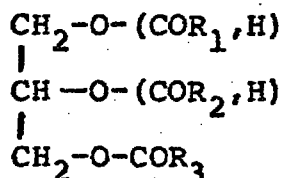


PROCESS FOR THE MANUFACTURE OF FATTY ACID NITRILES AND
GLYCEROL FROM GLYCERIDES, ESPECIALLY FROM NATURAL FATS
AND OILS

This invention relates to a process for converting mono-, di- and triglycerides of the formula



wherein R_1 , R_2 , and R_3 , identical or different, are aliphatic hydrocarbon radicals or mono-hydroxy substituted hydrocarbon radicals having from 3 to 23 C atoms, or mixtures of said glycerides in the liquid phase with ammonia yielding fatty acid nitriles of the formula $R_3(R_1, R_2)\text{-CN}$ and glycerol by passing gaseous ammonia optionally in admixture with an inert gas at elevated temperatures in the presence of a catalyst.

Fatty acid nitriles, which are important intermediates for the manufacture of amines, are produced by industrial processes, preferably from the corresponding fatty acids and ammonia in the presence of suitable catalysts. This synthesis, which has been known for quite a while, can be carried out in the liquid phase at a temperature in the range of from 250° to 350°C as well as in the gaseous phase at a temperature of from 320 to 380°C . Suitable catalysts for the reaction in the liquid phase are, for example, zinc oxide and manganese acetate, for the gaseous phase aluminum oxide or bleaching earth have been proposed. Detailed information about the aforesaid processes are found in "Methoden der Organischen Chemie" Houben-Weyl, volume 8, pages 330 et seq., Georg Thieme Verlag, Stuttgart, 1952, and in "Fatty Acids and their Industrial Applications", Marcel Dekker, New York, 1968, pages 909

et seq.. US Patent 2,589,232 describes a process for the manufacture of fatty acid nitriles by reaction of fatty acids with ammonia in the liquid phase in the presence of zinc or calcium salts of fatty acids. Another process in which titanate acid esters of short-chain aliphatic alcohols are used as catalysts and, besides fatty acids, the fatty acid esters of short-chain alcohols can be used as starting materials is described in US Patent 2,993,926. When, in the aforesaid processes, natural fats or oils are used, the free fatty acid or the short-chain fatty acid must be isolated first in a separate stage.

It has also been proposed to react natural fats or fatty acid esters of monohydric alcohols by reaction with ammonia and to obtain in this manner the corresponding fatty acid amides. Suitable catalysts in this process are, for example, metal oxides or calcium nitrate (cf. Japanese Patent Publications 70-35524 and 71-21846 and Japanese Patent Application 71-6614). The fatty acid amides can then be transformed in known manner into the fatty acid nitriles by dehydration in a second stage.

Japanese Patent Publication 72-26921 propose a process according to which natural fats can be transformed into fatty acid amides by reaction with aliphatic amines, and the glycerol formed is removed from the equilibrium as glycerol boric acid ester by the use of boric acid.

It would be desirable for economical reasons to dispose of a process in which natural fats or oils, i.e. native triglycerides, that may contain minor amounts of mono- or diglycerides, are directly transformed into the corresponding fatty acid nitriles without isolation of the

fatty acid amides or without detour over the free fatty acid or the short-chain fatty acid ester.

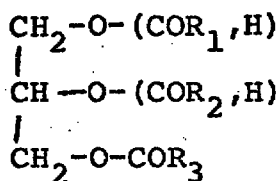
Attempts of this kind have already been made. British Patents 416,631 and 451,594 disclose a process for reacting hydroxy fatty acids or fatty acids, obtained from natural fats, with ammonia to obtain fatty acid nitriles, in the gaseous phase at a temperature of from 300 to 450°C in the presence of oxidic dehydration catalysts, preferably aluminum oxide. In the specifications it is said that the glycerides may be used directly although they cannot be evaporated under the specific conditions. In Example 3 of GB-PS 416,631 and in Examples 7 and 14 of GB-PS 451,594 reactions of castor oil, palm nut fat and coconut oil with ammonia at temperatures of from 350 to 400°C in the presence of bauxite are described. But nothing is said about the glycerol. We have found out that under the conditions of the said process, the glycerol is completely decomposed by thermal splitting. Hence, a valuable material is lost and moreover, the quality of the fatty acid nitriles obtained is noticeably impaired, especially as regards color and odor. Fatty acid nitriles constitute intermediates and for further processing high degrees of purity are required; consequently expensive purifying procedures are necessary to remove the decomposition products, so that the above process becomes completely uneconomic.

From British Patent Specification No. 477,463 a process is known in which the conversion of fatty acids into nitriles in the liquid phase preferably is performed without catalysts.

It is alleged in this British Patent Specification that glycerol can be obtained if glycerides are used as starting materials. An experimental verification of this process proved that only smallest traces of glycerol are formed besides high amounts of decomposition products of glycerol which contaminate the nitrile obtained. The use of cobalt salts of fatty acids as catalysts for conversion of free fatty acids to nitriles is known from US-Patent No. 2,493,637. French Patent No. 864,571 discloses for the conversion of adipic amide and acetic anhydride to adiponitrile the use of heavy metal salts of carboxylic acids as catalysts.

