

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 November 2003 (06.11.2003)

PCT

(10) International Publication Number
WO 03/091364 A2

(51) International Patent Classification⁷: **C10L 1/08**,
1/16, 10/00, 10/06

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(21) International Application Number: PCT/EP03/04359

(22) International Filing Date: 24 April 2003 (24.04.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02252946.5 25 April 2002 (25.04.2002) BP

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: DIESEL FUEL COMPOSITIONS

(57) Abstract: Use of a Fischer-Tropsch derived gas oil in a diesel fuel composition, optionally together with a detergent, to reduce and/or clean up engine fouling. Use of a Fischer-Tropsch derived gas oil, and/or of a fuel composition containing it, to clean a diesel engine. Method for assessing a diesel fuel composition, involving measurement of engine fouling levels. Diesel fuel composition based on a fuel or fuel blend comprising at least 30% w/w of a Fischer-Tropsch derived gas oil.



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Diesel fuel compositions

This invention relates to diesel fuel compositions, their preparation and their use in diesel engines, and to the use of certain types of fuel in diesel fuel compositions.

5 Typical diesel fuels comprise liquid hydrocarbon middle distillate fuel oils having boiling points from about 150 to 400°C. Examples of such fuels include the reaction products of Fischer-Tropsch methane condensation processes, for example the process known as Shell Middle
10 Distillate Synthesis (van der Burgt et al, "The Shell Middle Distillate Synthesis Process", paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985; see also the November 1989 publication of the same title from Shell International Petroleum Company
15 Ltd, London, UK). These Fischer-Tropsch derived gas oils are low in undesirable fuel components such as sulphur, nitrogen and aromatics and tend to lead to lower vehicle emissions. They are typically blended with other diesel base fuels, for instance petroleum derived gas oils, at
20 concentrations of for instance from 10 to 30% w/w, to modify the base fuel properties.

 Compression-ignition (diesel) engines running on conventional diesel fuels can suffer from the build up of combustion related deposits in their fuel injection
25 systems, in particular in the injector nozzles. This injector fouling can impair engine performance. To reduce fouling, a detergent-containing additive may be included in

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the fuel, or the proportion of heavier components in the fuel may be adjusted so as to lower its endpoint.

It has now been found that Fischer-Tropsch derived fuels can themselves contribute to a reduction in, and/or reversal of, injector fouling. A fuel composition
5 containing such components can therefore be used to help maintain and/or improve engine cleanliness.

According to a first aspect of the present invention there is provided the use of a Fischer-Tropsch derived gas
10 oil in a diesel fuel composition, for the purpose of reducing subsequent combustion related deposits in a diesel engine into which the fuel composition is introduced.

The Fischer-Tropsch derived gas oil may instead or in addition be used for the purpose of removing previously
15 incurred combustion related deposits (ie, to "clean up" the engine).

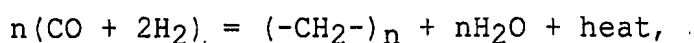
In the context of the present invention, "reducing" includes complete prevention and "removing" embraces both complete and partial removal. "Use" of the Fischer-Tropsch
20 derived gas oil in a fuel composition means incorporating the fuel into the composition, typically as a blend (ie, a physical mixture) with one or more other fuels, conveniently before the composition is introduced into the engine.

25 The Fischer-Tropsch derived gas oil should be suitable for use as a diesel fuel. Its components (or the majority, for instance 95% w/w or greater, thereof) should therefore have boiling points within the typical diesel fuel ("gas oil") range, ie, from about 150 to 400°C or from 170 to

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370°C. It will suitably have a 90% w/w distillation temperature of from 300 to 370°C.

By "Fischer-Tropsch derived" is meant that the fuel is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons:



in the presence of an appropriate catalyst and typically at elevated temperatures (eg, 125 to 300°C, preferably 175 to 250°C) and/or pressures (eg, 5 to 100 bar, preferably 12 to 50 bar). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

A gas oil product may be obtained directly from this reaction, or indirectly for instance by fractionation of a Fischer-Tropsch synthesis product or from a hydrotreated Fischer-Tropsch synthesis product. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, eg, GB-B-2077289 and EP-A-0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The

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desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-
5 decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4125566 and US-A-4478955.

Typical catalysts for the Fischer-Tropsch synthesis of
10 paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0583836 (pages 3 and 4).

15 An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (*supra*). This process produces middle distillate range products by conversion of a natural gas (primarily
20 methane) derived synthesis gas into a heavy long-chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. A version of the SMDS process, utilising a fixed-bed reactor
25 for the catalytic conversion step, is currently in use in Bintulu, Malaysia and its products have been used in petroleum derived gas oil blends in commercially available automotive fuels.

Gas oils prepared by the SMDS process are commercially
30 available for instance from the Royal Dutch/Shell Group of

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Companies. Further examples of Fischer-Tropsch derived gas oils are described in EP-A-0583836, EP-A-1101813, WO-A-97/14768, WO-A-97/14769, WO-A-00/20534, WO-A-00/20535, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83641, 5 WO-A-01/83647, WO-A-01/83648 and US-A-6204426.

