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(54) TREATMENT METHOD FOR REDUCING CONTAMINATING AGENTS IN LIQUID MIXTURES OF SUBSTITUTED HYDROCARBONS USED AS FUELS

(57) The invention relates to a treatment method for reducing contaminating agents in liquid mixtures of substituted hydrocarbons used as fuels, using a supersaturated mixture of ferrous oxide combined with the hydrocarbons, both solutions subsequently being separated by means of settling.

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Description

[0001] Method for refining hydrocarbons used as fuels.

Technical Field

[0002] Heterogeneous catalysis of hydrocarbons, refinement.

Background Art

[0003] Liquid hydrocarbons used as fuel, such as gasoline, gas oil or disel, the jet fuel, or the kerosene, are toxic and of high flammability. Vapors produced by their evaporation and substances created when burnt, such as carbon monoxide, nitrous oxides, non-burnt hidrocarbons, etc., contribute to air pollution. Also, burning these fuels additionally produce carbon dioxide, a greenhouse gas directly related to global climate change.

[0004] Concerned for environment pollution, Governments have passed legislation aimed to reduce pollutants from hydrocarbons used as fuels. At present time there is a need for more efficient refining methods. Prior art teaches well known desulfuration methods for hydrocarbon fractions with organic sulfur compounds impurities.

[0005] Prior art shows a number of alternative gasoline and diese' refining proceses, such as direct absorption methods (US4830733A, NAGT et al., 1989), bioprocessing methods (US5910440A, GROSSMAN et al., 1999), selective oxidation methods (US3341448A, FORD et al., 1967), and zeolites catalysing methods (MAXWELL, I. E.; STORK, W. H. J. Hydrocarbon processing with zeolites. Studies in Surface Science and Catalysis, 2001, vol. 137, p. 747-819).

[0006] However, all prior art methods have inconveniences. For example, many of such methods only can desulfurize hydrocarbons, but fail at reducing bencenes and harmful aromatic compounds. Additionally, in practice they also entail high costs that hinder their continuous use.

[0007] Even if prior art refining do remove some polluting components, fuel loses effectiveness as such compounds help in its combustion.

[0008] Therefore, a refining and catalysing method that removes polluting agents and provides benefits at low costs is required.

Summary of the invention

[0009] This invention claims a refining and catalysing method for liquid hydrocarbons used as fuel that eliminates sulfur, aromatic compounds, bencenes, xylenes, toluenes, and others, and oxidising available octanes to act as comburent during hydrocarbon combustion processes, producing better burning and more energy availability for industrial fuel uses.

[0010] The disclosed method is applicable to mixed fuels in the final hydrocarbon refining step, i.e., fuels that in current state of the art would be used as final products available in commerce to consumer public.

[0011] The disclosed method comprises mixing small solid ferrous oxide particles mixed with water vapor until a heterogeneous mixture is achieved. Said heterogeneous mixture is then poured into a container with substituted hydrocarbons used as fuel, and are combined and mixed constantly for a few minutes.

[0012] The result is fuel with a lower hydrocarbon count. In gasoline, cyclic hydrocarbons count is lower, and in diese' and jet fuel lineal hydrocarbon count is reduced.

[0013] The chemical reaction is no fully understood at the time of filing this application. Some studies (HAMADA, Hideaki, et al. Role of supported metals in the selective reduction of nitrogen monoxide with hydrocarbons over metal/alumina catalysts. Catalysis today, 1996, vol. 29, no 1, p. 53-57) teach that ferrous oxide particles catalyze propene oxidation with dioxygen.

[0014] Hence, an emulsion is produced which hydrocarbon refining properties are in-disputable, as may be appreciated in experimental evidence filed as Drawings in this technical document.

Technical Problem

[0015] Hydrocarbons used in commerce as fuel carry high concentrations of sulfur, aromatic compounds, bencenes, xylenes, toluenes, and others. Burning these fuels in internal combustion engines is not efficient enough to burn them all, and are therefore released in the atmosphere.

