(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 126 168**
B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **17.12.86**

(51) Int. Cl.^{4}: **C 11 C 3/12**

(21) Application number: **83104898.8**

(22) Date of filing: **18.05.83**

(54) Continuous selective reduction of edible oils and fats.

(43) Date of publication of application:
28.11.84 Bulletin 84/48

(45) Publication of the grant of the patent:
17.12.86 Bulletin 86/51

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(58) References cited:
FR-A-2 006 356
FR-A-2 175 223
US-A-3 565 830

(73) Proprietor: **UOP Inc.**
10 UOP Plaza Algonquin & Mt. Prospect Roads
Des Plaines Illinois 60016 (US)

(72) Inventor: **Rosen, Bruce Irvin**
10116 Old Orchard Court
Skokie Illinois 60076 (US)

(74) Representative: **Weber, Dieter, Dr. et al**
Dr. Dieter Weber und Klaus Seiffert
Patentanwälte Gustav-Freytag-Strasse 25
Postfach 6145
D-6200 Wiesbaden 1 (DE)

EP 0 126 168 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

Description

Background of the Invention

Although some edible oils are used per se, by far the largest portion are hydrogenated, or hardened, prior to their end use. The reason for such hydrogenation is to increase the stability of the final product. For example, processed soybean oil is susceptible to oxidation resulting in deterioration of its organoleptic properties upon storage even at ambient temperature. Where the oil is to be used at higher temperatures, for example, as a frying oil, the adverse organoleptic consequences of oxidation become even more pronounced.

The commonly accepted origin of oxidative deterioration is the presence of highly unsaturated components, such as the triene moiety, linolenate, in soybean oil. Partial hydrogenation to remove most of this component leads to a marked increase in the oxidative stability of the resulting product, thereby facilitating storage and permitting unobjectionable use at higher temperatures. Ideally, one desires this hydrogenation to be highly specific, reducing only triene to the diene, linoleate, without effecting cis to trans isomerization. In practice, this goal is unachievable.

The fats and oils which are the subject of this invention, hereinafter collectively referred to as fatty materials, are triglycerides of fatty acids, some of which are saturated and some of which are unsaturated. In vegetable oils, the major saturated fatty acids are lauric (12:0), myristic (14:0), palmitic (16:0), stearic (18:0), arachidic (20:0), and behenic (22:0) acids. The notation, "18:0", for example, means an unbranched fatty acid containing 18 carbon atoms and 0 double bonds. The major unsaturated fatty acids of vegetable oils may be classified as monounsaturated, chief of which are oleic (18:1) and erucic (22:1) acids, and polyunsaturated, chief of which are the diene, linoleic acid (18:2) and the triene, linolenic acid (18:3). Unhardened vegetable fats and oils contain virtually exclusively cis-unsaturated acids.

In the context of partial hydrogenation, the ultimate goal is the reduction of triene to diene without attendant trans acid formation or saturate formation. In practice, it is observed that partial reduction results in lowering both triene and diene and increasing the monoene, saturate, and trans levels. Because it is desired that the product of partial hydrogenation itself be a liquid oil relatively free of sediment or even cloudiness upon storage at, for example, 10°C, the formation of saturated and trans acids in such hydrogenation is a vexing problem. Removal of these solids, whose relative amount is measured by the Solid Fat Index (SFI), is a relatively costly and inefficient process attended by large losses associated with the separation of gelatinous solids from a viscous liquid. It is known in the art that such solids are composed largely of triglycerides containing at least one saturated fatty acid moiety and/or trans monounsaturated fatty acid moiety with the predominant culprits having at least 18 carbon atoms. It is further known in the art that fatty acid analysis alone may be an insensitive analytical tool, that is to say, two products of hydrogenation of, for example, soybean oil may show different SFI profiles while having virtually identical fatty acid analysis. This arises because the distribution of the saturated moieties in the triglyceride is important. The solubility in the soybean oil of disaturated triglycerides is much less than twice the amount of monounsaturated triglycerides, and the solubility of monounsaturated triglycerides may depend upon whether the other fatty acid moieties of the triclyceride are monounsaturated, diunsaturated, etc., and may also depend upon whether the saturated portion is at the one-or two-position of the triglyceride. Hence, hydrogenation of edible fats and oils is largely an empirical process, whose analytical tools include Solid Fat Index (SFI) supported by fatty acid analysis. The difficulty of achieving desirable results, in the context of selectivity in Solid Fat Index, has largely limited such hydrogenation to a batch type process. Although the transition from a batch to a continuous process, especially of the fixed bed type, is conceptually facile, it will be recognized by the skilled worker that impediments have been substantial.

