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(54) USE OF CRUDE OIL DERIVED AND GAS-TO-LIQUIDS DIESEL FUEL BLENDS

VERWENDUNG VON MISCHUNGEN VON DIESELKRAFTSTOFF AUF BASIS VON ROHÖL UND GAS-TO-LIQUIDS-DIESELKRAFTSTOFF

UTILISATION DE MELANGES DE CARBURANT DIESEL GTL ET DE DERIVES DE PETROLE BRUT

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WO-A-01/83648 **WO-A-03/087273**
GB-A- 2 387 175 **US-B1- 6 663 767**

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Description

Field of the Invention

[0001] The invention relates to the use of Gas-To-Liquids (GTL) diesel fuel as a blend component for at least a crude oil derived diesel fuel for reducing the NOx and soot emissions of the resulting diesel composition.

Background of the Invention

[0002] Synthetic fuels such as GTL (Gas To Liquids) diesel fuel have seen a significant rise in interest in recent years. They are considered to be extremely clean fuels, with negligible sulfur and aromatics, and are odor-free and have a cetane number of > 70. The GTL diesel fuel used in the examples in this patent specification was manufactured by means of the Sasol Slurry Phase Distillate (Sasol SPD™) process, which consists of three process steps, as depicted schematically in Fig. 1.

[0003] In the first step an auto-thermal reforming process is used to convert the natural gas into the synthesis gas, a mixture of CO and H_2. In a second step the synthesis gas is converted into a so-called syncrude containing predominantly paraffinic hydrocarbons, by a Fischer-Tropsch process. This syncrude is primarily in the form of waxes and distillates, which are further refined in a third, product upgrading step by means of mild hydro-processing, in order to produce products that meet commercial fuel specifications, such as diesel fuel and kerosene.

[0004] GB 2 387 175 A discloses a possible reduction of the soot emission of a diesel fuel by oxidizing the fuel to a certain point and then mixing it with certain oxygen-containing organic compounds. It does not address the problem of NOx reduction.

[0005] WO 03/087273 A1 discloses a method of increasing the cetane number of a gas oil product based on a petroleum derived gas oil by the addition of a Fischer Tropsch derived gas oil having a higher cetane number than the petroleum derived gas oil. NOx reduction is not mentioned.

[0006] WO 01/83848 A discloses a method of achieving emissions level of cracked stocks that are equivalent to or superior to base fuels while containing greater levels of aromatics and poylaromatics, where the base fuels are conventional, petroleum derived base fuels.

Summary of the Invention

[0007] The invention provides the use of a Gas-to-Liquids (GTL) diesel fuel, which GTL diesel has a density at 15 deg C of below 0.78 kg/l, a sulphur content of less than 1 mg/kg, polyaromatics below 0.1 mass%, and a cetane number above 65, as a blend component for at least a crude oil derived diesel fuel for reducing the NOx and soot emissions of the resulting diesel fuel composition, characterized in that the crude oil derived diesel fuel has a density at 15 deg C below 0.85 kg/l, a sulphur content of less than 10 mg/kg, a polyaromatics content of below 5 mass%, and a cetane number from 51 to 60 whereby the NOx and soot emissions of the resulting diesel fuel composition, when combusted in an engine, are non-linearly reduced to a higher degree than would be expected when considering the blending ratio of the GTL diesel to the crude oil derived diesel fuel.

[0008] The resulting diesel fuel composition may have less than 10 mg/kg sulphur.

[0009] The resulting diesel fuel composition may have less than 5 mass% polycyclic aromatics.

[0010] The crude oil derived diesel fuel may be a fuel meeting the EN590 specification.

[0011] The volumetric ratio range of the GTL: Crude derived diesel may be from 1:9 to 9:1.

[0012] The volumetric ratio range of the GTL: Crude derived diesel may be from 1:5 to 5:1.

[0013] The molar H:C ratio of the resulting diesel fuel composition the may be from 1.85:1 and 2.05:1.

[0014] The molar H:C ratio of the resulting diesel fuel composition may be from 1.9:1 and 2.00:1.

[0015] The resulting diesel fuel composition may have an ASTM D86 10% distillation temperature of from 180°C to 220°C.

