of pump **32** introducing it at a point below the deck or grid **28** which restrains the catalyst bed. The hydrogen and liquid fat entering the reaction zone are preheated by the recycle streams to substantially near the reaction temperature.

Catalyst may be added periodically through catalyst addition system **34** and may be likewise withdrawn through catalyst withdrawal system **36**. These are only schematically shown.

The effluent from the reactor leaves through line **38**, is then cooled in exchanger **24** and passed through high pressure separator **40**. The hydrogen is removed overhead in line **42**, depressured through valve **44**, scrubbed in scrubber **46**, and recycled through line **48** by booster compressor **50** back to the original feed line **20**.

The condensed liquid products, removed from the high pressure separator **40**, through line **52** are depressured by passing through valve **54**, and passed to a flash drum **56** from which the vapor products will be removed through line **58** and the liquid products through line **60**. Crude separation from the unconverted feed is accomplished in a typical fractionating device **62** from which products will be removed through line **64** and passed to subsequent separation and purification apparatus. Unconverted fat and heavier are removed through line **66**.

The liquid velocity in the reactor **26** required to expand the bed of catalyst at least 10% is a function of the viscosity of the liquid, the density of the liquid and the size and density of the catalyst particles in addition to the velocity of the liquid itself. The velocity of the gas must be such that it aids in maintaining the random motion of the catalyst particles but is less than that amount required to cause any of the catalyst to leave the reaction zone.

The use of such a system designated as an "ebullated" bed system, improves and eliminates most of the process deficiencies inherent in the older methods of producing fatty alcohols. For example, the temperature control within the reactor, in spite of the great exothermicity of the hydrogenation reaction, is maintained in the order of 1 to 5 degrees Fahrenheit through the reaction zone. This is accomplished by the random motion of the mixture of catalyst particles, liquid, and gas within the catalyst bed, complemented in this case by the internal recycle of liquid from the top of the reactor to the bottom. Such close temperature control eliminates the need for external heat exchange equipment, and much more importantly, eliminates the danger of overheating in any part of the reaction system. Thus the catalyst may be used at optimum temperatures without uncontrolled reactions occurring which produce products of inferior value, increase hydrogen use costs and complicate product recovery.

The turbulence produced in the reactor serves also to keep the hydrogen dispersed without any mechanical mixing device within the reactor. The turbulence thus results in very efficient contacting of feed liquids with hydrogen, increasing the rate of the desired hydrogenation reactions, and thereby decreasing the size of the reactor required to process a given quantity of feed.

The catalyst is maintained within the reaction zone and is not carried out with the liquid; thus the filtering operation conventionally required to remove catalyst from the products is eliminated, reducing overall plant capital cost and simplifying operations. In addition, the high density of the catalyst in the reaction zone (which may be from 5 to 70 pounds per cubic foot) provides much more available catalyst in the reaction zone than has been heretofore practiced. Since the catalyst concentration is high, it is possible to use somewhat less active catalysts than have been used and replace them with materials that are more rugged and more resistant to poisoning by sulfur. Obviously, the high catalyst density in the reactor to a large extent also reduces the reaction time necessary to carry out the reaction.

Since all catalysts ultimately become poisoned or deactivated, in the embodiment of our invention shown, facilities are provided to replace spent catalyst on a continuous or semi-continuous basis. The replacement rate, of course, varies with the quantity of poisons associated with the feed. Such continuous replacement of catalyst permits maintenance of a given catalyst activity indefinitely; consequently product distribution can be maintained indefinitely with no variations caused by operating with a fresh catalyst on one day and with a spent catalyst on another day. Thus such continuous replacement is an important factor in economizing the design of product recovery and purification equipment and in assuring constant product quality. It is important to note that operations at constant catalyst activity and selectivity are impossible with fixed bed continuous catalytic reaction systems and virtually impossible with batch reaction systems where spent catalyst must be re-used.

