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(54) Title: METHOD FOR DETECTING THE PRESENCE OF HYDROCARBONS DERIVED FROM METHANE IN A MIX-
TURE

(57) Abstract: Method for detecting the presence of hydrocarbons derived from naturally occurring methane, in particular Fischer-Tropsch derived hydrocarbon components, in a gaseous, liquid or solid refined hydrocarbon mixture wherein the method comprises a step of applying a spectroscopic method selected from isotope ratio mass spectrometry (IRMS) and TDLAS to the gaseous, liquid or solid refined hydrocarbon mixture and wherein the presence of hydrocarbons derived from naturally occurring methane is confirmed by a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -33 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB). Preferably, the method of the present invention is used for detecting the presence of Fischer-Tropsch derived hydrocarbon components in a lubricating composition.



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METHOD FOR DETECTING THE PRESENCE OF HYDROCARBONS DERIVED
FROM METHANE IN A MIXTURE

Field of the Invention

The present invention relates to a method for detecting the presence of any hydrocarbon derived from naturally occurring methane in a gaseous, liquid or solid refined hydrocarbon mixture. In particular, the present invention relates to a method for detecting the presence of Fischer-Tropsch derived hydrocarbons in a gaseous, liquid or solid refined hydrocarbon mixture.

Background of the Invention

Fischer-Tropsch derived hydrocarbon components are well known for use in various products, including, but not limited to, lubricating oil compositions and liquid fuel compositions. As is disclosed in for example D.J. Wedlock et al., "Gas-to-Liquids Base Oils to assist in meeting OEM requirements 2010 and beyond", presented at the 2nd Asia-Pacific base oil Conference, Beijing, China, 23-25 October 2007, the use of Fischer-Tropsch derived base oils in lubricating compositions such as engine oils, transmission fluids, and industrial lubricants can result in various performance benefits. Examples of performance benefits by the use of Fischer-Tropsch derived base oils mentioned in the above article include: improved oxidation stability properties, improved engine cleanliness, improved wear protection, improved emissions and improved after-treatment device compatibility. Also the Fischer-Tropsch derived base oils allow for the formulation of low-viscosity energy conserving formulations and exhibit very good cold flow properties, high viscosity indices and low volatility.

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Since the presence of Fischer-Tropsch derived hydrocarbon components in lubricating and fuel compositions provide highly desirable characteristics it would be useful to be able to quickly differentiate
5 between a product which contains Fischer-Tropsch derived hydrocarbon components and a product which does not contain Fischer-Tropsch derived hydrocarbon components. Quick differentiation between the compositions of different products is useful, for example, in the
10 detection of counterfeit lubricating oil compositions and other products.

Standard methods that can be used for detecting the presence of Fischer-Tropsch derived hydrocarbon components within product mixtures are analytical
15 chemistry techniques including various forms of chromatography and spectroscopy, however these methods can be costly and time consuming and are not always accurate or conclusive, especially in the case of mixtures of Fischer-Tropsch derived fluids and non-
20 Fischer-Tropsch derived fluids. In addition, these standard methods often require expert interpretation of results in order to reach a conclusion. It would therefore be desirable to provide an alternative method for detecting the presence of Fischer-Tropsch derived
25 hydrocarbon components, or any hydrocarbon derived from naturally occurring methane, in a mixture which obviates the problems of existing methods.

Summary of the Invention

According to a first aspect of the present invention
30 there is provided a method for detecting the presence of hydrocarbons derived from naturally occurring methane, in a gaseous, liquid or solid refined hydrocarbon mixture wherein the method comprises a step of applying a

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spectroscopic method selected from isotope ratio mass spectrometry (IRMS) and tunable diode laser absorption spectroscopy (TDLAS) to the gaseous, liquid or solid refined hydrocarbon mixture and wherein the presence of hydrocarbons derived from naturally occurring methane is confirmed by a $\delta^{13}\text{C}$ (difference in carbon-13 isotope content) value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -33 parts per thousand or less relative to the carbon-13 content of Vienna Pee Dee Belemnite (VPDB).