Suitably, in accordance with the present invention, the Fischer-Tropsch derived gas oil will consist of at least 70% w/w, preferably at least 80% w/w, more preferably at least 90% w/w, most preferably at least 95% w/w, of 10 paraffinic components, preferably iso- and linear paraffins. The weight ratio of iso-paraffins to normal paraffins will suitably be greater than 0.3 and may be up to 12; suitably it is from 2 to 6. The actual value for this ratio will be determined, in part, by the 15 hydroconversion process used to prepare the gas oil from the Fischer-Tropsch synthesis product. Some cyclic paraffins may also be present.

By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived gas oil has essentially no, or undetectable 20 levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. Further, the process as usually operated produces no or virtually no aromatic components. 25 The aromatics content of a Fischer-Tropsch gas oil, as determined by ASTM D 4629, will typically be below 1% w/w, preferably below 0.5% w/w and more preferably below 0.1% w/w.

The Fischer-Tropsch derived gas oil used in the 30 present invention will typically have a density from 0.76

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to 0.79 g/cm³ at 15°C; a cetane number (ASTM D613) greater than 70, suitably from 74 to 85; a kinematic viscosity from 2.0 to 4.5, preferably from 2.5 to 4.0, more preferably from 2.9 to 3.7, centistokes at 40°C; and a sulphur content
5 of 5 ppmw (parts per million by weight) or less.

Preferably it is a product prepared by a Fischer-Tropsch methane condensation reaction using a hydrogen/carbon monoxide ratio of less than 2.5, preferably less than 1.75, more preferably from 0.4 to 1.5, and
10 ideally using a cobalt containing catalyst. Suitably it will have been obtained from a hydrocracked Fischer-Tropsch synthesis product (for instance as described in GB-B-2077289 and/or EP-A-0147873), or more preferably a product from a two-stage hydroconversion process such as
15 that described in EP-A-0583836 (see above). In the latter case, preferred features of the hydroconversion process may be as disclosed at pages 4 to 6, and in the examples, of EP-A-0583836.

The level of combustion related deposits in a diesel
20 engine may be measured in its fuel injection system, with reference to the degree of fouling of the injector nozzles. Degree of nozzle fouling may be assessed in a number of ways, for instance visually, by measuring the mass of deposits in a fouled nozzle or by measuring the fluid flow
25 (for instance, fuel flow or more preferably air flow) properties of the fouled nozzle relative to those of the clean nozzle.

An appropriate test might for example determine the degree of nozzle fouling (conveniently in the form of a
30 percentage injector fouling index) under steady state

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conditions in a suitable diesel engine, for instance based on the change in air flow rate through one or more of the nozzles as a result of using the fuel composition.

Conveniently the results are averaged over all of the injector nozzles of the engine. A suitable test protocol, using an indirect injection diesel engine, is described below in connection with the experimental examples. The CEC standard test method F-23-T-00, which again involves injector nozzle air flow measurements, may also be used to assess engine fouling.

The invention may be applicable where the fuel composition is used or intended to be used in a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or in an indirect injection diesel engine. The fuel composition may be suitable for use in heavy and/or light duty diesel engines.

The amount of the Fischer-Tropsch derived gas oil used may be from 0.5 to 100% w/w of the overall diesel fuel composition, suitably from 1 to 60% w/w, preferably from 5 to 50% w/w, more preferably from 10 to 30% w/w. It may be desirable for the composition to contain 8% w/w or greater, more preferably 10% w/w or greater, most preferably 20% w/w or greater, of the Fischer-Tropsch gas oil.

Other fuel components of the composition may be diesel fuels of conventional type, typically comprising liquid hydrocarbon middle distillate fuel oils, for instance petroleum derived gas oils. Such fuel components will typically have boiling points within the usual diesel range of 150 to 400°C, depending on grade and use.

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The diesel fuel composition may, in order to achieve a reduction and/or removal of engine deposits, consist essentially of the Fischer-Tropsch derived gas oil - in other words it may contain a major proportion (by which is meant preferably 99% w/w or more of the fuel composition, more preferably 99.5% w/w or more, most preferably 99.8% w/w or more, even up to 100% w/w) of the Fischer-Tropsch derived gas oil, optionally with a minor proportion of one or more diesel fuel additives such as are known in the art but with no other diesel fuels.

The overall fuel composition preferably has a low or ultra low sulphur content, for instance at most 1000 ppmw (parts per million by weight), preferably no more than 500 ppmw, most preferably no more than 100 or 50 or even 10 ppmw. It preferably has a cetane number (ASTM D613) from 40 to 85, more preferably from 45 to 75. Its density will typically be from 0.75 to 0.9 g/cm³, preferably from 0.8 to 0.85 g/cm³, at 15°C.