It is, therefore, the object of the present invention to provide a one-stage process by which it is possible to produce fatty acid nitriles as well as glycerol in a high yield and in an economic reaction time from glycerides.

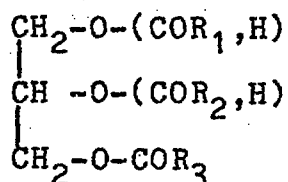
This objective is achieved in accordance with the invention by a process for converting mono-, di- and tri-glycerides of the formula



wherein R_1 , R_2 , and R_3 , identical or different, are saturated or mono- or multiple unsaturated hydrocarbon radicals or mono-hydroxy substituted hydrocarbon radicals having from 3 to 23 C atoms, or mixtures of said glycerides in the liquid phase with ammonia yielding fatty acid nitriles of the formula $R_3(R_1, R_2)\text{-CN}$ and glycerol by passing gaseous ammonia optionally in admixture with an inert gas at elevated temperatures in the presence of a

catalyst, which comprises contacting intimately the liquid glyceride with a flow of at least 200 liters ammonia per kilogram of glyceride and hour at temperatures of from 220 to 300°C in the presence of a salt of a carboxylic or sulfonic acid and a metal selected from the group of lead, zinc, cadmium, tin, titanium, zirconium, chromium, antimony, manganese, iron, nickel, and cobalt as catalysts, discharging the resulting product mixture with rapid removal of the glycerol formed from the reaction zone, and subjecting the product mixture to a phase separation into a fatty acid nitrile phase and glycerol/water phase.

Starting materials in the process of the invention are mono-, di and triglycerides of the formula



i.e. in this formula one or two fatty acid radicals can be replaced by hydrogen. The fatty acid radicals $R_1\text{CO-}$, $R_2\text{CO-}$ and $R_3\text{CO-}$ are derived from fatty acids having from 3 to 23 carbon atoms. The aliphatic hydrocarbon radicals R_1 , R_2 and R_3 can have a straight chain or they can be branched once or several times. The chains can be saturated or contain one or several multiple bonds, preferably double bonds. Optionally, they may be substituted with one hydroxyl group. Preferred starting materials in the process of the invention are, in the first place, natural fats which consist of mixtures of a preponderant proportion of triglycerides and smaller proportions of diglycerides and monoglycerides, and which for their part are mostly mixtures and contain different fatty acid radicals within the aforesaid limits, especially those having at least 8 carbon atoms. There are mentioned, by way of example, vegetable fats such as olive oil, coconut oil, palm nut oil, babussu oil, palm oil, peanut oil, rape oil, castor oil, sesame oil, ^{cotton oil} sunflower oil, soybean oil, hempseed oil, poppy oil, avocado oil, cotton seed oil, wheat germ oil, corn germ oil, pumpkin seed oil, grapeseed oil, coconut oil and vegetable tallows; furthermore animal fats such as beef tallow, lard, bone fat, mutton tallow, Japan tallow, whale oil and other fish oils, and cod liver oil. It is likewise possible to use uniform tri-, di- and mono-glycerides either isolated from natural fats or synthetized,

for example tributyrin, tricapronin, tricaprylin, tri-
caprinin, trilaurin, trimyristin, tripalmitin, tristearin,
triolein, trielaidin, trilinoliin, trilinolenin, monopal-
mitin, monostearin, monoolein, monocaprinin, monolaurin,
monomyristin, and mixed glycerides such as palmitodistearin,
distearoolein, dipalmitoolein and myristopalmitostearin.

Decisive for the success of the one-stage process of
the invention, i.e. the production of fatty acid nitrile
or of a mixture of fatty acid nitriles in a high purity
and high yield with the simultaneous production of glycerol
in a high yield are, above all, three process parameters,
namely the selection of the right temperature or tempera-
ture conditions, the rapid removal of the glycerol formed
from the reaction zone and the selection of the ^{/correct} catalyst.

To ensure a rapid removal of the glycerol from the
reaction zone a minimum amount of at least 200 liters of
ammonia should be passed through the reaction mixture per
kilogram of glyceride per hour, preferably at least 400
liters per kilogram of glyceride per hour. As regards the
ammonia current to be passed through there is no critical
upper limit, but economical considerations will limit
the amount of ammonia to about 1,000 liters, preferably
800 liters per kilogram of glyceride per hour. It proved
advantageous to add to the gaseous ammonia up to 30 % and
advantageously up to 15 %, calculated on the amount of
ammonia passed through, of an inert gas, for example
nitrogen.

Furthermore, in the process of the invention it is of
decisive importance that the reaction temperature during

the entire course of the reaction is maintained in the range of from 220 to 300°C, preferably 230 to 290°C. It proved advantageous to allow the temperature to rise from the beginning to the end of the process, either continuously or gradually, especially according to a temperature program. According to a preferred embodiment, the reaction is carried out at a temperature between about 220 and 240°C for a long time until about 30 to 70 % of the amount of glycerol to be expected theoretically are discharged from the reaction vessel, the temperature is then raised, during the course of about 30 minutes to 5 hours, either gradually or continuously, to about 270 to 400°C, whereupon the reaction is completed within the latter temperature range. The reaction is complete when no more liquid phase passes into the receiver.