Solution to Problem

[0016] A treatment method for reducing polluting agents in liquid substituted hydrocarbons used as fuel, comprising blending a heterogeneous mixture of ferrous oxide in water with said fuel, mixing or combining constantly the solution, allow the mixture to settle, and removing the aqueous solution of ferrous oxide and water by decantation.

Advantageous Effects of Invention

[0017] The fuel obtained as a result of applying the disclosed method contains a lower count of polluting compounds with sulfur, aromatic compounds, bencenes, xylenes, toluenes, and others. Additionally, it increases fuel burning efficiency, since during the chemical reaction hydrocarbons gain additional oxygen atoms that help as comburent.

Brief Description of Drawings

[0018] Disclosed embodiments and their advantages may be better understood making joint reference to the following description and attached figures. These figures do not limit in any way the disclosed compound's advantageous effects of its physicochemical interactions as catalyzer and refiner that a person having ordinary skill in the art may find, without departing from the disclosed embodiments' spirit and scope. All figures are graphics resulting from the analysis of the aforementioned hydrocarbon, performed by gas chromatography with a flame ionization detector (GC-FID) with MS Perkin Eimer Clarus 580 MS Clarus SQ 85, column Perkin Eimer Elite 5 MS 30 m x0.32 mm DI 0.25μm, and dicloromethane HPLC grade as control solvent, with an inyector temperature of 250°C, column temperature 50°C / 12 min, of 6°C / 1 min, and 120°C / 10 min, with an injection volume of 41, and a mobile Helium phase of 0-8 ml/min. These MS conditions were performed with ionization energy of 70 eV, a transfer temperature of 180°C, and an ionization source temperature of 200°C.

Fig.1 is the graphic result of the GC-FID analysis of a commercially available diese' sample, in which the X axis show minutes lapsed, and Y axis shows voltage in mV.

Fig.2 is the graphic result of the GC-FID analysis of a commercially available diese' sample, treated with the claimed compound and method, in which the X axis show minutes lapsed, and Y axis shows voltage in mV, and the hydrocarbon reduction is acknowledged.

Fig.3 is the graphic result of the GC-FID analysis of a commercially available gasoline sample, in which the X axis show minutes lapsed, and Y axis shows voltage in V.

Fig.4 is the graphic result of the GC-FID analysis of a commercially available gasoline sample, treated with the claimed compound and method, in which the X axis show minutes lapsed, and Y axis shows voltage in mV, and the hydrocarbon reduction is acknowledged.

Fig.5 is the graphic result of the GC-FID analysis of a commercially available jet fuel sample, in which the X axis show minutes lapsed, and Y axis shows voltage in mV.

Fig.6 is the graphic result of the GC-FID analysis of a commercially available jet fuel sample, treated with the claimed compound and method, in which the X axis show minutes lapsed, and Y axis shows voltage in mV, and the hydrocarbon reduction is acknowledged.

Description of Embodiments

[0019] There is a positive need for a method that reduces polutant agents in liquid substituted hydrocarbon-mixtures used as fuels. Prior art teaches a number of refining steps to convert oil into usable fuels in the industry. However, these fuels still have sulfur compounds, aromatic compounds, bencenes, xylenes, bencenes, toluenes, and others that do not burn adequately when used, and it is therefore necessary a better refining method to reduce fuels' polluting effects.

[0020] The process is achieved by supersaturating ferrous oxide in water. The ferrous oxide supersaturation process has been described by (MARTIN, Scot T. Precipitation and dissolution of iron and manganese oxides. Environmental Catalysis, 2005, p. 61-81.). This supersaturated solution serves as catalyzer for refining fuel.

[0021] The ferrous oxide supersaturated solution is mixed with the fuel. It is well known that the ferrous oxide supersaturated solution may be used in a proportion of up to 70% of said solution against 30% fuel. However, in the preferred embodiment, the mixture is done with 10% solution to 90% fuel, that is, 100 liters of ferrous oxide super-saturated solution for each 1,000 liters of fuel one wishes to refine.

