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(54) **A novel alternative fuel for diesel engines giving low emissions and high energy content**

(57) A novel alternative fuel is described consisting of 10.0 to 50.0 % alkylated mono-cyclic alkanes, 50.0 to 90.0 % non-cyclic alkanes and common additives, e.g. lubricating additives. The aromatics content of the fuel is below 1.0 % and the content of di- and poly-naphthenics are also below 1.0 %. Fuel according to the invention is as energy rich as conventional diesel oil, counted both per litre and per kilogram. Engine effect and torque increase by most engine speeds and loads, and the fuel consumption decreases. The fuel gives decreased regulated and unregulated emissions compared with con-

ventional diesel oil.

Decreases in the exhausts by 70 to 95 % has been measured for some of the most toxic compounds in diesel exhausts, for example acrolein, 1,3-butadiene and benzene. Fuel according to the invention has been tested in field trials under both winter and summer conditions without any operational problems that could be connected to the fuel. Cold start of engines down to minus 35 degrees Celsius has been tested without any problems.

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Description**References to other patents**

5 **[0001]** 1. WO 9805740 A1, 12th Feb. 1998 "Synthetic Diesel Fuel with Reduced Particulate Matter Emissions"

Other references

10 **[0002]** 2. Gjirja, S., Olsson, E., Eklund, A., and Hedemalm, P., "A New Paraphinic Fuel Impact on Emissions and Combustion Characteristics of a Diesel Engine", SAE paper 2002-01-2218.

[0003] 3. Nord, K., and Haupt, Dan, "Evaluating a Fischer-Tropsch fuel, Eco-Par™, in a Valmet Diesel Engine", SAE Paper 2002-01-2726.

[0004] 4. "The influence of the fuel on emissions from diesel engines in large off-road machines", SMP Svensk Maskinprovning AB and SP Statens Provnings- och Forskningsinstitut, Report PU 45850/02 and PU 40318/01.

Background

20 **[0005]** Rudolf Diesel himself used vegetable oils for the first diesel engines. Like many persons after him, he assumed that petroleum based oil would soon run out. The good availability for petroleum based oil the last decade has led to the development of diesel engines optimised for crude oil based middle distillates. Considerable progress has been made both in engine design and fuel formulation.

[0006] In later years, vegetable oils have had a renaissance due to the interest for reducing greenhouse gas emissions. In order to get good usability in modern engines, especially engines with high pressure injection, the vegetable oils are esterified before use. One common esterified vegetable oil is rape-seed methyl ester (RME).

25 **[0007]** An important disadvantage with RME and other esterified vegetable oils is that they solidify by temperatures below approximately minus 10 degrees Celsius. Esters of vegetable oils also often have insufficient storage stability and they may form deposits in the engines. Energy content, viscosity, colour, smell and other parameters are affected by variations between harvests, which makes relatively wide technical limits necessary in the technical standard for RME.

30 **[0008]** Many esters are also very good solvents, which might make it necessary to change sealings, bushings and fuel pipes before new vehicles can use RME. Despite extensive development efforts during many years, these basic difficulties have not yet been completely resolved.

35 **[0009]** Another development path has been to improve petroleum based diesel fuels by hydrogenating or hydrocracking them, a development step that also has reduced sulphur, aromatics and olefin content. Successful examples are e.g. the Californian CARB-diesel oil (sulphur content below 50 mg/kg) and the Swedish environmental class 1 diesel oil (sulphur content below 10 mg/kg). Reduced sulphur content and aromatics content have greatly reduced the emissions of toxic compounds, e.g. sulphur dioxide and polyaromatic hydrocarbons.

40 **[0010]** This path of development has however led to increased emissions of greenhouse gases, since the hydrogenation requires some energy. By hydrogenation aromatics and polyaromatics are transformed to the equivalent naphthenics. There is a substantial risk that these naphthenics are only partially combusted in the engine, with partial dehydrogenation as a result, and thus aromatics and polyaromatics are reformed and emitted with the exhaust. Many naphthenics with two or more rings are also relatively toxic, and their toxicity is generally not particularly well investigated. The natural lubricity of these fuels is usually inferior, normally 600 to 1000 HFRR wear scar according to ISO 12156, which makes lubricating additives mandatory.