Finally, the selection of the catalyst is of decisive importance to the process of the invention. Suitable catalysts are the lead, zinc, cadmium, tin, titanium, zirconium, chromium, antimony, manganese, iron, nickel, or cobalt salts of organic carboxylic and sulfonic acids. The said catalysts can be also used in the form of mixtures. The organic carboxylic and sulfonic acids from which derive the anions of the aforesaid salts preferably belong to the following groups:

linear or branched, open-chain carboxylic acids in which the chain is saturated or may contain one or several double bonds and have from 4 to 23, preferably 8 to 23 carbon atoms;

alkylcarboxylic acids, preferably alkylbenzenecarb-

oxylic acids and alkylnaphthalenecarboxylic acids carrying one or several alkyl radicals on the aromatic nucleus each having 1 to 23, preferably 1 to 12 carbon atoms; alkyl sulfonic acids and alkyl disulfonic acids with linear or branched alkyl radicals having 4 to 24, preferably 8 to 24 carbon atoms, the alkyl radicals possibly being substituted with OH groups, preferably with one OH group and in the alkyl chain the hydrogen atoms possibly being replaced partially or preferably completely by fluorine atoms, and alkylaryl sulfonic acids, preferably alkylbenzenesulfonic acids and alkylnaphthalenesulfonic acids (in each case the mono-, di- and trisulfonic acids being meant) carrying one or several linear or branched alkyl radicals on the aromatic nucleus each having 1 to 24 carbon atoms and possibly substituted with two and preferably with one carboxyl group.

From among the specified salts to be used as catalysts in the process of the invention there are especially preferred with regard to the cation the salts of lead, cadmium, iron, cobalt and more preferably of zinc.

With respect to the anion, the above group of sulfonic acids are preferred, and especially the alkylarylsulfonic acids of the latter group. Examples are:

n-dodecyl sulfonic acid, n-octadecyl sulfonic acid, isobutyl naphthalenesulfonic acid, n-butyl naphthalenesulfonic acid, isopropyl naphthalenesulfonic acid, cetyl benzenesulfonic acid, octadecyl benzenesulfonic acid, tetrapropylene benzenesulfonic acid and triisobutyl benzenesulfonic acid.

The salt to be used as catalysts in the process of the invention can be prepared by reacting the free acids with the corresponding metal oxides by known methods. The free sulfonic acids can be obtained by known sulfonation processes or from the corresponding alkali metal sulfonates, for example with the help of ion exchangers.

The aforesaid catalysts can be added directly in salt form. Alternatively, the respective metal oxide and the carboxylic acid or sulfonic acid can be added separately to the reaction mixture, whereupon the catalyst is formed in situ during the course of the reaction. In the process of the invention the aforesaid catalysts are added in an amount of from 0.5 to 75 % by weight, with a discontinuous operation preferably in an amount of from 1 to 25 % by weight, more preferably 1 to 10 % by weight, and with a continuous operation preferably in an amount of from 5 to 75 % by weight, more preferably 10 to 30 % by weight, the percentages being calculated on the glyceride used.

To carry out the process of the invention a suitable reaction vessel, for example a vessel ^{provided with} stirrer, is charged with the glyceride or glyceride mixture and the catalyst. The total amount of the catalyst can be added at the be-

ginning or a partial amount thereof and the remainder is then added in portions or continuously during the course of the reaction. The reaction vessel is provided with an equipment for gas inlet by which the flow of gas can be measured, a temperature measuring device, heating means and optionally with a stirrer. The reaction vessel is connected with a condensation apparatus consisting of one or preferably several receivers heated to about 60 to 120°C. After heating of the reaction vessel, optionally under nitrogen, and when the reaction temperature has been reached, ammonia is introduced. At the beginning, the product mixture collected in the condensation apparatus contains a higher proportion of crude glycerol. During the course of the reaction the proportion of fatty acid nitrile increases gradually and, towards the end of the reaction, substantially pure fatty acid nitrile is collected while the discharge of crude glycerol has ceased previously. The ammonia current (to which inert gas may be added as mentioned above) further ensures a rapid removal of the reaction water over the entire reaction period. After separation of the entrained water and optionally with the addition of fresh ammonia, the issuing gas current is recycled into the reaction. The discharged product mixture is collected in the condensation apparatus and separated into a fatty acid nitrile phase and a crude glycerol/water phase. The final phase separation is expediently carried out after discharge from the condensation apparatus and transfer into a separator, for example a vapor separator, at about

60 to 100°C. Residual glycerol is washed out of the fatty acid nitrile phase by means of water. The crude glycerol isolated from the aqueous phase, for example by distillation, can be purified by known methods (cf. Ullman "Enzyklopädie der Technischen Chemie" 1965, volume 7, pages 523 to 524), for example by distillation.

By the process of the invention it is possible to produce fatty acid nitriles and glycerol in excellent yields of at least 93 % up to 96 % and more of fatty acid nitrile and up to 95 % of crude glycerol, each time calculated on the theoretical yield on the basis of the glyceride used. The fatty acid nitrile obtained contains at most 2 % by weight of free fatty acids and up to 10 %^{weight}, in most cases, however, less than 6 %^{weight}, of fatty acid amides as by-products.

