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Description

This invention relates to the synthesis of esters under the influence of an activated lipase enzyme catalyst in non-aqueous media.

Many chemical reactions for the preparation of organic products are catalysed by enzymes which therefore find increasing use for this purpose on an industrial scale. Water is required to activate the enzyme from the inert and desiccated condition in which these materials are stored and marketed, often carried on an inert support such as kieselguhr which is itself highly water-absorbent. The introduction of the activated enzyme, therefore, introduces water into the reaction system to be catalysed by the enzyme. The products of many such organic reactions are however susceptible to hydrolysis which forms other products at the expense of the yield of desired product, by reversing or otherwise changing the course of the reaction. They are therefore conducted in water-immiscible, non-aqueous but not anhydrous liquid.

The tendency for the hydrolysis reactions to occur is a function of the water activity A_w of the reaction system in which the reaction takes place, rather than the "concentration" of water it contains. In a water-immiscible system with only a limited capacity for absorbing water, A_w may remain substantially at its maximum value $A_w=1$ throughout the reaction, thus promoting the production of excessive amounts of hydrolysis products, despite the low total water content.

The present invention is based on the discovery that after the catalyst is introduced, the water activity of the system may be substantially reduced to minimise hydrolysis while maintaining the catalyst in an active condition.

The water activity of the activated catalyst before adding to the reaction mixture must be greater than 0.5 preferably than 0.9. The water activity of the total reaction system must be sufficient to permit the catalyst to continue to function well and the desiccant selected accordingly, to reach an A_w giving the desired optimum combination of continued catalyst activity and reduced by-products. This A_w can be achieved by choosing the nature and amount of desiccant in accordance with its known adsorption isotherm, or by controlling the rate at which water is transferred from the gas phase, where this method is adopted, as may be estimated by conventional methods.

The water activity may be decreased in the process of the invention by a desiccant in contact with the vapour phase and the process in then carried out in a closed vessel affording a headspace, in contact with a suitable desiccant through which the gases in the vapour phase are circulated. Water vapour may also be removed by condensation using, for example, a cold insert in the vapour space and reduced pressure may be applied.

Desiccants which may be used include molecular sieves of suitable molecular dimensions to retain water vapour selectively, silica gel, alumina, magnesium sulphate and calcium chloride and these desiccants may also be used in the liquid phase. Others, e.g. sulphuric acid, may only be used in the vapour phase.

An important application of the invention is in the treatment of fats for edible or other purposes, in order to modify their physical characteristics by changing the fatty acid composition of the fat and/or their distribution in the glycerides. The use of enzymes to modify fats in this way, by interesterification with or without added free fatty acid to change the overall composition of the triglycerides of the fat, has been disclosed in our British Patent 1,577,933. In particular, fats may be upgraded to contain higher amounts of symmetrical disaturated, 2-oleyl triglycerides which are chiefly responsible for the outstanding melting performance of hard butters. By the improvement provided by the present invention these changes are accompanied with less production of undesirable hydrolysis products, in particular of partial glycerides which profoundly affect the properties of fats. The invention is also suitable for making fats for use in margarine and other emulsion food spreads.

The invention may also be used to improve the quality of natural fats by treatment to re-esterify the free fatty acid and/or partial glycerides which may be present. These impurities are usually produced by natural enzyme action on the fat, either *in vivo* or after the fat is extracted from its plant or animal source. Since each mole of free fatty acid is liberated with a corresponding equivalent of partial glyceride, the two species may be recombined to triglycerides by treatment in accordance with the invention. While there may already be present lipase enzymes, much is likely to be inactive and additional enzyme must be provided in accordance with the invention.

The process of the invention may be applied to batch or continuous operations and is preferably carried out at a temperature from 10 to 70°C, using a lipase enzyme catalyst activated with from 0.1 to 30% water by weight of the catalyst including the catalyst support which preferably comprises a diatomaceous earth, for example celite® or hydroxylapatite, titanium dioxide, alumina or silica. The lipase enzyme catalyst may be used in extracted form or it may be used in cells. It may be a free enzyme, usually water-soluble, or immobilised by binding as described.