Suitable feed for the process of our invention include the class of substances called fats and fatty oils. These fats and oils are derived from plants and animals in which they appear in quantity and in an easily available form. They are primarily a product of agriculture, although there is also considerable production from uncultivated tropical plants and from marine animals. Such fats and oils are essentially triglycerides, or esters of glycerol and long chain aliphatic acids, both saturated and unsaturated. However, it is germane and important to the value of our invention, that fats and oils as obtained from nature are highly contaminated with foreign substances which among other things contain sulfur and nitrogen which may act as catalyst poisons. One of the advantages of our invention is that the fats and oils used as feed do not have to be carefully pre-processed to minimize the content of such catalyst poisons before subjecting the feed to hydrogenation.

Although our invention is applicable to any vegetable, animal or marine fat and oil, it is specifically directed to fats and oils which are produced in large quantities such as tallow, lard, coconut oil, cottonseed oil, soybean oil, and linseed oil. It is particularly directed to raw inedible tallow and tallow greases which are in large supply and are relatively low in cost. The aliphatic chains in the triglycerides which compose tallow are predominantly of from 16 to 18 carbon atoms in length. As indicated previously, our invention will convert such inedible tallow to more valuable, higher quality alcohols of lower chain lengths than the C_{16} and C_{18} alcohols which would be normally produced from this feed.

The particular contact agents which are used in our invention increase the rates of the chemical reactions which are desirable to carry out and these may be termed to be catalytic. These agents are inexpensive materials whose catalytic action is relatively unaffected by poisoning by sulfur. Many inexpensive catalysts previously developed for petroleum technology may be utilized in the process of this invention. Alumina, combinations of silica and alumina and refined clays are effective catalysts for this invention. Combinations of silica and alumina are particularly effective possibly because of an acid function which seems to be developed by such a combination. These contact agents may be promoted with iron, cobalt, molybdenum, chromium, tungsten or nickel. When such promoters are used in this invention, catalytic action is obtained from the sulfides of the promoting element, rather than from the metal per se. Thus, copper and zinc are not preferred promoters since the sulfides of these elements are relatively inactive with respect to hydrogenation activity. The more precious Group VIII elements which include platinum, palladium, and rhodium are similarly not preferred as promoters because of their high cost.

The particle size of the catalyst employed depends on various factors which affect the liquid velocity in the reactor, the properties of the reactor liquid itself and the density of the catalyst. In all cases the upflowing gas and liquid velocities, for the particle size used, will place the contact agent in random motion in the reactor liquid and will expand the catalyst mass at least 10% above its settled state but will not permit significant loss of catalyst from the reactor and subsequent contamination of the product stream with catalyst. It has been demonstrated that pelleted or extruded catalyst of 1/16" diameter or less is effective for our invention. Unformed particulates of an average particle size in the range of 16 to 270 mesh are also effective. Preferably, this should be in the range of 30 to 200 mesh in which the diameter of the largest five percent of the particles is no more than three times the diameter of the smallest five percent of the particles. In all cases, the reactor bulk phase will contain at least 5 pounds of catalyst per cubic foot of catalyst-containing space, whereas the space above the bulk phase will contain less than 0.1 pound of catalyst per cubic foot without resorting to expansion of the reactor diameter at its top (i.e., addition of a so-called knockout or expansion zone) to effect this pronounced phase separation.

Reaction temperatures used in our invention are substantially above those in conventional practice in the hydrogenation of fats and oils. Such relatively high temperatures are required to reduce the aliphatic chain lengths of the alcohols which are produced, which involves hydrosplitting of carbon to carbon bonds as well as the more readily effected hydrosplitting of carbon to oxygen bonds. Reaction temperatures are generally above 600° F. A preferred range for the reaction temperatures which are employed is between 700° F. and 800° F.

It is important to limit hydrogen partial pressure in the reaction system, particularly with active catalyst, in order to minimize hydrogenation of the alcohol groups of the primary fatty alcohol and glycerine products. Control of hydrogen partial pressure may be effected by controlling the total pressure or the concentration of hydrogen in the reaction zone. This concentration is generally of the order of 50 to 90% and, with total pressures of from 500 p.s.i.g. to 2000 p.s.i.g., hydrogen partial pressures will be in the range of 250 p.s.i. to 1800 p.s.i. Selection of the optimum hydrogen partial pressure in this range will depend on feedstock, catalysts, temperature and degree of hydrosplitting required together with various other factors.