45 **[0011]** A third development path has been to produce synthetic fuels instead, so called Fischer-Tropsch fuels. These contain mainly non-cyclic compounds, n- and iso-alkanes. These fuels have been shown to produce very low levels of emissions of many toxic compounds (see, e.g. WO 9805740A1), but unfortunately to the price that current diesel engines are not always directly suitable for this kind of fuel. The cause of this is that the energy content per litre becomes relatively low, and simultaneously the cetane number, especially for the current n-alkanic fuels, is very high.

50 **[0012]** In total this gives the effect that torque, effect and efficiency in the engine decrease with Fischer-Tropsch fuels. Modifications of the engine can probably improve the efficiency, but to the price of reduced usability of conventional fuels in the engine. Pure Fischer-Tropsch fuels often have inferior cold flow properties due to the high level of n-alkanes, and have subsequently not found any substantial use in cold climates. The natural lubricity for these fuels is even lower than for hydrogenated fuels, usually in the interval 1.5 to 2.0, which deviates from conventional diesel oil.

Summary of the the invention

55 **[0013]** By using alkylated mono-cyclic alkanes blended with non-cyclic n- and iso-alkanes the energy content in the

fuels becomes high, measured either per litre or per kilogram, while the cetane number is kept at a reasonable level. The energy content can increase with up to 4 MJ/litre compared with a pure iso- and n-paraffinic fuel, and the cetane number can be adjusted within the range of 40 to about 70. The fuel will thereby be well adapted to conventional diesel engines of today, while emissions of toxic compounds are kept on a very low level. Torque, effect and efficiency will improve compared to other conventional fuels for diesel engines at most engine speeds and loads. By maximum load in combination with high engine speed, torque and effect may however be similar to other fuels, or even decrease slightly.

[0014] Since the fuel according to the innovation has low levels of di- and polycyclic hydrocarbons, the levels of toxic di- and polyaromatics in the emissions will be very low. Since the fuel contains only trace amounts of monoaromatics, the levels of benzene usually decrease in the exhausts. The size of the decrease is however dependent on engine design.

[0015] Other advantages with fuel according to the invention are:

- High flashpoint compared to conventional diesel oil, usually over 90 degrees celsius, gives a decreased risk of accidents and decreased risks of serious effects of accidents.
- Better natural lubricity than Fischer-Tropsch fuels, values under 700 micrometer wear scar are possible. Better natural lubricity gives lower wear in the engine, and lower risk of engine problems. Lower concentrations of lubricating additives are needed, which decreases technical complications and costs.
- Low total toxicity of both fuel and emissions to air, land and water.
- Good cold flow properties - Values of CFPP according to analysis method IP 309 or EN 116 below minus 40 degrees Celsius are possible to achieve.
- Totally miscible and compatible with all types of diesel fuel.
- No negative influence on engines that are adapted for or already use low sulphur diesel oil or esters of vegetable oils.
- Many different possible production methods and feedstocks. Fuels according to the invention can be produced by e.g. conventional oil refining and blending of suitable clean fractions, or by Fischer-Tropsch-synthesis with subsequent upgrading processes. The Fischer-Tropsch synthesis can in turn use all types of feedstocks that contain carbon and energy, e.g. natural gas, wooden chips, waste or biogas.

Description of a preferred embodiment of the invention

[0016] Fuel was prepared in the following way:

1. A mixture of 1-alkenes (alpha-olefins) and alkanes was produced with a Fischer-Tropsch process.
2. Mentioned olefines and alkanes were processed to mainly alkylated mono-cyclic alkanes in a commercially available upgrading process, by use of zeolite catalysts.
3. Mentioned alkylated mono-cyclic alkanes were mixed with about 60 % iso- and n-paraffins in the boiling point range of 180 to 360 degrees Celsius.
4. Commercially available additives, e.g lubricity improvers, were added.

[0017] Swedish "environmental class 1" diesel oil according to standard SS 15 54 35 is hereinafter referred to as "EC 1 diesel oil". Fuel according to the invention is compared with commercially available swedish diesel oil EC 1 in table 1. Swedish EC 1 diesel oil is usually produced today by hydrogenation and/or hydrocracking of crude oil based middle distillates in oil refineries. It can be noted that the content of aromatics, polyaromatics, di- and polynaphthenics are substantially lower for fuel according to the invention than for conventional diesel oil.