The free fatty acids and fatty acid amides contained in the discharged product mixture are suitably transformed into fatty acid nitriles by subjecting the mixture, after or optionally prior to the phase separation, to an after-reaction in the presence of ammonia and of the catalysts specified above.

To this after-reaction there can be subjected either the free fatty acids and fatty acid amides separated from the discharged fatty acid nitrile, optionally together with crude nitrile not yet discharged, or the whole fatty acid nitrile phase. In the following are described methods to carry out the after-treatment.

According to a preferred method a fractionation column is intercalated between the reactor and the con-

densation apparatus. In this column, which may be a mirror glass column or a well insulated tube, packed, for example, with Raschig rings, the fatty acid amides and free fatty acids, which are reaction intermediates, are separated and recycled into the reaction vessel, while the remaining product mixture passes into the receiver where it is collected with condensation as described above.

With the intercalation of the fractionation system, the process of the invention can be performed fully continuously in an especially simple manner. To this end, the glyceride as defined above^{is} first introduced into the reaction vessel together with the specified amount of catalyst or it is added in dosed quantities to an inert, non volatile solvent, for example paraffin oil.

The amount of ammonia to be introduced should be also in this case at least 200 liters per kilogram of glyceride per hour, but normally higher amounts than indicated above for a discontinuous operation are passed through.

The temperatures of the continuous process are advantageously in the range of from 220 to 270°C, preferably 230 to 250°C. During the reaction, the glyceride is continuously metered in. It is likewise possible to add continually a mixture of the glyceride with the catalyst. Fatty acid nitrile, glycerol and water are constantly discharged through the fractionation system while fatty acid amide and free fatty acid are continuously recycled into the process.

According to another variant of the after-treatment

the reaction is continued until the crude glycerol is substantially discharged (in the case of phase separation the phase of crude glycerol does no longer increase), the fatty acid nitrile phase resulting from the phase separation is recycled into the reactor and combined with the portion of fatty acid nitrile not yet discharged, in the reactor a temperature in the range of from 200 to 320°C is adjusted and the flow of ammonia is reduced to 5 to 150 liters per kilogram of fatty acid nitrile per hour, preferably to 15 to 100 liters per kilogram. If in the first stage of the reaction a sufficient amount of catalyst has been added (amount at the upper limit of the indicated range) fresh catalyst need not be added. Otherwise, an appropriate amount of catalyst should be added. Under these reaction conditions the fatty acid amides and fatty acids are quantitatively transformed into fatty acid nitriles, as can be ascertained by the formation of reaction water. This water is discharged together with the excess amount of ammonia, the water is separated and the ammonia is recycled, optionally with the addition of fresh ammonia. When the reaction is complete, the fatty acid nitrile in the reactor is suitably distilled to remove the catalyst.

Alternatively, the entire amount of fatty acid nitrile can be removed from the reactor, subjected to phase separation and then introduced into a second reactor (after-reactor) into which a catalyst is introduced as defined above. The after-treatment is carried out under the same conditions as the above process wherein a partial amount is recycled into reaction vessel. In this case,

too, the fatty acid nitrile should be worked up by distillation after termination of the after-treatment.

The latter method can be modified in a manner such that the entire fatty acid nitrile phase is continuously conducted under the specified conditions for example through a tube reactor.

Finally, the fatty acid nitrile phase obtained can be passed continuously over a solid bed of dehydration catalysts together with ammonia in an amount of 200 to 800 liters per kilogram of fatty acid nitrile per hour, preferably 300 to 600 l/kg, at a temperature of from 280 to 400°C, preferably 300 to 380°C. Suitable dehydration catalysts are, for example, aluminum oxide in the form of bauxite or hydrargillite, thorium oxide, zirconium oxide, aluminum phosphate, silica gel, active bleaching earth and the like, and mixtures thereof.

Surprisingly, the process of the invention makes it possible to produce not only fatty acid nitriles in excellent yields and in high purity but also glycerol in a high yield. By the after-treatment methods as described above the purity of the fatty acid nitrile is further improved so that it finally contains less than 2 % by weight, in most cases less than 0.1 % by weight of fatty acid amide and less than 1.5 % by weight and in most cases less than 0.1 % by weight of free fatty acid and is free from other by-products.

Fatty acid nitriles are important chemical intermediates, especially for the manufacture of primary amines and quaternary ammonium salts, which, for their part, are

mainly used as textile auxiliaries, flotation auxiliaries and cation-active surfactants in many industrial processes. Glycerol is an important chemical compound, for example for the manufacture of explosives, as additive for heat- and power transmission fluids, as moisture-conserving additive to skin creams, tooth pastes, soaps, tobacco and the like, as textile auxiliary, as solvent and in many other fields known to everybody skilled in the art.

The following examples illustrate the invention.