[0022] The supersaturated solution must be mixed by constant fluid blending, either by agitation, fluid recirculation, or barometric variations. In the preferred embodiment, 1 liter of this mixture must be mixed for at least one minute.

[0023] The result of said mixing is a hydrocarbon reduction in the final fuel. In [Fig.1] it is shown a graphic result of gas chromatography of a commercially available diese' sample. The first spike belongs to the dichloromethane used as control solvent. In [Fig.2] it is shown a graphic result of gas chromatography of a commercially available diese' after treatment with the claimed method. As one can appreciate according to the retention period shown in [Fig.2], the amount of lineal hydrocarbons has been reduced, which show the refining capabilities of this method.

[0024] In [Fig.3] it is shown the graphic result of gas chromatography of a commercially available gasoline sample. The firs spike belongs to the dichloromethane used as control solvent. In [Fig.4] it is shown the graphic result of gas chromatography of a sample of the same commercially available gasoline after being treated with the claimed method. As one can appreciate, the quantity of cyclic hydrocarbons has also decreased.

[0025] [Fig.5] belongs to the analysis to commercially available jet fuel, and [Fig.6] to the analysis of the same jet fuel after being treated with the claimed method. The results are similar to those of diese' and gasoline.

Industrial Applicability

[0026] This method is applicable to any industry in which fuel is used and there is a desire to reduce polluting combustion byproducts, and improve fuel efficiency.

Patent references

[0027]

PTL 1: US4830733A, NAGT et al., 1989
PTL 2: US5910440A, GROSSMAN et al., 1999
PTL 3: US3341448A, FORD et al., 1967

References other than patents

[0028]

NPL 1: MAXWELL, I. E.; STORK, W. H. J. Hydrocarbon processing with zeolites. Studies in Surface Science and Catalysis, 2001, vol. 137, p. 747-819

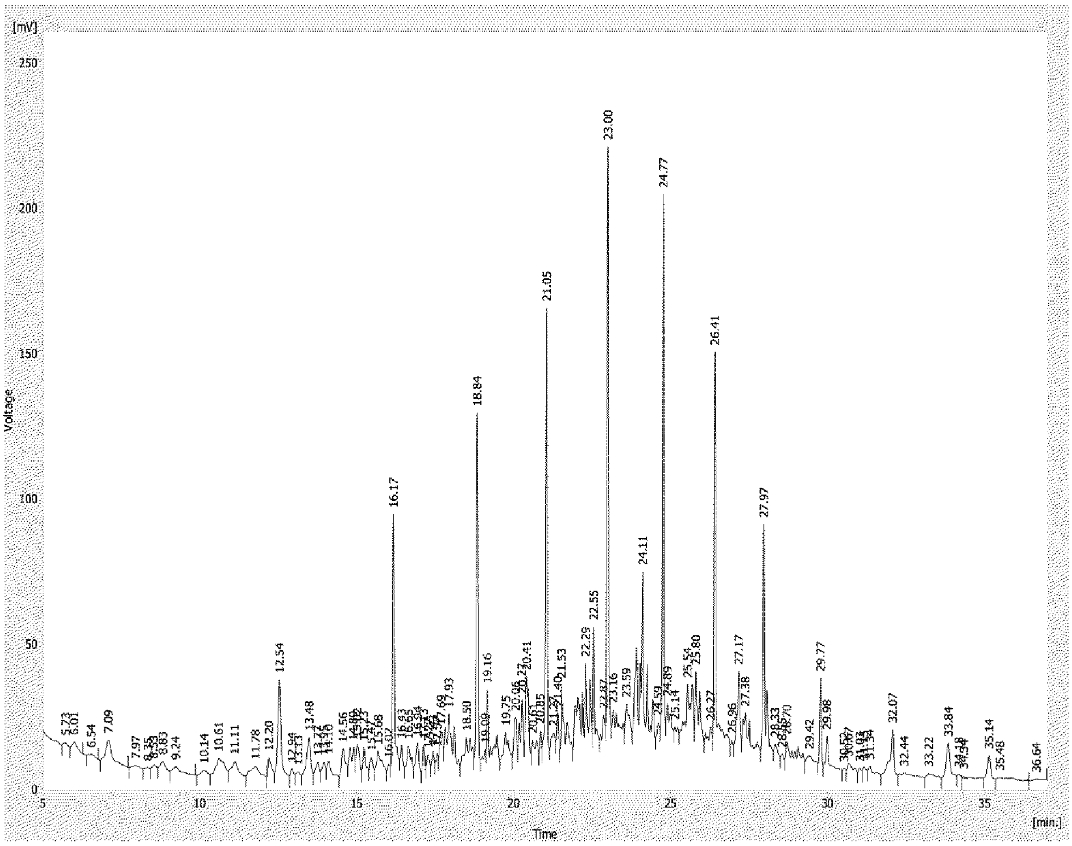
NPL 2: HAMADA, Hideaki, et al. Role of supported metals in the selective reduction of nitrogen monoxide with hydrocarbons over metal/alumina catalysts. Catalysis today, 1996, vol. 29, no 1, p. 53-57