[0016] GB 2 387 175 A discloses a possible reduction of the soot emission of a diesel fuel by oxidizing the fuel to a certain point and then mixing it with certain oxygen-containing organic compounds (see abstract and page 25, lines 22 to 25). The diesel fuels may be derived form various sources including petroleum or Fischer Tropsch synthesis.

[0017] WO 03/087273 A1 discloses a method for increasing the cetane number of a gas oil product based on a petroleum derived gas oil by the addition of a Fischer Tropsch derived gas oil having a higher cetane number than the petroleum derived gas oil. The amount of added Fischer Tropsch derived gas oil for reaching a target cetane number is less than the amount which would be added if the increase of the cetane number of the blend were linear.

[0018] The ASTM D86 10% distillation temperature of the resulting diesel fuel composition may be from 200°C to 215°C.

[0019] The resulting diesel fuel composition may have a flash point of between 60°C and 80°C, typically from 65°C to 78°C.

[0020] The resulting diesel fuel composition may have a density at 15°C of from 0.77 kg/l to 0.84 kg/l.

[0021] The resulting diesel fuel composition may have a density at 15°C of from about 0.8 kg/l to about 0.82 kg/l.

[0022] The resulting diesel fuel composition may have a lower heating value of from 42 500 kJ/kg to 43 800kJ/kg, usually from 43 100 kJ/kg to 43 600 kJ/kg, typically from 43 200 kJ/kg to 43 500 kJ/kg.

[0023] The use of Gas-to-Liquid diesel fuel as a blend component for a diesel fuel composition, which, when combusted in an engine, has reduced NOx and soot emissions, yields a composition comprising both crude oil derived diesel fuel meeting the European EN590 specification for sulphur-free diesel fuel (designated EU diesel), and the Gas-to-Liquids (GTL) diesel fuel, wherein the crude oil derived diesel fuel to Gas-to-Liquid diesel volumetric blend ratio may range from 1:99 to 99:1 and the composition may have a molar H:C ratio of between 1.8:1 and 2.1:1.

[0024] Reductions in both NOx and soot emissions are obtained which are greater than indicated by the blending ratio of the GTL diesel in the crude oil derived diesel fuel.

[0025] Thus, more than 70% of the reduction in both NOx and soot emissions which may be obtained with neat GTL diesel fuel, may be obtained with a 1:1 GTL:Crude derived diesel ratio.

[0026] More than 40% of the reduction in both NOx and soot emissions which may be obtained with neat GTL diesel, may be obtained with a 1:4 GTL:Crude derived diesel ratio.

[0027] However, in some embodiments the reduction in NOx emissions may be less than the reduction in soot emissions, and vice versa.

[0028] In some embodiments, the reduction in NOx may be minimal, however, the NOx will be reduced by the use of GTL diesel in accordance with the invention.

[0029] The properties of the composition and the blending ratios of the components are as described above for the composition.

Examples Involving the Invention

[0030] The effect of GTL diesel fuel blends on exhaust emissions and engine performance has been studied. EU diesel fuel was used as a reference fuel, in addition to being the base stock for the blends. The properties of test fuels used in the investigation are shown in Table 1.

Table 1 Properties of the fuels investigated in this study.

Property	Units	GTL 100% GTL diesel fuel	EU50 50:50 Blend EU:GTL	EU80 80:20 Blend EU:GTL	EU 2005 European sulphur-free diesel fuel
Density @ 15HC	kg/l	0.768	0.802	0.821	0.836
Density @ 20°C	kg/l	0.765	0.798	0.817	0.832
Cetane Number		71	62	58	54
Total Sulphur	mg/kg	< 1	4	6	7
D86 Distillation IBP	°C	169	157	174	193
5%	°C	180	193	204	214
10%	°C	187	201	212	221
20%	°C	200	215	225	233
30%	°C	219	231	240	248
40%	°C	235	248	256	264
50%	°C	251	264	270	277
60%	°C	267	277	282	287
70%	°C	283	291	294	299
80%	°C	297	305	307	313
90%	°C	312	322	324	332
95%	°C	321	337	339	354

(continued)

