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

(11) EP 2 922 935 B9

(12) CORRECTED EUROPEAN PATENT SPECIFICATION

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see

Description	**Paragraph(s) 16, 17, 25, 36-39, 41-48, 57**
Claims DE	**2, 3, 11**
Claims EN	**2, 3, 11**
Claims FR	**2, 3, 11**

(48) Corrigendum issued on:
19.12.2018 Bulletin 2018/51

(45) Date of publication and mention of the grant of the patent:
08.08.2018 Bulletin 2018/32

(21) Application number: **13814256.7**

(22) Date of filing: **18.11.2013**

(51) Int Cl.:
C11C 3/00 $^{(2006.01)}$
C11C 3/12 $^{(2006.01)}$
C10G 3/00 $^{(2006.01)}$
C01B 3/22 $^{(2006.01)}$
C10G 45/00 $^{(2006.01)}$

(86) International application number:
PCT/PL2013/000147

(87) International publication number:
WO 2014/081321 (30.05.2014 Gazette 2014/22)

---

(54) A METHOD OF OBTAINING PARAFFINIC HYDROCARBONS FROM NATURAL FAT

VERFAHREN ZUR HERSTELLUNG PARAFFINIERTER KOHLENWASSERSTOFFE AUS NATÜRLICHEM FETT

PROCÉDÉ D'OBTENTION D'HYDROCARBURES PARAFFINIQUES À PARTIR DE GRAISSE NATURELLE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **26.11.2012 PL 40177212**

(43) Date of publication of application:
30.09.2015 Bulletin 2015/40

(73) Proprietor: **Instytut Chemii Przemyslowej**
01-793 Warszawa (PL)

(72) Inventors:
- **OSAWARU, Osazuwa**
  PL-03-287 Warszawa (PL)
- **KIJENSKI, Jacek**
  PL-01-461 Warszawa (PL)
- **SMIGIERA, Ewa**
  PL-02-290 Warszawa (PL)
- **ZGUDKA, Anna**
  PL-05-071 Sulejówek (PL)
- **MIGDAL, Antoni**
  PL-01-991 Warszawa (PL)
- **NEMTUSIAK, Monika**
  PL-00-076 Warszawa (PL)
- **KAWALEC, Andrzej**
  PL-22-440 Krasnobród (PL)
- **RASINSKA, Iwona**
  PL-05-110 Jablonna (PL)

(74) Representative: **Twardowska, Aleksandra**
Kulikowska & Kulikowski
Roma Office Center
ul.Nowogrodzka 47A
00-695 Warszawa (PL)

(56) References cited:

WO-A2-2009/004180	**FR-A1- 2 917 424**
GB-A- 1 524 781	**US-A- 5 336 440**
US-A1- 2006 161 032	**US-A1- 2007 135 669**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The presented invention relates to a method of obtaining paraffinic hydrocarbons from natural fat, specifically, from waste vegetable oils, animal fat or algal oils.

[0002] The high cost involved in the mining and processing of fossil fuels, their depleting resources, and the limited global reserves of crude oil has caused greater interest in renewable resources. Most commonly, the fuels obtained from renewable resources are ethanol from maize and sugar, as well as vegetable oils used as diesel fuel. In the area of diesel fuel obtained from renewable sources, there are two sub-areas: *bio-diesel* (fatty acid methyl esters), described for instance in: D. Srivivas, J.K. Satyarthi, Catal. Surv. Asia, 2011, 15,145, E.F. Romalho et al., J. Therm. Anal. Calorim., 2011, 106, 825, C.L. Bianchi et al., Catal. Lett., 2010, 134, 179 and *green diesel,* i.e., green diesel fuel (paraffins obtained from the fatty acids present in vegetable oils and animal fat) which is known, for instance, from the US Patent 8,119,847. Methyl esters, mainly those of linear C_{14} to C_{22} carboxylic acids, may be used as fuel directly or mixed with diesel fuel from crude oil refining. The use of fatty acid methyl esters as diesel fuel requires costly modifications of diesel engines and of injectors. The use of biodiesel increases operating costs because of its low lubricity, and winter weather conditions significantly limit their applicability.

[0003] Taking into consideration the above-mentioned limitations in the use of biodiesel, alternative fuels are being sought. There is a potential for making green diesel (II and III generation biofuels) from renewable raw materials by converting fatty acids from triglycerides and/or free fatty acids originating from natural fat, especially waste vegetable oils, animal fat or algal oils to obtain linear aliphatic saturated hydrocarbons (paraffins). Green diesel has a high cetane number, which is necessary in maintaining the good performance of diesel engines (US Patent 8,119,847) and may be used as an independent fuel or mixed with diesel from crude oil, while its use does not actually require any engine modifications and it can be processed in existing refineries adapted to the refining of crude oil.

[0004] Recently, various types of waste materials are regarded as a source of raw materials for making other higher-value products. Vegetable oils, animal fat and various kinds of waste edible fat are part of the waste classified in the Waste Catalogue (Polish Journal of Laws Dz.U No. 112 of 2001, Item 1206), principally, in Group 2. Such waste must be disposed of properly so as not to create any environmental hazard. Algae with a high lipid content will be especially valuable (oil content in certain species is as high as above 80% of dry algal biomass) for it will constitute a raw material for third generation biofuels. The use of algae as energy plants has a huge potential because they quickly adapt to growth conditions, may be grown both in fresh and sea water, and also because land is not required for its production. Furthermore, due to the fact that two-thirds of the earth's surface is covered with water, algae will be a renewable source with a huge potential for the global energy needs.

[0005] A higher share of biocomponents in the market for liquid fuels and liquid biofuels for use in transport is an important element of sustainable development, leading to an improved energy security by diversifying fuel supply sources and reducing dependence on petroleum imports while, in addition, having a positive impact on natural environment through appropriate waste management. According to forecasts, a dynamic growth of the market for synthetic hydrocarbons obtained from biomass will be observed, as they will constitute a substitute of petroleum in the future.

[0006] Two methods of obtaining paraffins from fatty acids are described predominantly in the literature: *hydrodeoxygenation,* HDO (R-COOH + $3H_2$ →- R-CH_3 + $2H_2O$), and *decarboxylation* (R-COOH → R-H + CO_2), for example in J-G. Na et al., Catal. Today, 2012, 185, 313. In HDO, oxygen in the form of water is removed from fatty acids (hydrogenolysis). Typical hydrorefining catalysts, such as Ni/Mo or Co/Mo, are used in the HDO process. The HDO method ensures the production of pure hydrocarbons, which are fully compatible with conventional fuels, although it is energy-consuming because it requires the application of a high-pressure stream of hydrogen; it would be indispensable to minimize the use of hydrogen should the process be commercialized. Therefore, the process of decarboxylation of fatty acids, with CO_2 removal from the molecule, is a perfect alternative to HDO, though the hydrocarbons obtained are of one carbon atom less than in the molecule. In contrast to HDO, water is not produced in the decarboxylation process; this has a favorable effect, among others, on catalyst activity. On the other hand, both methods are conducted in batch systems at elevated pressures.