[0018] The fuel was tested first in a research engine consisting of an AVL 501 cylinder block with a Volvo cylinder head. The research engine had the following specifications (from ref. 2):

- Compression ratio 18.5:1

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- Bore-stroke 131-150 mm
- Cylinder volume 2.022 litre
- Nominal speed 1800 rpm
- Piston bowl 94.44 cm³
- Specification for injection 8 x 0.22 x 158, 1.4 mm protrusion

[0019] Test cycle ECE R49 was used, and comparison was made with commercially available diesel oil. Emissions of NO_x decreased with 13 % over the test cycle, emissions of HC decreased with 10 %, and emissions of soot decreased with 16 %. Emissions of carbon monoxide increased with 6 %. "Brake Specific Fuel Consumption", i.e. fuel flow per measured kWh effect, decreased by 2 %.

Table 1.

<i>Comparison between swedish EC 1 diesel oil and fuel according to the invention.</i>				
Parameter	Measurement standard	Unit	Fuel according to the invention	Diesel oil EC 1
Mono-aromatics	ASTM D 2425-93	wt-%	0,3	5,0
Di-aromatics	ASTM D 2425-93	wt-%	0,2	0,6
Poly-aromatics	SS 155116-97	mg/kg	<0,02	<0,02
Mono-cyclic naphthenes	ASTM D 2425-93	wt-%	25,4	41,5
Di-cyclic naphthenes	ASTM D 2425-93	wt-%	0,0	13,9
Poly-cyclic naphthenes	ASTM D 2425-93	wt-%	0,0	2,8
Density	ASTM D 4052	kg/m ³	790-800	810-820
Cold Filter Plugging Point (CFPP)	EN 116	°C	Below minus 36	-
Total sulphur content	EN ISO 14596:1998	mg/kg	1-2	2-3
Kinematic viscosity @ 40°C	ASTM D 445	mm ² /s	2,7-2,8	2,0
Cetane number	ASTM D 613	-	52-53	53-58
Oxidation stability	ASTM D 2274	mg/100 ml	0,1	1,2
Gross heat content	ASTM D 240	MJ/kg	46,0 - 47,0	42,0
Net heat content	ASTM D 240	MJ/kg	43,1	-
Hydrogen content	ASTM D 5291-96	% wt/wt	14,9-15,2	13,2-14,6

[0020] The fuel was subsequently tested in an engine designed for forestry machines, Valmet 620 DWRE, a 129 kW, 6 cylinder, 6.6-litre engine. Unregulated emissions were measured with GC-MS, and gave results according to table 2 (from ref. 3). All measured toxic emissions decreased, e.g. the highly toxic compounds acrolein, 1,3-butadiene and benzene.

Table 2.

<i>Unregulated emissions, comparison between fuel according to the invention and swedish EC 1 diesel oil. From ref. 3.</i>		
Chemical compound	Diesel oil EC 1, emissions measured according to ISO 8178 (mg/kWh)	Fuel according to the invention, emissions according to ISO 8178 (mg/kWh)
ethane	0,69	0,47

Table 2. (continued)

Unregulated emissions, comparison between fuel according to the invention and swedish EC 1 diesel oil. From ref. 3.

Chemical compound	Diesel oil EC 1, emissions measured according to ISO 8178 (mg/kWh)	Fuel according to the invention, emissions according to ISO 8178 (mg/kWh)
ethylene	55,4	33,2
acetylene	10,4	4,4
formaldehyde	0,47	0,46
acetaldehyde	1,4	0,41
acrolein	0,06	0,01
benzaldehyde	0,22	0,07
1,3-butadiene	0,35	0,025
benzene	1,91	0,49
toluene	1,06	0,36
O-xylene	0,46	0,08
M-xylene	0,22	0,10

[0021] The laboratory tests were concluded by measuring polyaromatics in particle phase and semivolatile phase in a somewhat smaller engine, Volvo TD40GJE. The average values of two measurements are shown in table 3.

Table 3.

Measurements of poly-aromatics in particle phase and semi-volatile phase in the exhausts from a Volvo TD40GJE engine. Average value of two measurements is shown, where only measurements over the detection limit have been used for the calculation of the average value. After reference 4.