NPL 3: MARTIN, Scot T. Precipitation and dissolution of iron and manganese oxides. Environmental Catalysis, 2005, p. 61-81.

Claims

1. Method for refining hydrocarbons used as fuels, wherein the method comprises; supersaturating ferrous oxide in water; mixing the super-saturated solution with liquid hydrocarbons used as fuel; combining the mixture until a homogeneous mixture is achieved; allowing the mixture to be decanted by mass difference; and separating the supersaturated solution from the liquid hydrocarbons.

[Fig. 1]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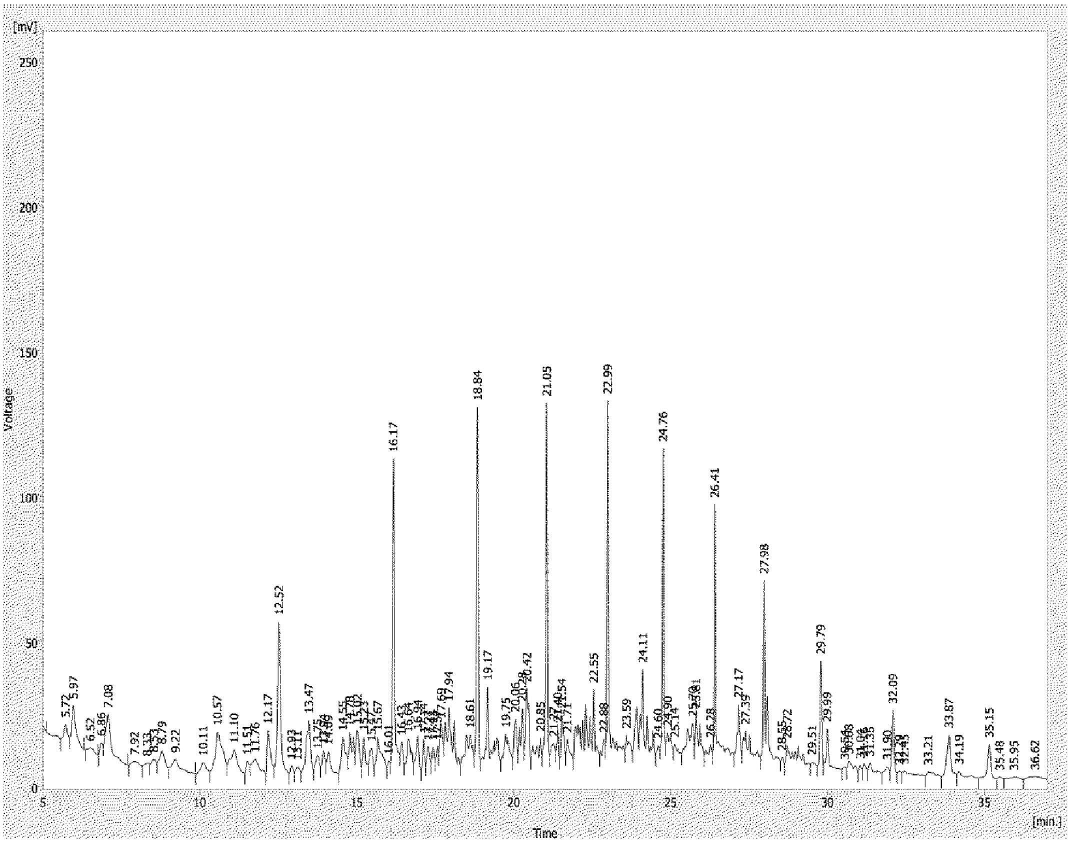
36.64