The Fischer-Tropsch derived gas oil may in particular be used to enhance the performance of a fuel or fuel blend which would otherwise cause relatively high levels of combustion related deposits, for instance a fuel having a relatively high endpoint and/or containing relatively high levels of aromatic components, and/or of a fuel or blend which causes, after three hours' engine running, a reduction in the achievable air flow rate through one or more of the engine nozzles of greater than 35 or 40 or 45% for instance measured using the test protocol described below.

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Although in general the diesel fuel composition may or may not contain additives, it is preferred that it includes a detergent, since this may enhance the cleaning effect of the Fischer-Tropsch derived gas oil. The first aspect of the present invention may therefore involve the use of both a Fischer-Tropsch derived gas oil and a detergent, in a diesel fuel composition, for the purpose of reducing subsequent combustion related deposits in a diesel engine into which the fuel composition is introduced and/or for the purpose of removing previously incurred combustion related deposits.

By "detergent" is meant an agent (suitably a surfactant) which can act to remove, and/or to prevent the build up of, combustion related deposits within the engine, in particular in the fuel injection system such as in the injector nozzles. Such materials are sometimes referred to as dispersant additives.

The Fischer-Tropsch derived gas oil, or alternatively the combination of the Fischer-Tropsch derived gas oil and the detergent, is preferably included in the fuel composition at a concentration sufficient to achieve a reduction in engine fouling (measured for instance as outlined above) of at least 5%, preferably at least 8%, more preferably at least 10%, most preferably at least 20%, as compared to that which results from using (under the same or comparable conditions) the same fuel composition but without the Fischer-Tropsch gas oil. Alternatively the reduction may be relative to the degree of engine fouling which results from the use (under the same or comparable conditions) of a fuel composition containing no, or less

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than 1% w/w, Fischer-Tropsch derived fuels and no, or less than 50 or even 20 ppmw of, detergent.

More preferably, the Fischer-Tropsch derived gas oil, or alternatively the combination of the Fischer-Tropsch derived gas oil and the detergent, is included at a concentration sufficient to remove, at least partially, combustion related deposits which have built up in the engine's fuel injection system, in particular in the injector nozzles, during a previous period of running using another diesel fuel (typically a fuel containing no, or less than 1% w/w, Fischer-Tropsch derived fuels and no, or less than 50 or even 20 ppmw of, detergent), when the engine is subsequently run on the Fischer-Tropsch fuel containing composition. This concentration is preferably sufficient to remove at least 5% of the previously incurred injector deposits (measured for instance as described above), more preferably at least 10%, most preferably at least 15 or 20 or 25 or 30%.

The removal of combustion related deposits may be achieved by running the engine on the Fischer-Tropsch fuel containing composition for instance for the same period of time as that during which the deposits accumulated, or more preferably for 75%, yet more preferably 50% or even 40% or 30%, of the period of deposit accumulation, conveniently under comparable conditions. Ideally at least partial removal of combustion related deposits is achieved by running the engine on the Fischer-Tropsch fuel containing composition for five hours or less, preferably for three hours or less, more preferably for two hours or less.

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Where the fuel composition includes a detergent, preferred concentrations lie in the range 20 to 500 ppmw active matter detergent based on the overall fuel composition, more preferably 40 to 500 ppmw, most preferably 40 to 300 ppmw or 100 to 300 ppmw or 150 to 300 ppmw. In the case of most commercially available detergent containing diesel fuel additives, this may mean that the additive is incorporated at levels higher than the standard recommended single treat rate, for example between 1.2 and 3 times, preferably between 1.5 and 2.5 times, such as about twice the standard single treat rate. Lower detergent levels (for example, corresponding to between 0.5 and 1.2 times, preferably the same as, the standard single treat rate) may however be used to help reduce or prevent further engine fouling and/or power loss.

Examples of detergents suitable for use in accordance with the present invention include polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (eg, polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557561 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

Detergent-containing diesel fuel additives are known and commercially available, for instance from Infineum (eg, F7661 and F7685) and Octel (eg, OMA 4130D).

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The fuel composition may contain other components in addition to the Fischer-Tropsch derived fuel and if applicable the detergent. Typically such components will be incorporated in fuel additives, for instance in combination with a detergent. Examples are lubricity enhancers such as EC 832 and PARADYNE™ (ex Infineum), HITEC™ E580 (ex Ethyl Corporation) and VEKTRON™ 6010 (ex Infineum) and amide-based additives such as those available from the Lubrizol Chemical Company, for instance LZ 539 C; dehazers, eg, alkoxyated phenol formaldehyde polymers such as those commercially available as NALCO™ EC5462A (formerly 7D07) (ex Nalco), and TOLAD™ 2683 (ex Petrolite); anti-foaming agents (eg, the polyether-modified polysiloxanes commercially available as TEGOPREN™ 5851 and Q 25907 (ex Dow Corning), SAG™ TP-325 (ex OSi) and RHODORSIL™ (ex Rhone Poulenc)); ignition improvers (cetane improvers) (eg, 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US-4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (eg, that sold commercially by Rhein Chemie, Mannheim, Germany as "RC 4801", a propane-1, 2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, eg, the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (eg, phenolics such as 2,6-di-tert-butylphenol, or

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phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); and metal deactivators.