Lipase enzyme catalysts used to effect changes in the composition of fats in the process of the invention may be selective or non-selective in action. Selective catalysts are preferentially reactive either towards the 1- and 3- or 2-positions of the glyceride molecule. They may be used in a process in which randomisation is correspondingly required in the 1- and 3-positions only, as in the production of a hard butter. The melting characteristics of these may be improved by augmenting the amount of saturated C_{16} and C_{18} fatty acid residues in the 1,3-positions of the triglycerides of a fat, while leaving unaffected

predominantly unsaturated fatty acid residues in the corresponding 2-position. For this purpose a 1,3-selective catalyst is used, e.g. *Rhizopus japonicus* lipase. Such catalysts are less effective in converting diglycerides by re-esterification to triglycerides, since they react only with 1,2(2,3)-diglycerides. There is however a relatively labile equilibrium between the 1:2-(2:3)- and 1:3-isomers, enabling continuous isomerisation to the reactive form as this is converted to the triglyceride by esterification of a 1- or 3-position under the influence of the catalyst. Moreover, 1,3-selective catalysts are preferably used in the invention when no overall isomerisation between triglycerides is required in a natural fat. Some natural fats are already random as regards their 1,3-positions and the effect of a 1,3-selective catalyst will therefore be merely to esterify any free fatty acid present, whether this is added or already present in the native fat, into the 1,3-position of glycerides. Glycerol may be added to combine with free fatty acid present to form partial glycerides where these leave the fat unaffected in the required properties. Non-selective catalysts may be used in the invention where their randomising effect on fatty acid residues in both the 1,3- and 2-positions is immaterial to the properties required. For example, the melting characteristics of lauric fats are little changed by complete randomisation.

The appropriate A_w for individual enzymes varies from one to another. Preferably, for example, *Rh. japonicus* lipase may be used below 0.3 and *Asp. niger* lipase below 0.4.

The invention is also applicable to the preparation of other esters, for example of wax esters which are esters of fatty alcohols.

Example 1

A mixture of 80 gms of palm mid-fraction with 40 gms stearic acid dissolved in 288 mls petroleum ether (BP 100 to 120°C) was selectively interesterified by stirring at 40°C in a vessel with a headspace of 900 mls, in the presence of 12.5 gms lipase-celite® catalyst previously wetted with 1.0 mls distilled water and allowed to stand 24 hours beforehand. The catalyst was prepared from *Rhizopus japonicus* lipase 2A ex Nagase and Co. Japan with an activity of 1600 lipase units/gram, in accordance with the method described in Example 2 of British patent specification No. 1,577,933, but using 1 part lipase per 5 parts celite® with 20 parts water.

The headspace gases were continuously circulated through a bed of 35 gms of $\frac{1}{8}$" pellets of molecular sieve type 4A ex BDH at 500 mls/minute to remove water vapour.

After six hours stirring was discontinued, the solvent distilled off and the product recovered and analysed for triglyceride (TG), diglyceride (DG) and free fatty acid (FFA).

The triglyceride was recovered and analysed for fatty acid residues. Water activity of the headspace was calculated from its temperature measurement and the water vapour pressure measured in the headspace by "Hydrolog" apparatus, Model No. WMY270 of Endress & Hauser. Results appear in Table III.

Comparative data was obtained by similar operations to Example 1 above, but without headspace circulation (Control A) and also with no water addition to the catalyst (Control B). The data obtained appear in Table I, all composition entries in which are by weight %. The Table includes an analysis obtained by calculation assuming 100% interesterification in the 1- and 3-positions. The water activity of Control A remained between 0.84 and 0.89 throughout.