[Fig. 2]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11.76
12.17
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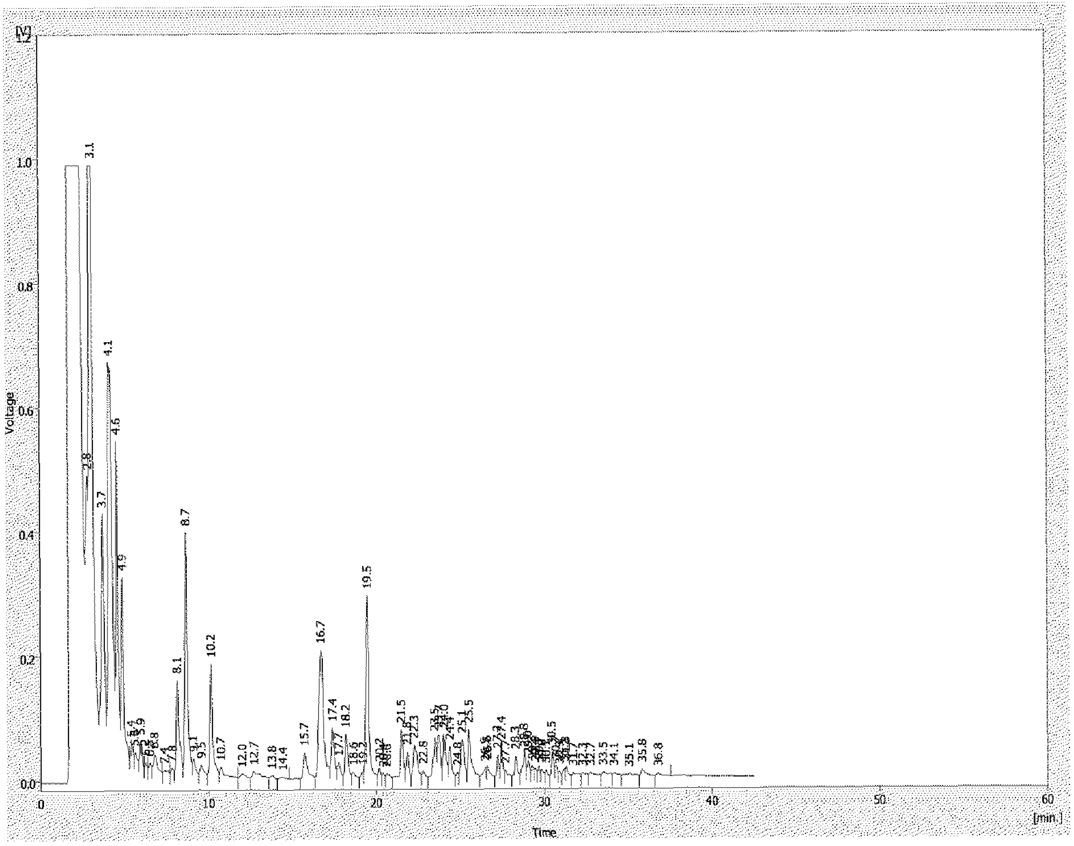
36.62