FR—A—2,175,223 discloses a continuous process for hydrogenating fatty acids by contacting them at a pressure of 6,9 to 69 bars and at a temperature of 93 to 232°C with a fixed mass of catalyst consisting essentially of palladium on alpha-alumina. The surface area and micropore volume of the alumina are not mentioned.

Thus US—A—2,971,016 describes the vapor-phase hydrogenation of unsaturated fatty acids and esters in a fluidized bed, which enables the disadvantages of liquid phase hydrogenation and the use of solid bed catalysts to be avoided. It will be recognized that vapor-phase hydrogenation is unfeasible for oils and fats. A continuous process based on a mixture of oil and suspended catalyst flowing along a turtuous path on the top surface of a series of perforated plates, with hydrogen admitted through the bottom face countercurrent to the oil flow and minimum mixing along the various plates, is the subject of US—A—3,634,471. The process described in US—A—3,792,067, which has had limited commercial application, is based on a turbulent two-phase gas-liquid flow with minimal back mixing, the liquid phase consisting of oil containing catalyst suspended therein. Both US—A—3,823,172 and US—A—3,988,329 describe continuous hydrogenation processes where the flowing mass of oil containing suspended catalyst is subject to high shear forces. US—A—3,444,221 describes a continuous process which requires a high ratio of liquid (catalyst suspended in oil) to gas phase using a plurality of reaction chambers.

The processes represented in the latter four references all suffer from the common disadvantage of necessitating the additional unit process of removal of suspended catalyst from partially hydrogenated oil, as by filtration. it is well known in the art that this unit process entails substantial product loss and requires use of relatively large amounts of filter aid, which adds to processing cost and presents subsequent disposal problems. Because use of a fixed bed continuous operation obviates the necessity of catalyst removal, such a mode of operation is greatly preferred. Both US—A—3,123,626 and US—A—3,123,627 describe fixed bed processes using sulfur- or nitrogen-poisoned nickel respectively, on a macroporous silica support. At least inpart, success of the method is attributable to the large pore structure of the support with catalyst contained within the pores. A diametrically opposed approach to fixed bed hydrogenation is described in US—A—4,163,750, where metals, including nickel and cobalt, are deposited almost entirely on the outer surfaces of the particles of the support. The support itself may be porous, and in fact advantages are ascribed to porous supports, such as porous carbon, as compared with non-porous supports, as stainless steel. The method of achieving surface deposition of the metal, which appears to be critical to the success of this process, does not seem to be disclosed.

Reports on the use of cobalt as a catalyst in the reduction of edible oils have been sparse. US—A—4,169,101 describes the use of micrometallic and ferromagnetic cobalt resulting from the decomposition of dicobalt octacarbonyl as a catalyst in the hydrogenation of edible oils. Although the process is there characterized as a selective hydrogenation, the data presented belie this description. It should be noted that in no reduction described by the patentee is the stearate (18:0) level under 7.8%, and even at such a relatively high saturate level the triene content is 2.4%. Thus, it is questionable whether the cited prior art method constitutes a selective hydrogenation of edible oils as that term is commonly used in the art, and this prior art method definitely is not selective as that term is defined within.

In the context of this application, a method of hydrogenation of edible oils is selective if it is capable of reducing the iodine value of soybean oil from about 10 to about 30 units with a concomitant increase in saturates of less than about 1.5% and a decrease in triene level to at least 3%, and where the Solid Fat Index of the partially hydrogenated product is less than about 5 ± 1 at 10°C, less than about 2 ± 0.5 at 21°C, less than 1.0 ± 0.5 at 27°C, and 0 ± 0.2 at 32°C.

It must be clearly recognized and understood that although this definition of selective hydrogenation utilizes a specific decrease in iodine value of a particular edible oil, a selective hydrogenation may cause a greater decrease in iodine value and/or be effected with a different edible oil. That is to say, the definition of selective hydrogenation does not restrict a selective hydrogenation to the conditions of its definition.

Description of the Invention

The object of this invention is to provide a continuous method of hydrogenation of edible oils and fats which method is highly selective.

The inventive method which comprises contacting a flowing mass of edible oils and fats at a temperature from about 150 to about 260°C in the presence of hydrogen at a pressure up to about 150 psig (1000 kPa gauge) with a fixed mass of catalyst consisting essentially of a catalytically active metal selected from Group VIII of the Periodic Table supported on alpha-alumina and recovering the resultant hydrogenated product is characterized in that the alpha-alumina support has a surface area less than 10 m^2/g and a micropore volume less than 0,1 ml/g.

The observation upon which the subject invention of this application is founded is that alpha-alumina of low surface area and low porosity functions at hydrogenation conditions as an effective support for catalytically active zerovalent metals selected from Group VIII of the Periodic Table including iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum in a fixed bed hydrogenation of edible fats and oils, affording partially hydrogenated product with the desired selectivity. This observation seems unknown in the prior art, and stands in sharp contrast to the prior art requirements of a porous support.