E X A M P L E 1:

The reaction was carried out in a heatable reactor having a capacity of 800 cc and provided with gas inlet, stirrer, internal thermometer and fractionation column in the form of a glass tube (length 20 cm, diameter 1.5 cm) packed with Raschig rings and a receiver system of three series-connected receivers in which the volatile reaction products are condensed. The reactor was charged with 495 g of tallow (saponification number 190, acid number 7.6) and 5 g of zinc dodecylbenzenesulfonate as catalyst. During heating the reactor was scavenged with nitrogen. The nitrogen was then replaced by gaseous ammonia which was conducted in a cycle in an amount of 600 l of NH_3 /kg of tallow·hour. During the reaction fresh gaseous ammonia was constantly added. The temperature in the reactor was as follows:

<u>reaction time (hr)</u>	<u>temperature in reactor</u>
3	230°C
0.75	230 → 250°C
0.25	230 → 260°C
0.25	260 → 270°C
1	270°C
0.5	270 → 290°C
1.25	290°C

The reaction of the tallow with ammonia was complete after a total reaction time of 7 hours. The tallow nitrile and glycerol were collected in 2 series-connected receivers, while in another receiver ammoniacal reaction water was condensed.

The glycerol and tallow nitrile collected as two phases in the two first receivers were separated and the tallow nitrile was washed with water. 413.7 g (93.6 %^{weight}) of tallow nitrile having an amide content of 1.8% and a tallow fatty acid content of 1.5 % by weight and 39.6 g (80.2 %) of pure glycerol were obtained after working up. (The yields given in parentheses here and in the following are calculated on the theoretical yield).

EXAMPLE 2:

The apparatus as described in Example 1, was charged with 495 g of beef tallow (saponification number 190, acid number 1.6) and 10 g of zinc dodecylbenzenesulfonate and, starting at 230°C, 600 l of NH_3 /kg of beef tallow·hr were passed through. The following temperature conditions were

maintained in the reactor:

<u>reaction time</u>	<u>temperature in reactor</u>
30 min	230°C
20 min	235°C
20 min	240°C
20 min	245°C
1 h 10 min	250°C
1 h 20 min	255°C
30 min	260°C
60 min	270°C
60 min	280°C
60 min	290°C

The total reaction time was 7.5 hours. The reaction products collected in the receivers were washed out with water and worked up. 408 g (92.3 %) of tallow nitrile having an amide content of 0.7 % by weight and a fatty acid content of 0.5 % by weight and 44.7 g (87.7 %) of crude glycerol were obtained. The isolated crude glycerol contained, according to the hydroxyl number of 1694, 81.2 % of glycerol, calculated on the tallow used.

EXAMPLE 3:

The apparatus described in Example 1 was charged with 445 g of industrial grade tallow (bleachable tallow, saponification number 186, acid number 12.6) and 9 g of zinc dodecylbenzenesulfonate and the mixture was reacted with ammonia under the conditions of Example 2. The reaction products discharged during the reaction over a period of 7.5 hours were combined and the glycerol was

washed out with water. After separation of the aqueous phase, 370.4 g (93.0 %) of tallow nitrile having an amide content of 0.5 % by weight and a fatty acid content of 0.3 % by weight could be isolated. Crude glycerol was obtained from the aqueous phase in a yield of 38.5 g (97.5 %). According to the OH number^{of 1683}, the yield of pure glycerol amounted to 84.0 %, calculated on the tallow used.

E X A M P L E 4:

The apparatus as described in Example 1 and additionally provided with a 70 cm mirror glass column packed with Raschig rings for fractionation was charged with 488 g of edible tallow (saponification number 190, acid number 2.4) and 5 g of zinc toluenesulfonate. During heating a weak nitrogen current was passed through the reactor. At 190°C, the nitrogen was replaced by 600 l of NH₃/kg of fat·hr. The reaction was continued for 3 hours at 230°C. The temperature was then raised from 230 to 270°C within 30 minutes and maintained at the higher level for a further 3.25 hours. After a total period of 6.75 hours all volatile reaction products from the reactor had passed the column. The mixture of glycerol and tallow nitrile collected in the receiver system was treated with water and, after working up of the two phases, tallow nitrile was obtained in a yield of 406 g (93.2 %) (1.7 % of amide and 0.5 % by weight of fatty acid) and pure glycerol was obtained in a yield of 40.1 g (80.1 %).

In the same apparatus and under the same conditions edible tallow was reacted in the presence of other cata-

lysts. In the following table the test results are summarized.

catalyst	reaction time hr	nitrile yield %	amide content % b.w.	yield of pure glycerol %
1 % b.w. of zinc perfluorohexane- sulfonate	6.25	93.8	0.9	78
1 % b.w. of zinc- isopropyl-naphtha- lenesulfonate	7	94	1.3	82
1 % b.w. of C ₁₅ /C ₁₈ - alkane-sulfonate	6.75	94	2	83
1 % b.w. of zinc salt of the reac- tion product of ben- zene, oleic acid and H ₂ SO ₄ (alkylbenzenesulfonic acid carrying a carboxyl group in the alkyl chain)	6	92	0.7	77

E X A M P L E 5:

In the apparatus as described in Example 4, 436 g of sunflower oil (saponification number 189, acid number 0.8) and 9 g of zinc dodecylbenzenesulfonate as catalyst were reacted under the conditions of Example 4 (reaction time 6.75 hours) with gaseous ammonia (690 l/kg of fat·hr). After working up, there were obtained 94.6 % of fatty nitrile (amide content 0.5 % by weight, fatty acid content 0.35 % by weight) and 91.2 % of crude glycerol (40.9 g) or 85.6 % of pure glycerol according to the OH number of 1717, calculated on the oil used.