TABLE I

Species	Feed	Product composition			
	Composition	Example 1	Control A Activated catalyst	Control B Dry catalyst	Complete interesterification (calculated)
TG	66.0	68.2	51.3	66.1	
FFA	33.3	30.6	40.0	32.3	
DG	0.7	1.2	8.7	1.7	
Fatty acyl residues in TG					
14:0	1.0	0.6	0.7	0.9	0.6
16:0	57.2	35.9	35.3	56.2	34.6
18:0	5.7	29.8	30.5	6.1	31.0
18:1	31.7	29.3	29.2	32.1	29.6
18:2	4.1	3.9	3.8	4.3	4.0
20:0	0.4	0.4	0.4	0.3	0.2

From Table I it is clear that a fatty acid composition, more nearly approximating to the theoretical than Control B, is obtained in Example 1, and with substantially less hydrolysis, in comparison with Control A, evident from the low diglyceride and FFA values.

Example 2

Partially hydrolysed palm mid-fraction was re-esterified using a lipase-celite® catalyst as used in Example 1. 10 gms of the catalyst were activated by mixture with 0.8 mls of distilled water and standing for 24 hours. The activated catalyst was then added to a solution of 100 gms of the partially hydrolysed palm mid-fraction in 200 gms of petroleum ether, BP 100 to 120°C, contained in a vessel with a headspace volume of approximately 900 mls in which the mixture was stirred for 6½ hours at 40°C while the headspace gases were continuously circulated at a rate of 650 mls/minute, through a bed of 35 gms molecular sieve type 4A. Reaction was then stopped, the composition of the reaction product determined and the fat removed. In Table II details of the composition are given, together with those of the original hydrolysed palm mid-fraction and others from comparative experiments, one using the dry catalyst without previous activation with water (Control B) and the other similarly activated catalyst but with no headspace gas circulation (Control A). The A_w of the reaction mass, measured as described in Example 1, is given in Table III. For the dry catalyst run it remained between 0.09 and 0.04.

TABLE II

	Wt %				
	TG	1,2 DG	1,3 DG	MG	FFA
Partially hydrolysed palm mid-fraction	76.8	13.1	1.0	ND	9.1
Example 2	87.6	4.3	3.4	ND	4.7
Control A	65.3	——17.9——		1.5	15.4
Control B	80.7	9.9	2.2	ND	7.2

With the activated catalyst extensive re-esterification is shown between the diglyceride and free fatty acid present, with the formation of triglyceride. With the dry catalyst only limited re-esterification is observed, with only a marginal increase in the amount of triglyceride present.

TABLE III
Water activity

Example	Time (hours) 0.5	1.0	2.0	3.0	4.0	5.0	6.0
1	0.53	0.33	0.17	0.15	0.11	0.08	0.07
2	0.50	0.35	0.24	—	0.13	—	0.05

Example 3

75 gms of palm mid-fraction was interesterified with half its weight of stearic acid in solution in 140 mls of hexane to which was added 7.5 gms of celite®-(Aspergillus Niger lipase ex Amano Pharmaceuticals, Japan) (AP6) lipase enzyme catalyst, previously moistened with 10% its weight of water and stood overnight. The catalyst was prepared as described in Example 2 of British patent specification No. 1,577,933 and the enzyme had the same activity as already given above. The reaction mixture also contained 12 gms of silica gel of 4 to 6 BSS mesh size that had been previously dried overnight at 105°C, and was stirred at 40°C for 24 hours.

The course of the reaction was followed by measuring the free fatty acid and stearate content in the triglycerides of samples recovered at intervals from the reaction mixture, the initial free fatty acid content being 1.17 Mmoles/gm. The stearate content of the triglycerides was obtained by measuring the C_{52} and C_{54} contents of the triglycerides by GLC and, using a calibration curve for stearate content calculated from fatty acid methyl determination (FAME), determined on a separate interesterification reaction. The initial stearate content was 6.1%.