Unless otherwise stated, the (active matter) concentration of each such additional component in the overall fuel composition is preferably up to 1% w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

It is particularly preferred that a lubricity enhancer be included in the fuel composition, especially when it has a low (eg, 500 ppmw or less) sulphur content. The lubricity enhancer is conveniently present at a concentration from 50 to 1000 ppmw, preferably from 100 to 1000 ppmw, based on the overall fuel composition.

The (active matter) concentration of any dehazer in the fuel composition will preferably be in the range from 1 to 20 ppmw, more preferably from 1 to 15 ppmw, still more preferably from 1 to 10 ppmw and advantageously from 1 to 5 ppmw. The (active matter) concentration of any ignition improver present will preferably be 600 ppmw or less, more preferably 500 ppmw or less, conveniently from 300 to 500 ppmw.

A second aspect of the present invention provides a method of operating a diesel engine, and/or a vehicle which is driven by a diesel engine, which method involves introducing into a combustion chamber of the engine a diesel fuel composition incorporating a Fischer-Tropsch derived gas oil, and optionally also a detergent, for the purpose of reducing subsequent combustion related deposits in the engine and/or removing previously incurred combustion related deposits in the engine.

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Preferred features of the second aspect of the invention, for instance regarding the engine type, the nature of the diesel fuel composition, the nature and concentration of the Fischer-Tropsch derived gas oil and if present the detergent, as well as of other components of the fuel composition, and the ways in which engine fouling may be assessed, may all be as described above in connection with the first aspect.

According to a third aspect of the invention, there is provided a diesel fuel composition which includes a major proportion of a fuel or fuel blend for an internal combustion engine of the compression ignition type, wherein the fuel or fuel blend comprises at least 30% w/w of a Fischer-Tropsch derived gas oil, preferably at least 40% w/w, more preferably at least 50% w/w, most preferably at least 60% w/w. The fuel or fuel blend may comprise up to 100% w/w of the Fischer-Tropsch derived gas oil, preferably up to 95% w/w, more preferably up to 90% w/w, most preferably up to 80% w/w or 70% w/w.

This fuel composition preferably also contains a minor proportion of a detergent-containing additive. By "minor proportion" is meant preferably less than 1% w/w of the fuel composition, more preferably less than 0.5% w/w (5000 ppmw) and most preferably less than 0.2% w/w (2000 ppmw); references to "major proportion" may be construed accordingly.

As described above, in accordance with the present invention a fuel or fuel blend may be additivated (additive-containing) or unadditivated (additive-free). If additivated, it will contain a minor proportion of one or

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more additives, in particular a detergent containing additive. Such additives may be added at various stages during the production of the fuel composition; those added at the refinery for example might be selected from anti-static agents, pipeline drag reducers, flow improvers (eg, 5 ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers) and wax anti-settling agents (eg, those commercially available under the Trade Marks "PARAFLOW" (eg, PARAFLOW™ 450, ex Infineum), "OCTEL" (eg, 10 OCTEL™ W 5000, ex Octel) and "DODIFLOW" (eg, DODIFLOW™ v 3958, ex Hoechst).

In accordance with a fourth aspect of the invention, there is provided a method of operating a diesel engine, and/or a vehicle which is driven by a diesel engine, which 15 method involves introducing into a combustion chamber of the engine a diesel fuel composition according to the third aspect.

A fifth aspect of the invention provides a process for the preparation of a diesel fuel composition, such as a 20 composition according to the third aspect, which process involves blending a Fischer-Tropsch derived gas oil with a non Fischer-Tropsch derived diesel fuel, optionally together with a detergent. Again the blending is ideally carried out with the aim of reducing subsequent combustion 25 related deposits in a diesel engine into which the fuel composition is introduced and/or for the purpose of removing previously incurred combustion related deposits in the engine.

The discovery that Fischer-Tropsch gas oils can at 30 least partly remove existing engine deposits may be put to

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use in the "clean-up" of a fouled engine. Thus, according to a sixth aspect of the present invention, there is provided the use of a Fischer-Tropsch derived gas oil, and/or of a fuel composition containing a Fischer-Tropsch .
5 derived gas oil, to clean (ie, to remove combustion related deposits from) the fuel injection system of a diesel engine. "Use" in this way means running the engine, or a part thereof such as its fuel injection system, on the gas oil or fuel composition for a period of time sufficient to
10 effect at least partial removal of the combustion related deposits. It need not necessarily involve driving the vehicle.

A Fischer-Tropsch derived gas oil, or a fuel composition containing such a gas oil, may therefore in
15 accordance with the invention be packaged together with instructions for its use to clean a diesel engine in the manner described above.

The sixth aspect of the invention also encompasses a method of cleaning the fuel injection system of a diesel
20 engine, by introducing into a combustion chamber of the engine a Fischer-Tropsch derived gas oil and/or a fuel composition containing a Fischer-Tropsch derived gas oil.