Property	Units	GTL 100% GTL diesel fuel	EU50 50:50 Blend EU:GTL	EU80 80:20 Blend EU:GTL	EU 2005 European sulphur-free diesel fuel
FBP	°C	329	346	350	360
Flash Point	°C	59	66	76	82
Kinematic Viscosity @ 40°C	mm^2/s	1.97	2.54	2.79	2.95
CFPP	°C	-19	-18	-17	-17
Cloud Point	°C	-18	-17	-15	-14
Total Aromatics*	% m/m	0.1	13.5	21.5	26.8
Bi- and Polycyclic aromatics*	% m/m	0.0	2.3	3.7	4.6
Hydrogen Content*	% m/m	15.0	14.3	13.8	13.5
H/C ratio (molar)*	-	2.10	1.98	1.91	1.86
Lower Heating Value*	MJ/kg	43.8	43.5	43.2	43.1
HFRR Wear Scar Diameter	μm	370	< 400	< 400	394
* Values for blends calculated according to blending ratio					

[0031] Dynamometer tests were conducted with a Mercedes Benz™ E220 CDI vehicle, using the New European Driving Cycle (NEDC) emission test, and without any changes to the basic EU3 emission level engine calibration or engine hardware. The vehicle was tested with its standard calibration without any adaptation, with EU diesel, the 1:1 blend and for the neat GTL fuel. The relevant test vehicle data are shown in Table 2.

Table 2 Test vehicle and engine data

Vehicle designation	Mercedes E 220 CDI Limousine
Model year	2003
Transmission	6-speed manual gearbox
Gross vehicle mass	2 145 kg
Engine designation	MB OM646, EU3 emission level
Displacement, configuration	2,2 L, in-line 4 cylinder, 4 valves per cylinder
Compression ratio	18 : 1
Fuel management	Common rail fuel injection (peak pressure 1 600 bar)
Air management	Turbocharged (VNT), intercooled
Emission control	Cooled EGR, inlet swirl control, close coupled and underfloor oxidation catalysts
Rated torque	340 Nm at 2 000 rev/min
Rated power	110 kW at 4 200 rev/min

[0032] The results of the unadapted vehicle emission tests are depicted in Fig. 2 for the EU diesel, EU50, and GTL diesel fuel. The averaged results for the test runs are presented as the percentages relative to the EU diesel reference fuel. FC indicates the volumetric fuel consumption.

[0033] For neat GTL diesel fuel, an unexpectedly high reduction of >90% for HC and CO emissions was observed.

The CO and HC reductions for the 50% blend scale roughly with the blending ratio. The NOx emissions were reduced marginally, with the 50% blend again showing about half the reduction of the neat GTL diesel fuel. The same applies for the HC+NOx data.

[0034] PM emissions were reduced by up to 30% with the GTL diesel. Surprisingly, a strong non-linear characteristic was evident with the 50% blend (EU50), which showed a reduction of approximately 22%.

[0035] The potential for further emission reductions with the test fuels, and including the optimisation of a limited number of software parameters in the Engine Control Unit (ECU) of the engine was then investigated. For this purpose, an engine mounted on a test bench was used. Steady state test runs were carried out at five operating points characteristic for NEDC emission test cycle. The software parameters investigated were the Exhaust Gas Recirculation (EGR) rate, the start of pilot injection (SOPI) and the start of main injection (SOMI). The five operating points are shown in Table 3

Table 3 Steady state engine test points chosen to reflect NEDC characteristics.

Engine Test Point	Engine Speed (rev/min)	bmep (bar)	Power (kW)	Description
1	1000	0	0	Pseudo Idle
2	1 600	3.3	9	Characteristic operating points for the NEDC emission test
3	2000	2	7	
4	2000	5	18	
5	2800	4	20	

[0036] Fig. 3 shows two examples of results obtained from the steady state test bench work. The figure depicts representative data for the effect of GTL diesel fuel and its blends on the soot - NOx trade-off characterisitc at two operating points, namely 1 600 rev/min and 3,3 bar bmep (brake mean effective pressure), and 2 000 rev/min and 5 bar bmep. In this case, the EGR rate was varied, while the SOPI and SOMI were kept constant and equal to the reference values. Soot emission levels were calculated from exhaust smoke levels determined by FSN (Filter Smoke Number) measurements.