In a specific embodiment, the metal selected from Group VIII of the Periodic Table is present at a level from about 25% based on alpha-alumina. In a preferred embodiment, the catalytically active zerovalent metal selected from Group VIII of the Periodic Table is iron, cobalt, nickelt, ruthenium, rhodium, palladium, osmium, iridium, or platinum. Preferred is cobalt or nickel. Nickel is especially preferred. In a still more specific embodiment, the vegetable oil is passed upflow over the fixed bed.

The method described herein is generally applicable to edible oils and fats. Because the partial hydrogenation of liquid oils to afford hardened, but still liquid, oils occupies a prominent part within the domain of hydrogenation of edible oils and fats, the method of this invention is particularly applicable to such partial hydrogenation. Thus, the described method of hydrogenation is especially useful to partially harden edible liquid oils whereby the iodine value (IV) is lowered from about 10 to about 30 units by hydrogenation, whereby the increase in saturates attending hydrogenation is less than about 1.5%, and whereby the triene level is reduced to about 3% or less. Such a partially hydrogenated product preferably has an SFI of less than about 5 ± 1 at 10°C, less than about 2 ± 0.5 at about 21°C, less than about 1.0 ± 0.5 at 27°C, and 0 + 0.2 at 33°C. The term "iodine value" is a measure of the total extent of unsaturation in an edible oil or fat as performed by a standard test. In the context of soybean oil, which is a particularly important liquid vegetable oil, partial hardening is continued to an IV drop of from about 15 to about 25 units, with the product having less than about 6% stearate and about 3% linolenate or less.

Although the method claimed herein is especially valuable when applied to the partial hydrogenation of liquid vegetable oils, it must be explicitly recognized that the selectivity of the claimed method is also manifested in more extensive hydrogenations. Thus, as is shown below, the claimed method may be used generally in hydrogenating edible oils whenever selective hydrogenation is desired.

The method of this invention is especially applicable to liquid vegetable oils. Examples of such oils include soybean oil, cottonseed oil, sunflower oil, safflower oil, rapeseed oil, corn oil, and liquid fractionations from palm oil. The application of this method to soybean oil is especially important. As will be recognized by those skilled in the art, partial hydrogenation of liquid oils to afford partially hardened liquid oils is especially demanding, hence it is to be expected that a method suitable for this task also is suitable for more extensive hydrogenation. Thus, the method described herein also is suitable for more extensive hydrogenation, where the IV of the product may be as low as about 70. Oils and fats which can be so hydrogenated include those above, their partially hydrogenated products, and also such feedstocks as palm oil.

The hydrogenation catalyst used in this method is essentially a catalytically active zerovalent metal selected from Group VIII of the Periodic Table deposited on low surface area alpha-alumina. It is to be understood that by alpha-alumina is meant alumina whose crystallinity as measured by X-ray diffraction corresponds to that characterized in ASTM file number 10—173. Although zerovalent Group VIII metals are widely used in this art area, they are generally used on supports, such as kieselguhr and alumina, of high surface area and large porosity. A discovery of this invention is that continuous hydrogenation using zerovalent Group VIII metal in a fixed bed mode can be successfully performed, in the context of the criteria elaborated above, only on an alpha-alumina support characterized by relatively low surface area and porosity. In particular, the hydrogenation catalyst of this method consists essentially of catalytically active zerovalent Group VIII metal on alpha-alumina with a surface area less than about 10 m^2 per gram, with a surface area less than about 5 m^2 per gram preferred. Additionally, the micropore volume of the support must be less than about 0.1 ml/g, with those supports having a micropore volume less than about 0.05 ml/g, being advantageous. The macropore volume of the supports used in this invention is related to the surface area of the support. Consequently the supports used herein are further characterized by a macropore volume less than about 0,6 ml/g, with a macropore volume under about 0,3 ml/g being preferred. By micropore volume is meant the total volume of pores under about 11,7 nm (117 angstroms) in size; by macropore volume is meant the total volume of pores greater than 11,7 nm (117 angstroms) in size.

It is believed that, because of transport problems associated with fatty materials in the smaller pores, the selectivity in hydrogenation of a catalyst of a given surface area, micro- and macropore volume will change with macropore distribution. In particular, it is believed that a distibution skewed toward relatively large pore sizes will favor selectivity. As an example, with other variables being held constant it is believed that a catalyst whose support contains 90% of its macropores larger than about 350 nm (3500 angstroms) will be more selective than one where 90% of the macropores are larger than 30 nm (300 angstroms), but only 10% larger than 350 nm (3500 angstroms).