Preferred features of the third to the sixth aspects of the invention, for instance regarding the nature and
25 concentrations of the Fischer-Tropsch derived gas oil, any detergent present and any other fuel components and additives present, may be as described above in connection with the first and second aspects of the invention.

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- According to a seventh aspect, the present invention provides a method for assessing the performance of a candidate diesel fuel composition, comprising the steps of:
- 1) measuring the level of combustion related deposits in a diesel engine running on a "standard" diesel fuel composition, which "standard" fuel composition contains no, or less than 1% w/w of, Fischer-Tropsch derived gas oils;
 - 2) subjecting the engine to a first test cycle running on the standard fuel composition;
 - 3) measuring the level of combustion related deposits in the engine after the first test cycle;
 - 4) calculating the increase in deposits during the first test cycle;
 - 5) subjecting the engine to a second test cycle running on the candidate diesel fuel composition;
 - 6) measuring the level of combustion related deposits in the engine after the second test cycle;
 - 7) calculating the increase in deposits (if any) during the second test cycle; and
 - 8) if applicable, calculating the extent of removal of deposits during the second test cycle.

The "standard" fuel composition suitably contains no, or less than 50 or even 20 ppmw, active matter detergent. It is suitably a low or ultra low sulphur diesel fuel, as described above, and is preferably unadditivated.

The level of combustion related deposits may be measured by assessing the degree of fouling of the injector nozzles in the fuel injection system of the engine, as described above.

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The test cycles involve running the engine on the relevant fuel composition for a given period of time and/or for a given number of miles. The tests may be conducted on the engine alone or driving a vehicle - in the latter case they may be conducted under simulated driving conditions (such as using a chassis dynamometer) or involve regular road driving (preferably under urban as opposed to motorway conditions). The engine running and/or driving conditions should be the same or comparable for both the first and the second test cycles.

By way of example, the duration of the first test cycle should be sufficient to cause a significant, and at least detectable, build up of combustion related deposits compared to that measured in step 1 of the test. A typical first test cycle might last from 1 to 5 hours, preferably 2 hours or more, more preferably 3 hours or more.

An appropriate duration for the second test cycle is typically from 10 to 100%, preferably from 50 to 100%, most suitably 100%, of that of the first test cycle. It may in cases be 80% or 75% or even 50% or less of the duration of the first test cycle. For assessing reductions in (as opposed to removal of) combustion related deposits, it may be up to 120% or 150% or even 200% of the duration of the first test cycle.

The engine used for the test may for instance be an indirect injection diesel engine, such as a Volkswagen™ Passat™ engine, for instance the Passat™ AAZ 1.9 TD engine. The test may be conducted on only a part of the engine (eg, the fuel injection system) or on a simulated engine or engine part.

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The assessment method of the invention is particularly applicable to a candidate diesel fuel composition which incorporates a Fischer-Tropsch derived gas oil, more particularly to one which also incorporates a detergent.

5 The method may therefore be used to identify and/or evaluate fuel compositions according to the third aspect of the invention.

The method may also be used to assess the performance of a diesel engine, and/or to assess the performance of a fuel injection system for use in a diesel engine, and/or to assess the performance of a vehicle driven by a diesel engine.

15 An eighth aspect of the present invention provides a diesel fuel composition which, when used as the candidate fuel composition in the assessment method of the seventh aspect, leads to removal of at least 5%, preferably at least 10% or 15% or 20% or 25% or 30%, of the combustion related deposits accumulated in the engine prior to step 5 of the test, when the duration of the second test cycle is the same as or less than, more preferably 80% or 75% or even 50% or less of, the duration of the first test cycle, and the duration of the first test cycle is preferably at least 2 hours, more preferably 3 hours or more.

25 Such a fuel composition ideally contains, in accordance with the present invention, a Fischer-Tropsch derived gas oil, preferably together with a detergent.

The present invention will be further understood from the following examples, which illustrate the effects of using Fischer-Tropsch derived gas oils in diesel fuel compositions, on the degree of fuel injector fouling.

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General

The two fuels used in the tests were a petroleum derived low sulphur diesel fuel F1 and a Fischer-Tropsch (SMDS) derived gas oil F2, both alone and in blends
5 containing varying proportions of the two. Their properties are shown in Table A.