[0037] It is evident that GTL diesel offers a significant reduction in terms of both soot emissions and NOx for all the EGR rates tested. The soot emission increase for decreasing NOx values follows the expected pattern, and enables a wide range of possible alternative software calibrations. Surprisingly, the strong non-linear behavior of the EU50 blend is again evident - this fuel exhibits almost the same benefits as neat GTL diesel fuel.

[0038] A design of experiments (DOE) method was used to numerically optimize the three software parameters simultaneously. The DOE predictions were verified by actual experiments, and an example of the results of the simultaneous optimisation of all three calibration parameters at each of the engine operating points is shown in Fig. 4. In this case the optimisation has been performed to minimise NOx emissions with the GTL diesel fuel. Reductions of between 30% and 75% were obtained, without compromising the other emissions, when compared to the EU diesel.

[0039] The measured data at the five steady-state test points was used to predict the emissions over the NEDC test cycle. Empirical factors were used to account for the differences between the steady-state and transient engine operation. All results from the selected operating points have been normalized and combined into one universal plot, shown in Fig. 5, to mimic the behavior in a NEDC test with an optimized calibration for each fuel. A surprisingly large reduction in soot and NOx appears to be possible for the GTL diesel fuel and the EU50 and EU80 blends. These reductions are possible without hardware changes to the engine.

[0040] The neat GTL would allow for a simultaneous soot and NOx reduction of at least 35% compared to the EU diesel calibration. For constant engine-out soot emission, a NOx reduction of 45% seems possible. Due to the non-linear response with the GTL blends, reductions in soot and NOx that are greater than expected when considering the blending ratio, could be obtained with the EU80 and EU50 fuels. This non-linear response is depicted graphically in Fig. 6.

[0041] A 50% GTL blend would recover approximately 85% of the soot/NOx benefits of neat GTL, while a 20% GTL blend would recover approximately 48% of the benefit. It should be noted that the results shown so far have been facilitated by a simple and cost-efficient software adaptation only. It is to be expected that further improvements will be possible if additionally hardware changes, e.g. in the injection system and/or the combustion chamber design are taken into account.

Claims

1. Use of Gas-to-Liquid (GTL) diesel fuel which has a density at 15 deg C of below 0.78 kg/l, a sulphur content of less than 1 mg/kg, polyaromatics below 0.1 mass%, and a cetane number above 65, as a blend component for at least a crude oil derived diesel fuel for reducing the NOx and soot emissions of the resulting diesel fuel composition, **characterized in that** the crude oil derived diesel fuel has a density at 15 deg C below 0.85 kg/l, a sulphur content of less than 10 mg/kg, a polyaromatics content of below 5 mass%, and a cetane number from 51 to 60, whereby the NOx and soot emissions of the resulting diesel fuel composition, when combusted in an engine, are non-linearly reduced to a higher degree than would be expected when considering the blending ratio of the GTL diesel to the crude oil derived diesel fuel.

2. Use as claimed in claim 1, wherein a 1:1 GTL:Crude derived diesel ratio is used, the reductions in both NOx and soot emissions for said ratio being greater than 70% of the reduction obtained with a 100% GTL diesel fuel.

3. Use as claimed in claim 1, wherein a 1: 4 GTL: Crude derived diesel ratio is used, the reductions in both NOx and soot emissions for said ratio being greater than 40% of the reduction obtained with a 100% GTL diesel fuel.

4. Use as claimed in claim 1, wherein the GTL to crude oil derived diesel ratio is from 99: 1 to 1:99 and the diesel fuel composition produced has a molar H: C ratio of between 1.8: 1 and 2.1:1.