The quantity of hydrogen supplied to the reaction zone may be, of course, considerably higher than the net hydrogen feed by recycling the hydrogen as shown in FIG. 1. The net hydrogen feed, approximately corresponding to the chemical requirements of the hydrosplitting reactions, will, in general, exceed 1 pound of hydrogen per hundred pounds of fat or oil fed and normally are in the range of 2 to 10 pounds of hydrogen per 100 pounds of feed.

FIG. 2 is a schematic flow diagram of a modified form of embodiment of this invention. It is generally analogous to the embodiment shown in FIG. 1. However, reactor **26** in FIG. 2 is constructed without the internal liquid recycle used in FIG. 1, with control of reactor temperatures accomplished substantially by the turbulence of solids, liquids, and gas within the reactor. Without the internal liquid recycle in reactor **26**, the liquid velocities in the reactor may be substantially below those in the corresponding reactor of FIG. 1. Thus, it is feasible to utilize catalyst of substantially smaller average particulate size.

This catalyst may be conveniently introduced into reactor **26** on a continuous basis by mixing with a small amount of liquid in vessel **70**, forming a slurry which is then pumped by pump **72** through line **74**, ultimately combining with the feed and hydrogen in line **14** and subsequently entering the reactor as before.

Although the amount of catalyst supplied on a continuous basis is very small compared to the amount of fat or oil fed, generally substantially below one pound of catalyst per 100 pounds of fat or oil, the catalyst concentration in reactor **26** always exceeds 5 pounds per cubic foot and may be as high as 70 pounds per cubic foot as mentioned previously. Even so, and although the reactor **26** is of uniform cross section, an interface **76** will be developed at the top of the reactor above which the catalyst concentration is less than 0.1 pound per cubic foot.

In the embodiment as shown in FIG. 2, mild hydrosplitting conditions are employed so that a substantial amount of feed triglycerides are unconverted. These are separated in fractionator **62** and proceed through lines **66** and **78**, and are then pumped using pump **80** ultimately to be recycled through line **82** to the reactor for additional conversion. The small net feed of catalyst will also be collected in the bottom of fractionator **62** and be similarly recycled.

Since catalyst must be withdrawn from the system equivalent to that fed, a small bleed stream of catalyst in unconverted feed is withdrawn from the system through valve **84** and line **86**. Thus the embodiment shown in FIG. 2 provides a continuous system in which finer catalyst and lower velocities may be used in reactor **26** with lower single pass feed conversion, to accomplish continuous operation with continuous or semi-continuous catalyst replacement and without contamination of the desired products with catalyst, to accomplish virtually the same end result as obtained in the embodiment of FIG. 1.

FIG. 3 provides a schematic flow diagram of a multistage embodiment of this invention. The systems for feeding hydrogen and fats, the first stage reactor system, and its accompanying downstream primary separation facilities are similar to that in FIG. 1. However, fractionator **62** is a multi-tray still from which light gases comprising hydrocarbons from methane to octane will be removed in the column vapor overhead effluent at line **64**, liquid products to be subsequently described will be removed from the middle of the column through line **88** (from which they will ultimately proceed to conventional separation and purification equipment) and fractionator bottoms are removed as liquid through line **66**.

The fractionator temperatures are controlled so that the products removed from line **88** includes glycerol, and the valuable C_{10}, C_{12} and C_{14} fatty alcohols. The higher boiling C_{16}, C_{18} and C_{20} alcohols issue from the column together with a small quantity of unconverted glycerides through line **66** and are then pumped using pump **90** to second stage reactor pressures, combined with hydrogen obtained from line **92**, reheated in **94** and still additionally heated in exchanger **96** to enter the second stage reactor **98**.