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Table A

<i>Fuel property</i>	<i>Test method</i>	<i>F1</i>	<i>F2</i>
Density @ 15 °C (g/cm ³)	IP 365/ASTM D4052	0.8403	0.7842
Distillation	IP 123/ASTM D86		
IBP (°C)		180.0	212.5
10%		220.0	248
20%		237.0	264
30%		251.5	277.5
40%		264.0	290.5
50%		276.0	300.5
60%		288.0	309
70%		301.0	316
80%		316.5	327
90%		338.0	332
95%		355.0	339
FBP		364.5	344
Cetane number	ASTM D613	52.9, 54.0 Jul '00	
Cetane index	IP 364/84	52.3	78.0
Cetane index	IP 380/94	52.7	93.7
Kinematic viscosity @ 40°C (centistokes)	IP 71/ASTM D445	3.020	3.467
Cloud point (°C)	IP 219	-9	1
Cold filter plugging point (°C)	IP 309	-26	-2
Sulphur (WDXRF) (ppmw)	ASTM D2622	280	<5
Carbon (% w/w)			85.1
Hydrogen (% w/w)			15.1
Calorific value (cal (IT)/g)			
Gross			11170
Net			10405
HPLC aromatics (% w/w):	IP 391 (mod)		
Mono		22.4	<0.1
Di		3.9	<0.1
Tri		0.3	<0.1
Total		26.6	<0.1

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The gas oil F2 had been obtained from a Fischer-Tropsch (SMDS) synthesis product via a two-stage hydroconversion process analogous to that described in
5 EP-A-0583836.

In the Example 3 tests, a commercially available detergent-containing additive A was added to the fuels and fuel blends. Additive A is a detergency additive available from Infineum which passes the Cummins L10 heavy duty
10 detergency test and contains inter alia a detergent, a lubricity additive, an anti-foam agent and a corrosion inhibitor. It was added at a concentration of 842 ppmw (double its standard treat rate); this resulted in an active matter detergent concentration of greater than 100
15 ppmw in the additivated fuel/blend.

The performance of the fuels and blends in an indirect injection (IDI) diesel engine was tested according to the following protocol, which assesses the degree of injector nozzle fouling under steady state conditions.

20 Injector fouling test protocol

The engine used was a Volkswagen™ Passat™ AAZ 1.9 TD indirect injection diesel engine having the following specification:

25	Bore x stroke:	79.5 x 95.5 mm
	No. of cylinders:	4 in line
	Swept volume:	1.896 litres
	Maximum rated power:	75 kW @ 4200 r/min
	Maximum rated torque:	140 Nm @ 2400 - 3400 r/min

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Engine features: turbocharger and EGR with
electronic control;
oxidation catalyst

EGR system: blanked off at turbo outlet.

5 Its fuel injection equipment (Bosch™) had the
following specification:

Injector body: 2FH KCA 275 77

Nozzle type: DNO SD 308

Nozzle needle lift: 0.81 mm (+/- 0.02)

10 Nozzle pre lift: 0.010 mm (+/- 0.001)

Nozzle opening pressure (1): 150 bar (+8/-0)

Nozzle opening pressure (2): 235 bar (+10/-0)

Nozzle nut torque: 70 Nm

15 Leakback test 100 bar down to 70 bar applied
pressure in 10-35 s (new nozzles)

Injection pump: VE No. 0 460 494 314.

The injector blanking plugs used were also Bosch™,
133-9802. High pressure injection pipes were used between
the injection pump and the injectors.

20 Prior to the start of each test, the four clean
nozzles were air flowed at a needle lift of 0.05 mm, and at
0.1 to 0.8 mm in steps of 0.1 mm, and the results recorded.
The fuel filter was also changed prior to each test, and
the fuel supply bled and the systems returned with 9 litres
25 of the test fuel or blend.

In order to limit flow variations between tests, steps
were taken to ensure that each nozzle needle remained in
its own nozzle and that the nozzle bodies and needles were
aligned in the same way for each test.

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Each test began with a 20 minute engine warm up cycle, using the same injectors as for the subsequent deposit accumulation stage. During the warm up the engine speed was 1500 r/min (+/- 25 r/min) and the applied torque 25 Nm (+/- 2.5 Nm).

Once oil and water temperatures had reached 90°C the engine ramped for 15 seconds to the deposit accumulation stage, for which the conditions were as follows:

Engine speed:	2000 r/min (+/- 20 r/min)
Torque:	90 Nm (+/- 1.25 Nm)
Duration:	3 hours (+/- 3 minutes)
Oil temp (into cooler):	90°C (+/- 4°C)
Coolant temp (out of engine):	90°C (+/- 4°C)
Fuel pressure to injection pump:	0.35 bar (gauge) (+/- 0.05 bar)
Nominal fuel flow:	5.1 kg/h (85 g/min)
Nominal fuel supplied:	35 litres.

The engine was allowed to stabilise for 5-7 minutes at these test conditions. A series of manual readings was taken, including a Bosch smoke measurement. After reaching test conditions but before starting the test, the engine was returned to idle and the blow by measured. Test conditions were then re-established.

The parameters listed in Table B below were recorded throughout the test.