5. Use as claimed in claim 4, wherein the molar H: C ratio is from 1.9: 1 and 2.00: 1.

Patentansprüche

1. Verwendung von Gasverflüssigungs (GTL)-Dieselkraftstoff, der bei 15 Grad C eine Dichte von weniger als 0,78 kg/l, einen Schwefelgehalt von weniger als 1 mg/kg, Polyaromaten von weniger als 0,1 Gew.-% und eine Cetanzahl höher als 65 aufweist, als Mischkomponente für wenigstens einen aus Erdöl gewonnenen Dieselkraftstoff zur Reduzierung von NOx- und Rußemissionen der daraus entstehenden Dieselkraftstoffzusammensetzung, **dadurch gekennzeichnet, dass** der aus Rohöl gewonnene Dieselkraftstoff bei 15 Grad C eine Dichte von weniger als 0,85 kg/l, einen Schwefelgehalt von weniger als 10 mg/kg, einen Polyaromatengehalt von weniger als 5 Gew.-% und eine Cetanzahl zwischen 51 und 60 aufweist, wobei die NOx- und Rußemissionen der daraus entstehenden Dieselkraftstoffzusammensetzung, wenn diese im Motor verbrannt wird, nichtlinear in einem größeren Ausmaß reduziert werden als zu erwarten wäre, wenn man das Mischverhältnis zwischen GTL-Diesel und aus Erdöl gewonnenem Dieselkraftstoff berücksichtigt.

2. Verwendung gemäß Anspruch 1, wobei ein Verhältnis von 1:1 zwischen GTL- und aus Erdöl gewonnenem Diesel verwendet wird, wobei bei dem genannten Verhältnis die Reduzierungen sowohl der NOx- als auch Rußemissionen höher als 70% der mit einem 100%igen GTL Dieselkraftstoff erzielten Reduzierung sind.

3. Verwendung gemäß Anspruch 1, wobei ein Verhältnis von 1:4 zwischen GTL- und aus Erdöl gewonnenem Diesel verwendet wird, wobei bei dem genannten Verhältnis die Reduzierungen sowohl der NOx- als auch Rußemissionen höher als 40% der mit einem 100%igen GTL Dieselkraftstoff erzielten Reduzierung sind.

4. Verwendung gemäß Anspruch 1, wobei das Verhältnis zwischen GTL- und aus Erdöl gewonnenem Diesel zwischen 99:1 und 1:99 liegt und die erzeugte Dieselkraftstoffzusammensetzung ein molares H:C-Verhältnis zwischen 1.8:1 und 2.1:1 aufweist.

5. Verwendung gemäß Anspruch 4, wobei das molare H:C-Verhältnis zwischen 1.9:1 und 2.00:1 liegt.

Revendications

1. Utilisation d’un carburant diesel selon la technologie "gaz en liquides" (GTL) ayant, à 15 degrés Celsius, une densité inférieure à 0,78 kg/l, une teneur en soufre inférieure à 1 mg/kg, des polyaromatiques inférieurs à 0,1% en masse, et un indice de cétane supérieur à 65, en tant que composant de mélange pour au moins un carburant diesel dérivé de pétrole brut en vue de réduire les émissions de NOx et de suies de la composition de carburant diesel en résultant, **caractérisé en ce que** le carburant diesel dérivé de pétrole brut présente, à 15 degrés Celsius, une densité inférieure

à 0,85 kg/l, une teneur en soufre inférieure à 10 mg/kg, une teneur en polyaromatiqes inférieure à 5% en masse, et un indice de cétane compris dans la page allant de 51 à 60, conduisant à ce que les émissions de NOx et de suies de la composition de carburant diesel en résultant, lorsque cette dernière est brûlée dans un moteur, sont réduites non linéairement à un degré plus élevé à ce que l'on pourrait s'attendre, vu le rapport de mélange entre le diesel GTL et le carburant diesel dérivé de pétrole brut.

2. Utilisation selon la revendication 1, dans laquelle un rapport entre le GTL et le diesel dérivé de pétrole brut de 1:1 est employé, les réductions à la fois en émissions de NOx et de suies pour ledit rapport étant supérieures à 70% de la réduction obtenue par un carburant diesel GTL de 100%.

3. Utilisation selon la revendication 1, dans laquelle un rapport entre le GTL et le diesel dérivé de pétrole brut de 1:4 est employé, les réductions à la fois en émissions de NOx et de suies pour ledit rapport étant supérieures à 40% de la réduction obtenue par un carburant diesel GTL de 100%.