[Fig. 3]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10.2
16.7
8.1
17.4
18.2
21.5
25.5
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35.1
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10
20
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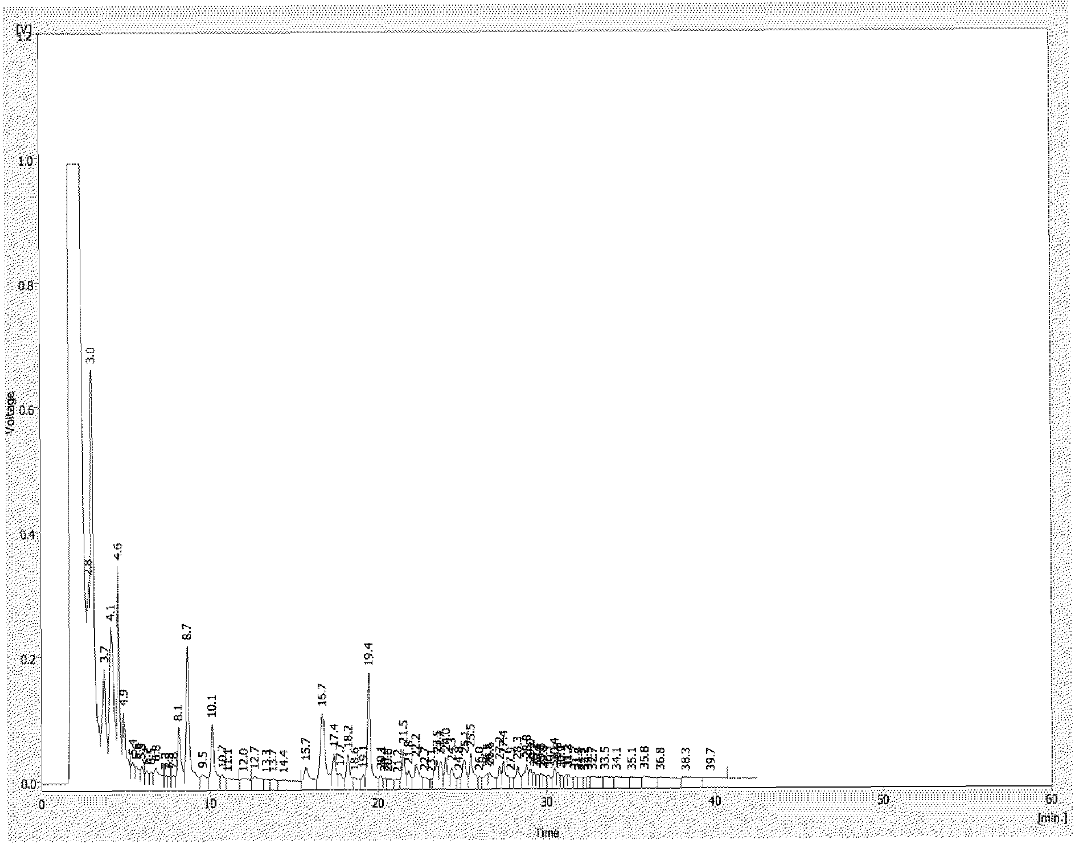
40
50
60
[min.]
Time

