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(54) Process for the selective hydrogenation of fatty acid derivatives and selectively hydrogenated fatty acid derivatives.

(57) A process for selectively hydrogenating a fatty acid derivative, such as a triglyceride fat or oil, having fatty acid moieties containing more than two double bonds as well as fatty acid moieties containing two double bonds comprises catalytic hydrogenation in the presence of at least 1.8 mol of ammonia per litre of fatty acid derivative. The high level of ammonia present allows increased selectivity to occur such that the fatty acid moieties containing more than two double bonds are highly selectively hydrogenated to moieties containing a two double bonds. Depending on the catalyst and derivative employed S_{II} values of at least 10 and trans-isomerisation of less than 5 mol% can be derived.

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PROCESS FOR THE SELECTIVE HYDROGENATION OF FATTY ACID DERIVATIVES AND SELECTIVELY HYDROGENATED FATTY ACID DERIVATIVES

The present invention relates to a process for the selective hydrogenation of unsaturated fatty acid derivatives. In particular the present invention relates to a process for the selective hydrogenation of fatty acid derivatives containing, in addition to fatty acids having two double bonds, fatty acids having more than two double bonds.

An area of major commercial importance in which such fatty acid derivatives occur is that of fats and oils which consist mainly of a mixture of triglyceride esters of fatty acids. The fatty acids usually contain about 16 to about 22 carbon atoms and may be saturated, e.g. stearic acid; mono-unsaturated, e.g. oleic acid; di-unsaturated, e.g. linoleic acid; or tri-unsaturated, e.g. linolenic acid or may even be unsaturated to a greater degree.

In the field of technology relating to oils and fats it is common to hydrogenate oils in order to remove at least partly the unsaturation present so as to obtain hydrogenated oil having the desired properties, such as a higher melting point and/or increased stability.

During the hydrogenation a number of reactions take place, both successively and simultaneously. For

example, in the hydrogenation of an oil containing linolenic acid, the hydrogenation reactions can be represented by the following simplified scheme:

linolenic acid $\xrightarrow{K_1}$ linoleic acid $\xrightarrow{K_2}$ oleic acid $\xrightarrow{K_3}$ stearic acid,

the rate constants of the reactions being indicated by K_1, K_2, etc. In addition side reactions occur, such as displacement and isomerisation of double bonds. Isomerisation gives rise to the conversion of cis-double bonds into trans-double bonds, the corresponding oils containing the trans-acids usually having a higher melting point. Oils and fats which have a high content of stearic acid have a melting point that for most applications is too high to be organoleptically acceptable. Formerly it was therefore usual to direct the hydrogenation in such a way that as little stearic acid was formed as possible, but that a high content of trans-oleic acid was still obtained, so that the oil had the desired melting point. Nowadays it is considered less desirable to apply cis-trans isomerisation since there is a preference for liquid, though stable, oils, which can be used as such or can serve as an ingredient for soft margarines which can be stored in the refrigerator.

The selectivity values of the hydrogenation reactions are usually defined as follows:

$$S_I = \frac{K_2}{K_3} \qquad S_{II} = \frac{K_1}{K_2}$$

When the S_I value of the reaction is high, small amounts of saturated acids are obtained. With a high S_{II} value it is possible to hydrogenate linolenic acid

and still retain a high percentage of the essential fatty acid linoleic acid. An isomerisation-selectivity value, abbreviated to S_i, indicates the amount of trans-isomers formed in relation to the degree of hydrogenation. As has alrady been observed, it is now desirable that the hydrogenation be influenced in such a way that the S_i value is as low as possible.

The selection of catalysts with which to perform the hydrogenation reaction can thus be important in order to ensure as far as possible that the desired hydrogenation reaction preferentially occurs and that only a minimum of isomerisation takes place.