4. Utilisation selon la revendication 1, dans laquelle le rapport entre le GTL et le diesel dérivé de pétrole brut est situé dans une fourchette allant de 99:1 à 1:99 et la composition de carburant diesel produite présente un rapport H:C molaire entre 1.8:1 et 2.1:1.

5. Utilisation selon la revendication 4, dans laquelle le rapport H:C molaire est entre 1.9:1 et 2.00:1.

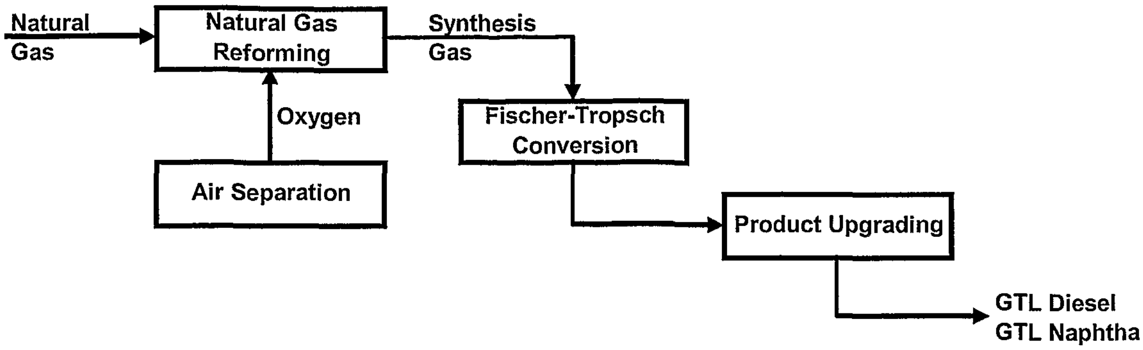

Fig. 1 Schematic Representation of the GTL Production Process.

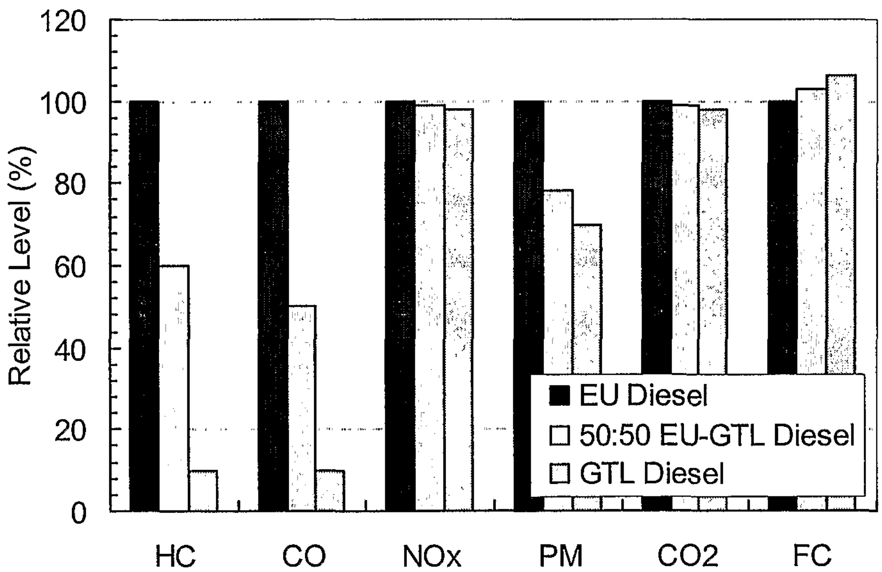

Fig. 2 Results of the chassis dynamometer tests in the NEDC.

