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(54) Title: A PROCESS FOR THE PREPARATION OF HYDROCARBON FUEL

(57) Abstract: The present invention provides a process for the preparation of hydrocarbon fuels, which comprises contacting fatty acid glycerides with alcohols in the presence of a solid, double metal cyanide catalyst at a temperature in the range of 150° to 200°C for a period of 2 - 6 hrs. and separating the catalyst from the above said reaction mixture to obtain the desired hydrocarbon fuel.



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“A PROCESS FOR THE PREPARATION OF HYDROCARBON FUEL”

FIELD OF THE INVENTION

The present invention relates to a process for the preparation of hydrocarbon
5 fuels. More particularly, it relates to an efficient process for producing hydrocarbon
fuel, which comprises contacting fatty acid glycerides with alcohols in the presence of
a solid, double metal cyanide catalyst.

The solid, double metal cyanide catalyst, used in the present invention is
10 described and disclosed in our co-pending Indian patent application no.
2723/DEL/2005.

BACKGROUND OF THE INVENTION

In recent years there has been a renewed interest in alternatives to petroleum-
15 based fuels. The alternative fuels must be technically acceptable, economically
competitive, environmentally acceptable and easily available. The need for these fuels
arises mainly from the standpoint of preserving global environment and concern about
long-term supplies of conventional hydrocarbon based fuels. Among the different
possible sources, diesel fuels derived from triglycerides (vegetable oil/animal fat)
20 present a promising alternative. Although triglycerides can fuel diesel engines their
viscosities and poor cold flow properties have led to investigation of various
derivatives. Fatty acid methyl esters derived from triglycerides and methanol known
as bio-diesel, have received the most attention. Vegetable oils are widely available
from a variety of sources. Unlike hydrocarbon-based fuels, the sulfur content of
25 vegetable oils is close to zero and hence the environmental damage caused by
sulphuric acid is reduced.

The main advantages of using bio-diesel are its renewability, better quality
exhaust gas emission, its biodegradability and given that all the organic carbon
30 present is photosynthetic in origin, it does not contribute to a rise in the level of CO₂
in the atmosphere and consequently to the greenhouse effect. Several processes for
transesterification of triglycerides have been developed: (1) Base-catalyzed
transesterification of glycerides with alcohol (catalysts - alkaline metal alkoxides and

hydroxides as well as sodium and potassium carbonates), (2) Direct acid-catalyzed esterification with alcohol (catalysts - Brönsted acids, preferably sulfonic acid and sulfuric acid), and (3) Conversion of oil to fatty acids and then to alkyl esters with acid catalysis. However, the former route (i.e., base catalyzed reaction) is the most economical and in fact, is in practice in several countries for bio-diesel production (J. Braz. Chem. Soc. Vol. 9, No. 1, Year 1998, pages 199-210; J. Am. Oil. Chem. Soc. Vol. 77, No. 12, Year 2000, pages 1263 – 1266; Fuel Vol. 77, No. 12, year 1998, pages 1389 – 1391; Bioresource Tech. Vol. 92, Year 2004, pages 55 – 64; Bioresource Tech. Vol. 92, Year 2004, pages 297 – 305; Renewable Sustainable Energy Rev. Vol. 9, Year 2005, pages 363 – 378). Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98%) of fatty acid alkyl esters in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%) (J. Food Composition and Analysis Year 2000, Vol. 13, pages 337 – 343). However, they require high quality oil and the absence of water, which makes them inappropriate for typical industrial processes (J. Braz. Chem. Soc. Vol. 9, No. 1, Year 1998, pages 199-210). Alkaline metal hydroxides (NaOH and KOH) are cheaper than metal alkoxides but require increasing catalyst concentration (1 – 2 mol%). NaOH is more superior to KOH as the latter and other alkali hydroxides yield more saponified products than the bio-fuel.