[0007] The US Patent 8,119,847 presents an invention based on a single-stage processing of vegetable oils and animal fat to paraffins by HDO in the presence of active metals and their mixtures (Ni, Co, Mo, W, Ni/Mo, Co/Mo), supported on graphite or oxides of aluminum and silicon, as well as zeolites (ZSM-5, ZSM-11, zeolite Y, mordenite, bata). The process was conducted in an autoclave at temperatures in the range of 250-450°C and hydrogen pressures in the range of 3.4-17.2 MPa. Paraffins were obtained, with high selectivity, in which the ratio of odd to even-numbered carbon atoms in the hydrocarbon chain were 2:1.

[0008] M. Snare et al., Fuel, 2008, 87, 933 reported a method to obtain hydrocarbons from vegetable oils and animal fat over Pd/C at temperatures in the range 300--360°C and at hydrogen pressures in the range 1.5-2.7 MPa. In addition to hydrocarbons, a significant amount of unreacted carboxylic acids was found in the product.

[0009] J-G. Na et al., Catal. Today, 2012, 185, 313 reported an innovative method to obtain paraffins in a decarboxylation reaction of fresh-water microalgae oil. The algal oil containing 36% triglycerides was initially subjected to pre-pyrolysis

(600°C, 1 hr) to obtain a product for decarboxylation containing C16 and C_{18} free fatty acids, hydrocarbons and compounds containing pure heteroatoms of nitrogen or sulfur. Volatile acids, aldehydes, ketones and furane compounds obtained during the pyrolysis process were separated from the stream which was directed for the decarboxylation process. The decarboxylation process was carried out in an autoclave in a temperature range of 350-400°C in the presence of hydrotalcites. C_{15} and C_{17} alkanes and also partly unreacted carboxylic acids were obtained mainly. The diesel fraction content was 35% after the first stage (pyrolysis) and 83.8% after decarboxylation.

[0010] Other Patent documents, such as WO2009/004180, US2007/0135669 or FR2917424, disclose a process comprising at least two stages for obtaining paraffins from oil, with a first stage in the presence of a metallic catalyst and a subsequent step in the presence of a metal oxide catalyst.

[0011] It was found that synthetic saturated aliphatic hydrocarbons (paraffins) may be obtained with high efficiency from natural fat and/or waste fat, by conducting the process according to the method of the invention under atmospheric pressure conditions in a continuous manner in the presence of heterogeneous catalysts.

[0012] In the method of the invention to obtain paraffinic hydrocarbons from natural fat and/or waste fat, in a coupled flow system, under atmospheric pressure, at an elevated temperature, in the presence of an inert gas, in the presence of heterogeneous catalysts a double-stage process is carried out whereby raw waste fat, or any other natural fat, is thermally transformed under strictly defined conditions (Fraction 1 is formed) in the first stage, and then the product obtained in the first stage is treated, in order to hydrogenate its olefin content, with hydrogen or with a mixture of hydrogen and carbon monoxide obtained in the selective decomposition of methanol (Fraction 2 is formed).

[0013] The fraction obtained in Stage I by the method of the invention (Fraction 1) may not be used directly as a biocomponent of fuels or as a biofuel because its hydrocarbons have a high degree of unsaturation, therefore, it requires further treatment by hydrogenation of its olefins (Fraction 2).

[0014] The thermodynamic conditions of the process of hydrogenation of Fraction 1, conducted with the use of methanol as a hydrogen donor, are much milder, compared with direct reduction with the use of hydrogen. It was found that the presence of carbon monoxide has a favorable effect on the hydrogenation of unsaturated compounds under atmospheric pressure, especially in reactions where the hydrogenation of compounds with a carbon chain length of more than C_{20} does not occur.

[0015] In the method of the invention to obtain paraffinic hydrocarbons from natural fat, specifically from waste vegetable oils, animal fat or algal oils, the process is performed in two stages, in a coupled flow-type system, in atmospheric pressure conditions, in the presence of heterogeneous catalysts following their thermal activation, preferably at a temperature of 450°C in a stream of air for 1 hour, so that in Stage I the fat and/or waste fat is heated at a temperature of 100-500°C, in the presence of an inert gas, in the presence of a catalyst in the form of a metal oxide on an oxide support or in the form of a mixture of at least two metal oxides on an oxide support, whereafter the product obtained in Stage I is treated, in the presence of an inert gas, at a temperature of 100-500°C, in the presence of a metallic catalyst on an oxide support, with hydrogen gas or with a mixture of hydrogen and carbon monoxide, obtained by the selective decomposition of methanol.

[0016] Preferably, the catalyst used in Stage I is CoO, NiO, FeO, MoO_3, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

[0017] Preferably, the catalyst used in Stage I is a mixture of metal oxides, preferably two or three metal oxides, selected from the group comprising CoO, NiO, FeO, MoO_3, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

[0018] Stage I of the process is preferably carried out at a catalyst load of 0.5-20 hr^{-1}.

[0019] Preferably, the inert gas used in Stage I is argon or nitrogen.

[0020] Preferably, in Stage II of the process, which is performed with the use of hydrogen gas, the catalyst used is Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

[0021] Preferably, in Stage II of the process, which is performed with the use of a mixture of hydrogen and carbon monoxide, the catalyst used is Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, most preferably Zr, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

[0022] Stage II of the process is preferably carried out at a catalyst load of 0.5-20 hr^{-1}.

[0023] Preferably, the inert gas used in Stage II is argon or nitrogen.

[0024] Preferably, the selective decomposition of methanol is carried out by subjecting the anhydrous methanol to a reduction reaction in a coupled flow-type system, in atmospheric pressure conditions, at a temperature of 80-350°C, in the presence of an inert gas, over a heterogeneous catalyst in the form of a metal oxide on an oxide support.

[0025] Preferably, the catalyst used for the selective decomposition of methanol is CoO, NiO, CuO, ZnO, FeO, MoO_3 while the oxide support is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

[0026] Preferably, the inert gas used in methanol decomposition is argon.

[0027] Preferably, methanol decomposition is carried out at a catalyst load of 0.5-20 hr^{-1}.

[0028] Preferably, the methanol decomposition catalyst is activated at a temperature of 450°C in a stream of air for 1 hour.

[0029] Preferably, the mixture of hydrogen and carbon monoxide from methanol decomposition is used for reducing the reaction catalyst, in Stage II of the process, from its starting form to a metallic form. It was found that the presence of carbon monoxide prevents agglomeration of the active phase of the catalyst during its reduction.