The second stage reactor is essentially identical in general design features with that used in the first stage and includes a distribution grid **100**, internal recycle line **102**, internal pump **104**, and catalyst entry and withdrawal systems **106** and **108** respectively. The catalyst in this second stage reactor, like that in the first stage reactor, is in a state of random motion and is expanded to occupy at least 10% greater volume than the settled state of the mass, maintaining in the reactor an interface below which the mass of solids exists at a concentration greater than 5 pounds per cubic foot and above which said solids are at a concentration of less than 0.1 pound per cubic foot without employing a settling zone or other disengaging device. Products issue from reactor **98** in line **110** and pass through exchanger **96** where they are partially cooled and from which they pass through line **112** to enter the primary recovery equipment consisting of vessels **40**, **56** and **62** as previously described.

In the multi-stage embodiment shown in FIG. 3, the fat is substantially completely converted in the first stage to glycerol and higher alcohols, the glycerol removed in line **88**, and the higher alcohols subsequently hydrosplit to the more valuable lower alcohols in second stage reactor **98**. Thus, this embodiment allows the use of different catalysts in reactors **26** and **98** and/or different operating conditions in the two reactors, so that catalyst and operating conditions in the first stage are preferential for cleavage of the carbon-oxygen bond, whereas the catalyst and operating conditions in the second stage reactor are chosen to provide maximum selectivity in the cleavage of the carbon-carbon bonds required to produce the more valuable fatty alcohols.

The specific separation scheme (generally embodied in fractionator **62**) in this case allows complete extinction of the less valuable higher alcohols. However, other variations of this embodiment can provide for some removal of these less valuable alcohols to the extent for which there is a market for them. Similarly, other schemes may provide for making equivalent separations to that in fractionator **62** using a vacuum still. In other variations, glycerine may be washed from the crude product using water scrubbing devices after which the alcohols may be separated by conventional distillation procedures. It is apparent to those skilled in the art that there are many other schemes for separating, recovering, and purifying the products as obtained from this invention and that we are not limited to any specific embodiment for such separation, recovery and purification.

Example 1

This example covers the use of the embodiment described in FIG. 1 in which it is desired to convert inedible beef tallow to fatty alcohols of relatively high detergency and value together with glycerine. The catalyst is extruded and of $\frac{1}{32}''$ diameter and has a surface area of 310 square inches per gram. Analysis of the fresh catalyst indicates 84% alumina, 3.5% CoO, and 12.5% MoO_3. The tallow feed has an iodine value of 44, and a saponification value of 195. Analysis of the long chain aliphatic groups of the tallow indicates about 25% saturated C_{16} groups, 25% saturated C_{18} groups, 40% unsaturated C_{18} groups, with the remainder consisting of other acid groups (and impurities).

Hydrogen is fed to the reactor system at a net rate corresponding to 2.5 pounds per hundred pounds of feed. Velocities in the reactor are maintained to provide a state of random motion in which the catalyst is expanded to occupy over 30% of its settled volume. Reactor catalyst density is 28 pounds per cubic foot; although the reactor has no disengaging section, catalyst density above the bulk phase interface is less than 0.005 pound per cubic foot. The reactor is maintained at a temperature of 750° F. and a total pressure of 2000 p.s.i.g., providing a hydrogen partial pressure of 1600 p.s.i. Catalyst is continually fed to the reactor and withdrawn at a rate of 0.10 pound per hundred pounds of feed. Feed space velocity is chosen to substantially convert all of the triglyceride feed.

The first column of Table I provides the yields from this case. Glycerol yield is substantial, approximating at least 80% of the theoretical. However, the most significant illustration of the value of the invention is provided by the relatively large quantity of lower alcohols (33.6%) produced, although as previously indicated, the composition of the tallow fed would correspond to certainly less than 10% yield of such lower alcohols, and probably to as little as 5% yield of these lower alcohols. Further evidence that substantial hydrosplitting of the higher alcohols has been attained is apparent from the significant quantities of hydrocarbons yielded as products, and by the fact that these hydrocarbons have chain links varying from 1 (methane) to 6 (hexane). The undetermined material probably consists of unconverted triglycerides, impurities, glycols, and lower alcohols. Total yields exceed 100% because of the consumption of about 2% hydrogen with the feed.