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Recently, enzymatic transesterification using lipase has become more attractive for bio-fuel production, since the glycerol produced as a by-product can easily be recovered and the purification of fatty acid esters is relatively simple to accomplish. However, the main hurdle to commercialize this system is the cost of lipase production (J. Mol. Catal. B: Enzymatic Vol. 17, Year 2002, pages 133 – 142).

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Use of immobilized lipases in the synthesis of fatty acid methyl esters from sunflower and soybean oils were reported by Soumanou and Bornscheuer and Watanabe et. al. (Enzy. Microbiol. Tech. Vol. 33, Year 2003, page 97; J. Mol. Catal. B: Enzymatic Vol. 17, Year 2002, pages 151 – 155). They found that the immobilized enzyme is active at least for 120 h during five batch runs without significant loss of activity. Among the various lipases investigated the enzyme from *Pseudomonas fluorescens* (Amano AK) exhibited the highest conversion of oil. Khare and Nakajima

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(Food Chem. Vol. 68, Year 2000, pages 153 – 157) also reported the use of immobilized lipase enzyme.

Cost is the major factor slowing the commercialization of biofuels.

5 Replacement of homogeneous catalyst by a solid catalyst eliminates the processing costs associated with the homogeneous catalysts. Leclercq et al. (J. Am. Oil. Chem. Soc. Vol. 78, Year 2001, page 1161) studied the transesterification of rapeseed oil in the presence of Cs-exchanged NaX and commercial hydrotalcite (KW2200) catalysts. At a high methanol to oil ratio of 275 and 22 h reaction time at methanol reflux, the

10 Cs-exchanged NaX gave a conversion of 70% whereas 34% conversion was obtained over hydrotalcite. ETS-4 and ETS-10 catalysts gave conversions of 85.7% and 52.7%, respectively at 220°C and 1.5 h reaction time (US Patent No. 5,508,457). Suppes et al (J. Am. Oil. Chem. Soc. Vol. 78, Year 2001, page 139) achieved a conversion of 78% at 240°C and >95% at 160°C using calcium carbonate rock as catalyst. Of late, Suppes

15 et al reported the use of Na, K and Cs exchanged zeolite X, ETS-10, NaX occluded with NaO_x and sodium azide in the transesterification of soybean oil with methanol (Appl. Catal. A: Gen. Vol. 257, Year 2004, page 213). Furuta et al (Catal. Commun. Vol. 5, Year 2004, pages 721 – 723) describe biodiesel production from soybean oil and methanol at 200 - 300°C using solid superacid catalysts of sulfated tin and

20 zirconium oxides with oil conversions over 90%. Use of tin complexes immobilized in ionic liquids for vegetable oil alcoholysis was reported by Abreu et al (J. Mol. Catal. A: Chem. Vol. 227, Year 2005, pages 263 – 267; J. Mol. Catal. A: Chem. Vol. 209, Year 2004, pages 29-33). Kim et al reported the use of heterogeneous base catalysts (Na/NaOH/Al₂O₃) for the methanolysis of vegetable oils

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US Patent No. 5,713,965 describes the production of biodiesel, lubricants and fuel and lubricant additives by transesterification of triglycerides with short chain alcohols in the presence of an organic solvent such as an alkane, arene, chlorinated solvent, or petroleum ether using *Mucor miehei* or *Candida Antarctica*-derived lipase

30 catalyst. Patents Nos. WO 00/05327 A1, WO 02/28811 A1, WO 2004/048311 A1, WO 2005/021697 A1 and WO 2005/016560 A1 and US Patents 5,578,090; 6,855,838; 6,822,105; 6,768,015; 6,712,867; 6,642,399; 6,399,800; 6,398,707; 6,015,440, also teach us the production of fatty acid alkyl esters using either lipase

catalysts or metal ion catalysts. Patent No. WO 2004/085583 A1 describes transesterification of fats with methanol and ethanol in the presence of a solid acid catalyst having ultrastrong-acid properties in a short time at around ordinary pressure.