[0030] In the process conducted according to the method of the invention, the starting raw material may be any kind of natural fat, including waste vegetable oils and waste animal fat from food processing as well as algal oils containing triglycerides and/or fatty free acids C_6-C_{22}, of which the sources may include rapeseed, palm, coconut, sunflower, soy, linseed, maize, or peanut oils, animal fat, poultry fat, marine fat, prehydrolyzed fats, i.e., rendering fat, oils from various species of algae, or combinations of two or more fats.

[0031] In the process conducted according to the method of the invention, a mixture of saturated and unsaturated aliphatic hydrocarbons, mainly C_6-C_{18} (Fraction 1), is obtained in Stage I while in Stage II (hydrogenation stage) the hydrogenation of the olefins contained in Fraction 1 takes place, as a result, a mixture of synthetic hydrocarbons which is enriched with saturated hydrocarbons (Fraction 2) is formed, mainly C_6-C_{18} and contains the particularly desirable C_{12}-C_{17} fraction. The obtained mixture of paraffinic hydrocarbons (Fraction 2 without olefins) may be used as an independent fuel or as a component of liquid fuels, mainly diesel, thus becoming an alternative fuel source. In Stage I of the process conducted by the method of the invention, products are formed mainly as the result of decarboxylation involving the fatty acids and/or triglycerides contained in the starting raw material. Other probable mechanisms of the formation of Fraction 1 include hydrodeoxygenation with hydrogen being formed *in situ* as well as catalytic cracking.

[0032] In the event of insufficient amount of paraffins obtained in Fraction 2, Stage II may be repeated by refluxing Fraction 2 to the reactor in Stage II of the process, thereby further enriching the hydrocarbon fraction in saturated hydrocarbons.

[0033] The green diesel formed in the process of the invention (Fraction 2 without olefins) has the properties required for it to be used as diesel fuel or for mixing with petrochemical products, for instance those with lower cetane numbers. The cetane number may be controlled by selecting the appropriate heterogeneous catalyst and process conditions. Green diesel has the desirable lubricity, viscosity and density, and is useful in the diesel engines currently in use.

[0034] The method of the invention is illustrated in the Examples. A feasible way to carry out illustrated in Examples VIII-X, while Examples XI-XV illustrate a combination of the two stages of the process conducted by the method of the invention.

Stage 1

Example I.

[0035] The process was conducted in a flow-type catalytic system, as shown in the figure, Fig. 1 (Stage I). Initially, the catalyst was thermally activated under nitrogen at a temperature of 450°C for 1 hour, then temperature was lowered to 100°C and the raw material, heated to 60°C, was started to be fed in (3 ml/hr). The process temperature was gradually elevated to 500°C and products were subjected to a chromatographic analysis.

[0036] The catalyst used was 5%NiO+10%MoO_3/SiO_2 in the amount of 1 g obtained from a single solution of precursors. The raw material used was Category III rendering fat (a hydrolyzed waste animal fat, whose composition is given in wt % in Table 1 - Sample I). The composition of the rendering fat depends on the season of the year.
Sample II was used in the examples that follow.

Table 1. Composition of raw material

Category III Rendering fat			
Composition*	**Systematic name (customary name)**	**Content [wt %]**	
		Sample I	**Sample II**
C14 : 0	Tetradecanoic acid (myristic acid)	2.4	1.7
C16 : 0	Hexadecanoic acid (palmitic acid)	15.8	21.8
C16 : 1	9-Hexadecenoic acid (palmitoleic acid)	5.4	5.5
C17 : 0	Heptadecanoic acid (margaric acid)	0.8	1.1
C18 : 0	Octadecanoic acid (stearic acid)	13.4	13.9
C18 : 1	9-Octadecenoic acid (oleic acid)	34.5	40.6
C18 : 2	(*Z,Z*)-9,12-Octadecadienoic acid (linoleic acid)	9	10.3
C18 : 3	(*Z,Z,Z*)-9,12,15-Octadecatrienoic acid (linolenic acid)	0.7	0

(continued)

Category III Rendering fat			
Composition*	**Systematic name (customary name)**	**Content [wt %]**	
		Sample I	**Sample II**
alcohols	methanol	5.4	0
	glycerin	2.5	0
other	esters, amides, other	10.1	5.1
*The first number denotes the number of carbon atoms in a molecule, while the second the number of double bonds.			

[0037] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 2.

Table 2.

Content [wt %]; catalyst 5%NiO+10%MoO_3/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [500°C] Fraction 1**	**Percentage in product**
C14 : 0	2.4	82	-	2.7
C16 : 0	15.8		1.3	
C16 : 1	5.4		-	
C17 : 0	0.8		-	
C18 : 0	13.4		-	
C18 : 1	34.5		1.4	
C18 : 2	9		-	
C18 : 3	0.7		-	
methanol	5.4	5.4	-	0
glycerin	2.5	2.5	-	0
Saturated hydrocarbons C_6-C_{18} *(including* C_{12}-C_{17}*)*	-	-	*38.3 (26.6)*	*93.5 (60.8)*
Unsaturated hydrocarbons C_6-C_{18} *(including* C_{12}-C_{17}*)*	-	-	*55.2 (34.2)*	
other	10.1	10.1	3.8 (including other alcohols 2.4)	3.8

Example II.

[0038] The process was conducted as in Example I. The catalyst used was 10%NiO+10%MoO_3/SiO_2 in the amount of 1 g obtained from a single solution of precursors, and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample II).

[0039] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 3.

Table 3.

Content [wt %]; catalyst 10%NiO+10%MoO_3/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [500°C] Fraction 1**	**Percentage in product**
C14 : 0	1.7	94.9	-	2.2
C16 : 0	21.8		0.3	
C16 : 1	5.5		-	
C17 : 0	1.1		-	
C18 : 0	13.9		0.8	
C18 : 1	40.6		1.1	
C18 : 2	10.3		-	
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*29.4 (26.5)*	*72.8 (55.4)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*43.4 (28.9)*	
other	5.1	5.1	25 (mainly benzene derivatives)	25

Example III.

[0040] The process was conducted as in Example I. The catalyst used was 10%NiO/SiO_2 in the amount of 1 g and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample I).

[0041] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 4.

Table 4.

Content [wt %]; catalyst 10% NiO/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [500°C] Fraction 1**	**Percentage in product**
C14 : 0	2.4	82	1.6	14.1
C16 : 0	15.8		5.3	
C16 : 1	5.4		0.7	
C17 : 0	0.8		-	
C18 : 0	13.4		1.8	
C18 : 1	34.5		4.7	
C18 : 2	9		-	
C18 : 3	0.7		-	
methanol	5.4	5.4	-	0
glycerin	2.5	2.5	-	0
Saturated hydrocarbons C_6-C_{18} (including C_{12}-C_{17})	-	-	*33.8 (23.6)*	*77.2 (45.4)*
Unsaturated hydrocarbons C_6-C_{18} (including C_{12}-C_{17})	-	-	*43.4 (21.8)*	
other	10.1	10.1	8.7 (including 1.4 ketones C_{17}, 2.9 acids C_7-C_{10})	8.7

Example IV.