Poly-aromatic compound	Detection limit (µg/kWh)	Fuel according to the invention (µg/kWh)		Swedish EC 1 diesel oil (µg/kWh)	
		Particle bound	Semi-volatile phase	Particle bound	Semi-volatile phase
Naphthalene	6	7,0	155,2	24,4	329,6
1-methylnaphthalene	12	Not detected (ND)	26,6	25,2	187,6
2-methylnaphthalene	12	ND	22,6	16,4	144,7
Acenaphthylene	12	ND	3,0	ND	27,0
Acenaphthene	12	ND	18,2	ND	25,1
Fluorene	12	ND	ND	30,2	33,0
Phenanthrene	12	ND	25,9	ND	33,7
Anthracene	12	ND	32,1	ND	ND
Fluoranthene	12	ND	ND	ND	ND
Pyrene	12	ND	ND	ND	ND
Bens(a)anthracene	40	ND	ND	ND	ND
Chrysene	40	ND	ND	ND	ND
Bens(b)fluoranthene	40	ND	ND	ND	ND
Bens(k)fluoranthene	40	ND	ND	ND	ND

Table 3. (continued)

Measurements of poly-aromatics in particle phase and semi-volatile phase in the exhausts from a Volvo TD40GJE engine. Average value of two measurements is shown, where only measurements over the detection limit have been used for the calculation of the average value. After reference 4.

Poly-aromatic compound	Detection limit (µg/kWh)	Fuel according to the invention (µg/kWh)		Swedish EC 1 diesel oil (µg/kWh)	
		Particle bound	Semi-volatile phase	Particle bound	Semi-volatile phase
Bens(a)pyrene	40	ND	ND	ND	ND
Total PAH over detection limit	-	7,0	283,6	96,2	780,7

[0022] Field tests with the fuel was subsequently performed in a group of vehicles during a 10-month period. No modifications were made in vehicles or engines. Summer- as well as winter driving was tested in all types of weather. Cold start of engines was tested down to minus 35 degrees Celsius. Vehicles of types described in table 4 participated in the field trials:

Table 4.

<i>Vehicles that participated in field trials, and number of driven kilometres.</i>			
Vehicle	Manufacturer and make	Model year	kilometers driven
Car	Mercedes 250 D	1993	23 100
Car	Volvo V70 TDI	1999	102 500
Lorry	Scania PM93	1992	36 600
Buss	Volvo B10M	1989	25 300
Tractor	Fiat 80-90	1984	Not Available (NA)
Tractor	Fiat 160-90	1993	NA
Wheel loader	Volvo BM4300	1982	NA

Table 5.

Fuel consumption for vehicles that participated in the field tests during the period that tests occurred. Total driven kilometres (km) per vehicle within brackets.

Vehicle	Manufacturer	Consumption swedish EC 1 diesel oil oct - dec 2000 1/10 km (driven km)	Consumption of fuel according to the invention jan - nov 2001 1/10 km (driven km)	Consumption Swedish EC 1 Diesel oil nov - dec 2001 1/10 km (driven km)
Car	Mercedes	0,76 (7900)	0,74 (23100)	0,77 (6200)
Car (taxi)	Volvo V70	0,72 (46500)	0,71 (102500)	0,73 (19900)
Lorry	Scania PM93	2,89 (9000)	2,92 (36600)	3,05 (10100)
Bus	Volvo B10M	3,67 (10070)	3,98 (25300)	3,69 (4900)

[0023] No functional problems that could be connected with the fuel could be discovered during the time the field trials occurred. Cold start down to minus 35 degrees Celsius was tested without problems. For most vehicles, with the exception of the bus, the fuel consumption was about similar with fuel according to the invention and swedish EC 1 diesel oil. The causes for the deviation for the bus (about 10 % higher fuel consumption) could not be found, but measurement faults could not be excluded.

Conclusions

[0024] Laboratory experiments have shown that fuel according to the invention has a significant positive impact not only on the emissions, but also on parameters connected to energetic parameters of the engine, e.g. efficiency and fuel consumption. Fuel according to the invention has proven to be efficient at all loads and rpms of the engine, and especially at high load and recommended rpm. It has been shown that the fuel can be used in an unmodified diesel engine with significant decreases in both regulated and unregulated emissions. Continued optimization of motor performance can be achieved by optimizing for example "start of injection time" (SOI), which can lead to further decreased emissions and even better fuel economy.