The concentration of Group VIII metal may range from 1 to about 25 percent by weight of alumina. The choice of metal loading will depend, inter alia, on the degree of selectivity and catalyst life desired in a particular operation. Metals selected from Group VIII of the Periodic Table include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Of these Group VIII metals, cobalt and nickel are preferred catalytically active components of the hydrogenation catalyst. Nickel is most especially preferred.

The cobalt catalyst used in the method of this invention typically is prepared by reducing a suitable cobalt salt impregnated on the support. Such reduction is most conveniently effected by a stream of hydrogen at a temperature between about 400 and about 600°C. Other methods are also satisfactory, as for example, the methods commonly employed to prepare Raney-type cobalt. The cobalt catalysts used in this invention are efective in amounts from about 0.01 to about 5% cobalt, based on edible oil hydrogenated, with the range from about 0.01 to about 1% being preferred, and with the lower end of this range being particularly preferred.

When a cobalt catalyst is employed hydrogenation conditions embrace a temperature from about 150 to about 300°C at a hydrogen pressure from atmospheric up to about 14 bar. Because the selectivity of hydrogenation seems to increase with increasing temperature and decreasing pressure, there is some advantage to operating at the highest possible temperature and lowest possible pressure consistent with an acceptable reaction rate. Operationally, a temperature range from about 200 to about 260°C is preferred. The preferred range of pressure is from about 3 to about 11 bar with a range from about 4 to about 8 bar being still more preferred.

When a nickel catalyst is employed hydrogenations are conducted at a temperature from about 150 to about 250°C, with the range of 175 to 225°C being preferred. Hydrogenations may be conducted at pressures up to about 11 bar. Freqyently there is some advantage to conducting such hydrogenations at a pressure less than about 4 bar and a pressure from about 1,5 to about 4 bar often is preferred.

The following description is applicable to a fixed bed operation, although it will be recognized that by suitable changes it may also be applicable to expanded or fluidized bed operation. The catalyst bed may be in the form of pellets, granules, spheres, extrudate, and so forth. The reactor is heated to the desired reaction temperature in a hydrogen atmosphere, often with a small hydrogen flow. After attainment of the desired temperature, the feedstock of edible fats and oils is made to flow over the fixed bed. The flow rate of the oil may be from about 0,2 to about 20 liquid hourly spaced velicity (LHSV) depending upon the degree of hydrogenation sought. When the flow of edible fats and oils is initiated, it is desirable to mix the hydrogen with said fats and oils so as to maintain the desired pressure. Often it is advantageous to admit excess hydrogen, maintaining pressure by partial venting. As the reaction proceeds and the activity of the catalyst bed decreases, adjustments may be made either in the LHSV or the temperature to maintain the desired characteristics of the product. Partially hardened oil is recovered as the effluent in a state suitable for further processing, such as blending, bleaching, or deodorization.

The flow may be either downflow, as in a trickle bed operation, or upflow, as in a flooded bed operation. By downflow is meant that the feedstock flows with gravity, that is, a trickle bed operation. By upflow is meant that the feedstock is made to flow against gravity, as in a flooded bed operation. Upflow is generally thought to be preferred to downflow because of a demonstrated enhanced selectivity of hydrogenation.

Although the reason for enhanced selectivity in the upflow mode is not known with certainty, it may arise from an overabundance of hydrogen at the catalyst surface in the downflow mode relative to a flooded bed operation.

One index of selectivity as used herein is the Solid Fat Index, as described above. Obtaining SFI date for large numbers of samples is laborious and time consuming. Another index of selectivity relied upon here and commonly used elwsewhere can be better understood from the following partial reaction sequence, where k is the rate constant for the indicated hydrogenation step.

$$18{:}3 \xrightarrow{k_3} 18{:}2$$

$$18{:}2 \xrightarrow{k_2} 18{:}1$$

$$18{:}1 \xrightarrow{k_1} 18{:}0$$

$$S_{LN} = k_3/k_2$$

$$S_{LO} = k_2/k_1$$

S_{LN} is termed the linolenate selectivity; a high value is characterized by relatively high yields of dienoic acid in the reduction of an unsaturated triglyceride containing thienoic acids. S_{LO} is the linoleate selectivity; a high value is characterized by relatively high yields of monoenoic acid in a reduction of an unsaturated triglyceride containing dienoic acids. An oil such as soybean oil contains both trienoic and dienoic acids, thus S_{LN} and S_{LO} may be measured simultaneously.

In the context of linolenate and linoleate selectivity, in a continuous method of hydrogenation as described herein where fatty material is passed upflow over a fixed catalyst bed, S_{LN} usually is greater than about 2, and S_{LO} usually is greater than 10, and generally will be greater than about 15.

The examples herein are cited for illustrative purposes only and are not to be construed as limiting this invention in any way.