In a preferred embodiment of the present invention the hydrocarbon derived from naturally occurring methane is a Fischer-Tropsch derived hydrocarbon.

It has surprisingly been found that the method of the present invention offers the ability to detect the presence of hydrocarbon(s) derived from methane such as Fischer-Tropsch derived hydrocarbon components in unknown mixtures using a single test method, in a quick and easy manner, requiring minimal interpretation.

Detailed Description of the Invention

As used herein the term gaseous, liquid or solid refined hydrocarbon mixture means a gaseous, liquid or solid hydrocarbon mixture that is produced via refining of a feedstock derived from a commercially viable crude oil or natural gas reservoir.

The term "naturally occurring methane" as used herein refers to methane obtained from a commercially viable petroleum or natural gas reservoir.

The method of the present invention can be used for detecting the presence of hydrocarbons derived from naturally occurring methane, such as Fischer-Tropsch derived hydrocarbon components, in a gaseous, liquid or solid refined hydrocarbon mixture. The method of the

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present invention is suitable for use with any gaseous, liquid or solid refined hydrocarbon mixture which contains at least one hydrocarbon derived from naturally occurring methane, such as a Fischer-Tropsch derived hydrocarbon component. In one embodiment of the present invention the gaseous, liquid or solid refined hydrocarbon mixture is a lubricating oil composition. In another embodiment of the present invention the gaseous, liquid or solid refined hydrocarbon mixture is a liquid fuel composition. The present invention is also suitable for other types of mixtures which contain a hydrocarbon derived from naturally occurring methane such as a Fischer-Tropsch derived hydrocarbon component.

The method of the present invention can be used for detecting any hydrocarbon derived from naturally occurring methane, not just hydrocarbons which are derived from a Fischer-Tropsch process. For example, there are alternative techniques for making heavier hydrocarbons from methane, such as methane oxidative coupling, the products of which will likely have similarly unique isotope composition to the Fischer-Tropsch derived products. However, in a preferred embodiment of the present invention the hydrocarbon derived from naturally occurring methane is a Fischer-Tropsch hydrocarbon component.

Fischer-Tropsch derived components are known in the prior art. By the term "Fischer-Tropsch derived components" as used herein is meant hydrocarbons that are, or are derived from, a synthesis product of a Fischer-Tropsch process. Examples of hydrocarbons produced via the Fischer-Tropsch process include *n*-paraffins, isoparaffins, kerosene, naphtha, gas oil,

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distillates, waxes, base oils, solvents, drilling fluids, and the like, and mixtures thereof.

Preferred Fischer-Tropsch derived components herein include Fischer-Tropsch derived base oils and Fischer-Tropsch derived fuel components such as kerosene, naphtha
5 and gas oil.

Typical hydrocarbons produced via the Fischer-Tropsch process comprise from 2 to 300 carbon atoms, preferably from 2 to 200 carbon atoms. Further,
10 hydrocarbons produced via the Fischer-Tropsch process typically have a kinematic viscosity at 40°C in the range of from 0.1 to 400 mm²/s, preferably in the range of from 0.1 to 200 mm²/s.

In a preferred embodiment of the present invention the gaseous, liquid or solid refined hydrocarbon mixture
15 is a lubricating oil composition comprising a Fischer-Tropsch derived base oil. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils for use as a base oil in a lubricating composition include
20 those, for example, disclosed in EP0776959, EP0668342, WO1997021788, WO2000015736, WO2000014188, WO2000014187, WO2000014183, WO2000014179, WO2000008115, WO1999041332, EP1029029, WO2001018156 and WO2001057166.