E X A M P L E 6:

This example is intended to demonstrate the preparation of fatty acid nitrile and glycerol directly from glycerides in continuous operation. A heatable, cyclindrical, 750 cc glass vessel was charged with 192 g of edible tallow and 7.5 g of zinc dodecylbenzenesulfonate. The reactor was provided with stirrer, internal thermometer, heated dropping funnel and 70 cm mirror glass column packed with Raschig rings. 600 l of ammonia per kg of fat·hr were introduced into the reactor from below at 230°C by means of a frit. Under these conditions, 1009 g of edible tallow mixed with 1 % by weight of zinc dodecylbenzene-sulfonate were added in dosed quantities over a period of 3 hours (27 to 29 g of tallow per hour). The volatile reaction products permanently discharged through the column were condensed in a receiver system. The tallow nitrile obtained was freed from glycerol by means of water. 1033 g (96.1 %) of tallow nitrile (amide content 1.4 % by weight) could be isolated. 115.4 g (95.5 %) of crude glycerol were isolated from the water.

E X A M P L E 7:

The apparatus described in Example 4 was charged with 486 g of edible tallow (saponification number 190, acid number 1.6) and 5 g of zinc dodecylbenzenesulfonate. At about 270°C, 500 l of NH_3 /kg of fat·hr were passed through the reaction mixture at a constant speed. The reaction time was 6.5 hours. The reaction products collected in the receivers were washed with water and worked up. 406 g (93.7 %) of tallow nitrile having an

amide content of 2.2 % by weight and a fatty acid content of 0.4 % by weight and 36.8 g (73.45 %) of pure glycerol, calculated on the tallow used, were obtained.

E X A M P L E 8:

The apparatus described in Example 4 was charged with 486 g of tallow (saponification number 187.5, acid number 11.1) and 4.25 g of the zinc salt of tallow fatty acid. During heating, 30 l of N_2 /hr were passed through the reactor and at 190°C the nitrogen was replaced by 600 l of NH_3 per kg of fat·hr. The reaction was complete after 13 hours. During the reaction the temperature was maintained for 3 hours at 230°C and then for 9.5 hours at 270°C. The reaction products collected in the receivers and discharged from the reactor were washed with water. 367.8 g (84.6 %) of tallow nitrile and 28.3 g (60.4 %) of pure glycerol were obtained, calculated on the tallow used.

E X A M P L E 9:

The apparatus described in Example 1 and provided with the fractionation system of Example 4 was charged with 445 g of beef tallow (saponification number 186, acid number 0.8) and 9 g of iron-dodecylbenzenesulfonate as catalyst. Starting at 230°C, 600 l of NH_3 /kg of fat·hr were passed through the tallow. The temperature was raised to 290°C within 7.25 hours. At the end of the reaction and after working up 364.1 g (91.4 %) of tallow nitrile having an amide content of 2.9 % by weight and a fatty acid content of 0.4 % by weight and 30.2 g (67.0 %) of pure glycerol were obtained, calculated on the tallow used.

E X A M P L E 10:

The apparatus described in Example 1 was charged with 445 g of beef suet (saponification number 190, acid number 0.2) and 9 g of lead dodecylbenzenesulfonate and, starting at 230°C, 600 l of NH_3 /kg of fat·hr were passed through. The reaction temperature was raised to 290°C within 7.25 hours. At the end of the reaction and after working up, 350.5 g (88.2 %) of nitrile having an amide content of 2.7 % by weight and a fatty acid content of 0.35 % by weight and 36.5 g (78.9 %) of pure glycerol were obtained.

E X A M P L E 11:

The apparatus described in Example 1 was charged with 445 g of soybean oil (saponification number 203.2) and 9 g of zinc dodecylbenzenesulfonate. Starting at 230°C, 600 l of NH_3 /kg of fat·hr were passed through the oil. The reaction temperature was raised ^{gradually} to 290°C within 7.25 hours. At the end of the reaction and after working up, 363.3 g (92.2 %) of soya nitrile having an amide content of 0.7 % by weight and a fatty acid content of 0.7 % by weight and 36.0 g (72.8 %) of pure glycerol were obtained, calculated on the oil used.

E X A M P L E 12:

The apparatus described in Example 1 was charged with 445 g of beef suet (saponification number 192, acid number 0.25) and 9 g of cadmium dodecylbenzenesulfonate. Starting at 230°C, 600 l of NH_3 /kg of fat·hr were passed through the fat. The reaction temperature was raised to 290°C within 6.5 hours. At the end of the

reaction and after working up, 373.6 g (94.2 %) of tallow nitrile having an amide content of 2 % by weight and a fatty acid content of 0.7 % by weight and 35.1 g (75.2 %) of pure glycerol were obtained.

E X A M P L E 13:

The apparatus described in Example 1 was charged with 445 g of beef suet (saponification number 192) and 9 g of cobalt dodecylbenzenesulfonate. Starting at 230°C, 600 l of NH₃/kg of fat·hr were passed through the fat. The reaction temperature was raised to 290°C within 7.25 hours. At the end of the reaction and after working up, 373 g (94 %) of tallow nitrile having an amide content of 4.9 % by weight and a fatty acid content of 0.8 % by weight and 40.3 g (86.4 %) of crude glycerol were obtained.