A catalytic process which aims to hydrogenate selectively fatty acid derivatives containing more than two double bonds with a minimum of isomerisation is disclosed in European Patent Application No. 0 021 528. In EP-A-0021528 the selective hydrogenation of triglyceride oils such as soya bean oil, rapeseed oil, linseed oil and fish oils is described in which fatty acids having more than two double bonds are reduced to fatty acids having two double bonds in the presence of other fatty acids having two double bonds, so-called essential fatty acids, whose content in the oil remains high. In addition isomerisation to the trans form of naturally occurring fatty acids having cis-double bonds is relatively low, so that stable liquid oils can be obtained which can be used as such or can be used in margarines that remain soft at refrigerator temperatures. A selectivity S_{II} of at most about 10 is claimed for the process described in EP-A-0021528, which comprises hydrogenating at a temperature of from -20°C to 100°C in the presence of a catalyst comprising palladium, platinum, rhodium or iridium which has been treated with dry ammonia in a molar ratio of ammonia to catalytically active metal of at least 100:1. It is stated that with increasing levels of ammonia treatment the selectivity achieved in hydrogenation

decreases and that when the mole ratios of ammonia to catalytically active metal are higher than 2000:1 no further increase in selectivity is achieved.

According to a first aspect of the present invention there is provided a process for the selective hydrogenation of unsaturated fatty acid derivatives having fatty acid moieties containing more than two double bonds and fatty acid moieties containing two double bonds, the process comprising catalytic hydrogenation at a temperature of from -20°C to 100°C in the presence of ammonia and a catalyst comprising at least one member selected from the group consisting of palladium, platinum, iridium and rhodium characteristed in that ammonia is present at a level of at least 1.8 mol/l with respect to the said fatty acid derivative.

It is to be understood that the present invention extends to the fatty acid derivatives so hydrogenated and to products incorporating the separated hydrogenated fatty acid derivatives.

We have now discovered that as the amount of ammonia is increased above the maximum level described in EP-A-0021528 the selectivity S_{II} value continues to rise.

The actual S_{II} value achieved in a particular case depends on the fatty acid derivative, the catalyst and the reaction conditions employed. Employing for example a palladium catalyst we have found however that S_{II} values of above about 10 can usually be achieved. In some instances even S_{II} values of more than 14 have been found at an ammonia concentration of 4 mol/l with respect to the fatty acid derivative. The selectivity of platinum as a catalyst is in general known to be less than that of palladium. However by means of the present process the S_{II} value is nonetheless increased even when platinum is employed. We have also found that the amount of ammonia when calculated with respect to the amount of fatty acid derivative present gives a better correlation with

selectivity S_{II}, than when measured with respect to the amount of catalyst present.

The present invention can thus provide a process that is easy to perform and that employs as a raw material dry ammonia which is not only readily available and relatively cheap, but which can also be removed readily from the hydrogenated fatty acid derivative.

As in the process described in EP-A-0021528 the present process can reduce the formation of trans-isomers to a low level. Unlike the process described in EP-A-0021528 however the present process can in addition give further increases in S_{II} values.

According to a second aspect of the present invention there is provided a fatty acid derivative which has been prepared by hydrogenation characterised in that the fatty acid derivative has an S_{II} value (as hereinbefore defined) of at least 10.

Preferably the fatty acid derivative has in addition a trans isomerisation content of less than 10 mol %. The actual amount will depend on the catalyst, the derivative and the reaction conditions employed. For example where the fatty acid derivative contains a high percentage of fatty acid moieties having more than two double bonds such as for instance in linseed oil the opportunity for trans-isomerisation to occur is greater and greater isomerisation may occur. Preferably however the fatty acid derivative has a trans-isomerisation content of less than 5 mol %. Moreover the fatty acid derivative preferably has a S_{II} value of at least 14 to 15.

In carrying out the present process the amount of ammonia present is preferably at least 2.5 mol/l with respect to the fatty acid derivative employed. A preferred upper limit for the ammonia concentration is 8 mol/l with respect to the fatty acid derivative employed. More preferably not more than 4 mol/l is employed.

As catalytically active metals, of which Pd and Pt are preferred, alloys of these metals can alternatively be used. Such catalytically active metals can contain so-called promotors, i.e. metals promoting the effect of the catalyst as far as its activity and/or selectivity are concerned, such as Cu, Ag, Au, Zn, Sn, Zr, Hf, V, Nb, Ta, Cr, Mo, W or Mn.

The catalyst can be used in the form of a porous metal, preferably in the form of small particles suspended in the system, such as palladium powder or a metal sol, obtained by reduction of a soluble compound of the metal with a reducing organo-metal compound. The metallic constituent can alternatively be supplied on a carrier. Suitable carriers for the catalyst include carbon, silicon oxide, aluminium oxide, kieselguhr and an ion-exchanging resin.