An essential feature of the method of the present invention is a step of applying a spectroscopic method selected from isotope ratio mass spectrometry (IRMS) and tunable diode laser absorption spectroscopy (TDLAS) to
25 the gaseous, liquid or solid refined hydrocarbon mixture in question.
30

In a preferred embodiment of the present invention, the spectroscopic method is selected from IRMS. IRMS is a more established technique than TDLAS and has high degree

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of accuracy. However, TDLAS may be able to achieve a comparable level of accuracy and is therefore mentioned herein as a possible spectroscopic method for use in the present invention, particularly if a hand-held and/or mobile application is required.

Isotope ratio mass spectrometry (IRMS) is a well known analytical technique which is a specific type of mass spectrometry. In IRMS, mass spectrometric methods are used to measure the relative abundance of isotopes in a given sample. It has been applied most commonly in chemistry, earth sciences and environmental sciences. In these fields it is used for the analysis of stable isotopes which is normally concerned with measuring isotopic variations arising from mass-dependent isotopic fractionation in natural systems.

As used herein the term Isotope Ratio Mass Spectrometry (IRMS) encompasses both GC-IRMS (Gas Chromatography IRMS) and EA-IRMS (elemental analyzer IRMS).

The IRMS technique allows the precise measurement of mixtures of naturally occurring isotopes. The IRMS technique and spectrometers for use therein have been described in, for example, US4866270, US5012052, US5432344 and US20090114809, all of which are incorporated herein by reference.

In the method of the present invention the chosen spectroscopic method, such as isotope ratio mass spectrometry (IRMS), is applied to the gaseous, liquid or solid refined hydrocarbon mixture in question for the purpose of detecting any hydrocarbon derived from naturally occurring methane in the mixture, in particular any GTL hydrocarbon components. The method of the present invention can unmistakeably differentiate between, for

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example, GTL base oils and crude-derived base oils, polyalphaolefin (PAO) base oils, and lubricant additives, but is also applicable to any other type of Fischer-Tropsch derived component such as those mentioned
5 hereinabove.

In the method of the present invention, the presence of hydrocarbons derived from naturally occurring methane such as Fischer-Tropsch derived hydrocarbon components is confirmed by a $\delta^{13}\text{C}$ value for the gaseous, liquid or
10 solid mixture as determined by a spectroscopic method selected from IRMS and TDLAS of -33 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB). The ^{13}C content measured by IRMS or TDLAS for Fischer-Tropsch derived components is lower than for any material derived
15 from crude oil, natural gas liquids, plants, or in general naturally occurring hydrocarbon compounds with 2 or more carbons per molecule.

In a preferred embodiment of the present invention, the presence of hydrocarbons derived from naturally
20 occurring methane, such as Fischer-Tropsch derived hydrocarbon components, is confirmed via a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -35 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB).

In a more preferred embodiment of the present invention, the presence of hydrocarbons derived from naturally occurring methane such as Fischer-Tropsch derived hydrocarbon components is confirmed via a $\delta^{13}\text{C}$
25 value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -40
30 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB).

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In an especially preferred embodiment of the present invention, the presence of hydrocarbons derived from naturally occurring methane such as Fischer-Tropsch derived hydrocarbon components is confirmed via a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -44 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB).

According to another aspect of the present invention there is provided a method of determining the amount of hydrocarbons derived from naturally occurring methane, in particular Fischer-Tropsch derived hydrocarbon components, in a gaseous, liquid or solid refined hydrocarbon mixture, wherein the method comprises the step of applying a spectroscopic method selected from isotope ratio mass spectrometry (IRMS) or TDLAS to the gaseous, liquid or solid refined hydrocarbon mixture in order to determine its $\delta^{13}\text{C}$ value and comparing the $\delta^{13}\text{C}$ value of the gaseous, liquid or solid refined hydrocarbon mixture to the known $\delta^{13}\text{C}$ values of non-methane derived components in the gaseous, liquid or solid refined hydrocarbon mixture. This quantitative determination may be conducted by estimating the minimum and maximum possible amounts of methane-derived components in an unknown mixture from the 95% confidence limits of the carbon-13 isotope content of pure non methane-derived materials and pure methane-derived components using the following two equations:

$$\text{estimated max \% methane - derived components} = \frac{(\delta^{13}\text{C measured by IRMS}) - (\text{Upper CI limit for } \delta^{13}\text{C non - methane - derived})}{(\text{Upper CI limit for } \delta^{13}\text{C methane - derived}) - (\text{Upper CI limit for } \delta^{13}\text{C non - methane - derived})} \cdot 100$$