[0042] The process was conducted as in Example I, at a temperature of 400°C. The catalyst used was 5%MoO_3/5%CoO/SiO_2 in the amount of 1 g obtained by impregnation, and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample II).

[0043] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 5.

Table 5.

Content [wt %]; catalyst 5%MoO_3/5%CoO/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [400°C] Fraction 1**	**Percentage in product**
C14 : 0	1.7	94.9	-	3.2
C16 : 0	21.8		1.5	
C16 : 1	5.5		-	
C17 : 0	1.1		-	
C18 : 0	13.9		1.7	
C18 : 1	40.6		-	
C18 : 2	18.3		-	
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*49.3 (43.1)*	*87.3 (74.4)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*38 (31.3)*	
other	5.1	5.1	9.5 (including 3 ketones, 1.6 esters)	9.5

Example V.

[0044] The process was conducted as in Example I, at a process temperature of 400°C. The catalyst used was 5%MoO_3/10%CoO/SiO_2 in the amount of 1 g obtained by impregnation, and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample II.

[0045] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 6.

Table 6.

Content [% wag]; catalyst 5%MoO_3/10%CoO/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [400°C] Fraction 1**	**Percentage in product**
C14 : 0	1.7	94.9	-	0
C16 : 0	21.8		-	
C16 : 1	5.5		-	
C17 : 0	1.1		-	
C18 : 0	13.9		-	
C18 : 1	40.6		-	
C18 : 2	18.3		-	

(continued)

Content [% wag]; catalyst 5%MoO_3/10%CoO/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [400°C] Fraction 1**	**Percentage in product**
Saturated hydrocarbons C_6-C_{17} *(including* C_{12}-C_{17}*)*	-	-	*53.1 (41.1)*	*93.5 (68.6)*
Unsaturated hydrocarbons C_6-C_{17} *(including* C_{12}-C_{17}*)*	-	-	*40.4 (27.5)*	
other	5.1	5.1	6.5 (including 5.2 ketones)	6.5

Example VI.

[0046] The process was conducted as in Example I at a temperature of 440°C. The catalyst used was 5%MoO_3/10%CoO/SiO_2 obtained by impregnation, in the amount of 6 g, and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample II). The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 7.

Table 7.

Content [wt %]; catalyst 5%MoO_3/10%CoO/SiO_2				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [440°C] Fraction 1**	**Percentage in product**
C14 : 0	1.7	94.9	-	3.3
C16 : 0	21.8		2.4	
C16 : 1	5.5		-	
C17 : 0	1.1		-	
C18 : 0	13.9		0.9	
C18 : 1	40.6		-	
C18 : 2	18.3		-	
Saturated hydrocarbons C_6-C_{17} *(including* C_{12}-C_{17}*)*	-	-	*43.1 (34.8)*	*86.8 (65)*
Unsaturated hydrocarbons C_6-C_{17} *(including* C_1-C_{17}*)*	-	-	*43.7 (30.2)*	
other	5.1	5.1	9.9 (including 6.1 ketones. 1.5 aldehydes)	9.9

Example VII.

[0047] The process was conducted as in Example I, at a temperature of 400°C. The catalyst used was 5%CoO/5%MoO_3/SiO_2 in the amount of 1 g obtained by dry impregnation, and the raw material was Category III rendering fat, whose composition in wt % is given in Table 1 - sample II).

[0048] The compositions of the raw material [wt %] and fraction 1 [wt %] are given in Table 8.

Table 8.

Content [wt %]; katalizator5%CoO/5%MoO$_3$/SiO$_2$				
Composition	**Before reaction**	**Percentage in raw material**	**After reaction [400°C] Fraction 1**	**Percentage in product**
C14 : 0	1.7	94.9	-	3
C16 : 0	21.8		1.1	
C16 : 1	5.5		-	
C17 : 0	1.1		-	
C18 : 0	13.9		-	
C18 : 1	40.6		1.9	
C18 : 2	18.3		-	
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*49.2 (42.0)*	*87.4 (73.1)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	-	-	*38.2 (31.1)*	
other	5.1	5.1	9.6 (including 3.5 ketones, 0.7 esters	9.6

Stage 2 (hydrogenation of the olefins contained in Fraction 1 from Stage 1 to Fraction 2)

[0049] The process of reduction of the olefins contained in Fraction 1 from Stage 1 is illustrated in the examples.

Example VIII.

[0050] The process was conducted in a flow-type, coupled catalytic system, composed of a methanol decomposition system and a Fraction 1 hydrogenation system, as shown in the figure, Fig. 1 (Stage II). The catalyst used for methanol decomposition was CoO/SiO$_2$ in the amount of 0.5 g, and the catalyst in Stage II was PdCl$_2$/Al$_2$O$_3$ in the amount of 0.5 g. The catalysts in both reactors (methanol decomposition and Stage II) were initially activated thermally in a stream of air at a temperature of 450°C for 1 hour, then temperature in the methanol decomposition reactor was lowered to 100°C, the stream of carrier gas was switched to argon, and then anhydrous methanol was fed in. The catalyst load was 10 h^{-1}. Methanol decomposition products were passed directly to the Stage II reactor to be contacted with the Stage II catalyst, reducing the active phase within an hour to the metal (Pd), within 1 hour, at a temperature of 450°C. Temperature in the catalytic bed in Stage II was then lowered to 100°C and the raw material (Fraction 1) from Example VI was fed in. The catalyst load was 1.5 h^{-1}. Temperature in Stage II was gradually elevated to 300°C and products were analyzed by chromatographic analysis.

[0051] The compositions of fraction 1 [wt %] and fraction 2 [wt %] are given in Table 9.

Table 9.

Composition	**Fraction 1 from Example VI [440°C]**	**Fraction 2 [300°C]**
C14 : 0	-	-
C16 : 0	2.4	0.9
C16 : 1	-	-
C17 : 0	-	-
C18 : 0	0.9	-
C18 : 1	-	-

(continued)

Composition	Fraction 1 from Example VI [440°C]	Fraction 2 [300°C]
C18 : 2	-	-
C18 : 3	-	-
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.1 (34.8)*	*79 (60.5)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.7 (30.2)*	*7.5 (3.6)*
other	9.9	12.6 (including esters)

Example IX

[0052] The process was conducted as in Example VIII, at a temperature of 400°C. The catalyst used for Stage II was H_2PtCl_6/Al_2O_3 in the amount of 0.5 g, and the product from Example VI was used as Fraction 1.