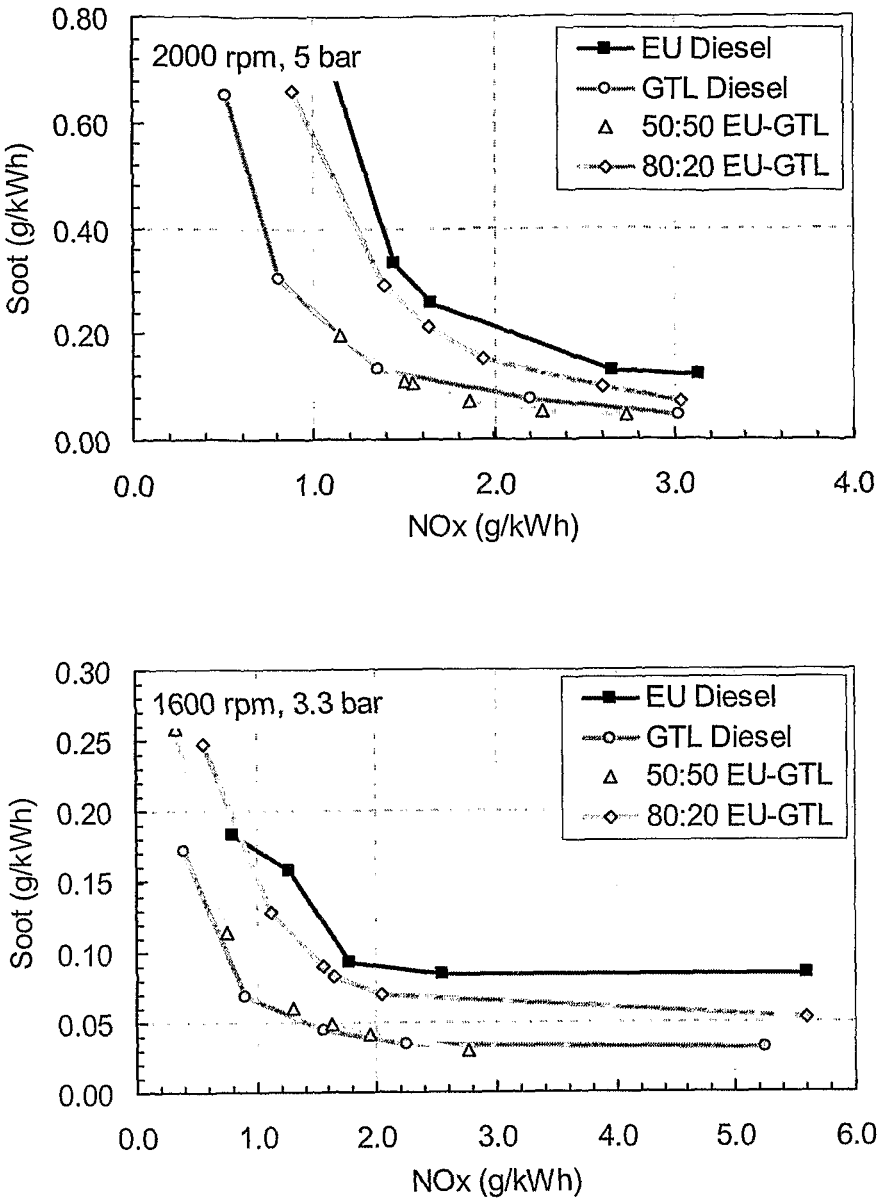

Fig. 3 Soot and NOx tradeoff at two operating points : 1600 rev/min and 3.3 bar bmep, and 2000 rev/min and 5 bar bmep.