Examples 1—4

All hydrogenations were conducted in a reactor of conventional design containing a fixed bed of about 50 ml catalyst. The rector had a preheater section for bringing feedstock to temperature and a heater for the reaction zone. The feedstock, which was soybean oil in these samples, was passed by a metering pump either upflow or downflow and mixed with hydrogen before the preheater stage. In all cases there was a net excess of hydrogen, that is, hydrogen in excess of that necessary for reaction was introduced into the reaction zone and excess hydrogen was vented so as to maintain a constant pressure.

Iodine values were determined by AOCS method CD1—25 or were calculated from the measured fatty acid distribution. Solid fat index was determined by AOCS method CD10—57. Fatty acid distribution was determined by AOCS method CE2—66. Macropore volume was determined by the mercury intrusion method as described in ANSI/ASTM D 2873—10 using the porosimeter of US—A—3,158,020.

The catalyst used in all runs consisted of 5% nickel on alpha-alumina, of surface area 3 m^2/g in the form of 1,6 mm spheres. It was prepared by mixing the alumina with an aqueous solution of nickel nitrate hexahydrate, evaporating the water while mixing, calcining the resulting solid at 450°C in air for 3—4 hours, then reducing the material in hydrogen for 2—4 hours at the same temperature. The alpha-alumina had the following macropore volume characteristics (in ml/g): 11,7—50 nm, 0.0000; 50—100 nm, 0.0003; 100—350 nm, 0.0000; 350—1750 nm, 0.2037; 17 50—58 33,3 nm, 0.0000. The micropore volume was less than about 0.03 ml/g.

Results of some typical hydrogenations are given in Table 1. Each period of an example corresponds to a four hour time interval. The SFI of some representative samples from upflow hydrogenation are given in Table 2. Values of S_{LN}. S_{LO} were calculated using a computer program furnished by the U.S. Department of Agriculture, Northern Regional Laboratories, as described in J. Amer. Oil Chemists Soc., 56, 664 (1979).

TABLE 1

Continuous Hydrogenation of Soybean Oil

Example 1, Downflow

Period	P,H_2 (bar)	T,(°C)	LHSV	H_2 flow l/hr	18:3	18:2	18:1	18:0	16:0	IV (calc)	S_{LN}	S_{LO}
2—4	2,7	195	6	11,3	4.2	37.6	36.4	10.8	11.1	107.2	1.3	1.9
5—10	1,7	195	6	11,3	5.0	43.8	32.9	7.4	11.2	117.1	1.5	2.0
11—15	1,7	210	6	11,3	4.5	43.0	34.1	7.8	10.5	115.6	1.7	2.4
16—19	1,7	210	8	11,3	5.5	47.1	30.6	6.2	10.5	122.5	1.6	2.5
20—33	1,7	210	4	11,3	3.9	41.2	36.0	8.3	10.6	112.6	1.8	2.6
34—39	4,3	195	6	11,3	4.9	44.2	32.0	8.5	10.5	116.9	1.6	1.7
40—45	4,3	165	6	11,3	5.8	48.1	28.5	6.9	10.7	123.1	1.6	1.4
46—48	1,7	165	6	11,3	6.4	50.9	27.0	5.1	10.6	128.1	1.7	2.2
49—51	1,7	165	4	11,3	5.8	49.4	28.9	5.5	10.5	125.4	1.9	2.7
52—54	4,3	165	4	11,3	5.2	45.5	30.7	8.1	10.5	118.7	1.6	1.6
55—58	4,3	195	6	11,3	5.3	45.4	30.6	8.3	10.5	118.7	1.5	1.5

Example 2, Downflow

Period	P,H_2 (bar)	T,(°C)	LHSV	H_2 flow l/hr	18:3	18:2	18:1	18:0	16:0	IV (calc)	S_{LN}	S_{LO}
1—10	4,3	150	6	11,3	4.7	40.2	34.7	9.3	11.2	116.6	1.3	1.9
11—16	4,3	180	6	22,6	3.5	32.2	37.6	15.5	11.2	97.2	1.2	1.7
19—20	2,7	180	6	22,6	4.4	42.3	34.3	8.6	10.5	114.1	1.7	2.1
21—24	1,7	180	6	22,6	5.0	46.4	31.9	6.1	10.7	120.7	1.9	2.8
25—28	1,7	180	4	19,3	4.4	44.7	33.8	6.5	10.6	118.1	2.0	3.2
29—32	2,7	180	4	19,3	4.1	42.4	34.9	8.1	10.5	114.2	2.9	2.4
33—35	4,3	180	4	19,3	3.8	38.6	35.6	11.4	10.5	107.5	1.6	1.8
36—38	4,3	150	6	19,3	6.1	48.1	28.2	6.8	10.9	123.3	1.3	1.3
39—40	4,3	180	4	19,3	4.3	41.0	33.9	10.3	10.4	111.5	1.6	1.7
41—44	4,3	180	3	19,3	3.7	38.4	37.9	10.1	10.5	108.3	1.6	2.3