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$$\begin{aligned}
 & \text{estimated min \% methane - derived components} \\
 & = \frac{(\delta^{13}\text{C measured by IRMS}) - (\text{Lower CI limit for } \delta^{13}\text{C non - methane - derived})}{(\text{Lower CI limit for } \delta^{13}\text{C methane - derived}) - (\text{Lower CI limit for } \delta^{13}\text{C non - methane - derived})} \cdot 100
 \end{aligned}$$

As mentioned above, in a preferred embodiment the method of the present invention can be used for detecting the presence of Fischer-Tropsch derived components in lubricating compositions. There is no limit to the type of lubricating oil compositions which can be used in the present invention, as long as the lubricating oil composition comprises at least one Fischer-Tropsch derived component, such as a Fischer-Tropsch derived base oil.

A lubricating oil composition typically comprises a base oil and one or more performance additives.

Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" in relation to base oils is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition of the present invention include those, for example, disclosed in EP0776959, EP0668342, WO1997021788, WO2000015736, WO2000014188, WO2000014187, WO2000014183, WO2000014179, WO2000008115, WO1999041332, EP1029029, WO2001018156 and WO2001057166.

Typically, the aromatics content of a Fischer-Tropsch derived base oil, (as measured by IP-368, ASTM D2007, ASTM D7419), will be less than about 1 wt.%, alternatively less than about 0.5 wt.% or in alternate embodiments, less than about 0.1 wt.%. The base oil can have a total paraffin content of at least about 80 wt.%,

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alternatively at least about 85 wt.%, alternatively at least about 90 wt.%, alternatively at least about 95 wt.%, or, in certain embodiments, at least about 99 wt.%. The Fischer-Tropsch derived base oil can have a saturates content (as measured by IP-368, ASTM D2007, ASTM D7419, or any other chromatographic method that will yield similar results) of greater than about 98 wt.%, alternatively greater than about 99 wt.%, or alternatively greater than about 99.5 wt.%. The Fischer-Tropsch derived base oil can further include a maximum *n*-paraffin content of about 0.5 wt.% and naphthenic compound content of from 0 to less than 20 wt.%, alternatively from about 0.5 to 10 wt.%, alternatively from about 1-5 wt.%, or alternatively from about 5-10 wt.%.

Typically, the Fischer-Tropsch derived base oil or base oil blend has a kinematic viscosity at 100°C (as measured by ASTM D 7042) in the range of from 1 to 35 mm²/s (cSt), alternatively from 1 to 25 mm²/s (cSt), alternatively from 2 to 20 mm²/s (cSt), or alternatively from 2 mm²/s to 12 mm²/s. The Fischer-Tropsch derived base oil can have a kinematic viscosity at 100°C (as measured by ASTM D 7042) of at least 2.5 mm²/s, alternatively at least 3.0 mm²/s (e.g., "GTL 3"). In certain embodiments, the Fischer-Tropsch derived base oil can have a kinematic viscosity at 100°C of not greater than 5.0 mm²/s, alternatively not greater than 4.5 mm²/s, alternatively not greater than 4.2 mm²/s (e.g., "GTL 4"). In other embodiments, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of not greater than 8.5 mm²/s, alternatively not greater than 8 mm²/s (e.g., "GTL 8"). Other grades of GTL products would also

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be possible, based upon the specific manufacturing process utilized to produce the GTL product.

Further, the Fischer-Tropsch derived base oil can have a kinematic viscosity at 40°C (as measured by ASTM D445) of from 10 to 100 mm²/s (cSt), alternatively from 15 to 50 mm²/s, alternatively from 50 to 80 mm²/s, alternatively greater than 100 mm²/s.