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Table B

	<u>Parameter</u>	<u>Nominal end of test value</u>
	Engine speed	2000 r/min
	Engine torque	90 Nm
5	Duration	3 hrs
	Water outlet temperature	90°C
	Oil inlet temperature	90°C
	Fuel flow	85-88 g/min
	Fuel pressure	0.4 bar
10	Fuel temperature	30-32°C
	Ambient air temperature	25-30°C
	Air filter temperature	23-27°C
	Inlet manifold temperature	84-88°C
	Inlet manifold pressure	1480-1510 mbar
15	Exhaust temperature (before catalyst)	325-340°C
	Exhaust back pressure	1770-1800 mbar

On completion of each test, the injectors were removed taking care not to disturb or contaminate the deposits on the nozzle faces. They were dismantled and the nozzles removed. The nozzle body and needle were dipped separately in clean n-heptane or another suitable solvent to remove excess fuel, taking care not to disturb the deposits, and then allowed to drain prior to drying in an oven at 50°C for a minimum of 1 hour.

The dried nozzles were allowed to cool to ambient temperature for a minimum of 1 hour. Their air flow was then measured at needle lifts of 0.05 mm, and at 0.1 to 0.8 mm in steps of 0.1 mm, and the results recorded.

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In order to ensure consistency between nozzle flows a reference nozzle was also flowed at lifts of 0.1, 0.2 and 0.3 mm before flowing the test nozzles clean and dirty.

The fouling level for each test was assessed by calculating a "fouling index" from the air flow data. For each nozzle, fouling numbers F_n were calculated using the flow rates measured at needle lifts of 0.1, 0.2 and 0.3 mm, with the nozzles clean and fouled:

$$F_n = \frac{\text{flow clean} - \text{flow fouled}}{\text{flow clean}} \times 100 \%$$

An average fouling number was then calculated for each nozzle from its three F_n values. The mean fouling index for the test was the average (mean) of the fouling numbers F_n from all four nozzles.

Example 1

This example demonstrates a reduction in engine fouling due to the use of a Fischer-Tropsch gas oil in a petroleum derived diesel fuel composition.

Using the above described injector fouling test, petroleum derived fuel F1 was compared with the Fischer-Tropsch derived F2 as well as with blends containing the two fuels in a range of proportions. The results are shown in Table 1.

Table 1

Experiment no.	Proportion of fuel F2 (% w/w)	Mean fouling index (%)
1.1	0 (ie, fuel F1 alone)	42.4
1.2	10	38.3
1.3	50	33.2
1.4	70	31.5
1.5	100	19.2

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These data establish a clear trend for reduced fouling with increasing levels of the Fischer-Tropsch gas oil. The gas oil alone leads to markedly lower engine deposits compared to the petroleum derived fuel alone. However even at a level of only 10% w/w, the blending of the Fischer-Tropsch oil with fuel F1 is associated with a significant reduction in fouling.

Example 2

This example demonstrates that a Fischer-Tropsch derived fuel may be used to "clean up" fouled injectors, ie, to remove deposits which have built up through use of another fuel.

Following experiment 1.1, in which fuel F1 alone resulted in a mean fouling index of 42.4%, the same injectors were subjected to further air flow measurements to confirm the nozzle condition (this re-flow yielded a mean fouling index of 39.6%) and then re-tested using the Fischer-Tropsch fuel F2 alone.

Surprisingly, the mean fouling index after the re-test had reduced to 28.5%, indicating not only a reduction in fouling levels using fuel F2 as opposed to F1, but also a significant degree of clean-up of previously accumulated engine deposits during use of F2.

Example 3

This demonstrates the cumulative benefits of using a Fischer-Tropsch derived diesel fuel and a detergent containing additive.

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Example 1 was repeated but with additive A (at twice its standard treat rate) added to each fuel or blend. The results are shown in Table 2.

Table 2

<i>Experiment no.</i>	<i>Proportion of fuel F2 (% w/w)</i>	<i>Mean fouling index (%)</i>
3.1	0 (ie, fuel F1 alone)	25.2
3.2	10	23.5
3.3	50	16.4
3.4	70	10.3
3.5	100	2.3

5

Comparing these results with those in Table 1, it is clear that inclusion of the detergent containing additive results in a further reduction in nozzle fouling for each fuel or blend tested. Again increasing levels of the Fischer-Tropsch fuel are associated with decreasing levels of fouling.

10

Thus, in accordance with the invention, a Fischer-Tropsch derived fuel may be combined with a detergent to provide yet further improvements in fouling performance in a diesel engine, either as or as part of a diesel fuel composition.

15

C L A I M S

1. Use of a Fischer-Tropsch derived gas oil in a diesel fuel composition, for the purpose of reducing subsequent combustion related deposits in a diesel engine into which the fuel composition is introduced and/or of removing
5 previously incurred combustion related deposits from the engine.
2. Use according to claim 1, wherein the amount of the Fischer-Tropsch derived gas oil used in the fuel composition is 10% w/w or greater.
- 10 3. Use according to claim 1 or claim 2, wherein the fuel composition includes a detergent.
4. A method of operating a diesel engine, and/or a vehicle which is driven by a diesel engine, which method involves introducing into a combustion chamber of the
15 engine a diesel fuel composition incorporating a Fischer-Tropsch derived gas oil, and optionally also a detergent, for the purpose of reducing subsequent combustion related deposits in the engine and/or removing previously incurred combustion related deposits in the engine.
- 20 5. Use of a Fischer-Tropsch derived gas oil, and/or of a fuel composition containing a Fischer-Tropsch derived gas oil, to remove combustion related deposits from a diesel engine.
6. Use according to claim 5, wherein the Fischer-Tropsch
25 derived gas oil and/or the fuel composition is used together with a detergent.