TABLE 1

Example 3, Upflow — Continuous Hydrogenation of Soybean Oil (continued)

Period	P,H_2 (bar)	T,(°C)	LHSV	H_2 flow l/hr	18:3	18:2	18:1	18:0	16:0	IV (calc)	% Trans	S_{LN}	S_{LO}
1—10	4,3	195		11,3	2.1	40.0	41.9	5.1	10.5	111.4	28.6	3.2	15.9
11—16	4,3	195		11,3	0.1	20.2	59.9	9.5	10.3	86.9	43.0	3.8	10.4
17—22	4,3	195	0.8	11,3	—	14.7	63.0	12.0	10.3	79.6	46.4	3.1	9.5
23—28	4,3	195	0.6	11,3	—	8.1	66.8	14.6	10.5	71.5	44.9	1.9	11.0
29—34	3,0	195	0,5	11,3	0.1	10.6	67.2	11.6	10.4	76.4	45.3	2.4	13.3
35—38	4,3	210	1	11,3	—	17.4	63.1	9.1	10.5	84.3	47.4	3.3	13.2
39—42	4,3	210	0.6	11,3	—	0.4	68.7	20.4	10.5	59.7	43.3	0.7	25.5
43—56	3.0	210	0.6	11,3	—	10.6	69.7	9.4	10.4	78.2	48.0	2.1	19.2
57—72	3,0	215	0.6	11,3	—	10.6	70.6	8.6	10.3	79.0	50.5	2.1	24.9
73—78	3,0	220	0.6	11,3	—	11.5	70.5	7.7	10.3	80.6	51.9	2.5	29.3
79—82	4,3	195	1	11,3	0.5	37.4	46.4	5.5	10.5	105.8	45.9	5.3	16.0
83—92	4,3	225	0.6	11,3	0.1	19.7	60.3	9.7	10.2	86.1	51.8	3.7	10.6
93—98	4,3	235	0.6	11,3	0.1	16.2	63.5	9.9	10.3	82.8	51.6	3.1	12.4
99—102	4,3	195	0.6	11,3	—	28.6	54.3	6.8	10.4	92.2	52.9	5.4	13.6
Example 4, Upflow													
1—10	4,3	195	3	11,3	3.0	41.1	41.0	5.0	10.0	114.0	27.7	2.4	65.0
11—16	3,0	195	0.6	11,3	—	16.5	63.0	10.3	10.2	82.7	45.7	3.1	11.5
17—20	3,0	195	0.6	2,8	0.5	27.9	55.0	6.6	10.2	96.6	42.8	3.3	17.2
21—24	3,0	205	0.6	11,3	0.5	13.9	64.2	11.4	10.2	80.4	46.1	1.7	11.4
25—28	3,0	215	0.6	11,3	—	0.6	75.0	14.2	10.2	65.5	46.3	0.8	38.3
29—32	3,0	195	0.6	11,3	—	13.2	66.9	9.9	10.1	80.2	47.1	2.7	15.9
33—39	3,0	225	0.6	11,3	—	0.5	75.1	14.3	10.2	65.3	46.1	0.7	44.3
37—48	3,0	235	0.6	11,3	—	1.9	70.5	15.5	10.4	64.0	45.5	1.1	20.4
49—52	3,0	195	0.6	11,3	—	11.5	68.6	9.3	10.7	78.9	48.2	2.4	17.9
53—62	3,0	235	0.6	11,3	—	6.7	71.7	11.0	10.5	73.5	48.7	1.8	19.8
63—66	3,0	240	0.6	11,3	—	9.4	71.3	9.0	10.4	77.6	51.0	2.2	23.7
67—70	3,0	245	0.6	11,3	—	6.2	73.8	9.8	10.3	74.2	50.2	1.8	26.9
71—74	3,0	250	0.6	11,3	—	3.2	74.9	11.5	10.5	69.8	49.8	1.3	27.6
75—78	3,0	195	0.6	11,3	0.3	20.0	62.7	6.8	10.4	89.1	51.9	2.7	23.1

TABLE 2

Solid Fat Index of Upflow Hydrogenation products

IV		109	75	69
SFI:	10°C	4.5	52	52
	21°C	1.7	40	41
	27°C	0.6	33	36
	33°C	0	18	22
	40°C	0	2.7	6.9

As is clearly shown by comparison of S_{LN}, S_{LO} measured in the upflow and downflow modes, the selectivity of continuous hydrogenation to various IV levels is enhanced when hydrogenation is performed upflow.