Example 2

This example illustrates the use of the embodiment of this invention indicated in FIG. 2. In this case the catalyst is bauxite which had been previously used for decolorizing a special petroleum product, and which is ground to an average particle size of 200 mesh before use. Analysis of this material indicated 92% Al_2O_3, 4% Fe_2O_3, and about 2% of non-volatile organic material (probably coke). After grinding, the contact agent is screened to 5% passing 270 mesh. The contact agent has a surface area of 55 square meters per gram.

The feed is tallow of virtually the same composition and properties used for Example 1. The net feed of hydrogen corresponded to about 2.8 pounds per hundred pounds of tallow fed. Velocities in the reactor are maintained to provide the state of random motion as indicated in Example 1. Expansion of the catalyst is 70% greater than the settled mass. Bulk phase catalyst density is 25 pounds per cubic foot. However, analysis of the stream at the top of the reactor indicated less than 0.08 pound of catalyst per cubic foot. The contact agent is continuously supplied to the reactor at a rate of 0.6 pound per hundred pounds of tallow fed. Reactor temperatures are 850° F. with a total pressure of 1000 p.s.i.g. to provide a hydrogen partial pressure of about 750 p.s.i. Space velocity is maintained to convert about 85% of the triglycerides in the feed single pass. Spent catalyst is withdrawn through line 86 at the same rate as fed, corresponding to 0.6 pound per hundred pounds of tallow; the catalyst is withdrawn as a slurry with about 1.8 pounds of unreacted triglycerides per hundred pounds fed. Table I again illustrates the results. High yields of glycerol are again obtained. The yield of the move valuable lower alcohols exceeds that obtained in Example 1 and collateral with higher yields of light hydrocarbons. The yield of undetermined by-products is very low, when it is considered that 1.8% of the 3.8% undetermined must be comprised by the unreacted triglycerides withdrawn through line **86** with the spent contact agent.

Example 3

This example illustrates the use of the two stage embodiment of this invention, a schematic representation of which is provided in FIG. 3.

In this example, reactor **26** (the first stage reactor) is charged with a cracking catalyst essentially consisting of over 99% of SiO_2 and Al_2O_3. This contact agent has a surface area of over 425 square meters per gram and is in the shape of beads all of which pass a 40 mesh screen but are maintained on a 60 mesh screen. The second stage reactor is charged with 1/32" extrudates of a catalyst containing 56% silica, 19% alumina, 6% nickel sulfide and 19% tungsten sulfide. This catalyst has an initial surface area of 275 square meters per gram. Internal recycle is provided in both reactors to maintain each of the catalysts in a state of random motion, expanded, in this case, over 35% of the respective settled volumes. The tallow feed is identical with that used in Example 1. The net hydrogen feed corresponds to 3.5 pounds per pound of tallow fed. The pressure in reactor **14** is 1800 p.s.i.g., whereas that in reactor **98** slightly exceeds 1700 p.s.i.g. Reactor **26** is maintained at a temperature of 705° F., whereas reactor **98** is maintained at 790° F.

Catalyst is continually replaced in both reactors; the replacement rate in reactor **26** is 0.04 pound per hundred pounds of feed, whereas that in reactor **98** is very low corresponding to about 0.005 pound per hundred pounds of fat fed. The bottoms material from fractionator **62** passing through line **66** into second stage reactor **98** corresponds to about 150 pounds per hundred pounds of tallow fed to reactor **26**.

Table I provides the results from Example 3. In this case, the yields of glycerol exceeds 95% of that which can be theoretically obtained in accordance with the analysis of the tallow. However, the conspicuous result obtained in this example is the yield of 64% of alcohols boiling in the C_{10} to C_{14} range of which more than 10 wt. percent was lauryl alcohol. Obviously, by more carefully controlled operation of fractionator **62**, the yields of higher alcohols will be nil; in the example as shown, a small amount of these alcohols is slopped into the product fraction. The high yields of lower alcohols are again reflected by the incremental yields of light hydrocarbons which are produced.