Production of diesel from pure soybean oil or coconut oil is not economical, so it is desirable to use cheaper alternative feedstocks such as animal fat or used cooked oil or oil from seeds of wild plants like jojoba and jatropha. Animal fat and used oil contain high amounts of free fatty acids (FFA) content. The FFA saponifies with the alkali-based transesterification catalyst leading to low yield, difficulties in separation of the products, and increase in production cost. In those cases a two step process wherein in the first step an acid catalyst esterifies the free fatty acids to methyl esters and in the second step a base catalyst transesterifies the triglycerides is generally employed in diesel preparation. An efficient solid catalyst, which can do this in a single-step is highly desirable.

The present invention deals with a process, which eliminates most of the above said drawbacks. In one form the present invention deals with production of hydrocarbon fuels (diesel oil) which comprises reaction of vegetable oils or fats with alcohols such as C1 — C5 alcohols at moderate conditions using a novel, solid, reusable double metal cyanide catalyst. The feedstock oil is a triglyceride or a mixture of fatty acids and glycerides. Preferably one of the metals of the double metal cyanide catalyst is Zn^{2+} while the other is a transition metal ion preferably Fe. Co-existence of Zn and Fe in the active site linking through cyano bridges makes it efficient to transform feedstocks containing fatty acids in a single step to fatty acid alkyl esters. The catalyst could be separated easily by centrifugation or by simple filtration and reused. Most importantly, the catalyst is highly efficient and only a small amount (~1 wt% of oil) is needed to carry out the reaction. The process is atom-efficient and the reaction conditions like temperature and pressure are only moderate. Unlike the conventional base catalysts the catalyst of the present invention is more efficient even in the presence of water impurity in oil. Hence, there are no limitations on the quality of oil that should be used with the catalysts of the present invention.

OBJECTIVES OF THE INVENTION

The main objective of the present invention to provide an efficient, reusable heterogeneous catalyst and a process for the preparation of hydrocarbon fuels in high yields.

Another object is to provide a single-step process for the production of hydrocarbon fuels from used oils or oils or fats containing significant amount of fatty acids.

Yet another object of one form of the present invention is to produce fuels by transesterification of vegetable oil or fat with alcohols such as C1 - C5 alcohols at moderate conditions and shorter reaction times.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a process for the preparation of hydrocarbon fuel, which comprises contacting fatty acid glycerides with an alcohol in the presence of a solid, double metal cyanide catalyst, at a temperature in the range of 150- 200°C, for a period of 2-6 hrs, cooling the above said reaction mixture to a temperature in the range of 20-35°C, filtering the above said reaction mixture to separate out the catalyst, followed by removing the unreacted alcohol from the resultant filtrate by vacuum distillation to obtain the desired hydrocarbon fuel.

In an embodiment of the present invention the molar ratio of fatty acid glyceride to alcohol used is in the range of 1 :6 to 1 : 12.

In yet another embodiment the concentration of solid, double metal cyanide catalyst used is 1-2 wt% of fatty acid glyceride.

In yet another embodiment the solid, double metal cyanide catalyst used has the molecular formula:



wherein, R is tertiary-butyl, M is a transition metal ion, x varies from 0 to 0.5, y varies from 3 - 5 and n is 10 or 12.

In yet another embodiment the transition metal ion used is Fe, Co, or Cr.

In yet another embodiment the hydrocarbon fuel obtained is C9 - C23 fatty acid methyl esters.

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In yet another embodiment the hydrocarbon fuel obtained is diesel oil.

In yet another embodiment the source of fatty acid glyceride used is vegetable oil or animal fat.

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In yet another embodiment the vegetable oil has C9 - C23 fatty acid alkyl esters, the oil being selected from the group consisting of coconut oil, sunflower oil, soybean oil, mustered oil, olive oil, cotton seed oil, rapeseed oil, margarine oil, jojoba oil, jatropha oil and mixtures thereof.