E X A M P L E 14:

The apparatus described in Example 1 which, instead of a fractionation system, was provided with a direct transition pipe from the reactor to the receiver system, was charged with 486 g of edible tallow (saponification number 187, acid number 0.8) and 1 % by weight of zinc dodecylbenzenesulfonate, calculated on the tallow. During the reaction 600 l of NH₃/kg of fat·hr were passed through the reaction mixture. The temperature was maintained for 3 hours at 230°C, and after temperature increase (0.5 hr) for 1.25 hours at 270°C. After a total period of 4.75 hours, the reaction was terminated. The reaction products discharged at 230°C and at 270°C were collected separately and worked up. The fatty acid nitrile isolated at 230°C had an amide content of 20 %

by weight, while the amide content of the product discharged at 270°C was found to be 9 % by weight. The amide content in the total amount of fatty acid nitrile was 10 % by weight.

EXAMPLE 15:

The apparatus described in Example 1 which, instead of the fractionation system, was provided with a direct connecting pipe from the reactor to the receiver system, was charged with 500 g of tallow (saponification number 189, acid number 0.9) and 2 % by weight of zinc dodecylbenzenesulfonate, calculated on the tallow. During the reaction 600 l of NH_3 /kg of fat·hr were passed through the reaction mixture. The temperature was maintained for 3 hours at 230°C, then raised by 10 centigrades and after every 30 minutes for a further 10 centigrades. The reaction was complete at 280°C after a reaction time of 5.25 hours. The ^{total} condensate was separated by means of water and at 80°C into fatty acid nitrile and glycerol/water. The isolated fatty acid nitrile had an amide content of 5.3 % by weight and a fatty acid content of 0.5 % by weight. The nitrile yield was 95.2 %. After working up, 91.4 % of pure glycerol were obtained.

EXAMPLE 16:

A heatable reactor equipped with gas inlet tube, stirrer and internal thermometer and connected with a receiver system (condensation system of one or several receivers and containers) was charged with 500 g of industrial grade tallow (saponification number 191.4, acid number 1.5) and 2 % by weight of zinc dodecylbenzenesul-

fonate, calculated on the tallow. The content of the reactor was heated to 230°C and 600 l of ammonia/kg of fat·hr were passed through the mixture. The temperature was maintained for 3 hours at 230°C and then raised to 260°C within 1.5 hours. After 4.5 hours the glycerol discharge was terminated and about one half of the crude fatty nitrile had been discharged. At this time of the reaction the throughput of ammonia was reduced to 60 l/kg of reaction mixture·hr and simultaneously the reaction temperature was raised to 290°C. During the temperature increase the glycerol-containing crude nitrile was washed with water and the nitrile freed from glycerol was recycled into the reactor heated to 290°C. After a reaction period of 6.5 hours altogether (after-reaction 2 hours) the tallow nitrile was discharged and freed from the catalyst by distillation. 417 g (93.2 %) of tallow nitrile having an amide content below 0.06 % by weight and an acid number of 0.1 and 42.9 g (82.7 %) of pure glycerol (according to the hydroxyl number) were obtained.

EXAMPLE 17:

The apparatus described in Example 1 was charged with 500 g of industrial grade tallow (saponification number 191.4, acid number 1.5) and 2 % by weight of zinc dodecylbenzenesulfonate, calculated on the tallow. During the course of the reaction, 600 l of ammonia per kg of fat and hour were passed through the reaction mixture, while the temperature was maintained for 3 hours at 230°C and then raised to 280°C within 2.25 hours. The total reaction time was 5.25 hours. During the reaction care was taken

that the temperature gradient between the sump and the transition was as low as possible. The condensate obtained was separated by a water wash into crude fatty nitrile and glycerol.

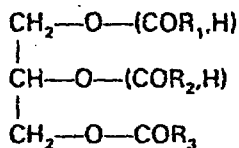
The isolated 432.8 g of crude fatty nitrile (amide content 6.1 % by weight) were introduced into a reactor provided with gas inlet tube, stirrer, internal thermometer and condensation system and 2 % by weight of zinc dodecylbenzenesulfonate were added. 60 l of ammonia per kg of reaction mixture and hour were passed through at 290°C, while the reaction water formed was discharged. The reaction time was 1 hour. After distillation of the reactor content, 415 g (93.1 %) of tallow nitrile having an amide content below 0.05 % by weight and an acid number of 0.1 and 47.3 g (91.2 %) of pure glycerol (according to hydroxyl number) were obtained.

COMPARATIVE EXAMPLE: ^{according to} (British Patent 451,594)

300 l of NH_3 /l of catalyst·hr and 50 g of beef suet per hour were passed from below at 320 to 360°C through a glass tube filled with 800 cc of granular aluminum oxide. A total amount of 1,342 g of beef suet was metered in. The volatile reaction products leaving the reactor at the head were collected in a receiver system, combined and then washed with water. 1,191 g of crude tallow nitrile (yield 99 %) were obtained, but its quality was poor (black and pungent odor). Glycerol could not be detected. The theoretical yield of glycerol would have been 140 g.