TABLE I.—YIELDS FROM EXAMPLES 1, 2 AND 3

Example	1	2	3
Embodiment	1	2	3
Yields, Weight Percent:			
Glycerol	8.4	9.3	10.5
Alcohols (C^{10}–C^{14})	33.6	49.2	64.0
Alcohols (C^{16}+)	43.0	21.0	1.3
Hydrocarbons	12.4	18.7	24.0
Undetermined	4.6	3.8	3.0

In the examples as provided, a single source of inedible tallow has been used as feed to illustrate the various differences in yields, and the wide flexibility of product distribution that can be obtained in the various possible embodiments of this invention. Actually, however, additional example can be provided for various other fats or oils which can be processed by this invention. It is again noted that the invention is not restricted by impurities present in these feeds and that the lowest grade feed materials are advantageously used.

We claim:

1. The process of conversion of inedible tallow to a mixture of fatty alcohols having at least a 10 percent concentration of alcohols containing between 10 to 14 carbon atoms which comprises melting the tallow and passing the molten tallow together with hydrogen at a rate of 2.0 to 4.0 pounds of hydrogen per 100 pounds of tallow upwardly through a contact zone containing a catalytic bed composed of a sulfur resistant catalytic contact agent selected from the group consisting of alumina and combinations of silica and alumina and promoted with elements from Groups VI–B and VIII of the periodic table at temperatures between 600 and 850° F. and at a total pressure within the range of 500 to 2000 p.s.i.g. and wherein the hydrogen partial pressure is within the range 250 p.s.i. to 1800 p.s.i., the velocity of the gas and liquid being such as to expand the catalytic bed at least 10 percent of its original volume and to create and maintain an interface below which the catalyst density is greater than 5 pounds per cubic foot and above which the catalyst density is less than 0.1 pound per cubic foot without employing disengaging devices and replacing the particulate contact agent in the bed at a rate between 0.001 and 1.0 pound of catalyst per 100 pounds of feed and drawing off the liquid product from above the interface.

2. The process as claimed in claim **1** wherein two contact zones are used and in which the glycerin and alcohols containing between 10 to 14 carbon atoms are removed from the effluent of the first contact zone prior to passing the effluent into the second contact zone.

3. The process as claimed in claim **1** wherein the catalytic agent is within the particle size range of from 16 to 270 mesh.

4. The process as claimed in claim **3** wherein the catalyst is promoted with a metal selected from the group consisting of iron, cobalt, molybdenum, chromium, tungsten and nickel.

5. The process of conversion of a feed containing triglycerides of alcohols containing between 16 and 20 carbon atoms to a mixture of fatty alcohols having at least a 10% concentration of alcohols containing between 10 to 14 carbon atoms which comprises melting the feed and passing the molten feed together with hydrogen at a rate of 2.0 to 4.0 pounds of hydrogen per 100 pounds of feed upwardly through a contact zone containing a catalytic bed composed of a sulfur resistant catalytic contact agent selected from the group consisting of alumina and combinations of silica and alumina and promoted with elements from Groups VI–B and VIII of the periodic table at temperatures between 600 and 850° F. and at a total pressure within the range of 500 and 2000 p.s.i.g. and wherein the hydrogen partial pressure is within the range 250 p.s.i. and 1800 p.s.i., the velocity of the gas and liquid being such as to expand the catalytic bed at least 10% of its original volume and to create and maintain an interface below which the catalyst density is greater than 5 pounds per cubic foot and above which the catalyst density is less than 0.1 pound per cubic foot without employing disengaging devices and replacing the particulate contact agent in the bed at a rate between 0.001 and 1.0 pound of catalyst per 100 pounds of feed and drawing off the liquid product from above the interface.

(References on following page)

References Cited

UNITED STATES PATENTS

2,109,844	3/1938	Lazier	260—638
2,118,001	5/1938	Andrews et al.	260—638
2,322,095	6/1943	Schmidt	260—638
2,750,429	6/1956	De Nora et al.	260—638
Re. 25,770	4/1965	Johanson	208—10

FOREIGN PATENTS

457,358	11/1936	Great Britain.
1,146,483	4/1963	Germany.
712,197	6/1965	Canada.

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