Also, in certain embodiments, the Fischer-Tropsch derived base oil can have a pour point (as measured according to ASTM D 5950) of less than about -10°C, alternatively less than about -20°C, alternatively less than about -30°C, alternatively less than about -40°C, and alternatively less than about -45°C.

The flash point (as measured by ASTM D92) of the Fischer-Tropsch derived base oil can be greater than 120°C, alternatively greater than 130°C, alternatively greater than 140°C.

The Fischer-Tropsch derived base oil can have a viscosity index (according to ASTM D 2270) in the range of from about 100 to 200. Alternatively, the Fischer-Tropsch derived base oil can have a viscosity index of at least 125, alternatively at least 130. In certain embodiments, the viscosity index is less than 180, alternatively less than 160, alternatively less than 150. In certain embodiments, the viscosity index can be between 125 and 180, alternatively between 130 and 160.

In the event the Fischer-Tropsch derived base oil contains a blend of two or more Fischer-Tropsch derived base oils, the above values apply to the blend of the two or more Fischer-Tropsch derived base oils.

As used herein, the term "base oil" may refer to a mixture containing more than one base oil. Suitable base oils for use in a lubricating oil composition in addition

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to the Fischer-Tropsch derived base oil described above include one or more of the mineral derived or synthetic base oils selected from Group I, II, III or V base oils or Group IV poly-alpha olefins (PAOs), and mixtures thereof. By "Group I", "Group II", "Group III", "Group IV" and "Group V" base oils as used herein are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for category I, II, III, IV and V. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, July 2009.

In certain embodiments, the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%, and most preferably more than 90 wt.% of a Fischer-Tropsch derived base oil. In an alternate embodiment, not more than 5 wt.%, alternatively not more than 2 wt.%, of the base oil is not a Fischer-Tropsch derived base oil. In certain preferred embodiments, 100 wt% of the base oil is based on one or more Fischer-Tropsch derived base oils.

Preferably the base oil or base oil blend that includes the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of between 2 and 35 cSt, alternatively between 2 and 10.5 cSt (according to ASTM D 445).

In certain embodiments, the total amount of base oil that is incorporated in the lubricating composition herein is preferably an amount in the range of from 60 to 99 wt.%, alternatively an amount in the range of from 65 to 90 wt.%, and in certain preferred embodiments, in an amount in the range of from 70 to 85 wt.%, with respect to the total weight of the lubricating composition.

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The lubricating oil composition herein preferably has a kinematic viscosity at 40°C in the range of from 2 mm²/s to 1000 mm²/s, preferably in the range of from 32 mm²/s to 220 mm²/s.

5 The lubricating oil compositions herein can also include various other optional components such as solvency boosters, detergents, anti-oxidants, viscosity modifiers, anti-wear additives, such as dispersants, extreme-pressure additives, friction modifiers, viscosity
10 index improvers, pour point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-corrosion agents, seal compatibility agents and additive diluent base oils, etc.

 As the person skilled in the art is familiar with
15 the above and other additives, these are not further discussed here in detail. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

20 The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt.%, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt.%, more preferably from 0.1 to 20.0 wt.%, based on the
25 total weight of the lubricating composition.

 The lubricating compositions herein may be conveniently prepared by admixing the one or more additives with the base oil(s).

30 The lubricant composition described herein can find a variety of uses as a lubricant, including but not limited to, passenger car engine oils, heavy duty diesel engine oils, transmission lubricants, turbine oils, air compressor lubricants, hydraulic fluids, gear oils,

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greases, transformer oils, marine lubricants, and the like.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Various base oils (including non-GTL base oils and GTL base oils), performance additives, base oil blends and lubricant products were subjected to EA-IRMS in order to measure their $\delta^{13}\text{C}$ % values relative to VPDB. A Costech ECS 4010 Elemental Analyzer was used. The Elemental Analyzer was interfaced to a Thermo ConFlo IV coupled to a Thermo Delta V Plus IRMS. Samples were combusted in a combustion column held at 1050°C. Excess oxygen from combustion was reduced using copper placed inside a column held at 650°C. Analyte CO_2 was separated from N_2 using a 3 meter GC column maintained at a constant 30°C. The helium carrier gas flow rate was 100 ml/min. Internal standards were used for data normalization and the reference material NBS-22 was used to verify the results. Results are shown in Tables 1 to 5 below.