[Fig. 4]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Voltage
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4.1
3.7
8.7
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18.2
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9.5
35.8
35.1
38.3
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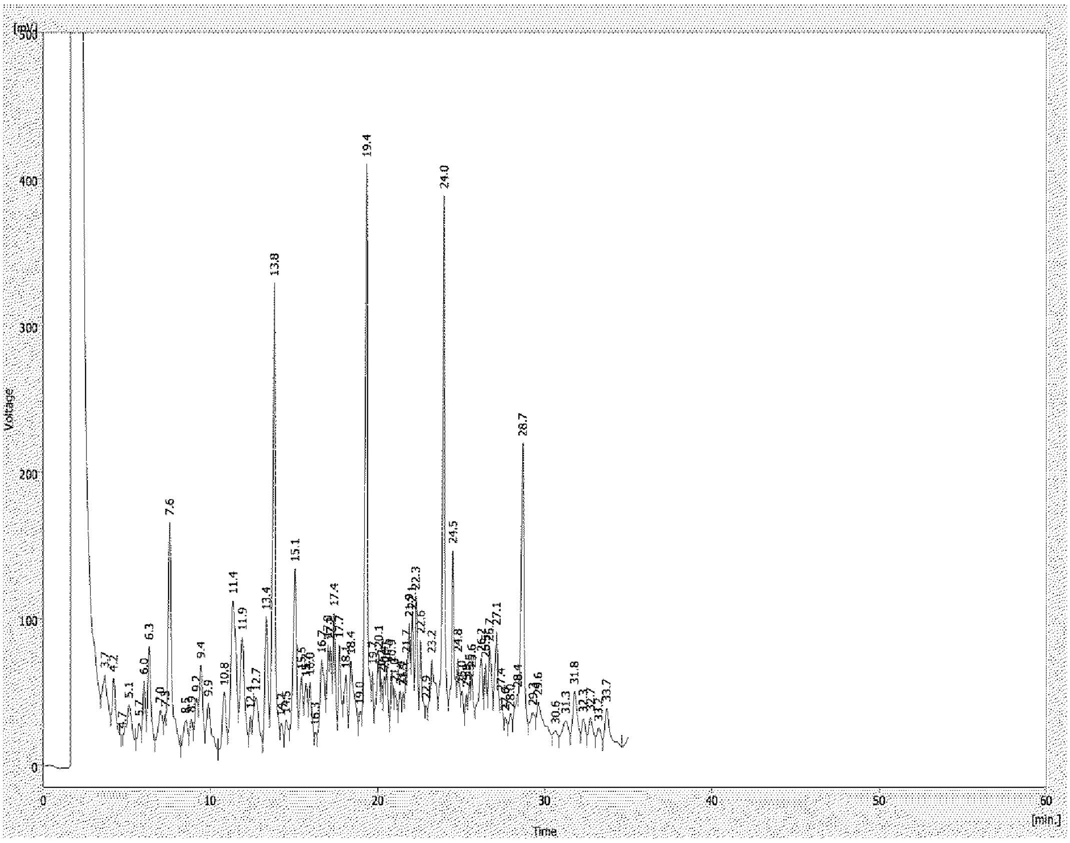
[min.]
Time