Example 5

The cobalt catalyst was prepared in the following general way. Material used as the support was mixed with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ containing an amount of cobalt sufficient to provide the desired catalyst loading. Water was removed by evaporation with mixing, and the resulting solid was calcined in air at 450°C for about 2 hours followed by reduction in a stream of hydrogen at about 450°C for about 2 hours.

TABLE 1

Properties of Alpha-Alumina

	alpha-Alumina
Apparent bulk Density, g/ml	1.4
Surface area, m^2/g	3
Micropore volume[a], ml/g	0.03
Macropore volume[b], ml/g	0.2

a. Micropore volume is the total volume of pores under about 11,7 nm in size.

b. Macropore volume is the total volume of pores greater than about 11,7 nm in size, as deterimined by ANSI/ASTM D 2873—10.

Example 6

Batch reactions were performed in a 350 cm^3 stirred autoclave using 55 ml soybean oil and 5 g of a 5% Co catalyst. After being purged with nitrogen, hydrogen was admitted and the temperature was adjusted to the desired point. When the desired temperature was attained, hydrogen pressure was adjusted and stirring was begun. Aliquots were taken at intervals and filtered through Celite prior to analysis. Representative results at 220°C and 4—8 bar hydrogen are presented in Table 2.

TABLE 2

Batch Reduction of Soybean Oil

IV (Calcd)	119.6	107.4
16:0	10.6	11.0
18:0	4.7	5.0
18:1	34.6	45.3
18:2	46.5	37.0
18:3	3.6	1.7

Examples 7 and 8

Hydrogenations were conducted in a reactor of conventional design containing a fixed bed of 15 to about 70 ml catalyst. The reactor had a preheater section for bringing feedstock to temperature and a heater for the reaction zone. The feedstock, which was soybean oil in these samples, was passed upflow by a metering pump and mixed with hydrogen before the preheater stage. In all cases there was a net excess of hydrogen, that is, hydrogen in excess of that necessary for reaction was introduced into the reaction zone and excess hydrogen was vented so as to maintain a constant pressure.

Iodine values were determined by AOCS method CD1—25 or were calculated from the measured fatty acid distribution. Solid fat index was determined by AOCS method CD10—57. Fatty acid distribution was determined by AOCS method CE2—66.

TABLE 3

Continuous Hydrogenation of Soybean Oil

Catalyst	Example	T. °C	Pressure bar	LHSV	H_2/Feed, moles/mole	18:3	18:2	18:1	18:0	16:0	IV (calc)	S_{LN}	S_{LO}
5% Co on alpha-alumina 1,6 mm	7	223	4,3	1,4	4,7	3,6	45,5	35,7	4,8	10,5	118,7	2,9	15,4
	8	220	7,0	2,2	8,0	4,3	46,7	33,8	4,7	10,6	121,0		

TABLE 4

Trans Cotnent of Partially Hardened Soybean Oil

Catalyst	IV	% Trans
5% Co on alpha alumina	123.1	18.4

Claims

1. A continuous method for the selective hydrogenation of edible oils and fats which comprises contacting a flowing mass of edible oils and fats at a temperature from 150 to 260°C in the presence of hydrogen at a pressure up to 150 psig (1000 kPa gauge) with a fixed mass of catalyst consisting essentially of a catalytically active metal selected from Group VIII of the Periodic Table supported on alpha-alumina and recovering the resultant hydrogenated product, characterized in that the alpha-alumina support has a surface area less than 10 m^2/g and a micropore volume less than 0,1 ml/g.

2. The method of Claim 1 wherein said edible oils and fats are liquid vegetable oils.

3. The method of Claim 2 wherein said liquid vegetable oil is selected from the group consisting of soybean oil, cottonseed oil, rapeseed oil, sunflower oil, corn oil, safflower oil, and liquid fractions from palm oil.

4. The method of Claim 2 wherein said oil is soybean oil and the contacting thereof with said catalyst is of duration sufficient to lower the iodine value from 10 to 30 units.

5. The method of Claim 1 wherein the catalytically active metal selected from Group VIII is nickel or cobalt.

6. The method of Claim 1 wherein the catalyst contains from 1 to 25% catalytically active zerovalent metal selected from Group VIII of the Periodic Table.

7. The method of Claim 1 wherein the surface area is less than 5 m^2/g, preferably 3 m^2/g.

8. The method of Claim 1 wherein the micropore volume is less than 0.05 ml/g.

9. The method of Claim 1 wherein the alpha-alumina is further characterized by a macropore volume less than 0.6 ml/g, preferably less than 0,3 ml/g.