Table 1 (Non-GTL Base Oils)

Base Oil Type	Trade Name	$\delta^{13}\text{C}$ (parts per thousand) relative to VPDB
Group I base oil	Shell Durban HVI 65 ¹	-26.9
	Shell Durban HVI 110 ¹	-26.8
	Shell Durban HVI 650 ¹	-26.6

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Group II base oil	Motiva Star 4 ²	-26.8
	Motiva Star 6 ²	-26.8
	Motiva Star 12 ²	-27.1
Group III base oil	Yubase 3 ³	-26.6
	Yubase 4 ³	-26.7
	Yubase 8 ³	-26.8
PAO base oil	Durasyn 168 PAO ⁴	-29.7
	Durasyn 164 PAO ⁴	-29.2
	Durasyn 166 PAO ⁴	-29.6
	Synfluid mPAO 40 cSt ⁵	-34.0
	Synfluid PAO 100 cSt ⁵	-32.3
	Synfluid PAO 5 cSt ⁵	-31.8

1. Commercially available from Shell
2. Commercially available from Motiva
3. Commercially available from SK
4. Commercially available from Ineos
5. Commercially available from Chevron Phillips
Chemical

Table 2 (Additives)

General Name	$\delta^{13}\text{C}$ ‰ (parts per thousand) relative to VPDB
Ester	-27.4
Copper passivator	-31.1
Hydraulic Oil additive package	-30.4
Transmission oil additive package	-28.6
Hydraulic oil additive package	-28.1
Hydraulic oil additive package	-28.6
Olefin Copolymer Viscosity Modifier in Mineral Oil Diluent	-28.1
Engine Oil Additive Package	-28.5
Engine Oil Additive Package	-28.7

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Engine Oil Additive Package	-28.0
Engine Oil Additive Package	-28.3
Engine Oil Additive Package	-28.2
Engine Oil Additive Package	-27.8
Engine Oil Additive Package	-29.3
Engine Oil Additive Package	-28.8
Olefin Copolymer Viscosity Modifier in Mineral Oil Diluent	-27.0
Engine Oil Additive Package	-28.2
Transmission oil additive package	-28.3
Hydraulic oil additive package	-28.3
Turbine oil additive package	-27.6
Aminic antioxidant	-27.5
Automotive gear oil package	-26.6
Engine Oil Additive package	-28.1
Engine Oil Additive package	-28.9
Engine Oil Additive package	-28.4
Engine Oil Additive package	-27.7
Olefin Copolymer Viscosity Modifier in Mineral Oil Diluent	-27.8

Table 3 (GTL Base Oils)

In Table 3 below "GTL 3" was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100°C (ASTM D445) of approximately 3 cSt (mm^2s^{-1}). GTL 3 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

In Table 3 below "GTL 4" was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100°C (ASTM D445) of approximately 4 cSt (mm^2s^{-1}). GTL 4 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby

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incorporated by reference.

In Table 3 below "GTL 8" was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100°C (ASTM D445) of approximately 8 cSt (mm^2s^{-1}). GTL 8 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

The $\delta^{13}\text{C}$ data in Table 3 covers a series of GTL 3, GTL 4, and GTL 8 samples from separate batches produced from 2012 to 2014.