[0053] The compositions of fraction 1 [wt %] and fraction 2 [wt %] are given in Table 10.

Table 10.

Composition	Fraction 1 from Example VI [440°C]	Fraction 2 [400°C]
C14 : 0	-	-
C16 : 0	2.4	-
C16 : 1	-	-
C17 : 0	-	-
C18 : 0	0.9	-
C18 : 1	-	-
C18 : 2	-	-
C18 : 3	-	-
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.1 (34.8)*	*76.7 (57)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.7 (30.2)*	*8.6 (5.4)*
other	9.9	14.7 (including esters)

Example X

[0054] The process was conducted in a single-stage flow-type catalytic system, composed of a glass reactor, as shown in the figure, Fig. 2 (Stage II). The catalyst was $PdCl_2/Al_2O_3$, used in the amount of 0.5 g and the process was conducted using compressed hydrogen. At the beginning, the catalyst was thermally activated in a stream of air at a temperature of 450°C for 1 hour, then the active phase was reduced for I hour to the metal (Pd), at a temperature of 450°C, using a compressed hydrogen fed directly to the Stage II reactor. The temperature in the catalytic bed was then lowered to 100°C and the raw material (Fraction 1 from Example VI) was fed in. The catalyst load was 1.5 h^{-1}. Temperature in Stage II was gradually elevated to 300°C and products were analyzed by chromatographic analysis.

[0055] The compositions of fraction 1 [wt %] and fraction 2 [wt %] are given in Table 11.

Table 11.

Composition	**Fraction 1 from Example VI [440°C]**	**Fraction 2 [300°C]**
C14 : 0	-	-
C16 : 0	2.4	0.3
C16 : 1	-	-
C17 : 0	-	-
C18 : 0	0.9	-
C18 : 1	-	-
C18 : 2	-	-
C18 : 3	-	-
Saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.1 (34.8)*	*79.5 (59.0)*
Unsaturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17})	*43.7 (30.2)*	*5.8 (3.4)*
other	9.9	14.4 (including esters)

Stage I and Stage II combined

[0056] A double-stage process composed of Stages I and II is illustrated in the Examples.

Example XI

[0057] The process was conducted in a flow-type catalytic system shown in the figure. Fig. 1 (Stage I and II). At the beginning, the catalysts of both stages were initially activated thermally (I -5%MoO_3/10%CoO/SiO_2 in the amount of 9 g, II - 10%ZrO_2/Al_2O_3 in the amount of 4 g), obtained by impregnation in a stream of argon at a temperature of 450°C for 1 hour, then the Stage II catalyst was reduced from its original form to its metallic form using hydrogen from the decomposition of anhydrous methanol (350°C, catalyst 10%CoO/SiO_2) at a temperature of 450°C for 1 hour, which was fed at a rate of 0.9 ml/hr. The temperature in the Stage I and Stage II reactors was lowered to 100°C and the raw material was fed in preheating to a temperature of 60°C at the rate of 10 ml/hr. The raw material was Category III rendering fat, Sample II. The temperature in both Stages was gradually elevated to 440°C (Stage I) and 300°C (Stage II), respectively, and after a stable condition was reached (about 1 hr) the major product (Fraction 2) was collected.

[0058] In Fraction 2 (at a 99% conversion), only saturated hydrocarbons C_6-C_{17} (including C_{12}-C_{17}) in the amount of 85% (80%), respectively, and esters in the amount of 15% were obtained.

Example XII

[0059] The process was conducted as in Example XI, the temperature used in Stage II was 400°C. The raw material used was a waste refined rapeseed oil of the following composition: C16:0 (10%), C18:0 (1.1%), C18:1 (46%), C18:2 (13%), C18:3 (4.5%), other (25.4%). The catalyst in Stage II was 10%Pd/Al_2O_3. In Fraction 2 (at a 100% conversion) the following hydrocarbons were obtained: saturated C_6-C_{18} (including C_{12}-C_{17}) 85% (66%) respectively, unsaturated C_6-C_{18} (including C_{12}-C_{17}), 7.2% (6%) respectively, and other products - 7.8% (mainly esters and alcohols).

Example XIII

[0060] The process was conducted as in Example XI, the temperature in Stage II was 500°C. The raw material used was waste animal fat (pork lard) of the following composition: C14:0 (3%), C16:0 (30%), C18:0 (15%), C18:1 (45%), C18:2 (5%), other (2%). The catalyst in Stage II was 10%Pd/Al_2O_3. In fraction 2 (at a 100% conversion) the following hydrocarbons were obtained: saturated C_6-C_{18} (including C_{12}-C_{17}) 80% (63%) respectively, unsaturated C_6-C_{18} (including C_{12}-C_{17}) 8% (3%) respectively, and other products - 12% (mainly esters and alcohols).

Example XIV

[0061] The process was conducted as in Example XI. The raw material used was a mixture of palmitic acid C16:0 and stearic acid C18:0 as a composition model of an algal oil after pyrolysis (Chlorella sp.) at a molar ratio of C16:0 to C18:0 of 1:0.7, respectively. The catalyst in Stage II was 10%Pd/Al_2O_3. In fraction 2, saturated C_{15} and C_{17} hydrocarbons were obtained with a yield of 75%.

Example XV

[0062] The process was conducted as in Example XI. The catalyst used in Stage II was 10%Pd/Al_2O_3. The raw material used was a waste hydrolyzed poultry fat of the following composition: C14:0 (1%), C16:0 (24%), C16:1 (6%), C18:0 (8%), C18:1 (29%), C18:2 (22%), other (10%). The catalyst used in Stage II was 10%Pd/Al_2O_3. In fraction 2 (at a 100% conversion) the following hydrocarbons were obtained: saturated C_6-C_{17} (including C_{12}-C_{17}) 85% (65%) respectively, unsaturated C_6-C_{17} (including C_{12}-C_{17}) 5% (2%) respectively, and other products - 10% (mainly esters).

Claims

1. A method of obtaining paraffinic hydrocarbons from natural fat, specifically from waste vegetable oils, animal fat or algal oils, **wherein** the process is performed in two stages, in a coupled flow-type system, under atmospheric pressure conditions, in the presence of heterogeneous catalysts, following their thermal activation, preferably at a temperature of 450°C in a stream of air for 1 hour, so that in Stage I the fat and/or waste fat is heated at a temperature range of 100-500°C, in the presence of an inert gas, in the presence of a catalyst in the form of a metal oxide on an oxide support or in the form of a mixture of at least two metal oxides on an oxide support, whereafter the product obtained in Stage I is treated, in the presence of an inert gas, at a temperature range of 100-500°C, in the presence of a metallic catalyst on an oxide support, with hydrogen gas or with a mixture of hydrogen and carbon monoxide, obtained by the selective decomposition of methanol.