The amount of catalytically active metal which is employed in the hydrogenation, is not critical and may vary from about 1 mg/kg to about 10 g/kg, preferably from 35 mg/kg to 1g/kg, calculated on the basis of the metal catalyst with respect to the compound to be hydrogenated. The optimum amount depends inter alia on the form of the catalyst, whether the catalyst has been applied on a carrier or not, on the unsupported surface area of the catalyst, on the catalytic activity of the metal that is used and on the amount of ammonia that is to be added.

Conversely the activity, selectivity and the formation of trans-isomers that are effected in the hydrogenation with the addition of a certain amount of ammonia will depend on the amount and the type of catalyst. In addition the quality of the fatty acid derivative and any prior treatment it may have had can influence the hydrogenation characteristics of the various amounts of ammonia added.

In carrying out a process embodying the present invention, the compound to be hydrogenated can

be dissolved or dispersed in an organic liquid such as hydrocarbon, for instance hexane, or a ketone. Good results can alternatively be obtained with alcohols, but in that case alcoholysis or in the case of oils and fats interesterification may take place; consequently, when alcoholysis or interesterification is desired, alcohols can be used.

The ratio of organic liquid to fatty acid derivative is not critical but is preferably not higher than about 20:1. The hydrogenation can alternatively be carried out on the fatty acid derivative in the absence of an added solvent or the like.

In general the hydrogenation can be carried out in any suitable apparatus such as a reaction vessel with a stirrer, or when done continuously in a series of reaction vessels with stirrers. Good results can also be obtained when hydrogenation takes place over a column of catalyst particles.

Preferably the process is performed so that the catalyst is pre-treated with dry ammonia before hydrogenation commences. If desired liquid ammonia can be employed. Preferably however the hydrogenation is carried out by suspending the catalyst in the fatty acid derivative to be hydrogenated or a solution or suspension thereof and subsequently introducing dry ammonia, optionally under pressure, until the desired ammonia concentration has been reached, after which the hydrogenation is started by introducing hydrogen. If desired, the hydrogen supplied can contain still more ammonia.

The temperature at which the hydrogenation is carried out should not exceed 100°C. Good results with active catalysts can be obtained at temperatures from -20°C. Preferably hydrogenation is arranged to take place at a temperature of from 10°C to 60°C.

The reaction can be carried out under atmospheric

pressure or at a higher pressure. Preferably the pressure will vary from 100 to 2500 kPa. Naturally, if it is desired to work at a temperature above the boiling point of any liquid employed, a pressure above atmospheric pressure should be applied.

The process can be controlled in a known manner, for example by stopping the hydrogenation when a previously calculated amount of hydrogen has been absorbed. Catalyst and ammonia removal can be performed in a conventional manner.

Examples of fatty acid derivatives that can be hydrogenated by means of the present process include: triglyceride fats and oils such as soya bean oil, rapeseed oil, linseed oil, fish oils, tallow and similar animal fats, palm oil; fatty acid esters, such as the methyl-, ethyl- and other alkyl esters; soaps; and alcohols.

The hydrogenated products can be used as frying oils, table oils, as raw material for margarine or as raw material for the preparation of stable products such as soaps, esters, etc. Conventional techniques can be employed for their preparation.

Embodiments of the present invention will now be described by way of example only with reference to the following worked Examples.

In some of the Examples the sum of the amount of components is less than 100%, as less important fatty acid components such as C_{14-}, C_{17-}, C_{20-} and C_{22} fatty acids have not been mentioned. The composition of the substrates before and after hydrogenation is given in mol.%. Other percentages have been calculated by weight.

In the Tables the fatty acids have been indicated by the number of carbon atoms present therein and the number of double bonds, i.e. C18:3 means linolenic acid and isomers, C18:2 linoleic acid and isomers, etc.

EXAMPLE 1

Hydrogenations were carried out in an autoclave with a volume of 1 dm^3 and provided with a heating coil, through which thermostated water could be passed, a stirrer, an inlet for gases, a device for taking samples and a manometer.