Table 3

Description	$\delta^{13}\text{C}$ (parts per thousand) relative to VPDB
GTL 4	-44.6
GTL 8	-44.7
GTL 3	-45.3
GTL 8	-46.4
GTL 3	-45.1
GTL 8	-46.9
GTL 4	-45.8
GTL 8	-46.7
GTL 3	-45.2
GTL 3	-44.9
GTL 8	-46.9
GTL 4	-45.5
GTL 8	-47.2
GTL 8	-46.9
GTL 4	-46.3
GTL 8	-46.3
GTL 3	-45.4
GTL 4	-46.4
GTL 8	-46.4
GTL 3	-45.2

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GTL 4	-45.9
GTL 8	-46.7
GTL 3	-45.1
GTL 8	-46.4
GTL 8	-46.6
GTL 4	-46.5
GTL 8	-47.2
GTL 3	-45.2
GTL 4	-46.4
GTL 8	-47.1
GTL 4	-46.3
GTL 3	-45.3
GTL 4	-45.9
GTL 4	-45.9
GTL 8	-46.5
GTL 8	-46.7
GTL 3	-45.5
GTL 4	-45.0
GTL 4	-45.7
GTL 4	-45.5
GTL 4	-45.4

Table 4 - Means and 95% Confidence Intervals for Each Set of Example Data

			95% Confidence Interval for Mean	
	Count	Mean	Lower limit	Upper limit
Group I base oil	3	-26.8	-28.2	-25.3
Group II base oil	3	-26.9	-28.4	-25.4

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Group III base oil	3	-26.7	-25.8	-27.6
PAO base oil	6	-31.1	-32.1	-30.1
GTL base oil	41	-46.0	-47.2	-44.6
Additives	27	-28.3	-28.7	-27.9

Table 5 (Commercially Available Lubricants Not Containing GTL Base Oils and Quantitative Estimates of Fischer-Tropsch Content for Each)

Trade Name	$\delta^{13}\text{C}$ (parts per thousand) relative to VPDB	Estimated minimum % Fischer-Tropsch components	Estimated maximum % Fischer-Tropsch components
Mobil 1 Full Synthetic 5W-30	-29.2	0	19.1
Kendall GT 5W-30 Liquid Titanium Full Synthetic	-26.8	0	7.4
Castrol Edge Full Synthetic 5W-30 (Russia)	-27.6	0	11.3

Discussion

The results set out in Tables 1 to 5 show that the GTL base oils and base oil blends containing GTL base oil give a much lower $\delta^{13}\text{C}$ % value relative to VPDB as measured by IRMS than non-GTL base oils, lubricant additives and lubricating compositions not containing GTL base oils. It is expected that all commercially available non-GTL base oils and commercially available lubricant

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additives will have greater carbon-13 content (thus greater $\delta^{13}\text{C}$ value) than GTL base oils. Methane from commercially viable petroleum or natural gas reservoirs contains a lesser amount of carbon-13 than higher molecular weight hydrocarbons from commercially viable petroleum or natural gas reservoirs, thus GTL products contain less amounts of carbon-13 than products derived from higher molecular weight hydrocarbons from commercially viable petroleum or natural gas reservoirs.

This observation is explained by that fact that $^{12}\text{C}-^{12}\text{C}$ bonds break at a faster rate than $^{13}\text{C}-^{12}\text{C}$ and $^{13}\text{C}-^{13}\text{C}$ bonds, thus methane that is formed from the breakdown of larger hydrocarbons in a commercially viable petroleum or natural gas reservoir will contain a lesser amount of carbon-13 than higher molecular weight hydrocarbons from commercially viable petroleum or natural gas reservoirs. These results demonstrate that the method of the present invention can be used as a quick and easy way to detect the presence of GTL components in a lubricant composition.