2. A method as claimed in Claim 1, **wherein** the catalyst used in Stage I is CoO, NiO, FeO, MoO_3, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

3. A method as claimed in Claim 1, **wherein** the catalyst used in Stage I is a mixture of metal oxides, preferably two or three metal oxides, selected from the group comprising CoO, NiO, FeO, MoO_3, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

4. A method as claimed in Claim 1, **wherein** Stage I is performed at a catalyst load of 0.5-20 hr^{-1}.

5. A method as claimed in Claim 1, **wherein** in Stage I argon or nitrogen is used as inert gas.

6. A method as claimed in Claim 1, **wherein** in Stage II, which is performed with the use of hydrogen gas, the catalyst used is Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

7. A method as claimed in Claim 1, **wherein** in Stage II, which is performed with the use of a mixture of hydrogen and carbon monoxide, the catalyst used is Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, most preferably Zr, and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

8. A method as claimed in Claim 1, **wherein** Stage II is performed at a catalyst load of 0.5-20 hr^{-1}.

9. A method as claimed in Claim 1, **wherein** in Stage II argon or nitrogen is used as the inert gas.

10. A method as claimed in Claim 1, **wherein** the selective decomposition of methanol is effected by subjecting the anhydrous methanol to a reduction reaction in a coupled flow-type system, in atmospheric pressure conditions, at a temperature range of 80-350°C, in the presence of an inert gas, in the presence of a heterogeneous catalyst in the form of a metal oxide on an oxide support.

11. A method as claimed in Claim 1 or 10, **wherein** the catalyst used for the selective decomposition of methanol is CoO, NiO, CuO, ZnO, FeO, MoO_3 and the oxide support used is SiO_2, Al_2O_3, TiO_2, MgO, the aluminosilicate halloysite.

12. A method as claimed in Claim 1 or 10, **wherein** argon is used as the inert gas for decomposition of methanol.

13. A method as claimed in Claim 1 or 10, **wherein** decomposition of methanol is performed at a catalyst load of 0.5-20 hr^{-1}.

14. A method as claimed in Claim 1 or 10 or 11, **wherein** the catalyst for decomposition of methanol is activated at a temperature of 450°C in a stream of air for 1 hour.

15. A method as claimed in Claim 1, **wherein** the mixture of hydrogen and carbon monoxide from methanol decomposition is used for reducing the reaction catalyst from its original form to a metallic form in Stage II.

Patentansprüche

1. Verfahren zur Gewinnung von paraffinischen Kohlenwasserstoffen aus natürlichem Fett, insbesondere aus pflanzlichen Abfallölen, tierischem Fett oder Algenölen, **wobei** das Verfahren in einem gekoppelten Fließsystem, unter atmosphärischen Druckbedingungen, in Gegenwart von heterogenen Katalysatoren, nach ihrer thermischen Aktivierung, vorzugsweise bei einer Temperatur von 450°C in einem Luftstrom für 1 Stunde, in zwei Stufen durchgeführt wird, so dass in Stufe I das Fett und/oder das Abfallfett auf einen Temperaturbereich von 100-500°C, in Gegenwart von einem Inertgas, in Gegenwart von einem Katalysator in Form von einem Metalloxids auf einem Oxidträger oder in Form von einer Mischung von mindestens zwei Metalloxiden auf einem Oxidträger, erhitzt wird, wonach das in Stufe I erhaltene Produkt, in Gegenwart von einem Inertgase, in einem Temperaturbereich von 100-500°C, in Gegenwart von einem metallischen Katalysator auf einem Oxidträger, mit Wasserstoffgas oder mit einer Mischung von Wasserstoff und Kohlenmonoxid behandelt wird, die durch selektive Zersetzung von Methanol erhalten wird.

2. Verfahren nach Anspruch 1, **wobei** der in Stufe I verwendete Katalysator CoO, NiO, FeO, MoO_3 ist, und der verwendete Oxidträger SiO_2, Al_2O_3, TiO_2, MgO, der Aluminosilicat Halloysit ist.

3. Verfahren nach Anspruch 1, **wobei** der in Stufe I verwendete Katalysator eine Mischung aus Metalloxiden, vorzugsweise zwei oder drei Metalloxiden, ausgewählt aus der Gruppe umfassend CoO, NiO, FeO, MoO_3 ist, und der verwendete Oxidträger SiO_2, Al_2O_3, TiO_2, MgO, der Aluminosilicat Halloysit ist.

4. Verfahren nach Anspruch 1, **wobei** Stufe I bei einer Katalysatorbelastung von 0.5-20 hr^{-1} durchgeführt wird.

5. Verfahren nach Anspruch 1, **wobei** in Stufe I Argon oder Stickstoff als Inertgas verwendet wird.

6. Verfahren nach Anspruch 1, **wobei** in Stufe II, die unter Verwendung von Wasserstoffgas durchgeführt wird, der verwendete Katalysator Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, Fe ist, und der verwendete Oxidträger SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2 ist.

7. Verfahren nach Anspruch 1, **wobei** in Stage II, die unter Verwendung einer Mischung von Wasserstoff und Kohlenmonoxid durchgeführt wird, der verwendete Katalysator Pd, Ru, Pt,Rh, Co/Mo, Ni/Mo, Mo, W, Fe ist, am meisten bevorzugt Zr, und der verwendete Oxidträger SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2 ist.

8. Verfahren nach Anspruch 1, **wobei** Stufe II bei einer Katalysatorbelastung von 0.5-20 hr^{-1} durchgeführt wird.

9. Verfahren nach Anspruch 1, **wobei** in Stufe II Argon oder Stickstoff als Inertgas verwendet wird.

10. Verfahren nach Anspruch 1, **wobei** die selektive Zersetzung von Methanol erfolgt, indem das wasserfreie Methanol einer Reduktionsreaktion in einem gekoppelten Fließsystem, unter Atmosphärendruckbedingungen, in einem Temperaturbereich von 80-350°C, in Gegenwart eines Inertgases, in Gegenwart eines heterogenen Katalysators, in Form von einem Metalloxids auf einem Oxidträger, unterworfen wird.

11. Verfahren nach Anspruch 1 oder 10, **wobei** der für die selektive Zersetzung von Methanol verwendete Katalysator CoO, NiO, CuO, ZnO, FeO, MoO_3 ist und der verwendete Oxidträger SiO_2, Al_2O_3, TiO_2, MgO, der Aluminosilicat Halloysit ist.

12. Verfahren nach Anspruch 1 oder 10, **wobei** Argon als Inertgas zur Zersetzung von Methanol verwendet wird.

13. Verfahren nach Anspruch 1 oder 10, **wobei** die Zersetzung von Methanol bei einer Katalysatorbelastung von 0.5-20 hr^{-1} durchgeführt wird.