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In yet another embodiment the alcohol used is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and the mixtures thereof.

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In yet another embodiment the solid double metal cyanide complex catalyst used is easily separable from the reaction mixture and is reusable in several recycling experiments without significant loss in activity.

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In yet another embodiment the mol% conversion of oil or fat to hydrocarbon fuel obtained is in the range of 90-95 mol% based on isolated glycerol yield and the fuel selectivity is greater than 95%.

DETAIL DESCRIPTION OF THE INVENTION

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In the investigations leading to the present invention, it was found that the double metal cyanide catalysts are highly efficient and could be easily separated from the products for further reuse. The prior art catalysts, mineral acid, alkali bases and lipases need additional expenses for catalyst separation. An easily separable catalyst system e.g., the catalyst of the present invention is beneficial and leads to an economic and eco-friendly process. Hence, the solid catalysts of the present invention are not only efficient but avoid the tedious process of catalyst recovery characteristic

of the prior art processes. The present catalyst system is efficient without using any additional solvent.

The solid, double metal cyanide catalyst has the molecular formula:



where, R is tertiary-butyl, x varies from 0 to 0.5, y varies from 3 – 5 and n is 10 or 12.

The catalyst has the physicochemical characteristics listed in Table 1.

10 TABLE-1: Physicochemical characteristics of the double metal cyanide (Fe-Zn) catalyst.

<u>Textural Characteristics:</u>	
Total surface area (S_{BET})	38.4 m ² /g
External surface area ($S_{\text{Extn.}}$)	24.1 m ² /g
Micropore area	14.3 m ² /g
Average pore diameter	3.9 nm
Total pore volume	0.037 cc/g
<u>Elemental analysis:</u>	
%C-content	23.3
%H-content	2.24
%N-content	17.3
<u>Morphology (SEM):</u>	Spherical shaped particles
<u>Spectral characteristics:</u>	
FT-IR band positions (in cm ⁻¹)	2096 (ν(C≡N)), 1230 (ν(C-O)), 500 (ν(Fe-C))
Diffuse reflectance UV-visible bands (in nm)	405, 330, 278, 236 and 208

The catalyst of the present invention is prepared as described in EXAMPLE 1 by reacting an aqueous ZnCl₂ solution, an aqueous K₄Fe(CN)₆ solution and a tri-block copolymer poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethyleneglycol) (EO₂₀-PO₇₀-EO₂₀; molecular weight of about 5800) dissolved in 15 tert.-butanol at ambient conditions (25 - 40°C) and activating at 170 – 200°C.

In still yet another embodiment, the concentration of said catalyst in the reaction mixture is 1 – 2 wt% of oil.

It is a feature of the process of the present invention that it eliminates the saponification. It is another feature of the process of present invention that the catalyst is a solid and the reaction takes place in a heterogeneous condition, the product fuel is a liquid and the solid catalyst can be easily separated from products by centrifugation/filtration for further reuse. In still yet another feature, the reaction is conducted without using any solvent.

The present invention is illustrated herein below with examples, which are illustrative only and should not be construed to limit the scope of the present invention in any manner.

EXAMPLE 1

This example illustrates the preparation of the Fe-Zn double metal cyanide catalyst of the present invention. In a typical catalyst preparation, $K_4[Fe(CN)_6]$ (0.01 mol) was dissolved in double distilled water (40 ml) (Solution-1). $ZnCl_2$ (0.1 mol) was dissolved in a mixture of distilled water (100 ml) and tertiary-butanol (20 ml) (Solution)-2. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}-PO_{70}-EO_{20}$; molecular weight of about 5800) (15 g) was dissolved in a mixture of 2 ml of distilled water and 40 ml of tertiary-butanol (Solution-3). Solution-2 was added to solution-1 over 60 min at 50°C with vigorous stirring. White precipitation occurred during the addition. Then, solution-3 was added to the above reaction mixture over a period of 5 min and stirring was continued for further 1 hr. The solid cake formed was filtered, washed with distilled water (500 ml) and dried at 25°C for 2-3 days. This material was activated at 180 - 200°C for 4 hr. prior to using it in the reactions.