[0025] Field tests have shown that fuel according to the invention functions well under both summer- and winter conditions. No functional problems that have been connected to the fuel have been possible to identify. Cold start down to minus 35 degrees Celsius has been tested in field trials without any problems.

Definitions

[0026] "hydrogenation": double bonds in aromatics and olefins are saturated with hydrogen gas by the use of a catalyst, and naphthenes and/or paraffins are formed.

[0027] "hydrocracking": cracking of larger hydrocarbon molecules into smaller molecules, by use of hydrogen gas (H₂) and catalyst. Usually, double bonds in aromatics and olefins are saturated simultaneously, and naphthenes and/or paraffins are formed.

[0028] "poly-aromatics": aromatic compounds with three or more carbon rings.

[0029] "di-aromatics": aromatic compounds with two carbon rings.

[0030] "naphthenics": cyclic, non-aromatic hydrocarbons that are e.g. produced by hydrogenation of corresponding aromatic compounds. Naphthenics also occur naturally in some types of crude oils.

[0031] "poly-cyclic naphthenes": cyclic, non-aromatic hydrocarbons with three or more carbon rings.

Acknowledgements

[0032] Tests in laboratory engine AVL 501/Volvo have been conducted by Dr. Savo Gjirja and professor Erik Olsson of Chalmers Institute of Technology, and in part financed by Saab AB. Tests in Valmet forestry engines have been conducted by Luleå Technical University, SMP and Swedish National Testing and Research Institute (SP). The latter tests have in part been financed by Skogforsk, and in part by the Swedish National Road Administration. Vehicle tests have been conducted by Framtidsbränslen AB, with financing mainly from the Regional Council of the region of Väster-norrland, Sweden. The Regional Council of Västra Götaland has financed this patent application within project Dnr RUN 627-0197-02.

Claims

1. A liquid fuel for diesel engines (compression ignition engines) that substantially has a boiling point interval between 160 and 360 degrees celsius, consisting of:

a) as characterizing ingredient approximately 10.0 to 50.0 % alkylated monocyclic naphthenes, mentioned monocyclic naphthenes with following chemical structure:

- A carbon ring consisting of five or six carbon atoms,
- At least three but maximum fifteen carbon atoms in one or several alkyl chains,
- Mentioned alkyl chains are each attached to one of the carbon atoms in mentioned carbon ring with one chemical single-bond,

b) approximately 50.0 to 90.0 % non-cyclic alkanes, branched or non-branched,

c) common additives, e.g. lubricating additives and oxygenates compatible with diesel oil.

2. A fuel according to claim 1 that has a total aromatic content according to ASTM D5186 below 1.0 weight-%.

3. A fuel according to claim 2 that has a content of cyclic naphthenes with two or more carbon rings according to ASTM D2425-93 below 1.0 weight-%.

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4. A fuel according to claim 3 that has a natural lubricity (without lubricating additives) measured according to ISO 12156 below approximately 750 micrometers HFRR wear scar.
5. A fuel according to claim 4 that has a sulphur content according to EN ISO 14596:1998 below 10.0 mg/kg.
6. A fuel according to claim 5 that has a cold flow plugging point (CFPP) according to EN116 below minus 20 degrees Celsius.
7. A fuel according to claim 6 that has a gross heat content according to ASTM D 240 and ASTM D 4052 above 35.0 MJ/litre.
8. A fuel according to claim 7 that has a cetane number according to ASTM D 613 between 40 and 70.



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EUROPEAN SEARCH REPORT

Application Number
EP 04 44 5020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P, X	WO 03/078550 A (CHEVRON USA INC) 25 September 2003 (2003-09-25) * paragraphs '0024!', '0025!', '0031!', '0043!', '0044!', '0079!; claims 1,6-8,10; figure 3; example 2 *	1-8	C10L1/08
A	WO 92/14804 A (CENTURY OILS AUSTRALIA) 3 September 1992 (1992-09-03) * claim 1; examples 2,3 *	1-8	
A	US 5 718 820 A (COMPANY JEAN CLAUDE ET AL) 17 February 1998 (1998-02-17) * claim 1 *	1-8	
A	US 3 835 022 A (FRAYER J ET AL) 10 September 1974 (1974-09-10) * claim 1 *	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 26 May 2004	Examiner Deurinck, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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