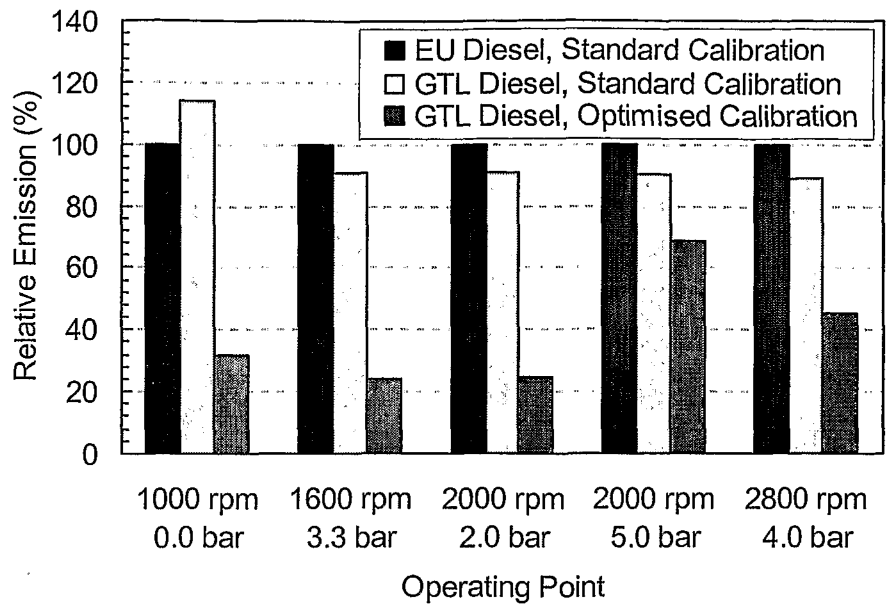

Fig. 4 Relative NOx emissions with GTL diesel fuel after calibration optimisation

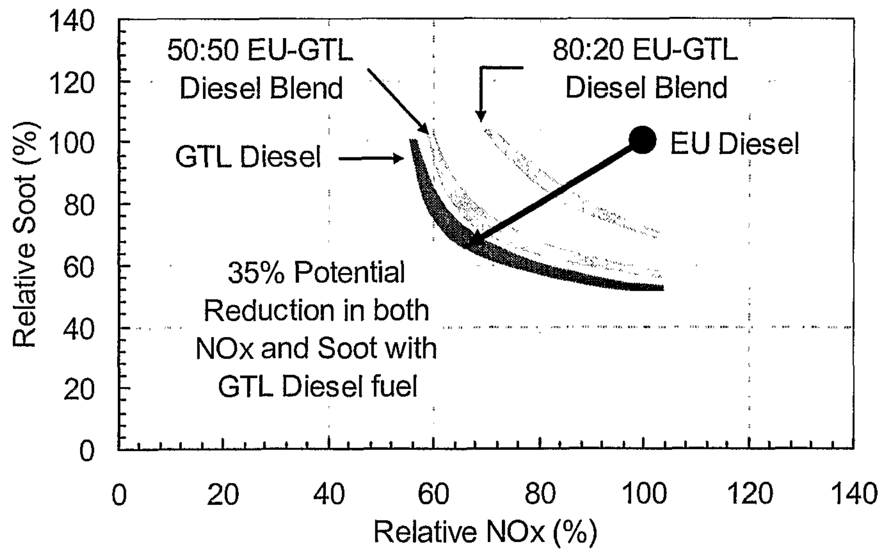

Fig. 5 Projected soot and NOx tradeoff for all investigated GTL fuels with DOE computed individual optimized software adaptation.

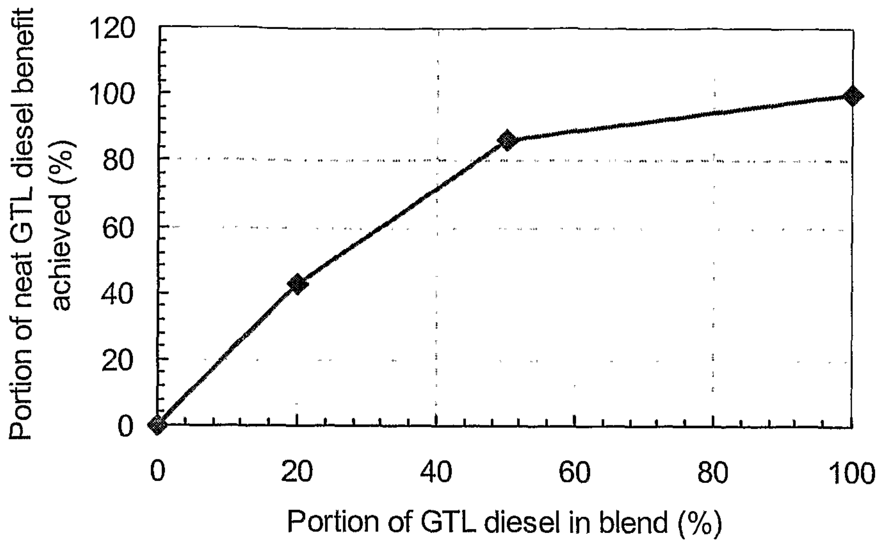

Fig. 6 Non-linear response in the projected emission reductions with blends of GTL and sulphur free European diesel fuel

REFERENCES CITED IN THE DESCRIPTION

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