EXAMPLE 2

This example describes the preparation of fatty acid methyl esters (diesel oil) from coconut oil and methanol. In a typical reaction, coconut oil (5 g), methanol (oil : methanol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt%

of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was closed and placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C.

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First, catalyst was separated by centrifugation/filtration from the reaction mixture. Then, by vacuum distillation unreacted alcohol in the reaction mixture was removed. Pet ether (60 ml) and methanol (20 ml) were added to separate out the glycerol by-product from the reaction mixture. The methanol layer containing glycerol by-product was separated. This process of glycerol separation was repeated 2-3 times. Glycerol was isolated by distilling out methanol under vacuum. Later, the ether portion was distilled out to obtain the esterified products. A portion of the esterified products (100 mg) was diluted with dichloromethane (1 g) for analysis by gas chromatography. The products were identified by GC-MS.

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EXAMPLE 3

This example illustrates the preparation of fatty acid methyl esters (diesel oil) from sunflower oil and methanol. In a typical reaction, sunflower oil (5 g), methanol (oil : methanol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was closed and placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

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EXAMPLE 4

This example describes the preparation of fatty acid methyl esters (diesel oil) from soybean oil and methanol. In a typical reaction, soybean oil (5 g), methanol (oil : methanol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was then placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure

at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

EXAMPLE 5

5 This example describes the preparation of fatty acid methyl esters (diesel oil) from margarine oil and methanol. In a typical reaction, margarine oil (5 g), methanol (oil : alcohol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was then placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH
10 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

EXAMPLE 6

15 This example describes the preparation of fatty acid methyl esters (diesel oil) from used/cooked margarine oil and methanol. In a typical reaction, used/cooked margarine oil (5 g), methanol (oil : alcohol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was then placed in a rotating synthesis reactor
20 (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

EXAMPLE 7

25 This example describes the preparation of fatty acid alkyl esters (hydrocarbon fuel) from coconut oil and butanol. In a typical reaction, margarine oil (5 g), butanol (oil : alcohol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was then placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH
30 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

EXAMPLE 8

This example describes the preparation of hydrocarbon fuel from sunflower oil and butanol. In a typical reaction, sunflower oil (5 g), butanol (oil : alcohol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was sealed and placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

EXAMPLE 9

This example illustrates the preparation of hydrocarbon fuel from margarine oil and propanol or butanol. In a typical reaction, margarine oil (5 g), propanol or butanol (oil : alcohol molar ratio = 1 : 6) and double metal cyanide Fe-Zn catalyst (50 mg; 1 wt% of oil) were charged into a 100 ml stainless steel autoclave having a teflon-liner. The autoclave was closed and placed in a rotating synthesis reactor (Hiro Co., Japan, Mode- KH 02; rotating speed = 30 rpm) and the reaction was conducted at autogeneous pressure at 170°C for 4 hr. It was then allowed to cool to 25°C. The products were isolated by distillation in vacuum.

TABLE-2 lists the results of catalytic activity studies exemplified in Examples 2 – 9.

TABLE-2: Hydrocarbon fuel preparation: catalytic activity of double metal cyanides