In the autoclave soya bean oil was hydrogenated at a temperature of 25°C and under a pressure up to 1200 kPa, the partial pressure of hydrogen of which amounted to 200 kPa. In each experiment the autoclave was charged with 100 mg of palladium per kg of oil of a 5% Pd/C (5% of palladium on a carbon carrier) catalyst, 250 ml of soya bean oil and 250 ml of hexane. The reactor was degassed several times, flushed with argon and charged with different amounts of ammoniacal gas (see column I of Table I). Thereafter the reactor was charge with hydrogen and at intervals hydrogen was introduced to bring the pressure to 1200 kPa. The course of the hydrogenation was followed on the basis of the intake of hydrogen as indicated by the manometer. At certain intervals samples were taken to determine the fatty acid composition and the trans-isomer content as indicated in Table I.

TABLE I

AMOUNT OF AMMONIA ADDED (MMOL)	NH_3 ON OIL (MOL/L)	HYDROGENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%) C16:0	C18:0	C18:1	C18:2	C18:3	TRANS (MOL%)	S II
		Starting Oil	10.6	4.0	23.0	53.0	7.0	<1	
500	2.0	85	10.6	4.0	30.3	51.6	2.0	5	10.3
600	2.4	86	10.6	4.0	30.0	51.9	2.0	6	10.9
700	2.8	102	10.6	4.0	29.6	52.3	2.0	5	11.7
775	3.1	82	10.6	4.0	29.5	52.5	2.0	5	12.1
875	3.5	111	10.6	4.0	28.9	53.0	2.0	5	13.4
975	3.9	147	10.6	4.0	28.5	53.4	2.0	5	14.6

EXAMPLE 2

The procedure of Example 1 was repeated, during which 975 mmol of ammonia were added and the partial pressure of hydrogen was increased to 1300 kPa.

The results are given in Table II.

TABLE II

HYDROGEN PRESSURE (kPa)	NH_3 ON OIL (MOL/L)	HYDRO-GENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%) C16:0	C18:0	C18:1	C18:2	C18:3	TRANS (MOL%)	S II
		Starting Oil	10.6	4.0	28.0	53.0	7.0	<1	
200	3.9	147	10.6	4.0	28.5	53.4	2.0	5	14.6
1300	3.9	103	10.6	4.1	29.2	52.5	2.0	5	12.1

EXAMPLE 3

Linseed oil was hydrogenated according to the procedure described in Example I, but at a temperature of 25°C and under a pressure of 1050 kPa. The autoclave was charged with 200 mg palladium per kg of oil as a 5% Pd/C catalyst, 250 ml linseed oil and 250 ml hexane.

The added ammonia amounted 975 mmol.

The results are given in Table III.

TABLE III

HYDROGENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%) C16:0	C18:0	C18:1	C18:2	C18:3	TRANS (MOL%)	S_{II}
Starting oil	6.0	4.6	13.5	14.8	53.8	<1	
420	6.0	4.3	30.4	54.6	2.0	24	13.1

The relatively high trans-isomerisation content arises from the high C18:3 content in unhydrogenated linseed oil.

EXAMPLE 4

The procedure of Example I was repeated with the exception that platinum was used as the catalyst. The temperature employed was 35°C and the pressure was 900 kPa. The autoclave was charged with 150 mg platinum per kg of oil as a 5% Pt/C catalyst and 500 ml soyabean oil. No organic liquid was added.

The added ammonia amounted to 1050 mmol.

The results are given in Table IV.

TABLE IV

HYDROGENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%) C16:0	C18:0	C18:1	C18:2	C18:3	TRANS (mol%)	S_{II}
Starting oil	10.6	4.0	24.0	53.0	7.0	<1	
144	10.6	5.4	34.3	45.8	2.0	2	5.1

The relatively low S_{II} value is due to the use of a Pt cata lyst. The S_{II} value obtained is however substantially higher than that obtained in a similar experiment in which a lower amount of ammonia was employed.

As a comparative example, Example 7 from EP-A-0021528 is reproduced below.

The hydrogenation of soyabean oil was carried out at a pressure of up to 1000 kPa using platinum as a catalyst at 20°C in an autoclave of 0.3 dm^3 volume, which was provided with an inlet for gases, a manometer, a stirrer and a sampling device.