Claims

1. A process for converting mono-, di- and triglycerides of the formula



wherein R_1 , R_2 , and R_3 , identical or different, are aliphatic hydrocarbon radicals or mono-hydroxy substituted hydrocarbon radicals having from 3 to 23 C atoms, or mixtures of said glycerides in the liquid phase with ammonia yielding fatty acid nitriles of the formula R_1 , R_2 , R_3 -N and glycerol by passing gaseous ammonia optionally in admixture with an inert gas at elevated temperatures in the presence of a catalyst, which is characterised by contacting intimately the liquid glyceride with a flow of at least 200 liters ammonia per kilogram of glyceride and hour at temperatures of from 220 to 300°C in the presence of a salt of a carboxylic or sulfonic acid and a metal selected from the group of lead, zinc, cadmium, tin, titanium, zirconium, chromium, antimony, manganese, iron, nickel, and cobalt as catalysts, discharging the resulting product mixture with rapid removal of the glycerol formed from the reaction zone, and subjecting the product mixture to a phase separation into a fatty acid nitrile phase and glycerol/water phase.

2. The process according to claim 1, characterised by raising the temperature gradually or continuously from 20°C to 300°C during the course of the reaction.

3. The process according to claims 1 and 2, characterised by maintaining in the starting phase of the reaction a temperature level in the range of from about 220 to about 240°C until between 30 and 70 percent of the theoretical amount of glycerol is removed from the reaction, then raising the temperature over a period from about 0.5 to about 5 hours to a temperature level in the range of from about 270 to about 300°C and completing the reaction.

3. The process according to claims 1 to 3, characterised by subjecting fatty acids and fatty acid amides contained in said discharged product mixture to an after-treatment, optionally following the phase separation, in the presence of ammonia and of the catalysts as defined in claim 1.

5. The process according to claims 1 to 4, characterised by subjecting the discharged product mixture to fractionation prior to the phase separation whereby recycling fatty acids and fatty acid amides contained in said discharged product mixture into the reaction.

6. The process according to claims 1 to 4, characterised by continuing the reaction until substantially the entire amount of glycerol is discharged, combining the fatty acid nitrile phase following the phase separation with the unremoved nitrile portion and treating said combined nitriles with a flow of ammonia of from 5 to 150 liters ammonia per kilogram fatty acid nitril and hour at temperatures of from 200 to 320°C in the presence of the catalysts as defined in claim 1.

7. The process according to claims 1 to 6, characterised by carrying out the reaction in the presence of lead, cadmium, iron, cobalt and zinc salts of alkylarene-sulfonic acids wherein the alkyl radicals have 1 to 24 carbon atoms, optionally substituted with one or two carboxylic groups, as catalysts.

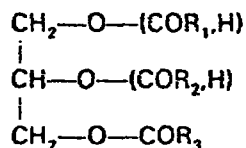




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Claims

1. A process for converting mono-, di- and triglycerides of the formula



wherein R_1 , R_2 , and R_3 , identical or different, are aliphatic hydrocarbon radicals or mono-hydroxy substituted hydrocarbon radicals having from 3 to 23 C atoms, or mixtures of said glycerides in the liquid phase with ammonia yielding fatty acid nitriles of the formula R_1 (R_2 , R_3)-N and glycerol by passing gaseous ammonia optionally in admixture with an inert gas at elevated temperatures in the presence of a catalyst, which is characterised by contacting intimately the liquid glyceride with a flow of at least 200 liters ammonia per kilogram of glyceride and hour at temperatures of from 220 to 300°C in the presence of a salt of a carboxylic or sulfonic acid and a metal selected from the group of lead, zinc, cadmium, tin, titanium, zirconium, chromium, antimony, manganese, iron, nickel, and cobalt as catalysts, discharging the resulting product mixture with rapid removal of the glycerol formed from the reaction zone, and subjecting the product mixture to a phase separation into a fatty acid nitrile phase and glycerol/water phase.

2. The process according to claim 1, characterised by raising the temperature gradually or continuously from 20°C to 300°C during the course of the reaction.

3. The process according to claims 1 and 2, characterised by maintaining in the starting phase of the reaction a temperature level in the range of from about 220 to about 240°C until between 30 and 70 percent of the theoretical amount of glycerol is removed from the reaction, then raising the temperature over a period from about 0.5 to about 5 hours to a temperature level in the range of from about 270 to about 300°C and completing the reaction.

3. The process according to claims 1 to 3, characterised by subjecting fatty acids and fatty acid amides contained in said discharged product mixture to an after-treatment, optionally following the phase separation, in the presence of ammonia and of the catalysts as defined in claim 1.

5. The process according to claims 1 to 4, characterised by subjecting the discharged product mixture to fractionation prior to the phase separation whereby recycling fatty acids and fatty acid amides contained in said discharged product mixture into the reaction.

6. The process according to claims 1 to 4, characterised by continuing the reaction until substantially the entire amount of glycerol is discharged, combining the fatty acid nitrile phase following the phase separation with the unremoved nitrile portion and treating said combined nitriles with a flow of ammonia of from 5 to 150 liters ammonia per kilogram fatty acid nitrile and hour at temperatures of from 200 to 320°C in the presence of the catalysts as defined in claim 1.

7. The process according to claims 1 to 6, characterised by carrying out the reaction in the presence of lead, cadmium, iron, cobalt and zinc salts of alkylarene-sulfonic acids wherein the alkyl radicals have 1 to 24 carbon atoms, optionally substituted with one or two carboxylic groups, as catalysts.