Example No.	Oil	Alcohol	Oil conversion based on isolated glycerol yield (mol%)	Alkyl esters selectivity (mol%)
Example 2	Coconut oil	Methanol	92.5	Methyl caprylic ester (8.7%)+ Methyl capric ester (5.8) + Methyl lauric ester (45.6) + methyl myristic ester (18.4) + Methyl Palmitic ester (7.9%) + Methyl (oleate + stearate+linoleate) esters (13.7)
Example 3	Sunflower oil	Methanol	92.3	Methyl Palmitic ester (6.8%) + Methyl (oleate + stearate+linoleate) esters (92.0)
Example 4	Soybean oil	Methanol	92.0	Methyl esters (99%)
Example 5	Margarine	Methanol	93.0	Methyl palmitate (10.1%) + Methyl (oleate + stearate+linoleate) esters (88.2)
Example 6	Used/Cooked margarine	Methanol	92.8	Methyl palmitate (10%) + Methyl (oleate + stearate+linoleate) esters (88.0)
Example 7	Coconut oil	Butanol	92.0	Butyl caprylic ester (9.5%)+ Butyl capric ester (8.0) + Butyl lauric ester (45.1) + Butyl myristic ester (19.6) + Butyl palmitic ester (9.2%) + Butyl (oleate + stearate+linoleate) esters (8.3)
Example 8	Sunflower oil	Butanol	91.0	Butyl palmitic ester (8.7%) + Butyl (oleate + stearate+linoleate) esters (91.1)
Example 9	Margarine	Propanol	93.7	Propyl palmitate (12.7%) + Propyl (oleate + stearate+linoleate) esters (86.5)
Example 9	Margarine	Butanol	92.1	Butyl palmitate (13.5%) + Butyl (oleate + stearate+linoleate) esters (86.0)

ADVANTAGES

1. The process has the combined unique advantages of high conversion accompanied with high selectivity for hydrocarbon fuels.
- 5 2. The catalyst can be easily separated from the product mixture and no issues related to saponification are encountered.
3. The catalyst of the present invention is highly efficient for the preparation of hydrocarbon fuel from vegetable oil or fat and C1 – C5 alcohols.

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CLAIMS

1. A process for the preparation of hydrocarbon fuel, which comprises
5 contacting fatty acid glycerides with an alcohol in the presence of a solid, double
metal cyanide catalyst, at a temperature in the range of 150- 200°C, for a period of 2-
6 hrs., cooling the above said reaction mixture to a temperature in the range of 20-
35°C, filtering the above said reaction mixture to separate out the catalyst, followed
by removing the unreacted alcohol from the resultant filtrate by vacuum distillation to
10 obtain the desired hydrocarbon fuel.
2. A process as claimed in claim 1, wherein the molar ratio of fatty acid
glyceride to alcohol used is in the range of 1:6 to 1:12.
- 15 3. A process as claimed in claim 1, wherein the concentration of solid, double
metal cyanide catalyst used is 1-2 wt% of fatty acid glyceride.
4. A process as claimed in claim 1, wherein the solid, double metal cyanide
catalyst used has a molecular formula:
20
$$\text{Zn}_3\text{M}_2(\text{CN})_n(\text{ROH})_x\text{ZnCl}_2.y\text{H}_2\text{O}$$

wherein, R is tertiary-butyl, M is a transition metal ion, x varies from 0 to 0.5, y
varies from 3 – 5 and n is 10 or 12.
5. A process as claimed in claim 4, wherein the transition metal ion used is
25 selected from Fe, Co and Cr.
6. A process as claimed in claim 1, wherein the hydrocarbon fuel obtained is
C₉ – C₂₃ fatty acid alkyl esters.
- 30 7. A process as claimed in claim 1, wherein the hydrocarbon fuel obtained is
diesel oil.

8. A process as claimed in claim 1, wherein the source of fatty acid glyceride used is vegetable oil or animal fat.
9. A process as claimed in claim 8, the vegetable oil used is selected from the group consisting of coconut oil, sunflower oil, soybean oil, mustard oil, olive oil, cotton seed oil, rapeseed oil, margarine oil, jojoba oil, jatropha oil and mixtures thereof.
10. A process as claimed in claim 1, wherein the alcohol used is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and the mixtures thereof.
11. A process as claimed in claim 1, wherein the mol% conversion of oil or fat to hydrocarbon fuel obtained is in the range of 90-95 mol% based on isolated glycerol yield and the fuel selectivity is greater than 95%.