14. Verfahren nach Anspruch 1 oder 10 oder 11, **wobei** der Katalysator zur Zersetzung von Methanol bei einer Temperatur von 450°C in einem Luftstrom für 1 Stunde aktiviert wird.

15. Verfahren nach Anspruch 1, **wobei** die Mischung aus Wasserstoff und Kohlenmonoxid aus Methanolzersetzung zur Reduktion des Reaktionskatalysators von seiner ursprünglichen Form zu einer metallischen Form in Stufe II verwendet wird.

Revendications

1. Un procédé d'obtention d'hydrocarbures paraffiniques à partir de graisse naturelle, de façon spécifique à partir d'huiles végétales, de graisse animale ou d'huiles d'algue usagées, **caractérisé en ce que** le processus est effectué en deux stades, dans un système de type à écoulement couplé, dans des conditions de pression sous atmosphérique, en présence de catalyseurs hétérogènes, après leur activation thermique, de préférence à une température de 450°C sous un courant d'air pendant 1 heure, de telle sorte que dans le stade I la graisse et/ou la graisse usagée est chauffée à une plage de température de 100-500°C, en présence d'un gaz inerte, en présence d'un catalyseur sous la forme d'un oxyde métallique sur un support d'oxyde ou sous la forme d'un mélange d'au moins deux oxydes métalliques sur un support d'oxyde, après quoi le produit obtenu dans le Stade I est traité, en présence d'un gaz inerte, à une plage de température de 100-500°C, en présence d'un oxyde métallique sur un support d'oxyde, avec de l'hydrogène gazeux ou avec un mélange d'hydrogène et de monoxyde de carbone, obtenu dans la décomposition sélective du méthanol.

2. Un procédé selon la revendication 1, **caractérisé en ce que** le catalyseur utilisé dans le Stade I est CoO, NiO, FeO, MoO_3, et le support d'oxyde utilisé est SiO_2, Al_2O_3, TiO_2, MgO, aluminosilicate de l'halloysite.

3. Un procédé selon la revendication 1, **caractérisé en ce que** le catalyseur utilisé dans le Stade I est un mélange d'oxydes métalliques, de préférence deux ou trois oxydes métalliques, sélectionnés dans le groupe comprenant CoO, NiO, FeO, MoO_3, et le support d'oxyde utilisé est SiO_2, Al_2O_3, TiO_2, MgO, aluminosilicate de l'halloysite.

4. Un procédé selon la revendication 1, **caractérisé en ce que** le Stade I est effectué à une charge du catalyseur de 0.5-20 hr^{-1}.

5. Un procédé selon la revendication 1, **caractérisé en ce que** pendant le Stade I l'argon ou l'azote est utilisé en tant qu'un gaz inerte.

6. Un procédé selon la revendication 1, **caractérisé en ce que** pendant le Stade II, qui est effectué avec l'usage de l'hydrogène gazeux, le catalyseur utilisé est Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, et le support d'oxyde utilisé est SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

7. Un procédé selon la revendication 1, **caractérisé en ce que** pendant le Stade II, qui est effectué avec l'usage d'un mélange d'hydrogène et de monoxyde de carbone, le catalyseur utilisé est Pd, Ru, Pt, Rh, Co/Mo, Ni/Mo, Mo, W, Fe, de toute préférence Zr, et le support d'oxyde utilisé est SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2.

8. Un procédé selon la revendication 1, **caractérisé en ce que** le Stade II est effectué à une charge du catalyseur de 0.5-20 hr^{-1}.

9. Un procédé selon la revendication 1, **caractérisé en ce que** pendant le Stade II l'argon ou l'azote est utilisé en tant que le gaz inerte.

10. Un procédé selon la revendication 1, **caractérisé en ce que** la décomposition sélective du méthanol est effectuée en soumettant le méthanol anhydre à une réaction de réduction dans un système de type à écoulement couplé, dans des conditions de pression sous atmosphérique, à une plage de température de 80-350°C, en présence d'un gaz inerte, en présence d'un catalyseur hétérogène sous la forme d'un oxyde métallique sur un support d'oxyde.

11. Un procédé selon la revendication 1 ou 10, **caractérisé en ce que** le catalyseur utilisé pour la décomposition

sélective de méthanol est CoO, NiO, CuO, ZnO, FeO, MoO_3 et le support d'oxyde utilisé est SiO_2, Al_2O_3, TiO_2, MgO, aluminosilicate de l'halloysite.

12. Un procédé selon la revendication 1 ou 10, **caractérisé en ce que** l'argon est utilisé en tant que le gaz inerte pour la décomposition du méthanol.

13. Un procédé selon la revendication 1 ou 10, **caractérisé en ce que** la décomposition du méthanol est effectuée à une charge du catalyseur de 0.5-20 hr^{-1}.

14. Un procédé selon la revendication 1 ou 10 ou 11, **caractérisé en ce que** le catalyseur pour la décomposition du méthanol est activé à une température de 450°C sous un courant d'air pendant 1 heure.

15. Un procédé selon la revendication 1, **caractérisé en ce que** le mélange d'hydrogène et de monoxyde de carbone obtenu dans la décomposition sélective du méthanol est utilisé pour la réduction du catalyseur de réaction de sa forme originale à une forme métallique dans le Stade II.