The analytical results are reported in Table IV, together with those from control experiments in one of which the catalyst was activated as before but no silica gel with added to the reaction mass (Control A). In the other (Control B) silica gel was moistened instead of the catalyst with the same amount of water as before. Water activities of silica gel samples were determined at 20°C using a SINA Equihygroscope. In Example 3 initial water activity of the silica gel was 0.18; after reaction 0.28 and in Control B 0.35 and 0.34 respectively. Initial water activity of the catalyst in Example 3 was >0.95. Water solubility in the hexane solution of fat was 0.06% w/v, determined by a micro Karl Fischer method using an "Aquatest" apparatus.

TABLE IV

	Example 3	Control A	Control B
Stearate % in triglyceride after 500 min.	19.0	20.6	10.7
Stearate % in triglyceride after 24 hr.	24.9	25.4	17.8
Increase in FFA (Mmole/g) after 500 min	0.14	0.22	0.13
after 24 hr.	0.16	0.27	0.15

Table IV shows that whereas in Example 3 virtually no more free fatty acid is generated than with the relatively inactive dry catalyst and substantially less than that using the activated catalyst without the silica gel to reduce the water activity as shown in the Table, almost as much stearate is produced in the Example as in the absence of A_w control using the active catalyst.

Example 4

A solution of 100 gms of palm oil in 200 gms of petroleum ether of BP 100 to 120°C was stirred in a vessel with a headspace volume of approximately 900 mls, in contact with 10 gms of a lipase-celite® catalyst prepared as described in Example 1 above from *R. japonicus* lipase and a mixture of 1 ml of water and 0.5 mls of glycerine with which the catalyst had been activated by standing for 24 hours beforehand at 20°C. The mixture was maintained in the vessel at 40°C while the headspace gases were continuously circulated at a rate of 650 mls/minute, through a bed of 35 gms of molecular sieve type 4A. After 24 hours reaction was stopped, the solvent removed and the palm oil recovered and analysed. Further data appearing in Table V includes an analysis of product from the palm oil treated with active catalyst as in Example IV but with no headspace gas circulation.

TABLE V

	TG	FFA	DG	MG
Original palm oil	92.3	2.7	5.0	ND
Esterified palm oil Example IV	89.1	0.7	10.2	ND
Control	67.5	14.2	18.3	1.5

It will be seen that as a result of the reaction in Example 4 most of the free fatty acid present in the original oil is esterified during the reaction to yield predominantly additional diglyceride. No monoglycerides were detected either in the original palm oil or in the esterified product of Example 4, but in the Control a significant amount was produced.

Example 5

This Example illustrates the effect of the invention on the preparation of oleyl ricinoleate. 0.25 g celite® lipase catalyst prepared as in Example 1 was hydrated by mixing with 0.025 ml water and standing overnight, to give an A_w of greater than 0.95. 0.5 g oleyl alcohol and 0.56 g castor oil fatty acids were dissolved in hexane to give 5 ml solution. The hydrated lipase catalyst was added, immediately followed by 1.2 g silica gel M.F.C. grade ex Hopkin & Williams that had been dried overnight at 105°C. It may be calculated that this silica gel would take up water present on the catalyst so as to reduce A_w below 0.6. This reaction mixture was stirred at 40°C for 2 hrs, then a sample of the organic phase removed for analysis. For comparison, two similar reactions were carried out: omitting the silica gel (Control A); and using unhydrated catalyst and no silica gel (Control B).

The products were analysed. No ricinoleate polymers were detected in any sample. In addition to unchanged reactants the samples contained oleyl ricinoleates: 76.2% in the example and 41.2% (Control A) and 7.7% (Control B).

Claims

1. Process for the synthesis of esters under the influence of an activated lipase enzyme catalyst, characterised by the combination of first activating a supported lipase enzyme by contact with water, to a water activity greater than 0.5, then without drying the catalyst, contacting a water-immiscible organic liquid comprising hydroxyl and fatty acid residues with the catalyst, in the presence of desiccant means to reduce the water activity of the resulting composition, and recovering esters therefrom.