10. The method of Claim 1 wherein the contacting is performed in the upflow mode.

Patentansprüche

1. Kontinuierliches Verfahren zur selektivien Hydrierung eßbarer Öle und Fette, bei dem man eine fließende Masse eßbarer Öle und Fette bei einer Temperatur von 150 bis 260°C in Gegenwart von Wasserstoff bei einem Druck von bis zu 150 psig (1000 kPa Überdruck) mit einer ortsfesten Katalysatormasse, die im wesentlichen aus einem katalytisch aktiven Metall aus der Gruppe VIII des periodensystems auf einem alpha-Tonerdeträger besteht, in Berührung bringt und das resultierende hydrierte Produkt gewinnt, dadurch gekennzeichnet, daß der alpha-Tonerdeträger eine Oberfläche kleiner als 10 m^2/g und ein Mikroporenvolumen kleiner als 0,1 ml/g hat.

2. Verfahren nach Anspruch 1 bei dem die eßbaren Öle und Fette flüssige pflanzliche Öle sind.

3. Verfahren nach Anspruch 2, bei dem das flüssige pflanzliche Öl aus der Gruppe Sojabohnenöl, Baumwollsamenöl, Rapssamenöl, Sonnenblumenöl, Maisöl, Safranblumenöl und flüssiger Fraktionen von Palmöl ausgewählt ist.

4. Verfahren nach Anspruch 2, bei dem das Öl Sojabohnenöl ist und dessen Behandelung mit dem Katalysator ausreichend lange erfolgt, um den Jodwert von 10 auf 30 Einheiten zu senken.

5. Verfahren nach Anspruch 1, bei dem das katalytisch aktive Material aus der Gruppe VIII Nickel oder Kobalt ist.

6. Verfahren nach Anspruch 1, bei dem der katalysator 1 bis 25% katalytisch aktives nullwertiges Metall aus der Gruppe VIII des Periodensystems enthält.

7. Verfahren nach Anspruch 1, bei dem die Oberfläche kleiner als 5 m^2/g, vorzugsweise 3 m^2/g ist.

8. Verfahren nach Anspruch 1, bei dem das Mikroporenvolumen kleiner als 0,05 ml/g ist.

9. Verfahren nach Anspruch 1, bei dem die alpha-Tonerde zusätzlich durch ein Makroporenvolumen kleiner als 0,6 ml/g, vorzugsweise kleiner als 0,3 ml/g gekennzeichnet ist.

10. Verfahren nach Anspruch 1, bei dem die Behandlung in Aufstromflußweise erfolgt.

Revendications

1. Procédé continu pour l'hydrogénation sélective d'huiles et graisses comestibles qui comprend la mise en contact d'une masse en écoulement d'huiles et graisses comestibles à une température de 150 à 260°C en présence d'hydrogène à une pression allant jusqu'à 1000 kPa au manomètre (150 livres par pouce carré au manomètre) avec une masse fixe de catalyseur consistant essentiellement en un métal

catalytiquement actif choisi dans le groupe VIII du Tableau Périodique sur support d'alpha-alumine et la récupération du produit hydrogéné résultant, procédé caractérisé en ce que le support d'alpha-alumine a une surface spécifique inférieur à 10 m²/g et un volume de micropores inférieur à 0,1 ml/g.

2. Procédé selon la revendication 1, dans lequel lesdites huiles et graisses comestibles sont des huiles végétales liquides.

3. Procédé selon la revendication 2, dans lequel ladite huile végétale liquide est choisie dans le groupe constitué par l'huile de soja, l'huile de graines de coton, l'huile de colza, l'huile de tournesol, l'huile de maïs, l'huile de carthame, et des fractions liquides d'huile de palme.

4. Procédé selon la revendication 2, dans lequel ladite huile est de l'huile de soja, et sa mise en contact avec ledit catalyseur a une durée suffisante pour abaisser l'indice d'iode de 10 à 30 unités.

5. Procédé selon la revendication 1, dans lequel le métal catalytiquement actif choisi parmi le groupe VIII est le nickel ou le cobalt.

6. Procédé selon la revendication 1, dans lequel le catalyseur contient d' 1 à 25% de métal catalytiquement actif à valence nulle choisi dans le Groupe VIII du Tableau Périodique.

7. Procédé selon la revendication 1, dans lequel la surface spécifique est inférieur à 5 m²/g, de préférence de 3 m²/g.

8. Procédé selon la revendication 1, dans lequel le volume des micropores est inférieur à 0,05 ml/g.

9. Procédé selon la revendication 1, dans lequel l'alpha-alumine est encore caractérisée par un volume de macropores inférieur à 0,6 ml/g, de préférence inférieur à 0,3 ml/g.

10. Procédé selon la revendication 1, dans lequel la mise en contact est effectuée dans le mode d'écoulement ascendant.