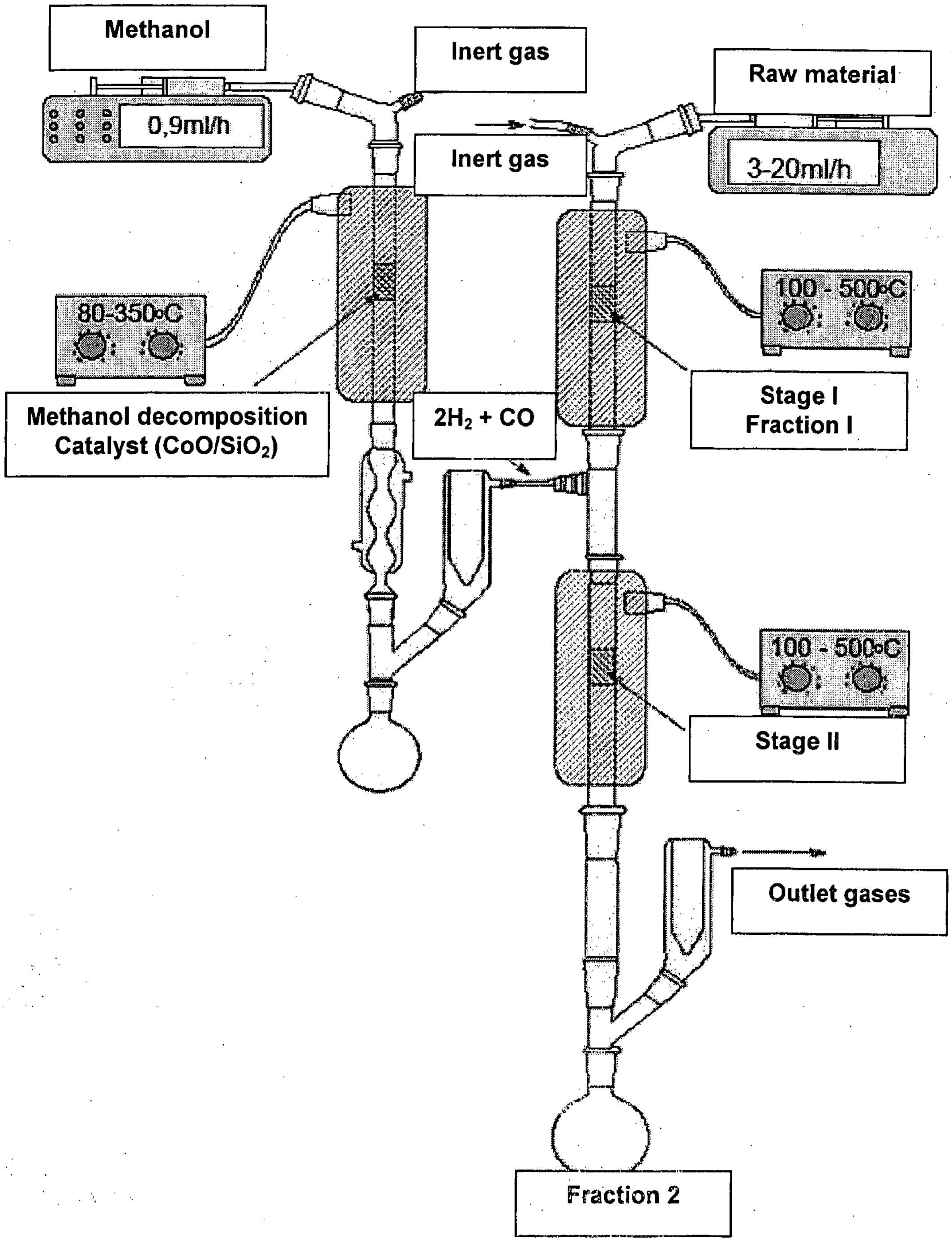

Fig. 1. A system for obtaining paraffinnic hydrocarbons from natural fat using hydrogen from methanol decomposition (under atmospheric pressure conditions)

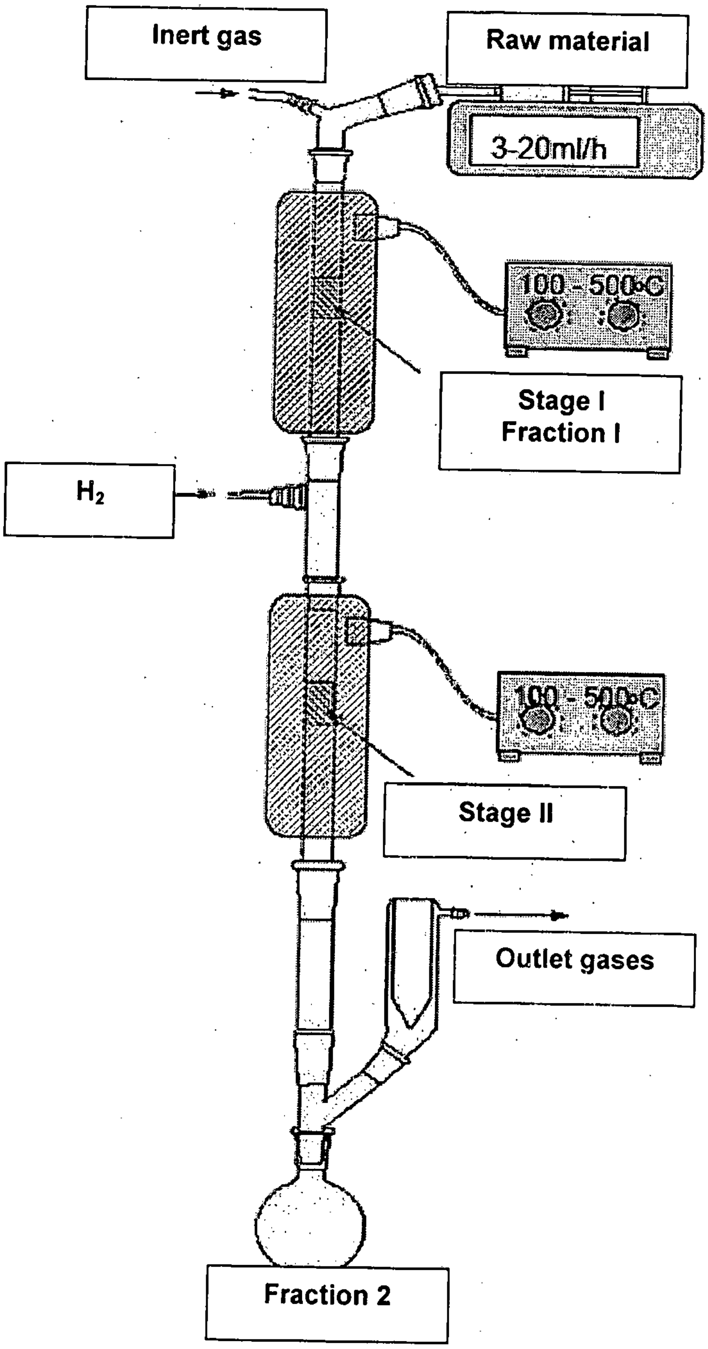

Fig. 2 A system for obtaining paraffinnic hydrocarbons from natural fat using hydrogen gas (under atmospheric pressure conditions)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 8119847 B **[0002] [0003] [0007]**
- WO 2009004180 A **[0010]**
- US 20070135669 A **[0010]**
- FR 2917424 **[0010]**

Non-patent literature cited in the description

- **D. SRIVIVAS ; J.K. SATYARTHI.** *Catal. Surv. Asia,* 2011, vol. 15, 145 **[0002]**
- **E.F. ROMALHO et al.** *J. Therm. Anal. Calorim.,* 2011, vol. 106, 825 **[0002]**
- **C.L. BIANCHI et al.** *Catal. Lett.,* 2010, vol. 134, 179 **[0002]**
- **J-G. NA et al.** *Catal. Today,* 2012, vol. 185, 313 **[0006] [0009]**
- **M. SNARE et al.** *Fuel,* 2008, vol. 87, 933 **[0008]**