The reactor was charged with 200 mg of a 5% platinum-on-carbon catalyst, 25 ml soyabean oil and 75 ml hexane. The autoclave was degassed two or three times, flushed with nitrogen and charged with gaseous ammonia.

The reactor was subsequently charged with hydrogen. The progress of the hydrogenation was followed on the basis of the hydrogen uptake as indicated by the manometer. At regular intervals samples were taken to determine the fatty acid composition and the transisomer content. The results are given in Table IVa.

TABLE IVa

AMOUNT OF AMMONIA ADDED (MMOL.)	HYDROGENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%) C16:0	C18:0	C18:1	C18:2	C18:3	TRANS (MOL%)
	Starting Oil	10.7	4.0	25.3	53.1	6.7	<1
	(45	10.7	5.3	31.7	48.1	4.1	<1
70	(90	10.6	6.1	37.9	43.1	2.2	<1
	(130	10.7	7.6	45.8	39.9	0.9	<1

EXAMPLE 5

Soya bean oil was hydrogenated to a C18:3 content of 1% to obtain an oil with good frying properties. The hydrogenation was performed by a procedure similar to that described in Example 1, but at a temperature of 35°C and under a pressure of 1050 kPa. An autoclave with a volume of 2 dm^3 was charged with 75 mg palladium per kg of oil at a 5% Pd/C catalyst and 1000 ml soya bean oil. No organic liquid was added.

The added ammonia amounted to 1800 mmol.

The results are given in Table V.

TABLE V

HYDROGENATION TIME (MIN)	FATTY ACID COMPOSITION (MOL%)					TRANS (MOL%)	S_{II}
	C16:0	C18:0	C18:1	C18:2	C18:3		
Starting oil	10.6	4.0	24.0	53.0	7.0	<1	
107	10.6	4.0	32.9	50.1	1.03	9	11.3

CLAIMS:

1. A process for the selective hydrogenation of unsaturated fatty acid derivatives containing both fatty acid moieties having more than two double bonds and fatty acid moieties having two double bonds, the process comprising catalytic hydrogenation at a temperature of from -20°C to 100°C in the presence of ammonia and a catalyst comprising at least one member selected from the group consisting of palladium, platinum, iridium and rhodium characterised in that ammonia is present at a level of at least 1.8 mol/l with respect to the said fatty acid derivative.

2. A process according to claim 1 wherein the ammonia is present at a level of at least 2.5 mol/l with respect to the fatty acid derivative.

3. A process according to claim 1 or claim 2 wherein the ammonia is present at a level of not more than 8 mol/l with respect to the fatty acid derivative.

4. A process according to claim 3 wherein the ammonia is present at a level of not more than 4 mol/l with respect to the fatty acid derivative.

5. A process according to any one of the preceding claims wherein the catalyst is pretreated with ammonia prior to the commencement of the hydrogenation reaction.

6. A process according to any one of the preceding claims wherein the fatty acid derivative is hydrogenated whilst dissolved or dispersed in an organic liquid.

7. A process according to any one of the preceding claims wherein hydrogenation takes place at a temperature of from 10°C to 60°C.

8. A process according to any one of the preceding claims wherein ammonia is introduced into a suspension of the catalyst in the fatty acid derivative, or a solution or suspension thereof, and subsequently hydrogen is introduced.

9. A process according to claim 8 wherein further ammonia is introduced during the hydrogenation.

10. A process according to any one of the preceding claims wherein the said fatty acid derivative is an edible triglyceride oil.

11. A process according to any one of the preceding claims including separating the fatty acid derivative from the reaction mixture.

12. A fatty acid derivative prepared according to the process of claim 11.

13. A fatty acid derivative prepared by hydrogenation characterised in that the fatty acid derivative has an S_{II} value (as herein defined) of at least 10.

14. A fatty acid derivative according to claim 13 having an S_{II} value of at least 14.

15. A fatty acid derivative according to claim 13 or claim 14 having a trans-isomerisation content of less than 10 mol %.

16. A fatty acid derivative according to any one of claims 12 to 15 wherein the fatty acid derivative is an edible triglyceride fat or oil.

17. Foodstuff incorporating an edible triglyceride fat or oil according to claim 16.