[Fig. 5]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22.3
22.6
22.9
23.2
24.0
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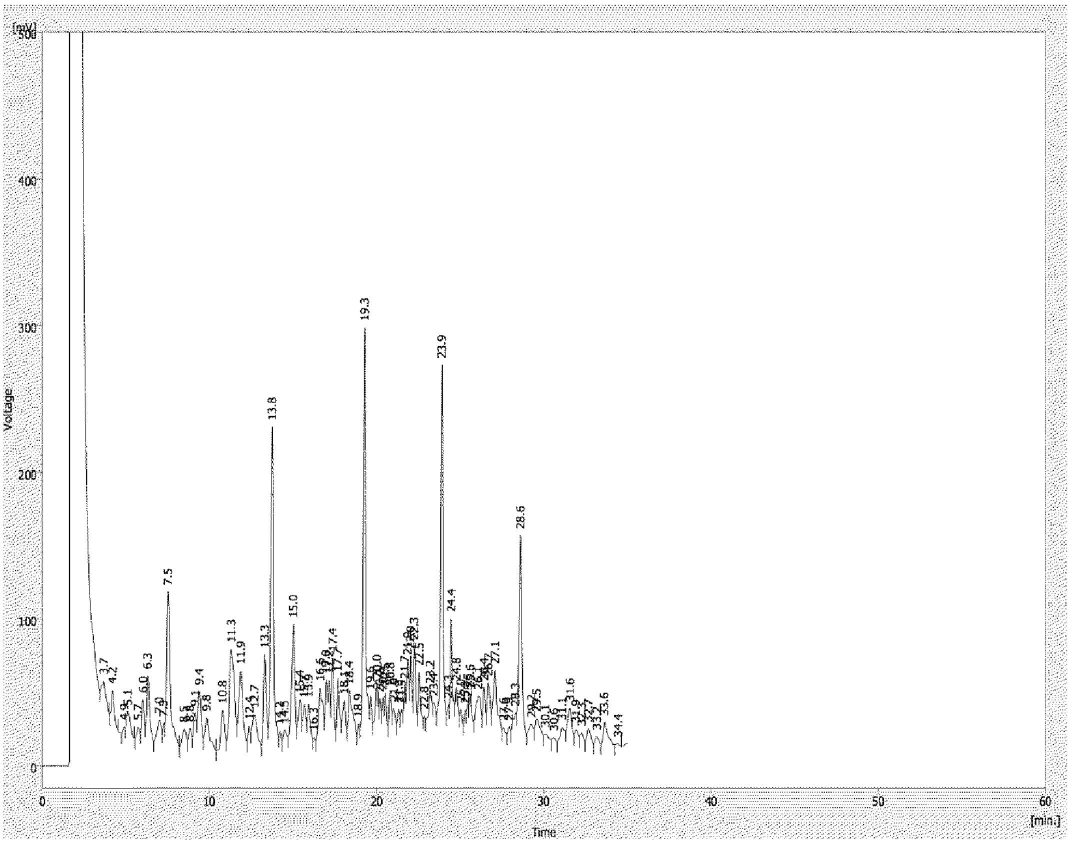
33.7

[Fig. 6]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31.6
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34.4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2016/055210

A. CLASSIFICATION OF SUBJECT MATTER

C10G29/16 (2006.01)
C10G29/00 (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, INVENES, WPI, DB-TXT, NPL, XPESP, CAS.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004108252 A1 (DE SOUZA WLADMIR FERRAZ) 10/06/2004, paragraphs 1, 19, 25, 30-36 and 39-42; claims 1 and 6; figures 6-8.	1
A	JP S4811321B B1 (NEGISHI, N. ET AL.) 12/04/1973, (Abstract) World Patent Index [on line]. London (United Kingdom) Thomson Publications, LTD. [Retrieved the 27/01/2017] DW 197316, Accession Number 1973-22480U.	1
A	CN 101067100 A (LI YUWEN BI SHU) 07/11/2007, (Abstract) World Patent Index [on line]. London (United Kingdom) Thomson Publications, LTD. [Retrieved the 27/01/2017] DW 200825, 201170, N° of access 2008-D30050.	1
A	US 2012215044 A1 (LIU CHIUNG-FANG ET AL.) 23/08/2012, claim 1.	1

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure use, exhibition, or other means.
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents , such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 31/01/2017	Date of mailing of the international search report **(10/02/2017)**
Name and mailing address of the ISA/ OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Facsimile No.: 91 349 53 04	Authorized officer N. Martín Laso Telephone No. 91 3493278

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2016/055210

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Form PCT/ISA/210 (patent family annex) (January 2015)

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- US 4830733 A, NAGT **[0005] [0027]**
- US 5910440 A, GROSSMAN **[0005] [0027]**
- US 3341448 A, FORD **[0005] [0027]**

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- **MAXWELL, I. E. ; STORK, W. H. J.** Hydrocarbon processing with zeolites. *Studies in Surface Science and Catalysis,* 2001, vol. 137, 747-819 **[0005] [0028]**
- **HAMADA, HIDEAKI et al.** Role of supported metals in the selective reduction of nitrogen monoxide with hydrocarbons over metal/alumina catalysts. *Catalysis today,* 1996, vol. 29 (1), 53-57 **[0013] [0028]**
- **MARTIN, SCOT T.** Precipitation and dissolution of iron and manganese oxides. *Environmental Catalysis,* 2005, 61-81 **[0020] [0028]**