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7. A method for assessing the performance of a candidate diesel fuel composition, comprising the steps of:

- 1) measuring the level of combustion related deposits in a diesel engine running on a standard diesel fuel composition, which standard fuel composition contains no, or less than 1% w/w of, Fischer-Tropsch derived gas oils;
- 2) subjecting the engine to a first test cycle running on the standard fuel composition;
- 3) measuring the level of combustion related deposits in the engine after the first test cycle;
- 4) calculating the increase in deposits during the first test cycle;
- 5) subjecting the engine to a second test cycle running on the candidate diesel fuel composition;
- 6) measuring the level of combustion related deposits in the engine after the second test cycle;
- 7) calculating the increase in deposits (if any) during the second test cycle; and
- 8) if applicable, calculating the extent of removal of deposits during the second test cycle.

8. A diesel fuel composition which, when used as the candidate fuel composition in a method according to claim 7, leads to removal of at least 5% of the combustion related deposits accumulated in the engine prior to step 5 of the test, when the duration of the second test cycle is the same as or less than that of the first test cycle.

9. A diesel fuel composition which includes a major proportion of a fuel or fuel blend for an internal combustion engine of the compression ignition type, wherein

the fuel or fuel blend comprises at least 30% w/w of a Fischer-Tropsch derived gas oil.

10. A diesel fuel composition according to claim 9, additionally comprising a detergent.

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 November 2003 (06.11.2003)

PCT

(10) International Publication Number
WO 2003/091364 A3

(51) International Patent Classification⁷: **C10L 1/08**,
1/16, 10/00, 10/06

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(21) International Application Number:
PCT/EP2003/004359

(22) International Filing Date: 24 April 2003 (24.04.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02252946.5 25 April 2002 (25.04.2002) EP

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

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(88) Date of publication of the international search report:
1 April 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIESEL FUEL COMPOSITIONS

(57) Abstract: Use of a Fischer-Tropsch derived gas oil in a diesel fuel composition, optionally together with a detergent, to reduce and/or clean up engine fouling. Use of a Fischer-Tropsch derived gas oil, and/or of a fuel composition containing it, to clean a diesel engine. Method for assessing a diesel fuel composition, involving measurement of engine fouling levels. Diesel fuel composition based on a fuel or fuel blend comprising at least 30% w/w of a Fischer-Tropsch derived gas oil.

WO 2003/091364 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/04359

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/08 C10L1/16 C10L10/00 C10L10/06

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)

IPC 7 C10L

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 814 109 A (COOK BRUCE R ET AL) 29 September 1998 (1998-09-29) page 1, line 62 - line 66 claims 1,5,6	4,8,9 1-3,5,6
X A	----- WO 01 49812 A (CHEVRON USA INC) 12 July 2001 (2001-07-12) page 3, line 11 - line 23 page 4, line 13 - line 21 examples	4,8,9 1-3,5,6
X A	----- US 6 369 286 B1 (O'REAR DENNIS J) 9 April 2002 (2002-04-09) claims 1,8 column 4, line 7 - line 12 column 4, line 48 - column 5, line 5 ----- -/--	4,8-10 1-3,5,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

2 September 2003

Date of mailing of the international search report

11 03 03

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PC EP 03/04359

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DE 683 927 C (RUHRCHEMIE AKT GES) 18 November 1939 (1939-11-18) the whole document</p> <p>-----</p>	1-6,8-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/04359

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-6, 8-10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-6, 8-10

1.1. claims: 1-3, 5, 6

Use of a Fischer-Tropsch derived gas oil in a diesel fuel composition for the purpose of reducing or removing combustion-related deposits from a diesel engine.

1.2. claim: 4

A method of operating a diesel engine and/or vehicle, which method involves introducing into a combustion chamber of the engine a diesel fuel composition incorporating a Fischer-Tropsch derived gas oil.

1.3. claims: 8-10

A diesel fuel composition.

2. claim: 7

A method for assessing the performance of a diesel fuel composition with regard to the formation or removal of combustion-related deposits in a diesel engine.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC/EP 03/04359

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DE 683927	C	18-11-1939	NONE	

EP 1497398

(54) 名稱：柴油機燃料合成物

(57) 摘要：把柴油機燃料成份中的以費-托合成法取得的瓦斯油，選擇性地與一清潔劑一起使用，以減少及/或清除發動機污穢。使用由費-托合成法取得的瓦斯油及/或含上述瓦斯油燃料合成物清洗柴油發動機。評估柴油機燃料合成物的方法涉及測定發動機的污穢程度。以最少含有費-托合成法取得的瓦斯油百分之三十質量分率(w/w)的燃料或混合燃料為基準的柴油機燃料合成物。