2. Process according to Claim 1 wherein the organic liquid comprises a glyceride oil or fat or product thereof.

3. Process according to Claim 1 or 2, wherein free fatty acid is present in the composition.

4. Process according to any of the preceding claims wherein the lipase support comprises diatomaceous earth or hydroxylapatite, titanium dioxide, alumina or silica.

5. Process according to any of the preceding Claims wherein the composition comprises a dispersion in a hydrocarbon.

6. Process as claimed in any preceding claim, wherein the enzyme comprises *Aspergillus niger* lipase and the water activity is reduced to less than 0.4.

7. Process as claimed in any of the preceding Claim 1 to 5 wherein the enzyme comprises *Rhizopus japonicus* lipase and the water activity is reduced to less than 0.3.

8. Process according to any of the preceding Claims wherein the enzyme is activated with from 1.1 to 30% water by weight of the catalyst, including any catalyst support.

9. Process according to any of the preceding Claims wherein the desiccant means comprises a molecular sieve, silica gel, alumina, magnesium sulphate or calcium chloride.

10. Process according to Claim 9 wherein the desiccant is in contact with the vapour phase of the composition.

11. Process according to any of the preceding claims which is carried out at a temperature from 10 to 70°C.

Patentansprüche

1. Verfahren zur Synthese von Estern unter Einwirkung eines aktivierten Lipaseenzymkatalysators, dadurch gekennzeichnet, daß in Kombination zunächst ein sich auf einem Träger befindendes Lipaseenzym durch Kontakt mit Wasser auf eine Wasseraktivität von mehr als 0,5 aktiviert wird, dann, ohne Trocknen des Katalysators, eine mit Wasser unmischbare organische Flüssigkeit, die Hydroxyl- und Fettsäurereste enthält, mit dem Katalysator in Gegenwart eines Trocknungsmittels in Kontakt gebracht

* C L M S *

TABLE V

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The products were analysed. No ricinoleate polymers were detected in any sample. In addition to unchanged reactants the samples contained oleyl ricinoleates: 76.2% in the example and 41.2% (Control A) and 7.7% (Control B).

Claims

1. Process for the synthesis of esters under the influence of an activated lipase enzyme catalyst, characterised by the combination of first activating a supported lipase enzyme by contact with water, to a water activity greater than 0.5, then without drying the catalyst, contacting a water-immiscible organic liquid comprising hydroxyl and fatty acid residues with the catalyst, in the presence of desiccant means to reduce the water activity of the resulting composition, and recovering esters therefrom.

2. Process according to Claim 1 wherein the organic liquid comprises a glyceride oil or fat or product thereof.

3. Process according to Claim 1 or 2, wherein free fatty acid is present in the composition.

4. Process according to any of the preceding claims wherein the lipase support comprises diatomaceous earth or hydroxylapatite, titanium dioxide, alumina or silica.

5. Process according to any of the preceding Claims wherein the composition comprises a dispersion in a hydrocarbon.

6. Process as claimed in any preceding claim, wherein the enzyme comprises *Aspergillus niger* lipase and the water activity is reduced to less than 0.4.

7. Process as claimed in any of the preceding Claim 1 to 5 wherein the enzyme comprises *Rhizopus japonicus* lipase and the water activity is reduced to less than 0.3.

8. Process according to any of the preceding Claims wherein the enzyme is activated with from 1.1 to 30% water by weight of the catalyst, including any catalyst support.

9. Process according to any of the preceding Claims wherein the desiccant means comprises a molecular sieve, silica gel, alumina, magnesium sulphate or calcium chloride.