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C L A I M S

1. Method for detecting the presence of hydrocarbons derived from naturally occurring methane in a gaseous, liquid or solid refined hydrocarbon mixture wherein the method comprises a step of applying a spectroscopic method
5 selected from isotope ratio mass spectrometry (IRMS) and tunable diode laser absorption spectroscopy (TDLAS) to the gaseous, liquid or solid refined hydrocarbon mixture and wherein the presence of hydrocarbons which have been derived from naturally occurring methane are confirmed by
10 a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -33 parts per thousand or less relative to the carbon-13 content of Vienna Pee Dee Belemnite (VPDB).
2. Method according to Claim 1 wherein the presence of
15 hydrocarbons derived from naturally occurring methane are confirmed via a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -35 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB).
- 20 3. Method according to Claim 1 or 2 wherein the presence of hydrocarbons derived from naturally occurring methane are confirmed via a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined by IRMS or TDLAS of -40 parts per thousand or less relative to Vienna
25 Pee Dee Belemnite (VPDB).
4. Method according to any of Claims 1 to 3 wherein the presence of hydrocarbons derived from naturally occurring methane are confirmed via a $\delta^{13}\text{C}$ value for the gaseous, liquid or solid refined hydrocarbon mixture as determined

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by IRMS or TDLAS of -44 parts per thousand or less relative to Vienna Pee Dee Belemnite (VPDB).

5 5. Method according to any of Claims 1 to 4 wherein the hydrocarbons derived from naturally occurring methane are hydrocarbons produced via the Fischer-Tropsch process.

6. Method according to Claim 5 wherein the hydrocarbons produced via the Fischer-Tropsch process are selected from *n*-paraffins, isoparaffins, kerosene, naphtha, gas oil, distillates, waxes, base oils, solvents, drilling fluids, and mixtures thereof.

7. Method according to Claim 5 or 6 wherein the hydrocarbons produced via the Fischer-Tropsch process comprise from 2 to 300 carbon atoms.

8. Method according to any of Claims 5 to 7 wherein the hydrocarbons produced via the Fischer-Tropsch process have a kinematic viscosity at 40°C in the range of from 0.1 to 400 mm²/s.

9. Method of determining the amount of hydrocarbons derived from naturally occurring methane in a gaseous, liquid or solid refined hydrocarbon mixture, wherein the method comprises the step of applying a spectroscopic method selected from isotope ratio mass spectrometry (IRMS) and TDLAS to the gaseous, liquid or solid refined hydrocarbon mixture in order to determine its $\delta^{13}\text{C}$ value and comparing the $\delta^{13}\text{C}$ value of the gaseous, liquid or solid refined hydrocarbon mixture to the known $\delta^{13}\text{C}$ values of non-methane derived components in the gaseous, liquid or solid refined hydrocarbon mixture.

10. Method according to any of Claims 1 to 9 wherein the gaseous, liquid or solid refined hydrocarbon mixture is a lubricating oil composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058077A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N33/28
ADD.

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)
G01N

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)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MCCOLLOM T M ET AL: "The influence of carbon source on abiotic organic synthesis and carbon isotope fractionation under hydrothermal conditions", GEOCHIMICA ET COSMOCHIMICA ACTA, PERGAMON PRESS, NEW YORK, NY, US, vol. 74, no. 9, 1 May 2010 (2010-05-01), pages 2717-2740, XP026994241, ISSN: 0016-7037 [retrieved on 2010-02-17] the whole document ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

24 June 2016

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058077

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	T. M. MCCOLLOM: "Laboratory Simulations of Abiotic Hydrocarbon Formation in Earth's Deep Subsurface", REVIEWS IN MINERALOGY AND GEOCHEMISTRY, vol. 75, no. 1, 1 January 2013 (2013-01-01), pages 467-494, XP055229292, US ISSN: 1529-6466, DOI: 10.2138/rmg.2013.75.15 the whole document -----	1-10
A	ZHIFU WEI ET AL: "Abiogenic gas: Should the carbon isotope order be reversed?", JOURNAL OF PETROLEUM SCIENCE AND ENGINEERING, ELSEVIER, AMSTERDAM, NL, vol. 84, 29 January 2012 (2012-01-29), pages 29-32, XP028418726, ISSN: 0920-4105, DOI: 10.1016/J.PETROL.2012.01.019 [retrieved on 2012-02-07] the whole document -----	1-10