10. Process according to Claim 9 wherein the desiccant is in contact with the vapour phase of the composition.

11. Process according to any of the preceding claims which is carried out at a temperature from 10 to 70°C.

Patentansprüche

1. Verfahren zur Synthese von Estern unter Einwirkung eines aktivierten Lipaseenzymkatalysators, dadurch gekennzeichnet, daß in Kombination zunächst ein sich auf einem Träger befindendes Lipaseenzym durch Kontakt mit Wasser auf eine Wasseraktivität von mehr als 0,5 aktiviert wird, dann, ohne Trocknen des Katalysators, eine mit Wasser unmischbare organische Flüssigkeit, die Hydroxyl- und Fettsäurereste enthält, mit dem Katalysator in Gegenwart eines Trocknungsmittels in Kontakt gebracht

wird, um die Wasseraktivität der anfallenden Zusammensetzung herabzusetzen, und hieraus Ester gewonnen werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die organische Flüssigkeit ein Glyceridöl oder -fett oder ein Produkt davon enthält.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß freie Fettsäure in der Zusammensetzung vorliegt.

4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Lipaseträger Diatomeenerde oder Hydroxylapatit, Titandioxid, Aluminiumoxid oder Siliciumdioxid enthält.

5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Zusammensetzung eine Dispersion in einem Kohlenwasserstoff enthält.

6. Verfahren nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Enzym *Aspergillus niger*-Lipase enthält und die Wasseraktivität auf weniger als 0,4 herabgesetzt wird.

7. Verfahren nach irgendeinem der vorhergehenden Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Enzym *Rhizopus japonicus*-Lipase enthält und die Wasseraktivität auf weniger als 0,3 herabgesetzt wird.

8. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Enzym mit 1,1 bis 30% Wasser, bezogen auf das Gewicht des Katalysators, einschließlich des gesamten Katalysatorträgers, aktiviert wird.

9. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Trocknungsmittel ein Molekularsieb, Silicagel, Aluminiumoxid, Magnesiumsulfat oder Calciumchlorid enthält.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Trocknungsmittel mit der Dampfphase der Zusammensetzung in Kontakt steht.

11. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es bei einer Temperatur von 10 bis 70°C durchgeführt wird.

Revendications

1. Procédé de synthèse d'esters sous l'influence d'un catalyseur enzymatique de type lipase activée, caractérisé par la combinaison, en premier lieu, de l'activation d'une enzyme de type lipase supportée au contact de l'eau, jusqu'à une activité d'eau supérieure à 0,5, puis, sans sécher le catalyseur, de la mise en contact d'un liquide organique non miscible à l'eau comprenant des restes hydroxyle et acide gras avec le catalyseur, en présence d'un dispositif desséchant pour réduire l'activité d'eau de la composition résultante, et de la récupération des esters dans cette composition.

2. Procédé selon la revendication 1, dans lequel le liquide organique comprend une huile ou graisse de type glycéride ou un de ses produits.

3. Procédé selon la revendication 1 ou 2, dans lequel un acide gras libre est présent dans la composition.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le support de la lipase comprend de la diatomite ou de l'hydroxylapatite, du bioxyde de titane, de l'alumine ou de la silice.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition comprend une dispersion dans un hydrocarbure.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'enzyme comprend la lipase de Aspergillus niger et l'activité d'eau est réduite à moins de 0,4.

7. Procédé selon l'une quelconque des revendications 1 à 5 précédentes, dans lequel l'enzyme comprend la lipase de *Rhizopus japonicus* et l'activité d'eau est réduite à moins de 0,3.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'enzyme est activée avec de 1,1 à 30% d'eau en poids du catalyseur, y compris tout support de catalyseur.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le dispositif desséchant comprend un tamis moléculaire, du gel de silice, de l'alumine, du sulfate de magnésium ou du chlorure de calcium.

10. Procédé selon la revendication 9, dans lequel le desséchant est en contact avec la phase vapeur de la composition.

11. Procédé selon l'une quelconque des revendications précédentes, réalisé à une température de 10 à 70°C.