(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 832 829 B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
28.12.2016 Bulletin 2016/52

(21) Application number: **13770302.1**

(22) Date of filing: **20.02.2013**

(51) Int Cl.:
C10L 1/04 (2006.01) ***C10L 1/196*** (2006.01)
C10L 10/16 (2006.01)

(86) International application number:
PCT/JP2013/000948

(87) International publication number:
WO 2013/145535 (03.10.2013 Gazette 2013/40)

(54) **GAS OIL COMPOSITION**

GAS-ÖL-ZUSAMMENSETZUNG

COMPOSITION DE GAZOLE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **30.03.2012 JP 2012079570**

(43) Date of publication of application:
04.02.2015 Bulletin 2015/06

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Description

TECHNICAL FIELD

[0001] The present invention relates to a gas oil composition, in particular to a gas oil composition which can be used in a very low temperature environments.

BACKGROUND ART

[0002] In general, a gas oil composition is produced by blending one or more types of blendstocks produced by subjecting a straight gas oil or straight kerosene, produced through an atmospheric distillation unit of crude oil to hydrorefining or hydrodesulfurization. In particular, it is often the case that the blend ratio of the foregoing kerosene blendstock and gas oil blendstock is controlled in order to ensure low temperature fluidity during a winter season. If necessary, the blendstocks are blended with additives such as cetane number improvers, detergents, and cold flow improvers.

[0003] In recent years, the use of Fischer Tropsch synthetic oil (hereinafter, referred to as "FT synthetic oil") obtained by Fischer Tropsch synthesis using carbon monoxide and hydrogen as feedstocks, as one of alternative fuels for a petroleum-based fuel is considered. When gas oil for diesel fuel is produced from FT synthetic oil, gas oil free of sulfur content can be obtained. Thus, the FT synthetic gas oil is preferable in terms of reducing environmental impact.

[0004] However, the above-described FT synthetic oil has a relatively high content of straight-chain saturated hydrocarbon (normal paraffin) compounds. It has been pointed out that in particular when heavy normal paraffin compounds are contained, there is the possibility that they would deposit in the form of wax. Further, the FT synthetic blendstock is a hydrocarbon mixture containing predominantly the aforesaid normal paraffin and saturated hydrocarbons having a side chain (isoparaffin) and thus generally has poor oil solubility. Accordingly, there is a case that additives to be dissolved in fuel oils such as gas oil, highly relying on their oil soluble groups (straight-chain alkyl group or the like) would be hardly dissolved. With this being the situation, there has been a problem in that gas oil derived from FT synthetic oil cannot be used in a low temperature environment.

[0005] In order to solve the above problem, various techniques have been developed. For example, JP 2007-270109 A (PTL 1) discloses a technique of adding and mixing a lubrication improver and a cold flow improver to and with a FT synthetic gas oil composition having a certain composition to thereby improve the fluidity in a low temperature environment.

[0006] WO 00/20535 A1 (PTL 2) discloses a synthetic gas oil and addresses the problems related to cold flow in paraffinic synthetic oils.

CITATION LIST

Patent Literature

[0007]

PTL 1: JP 2007-270109 A
PTL 2: WO 00/20535 A1

SUMMARY OF INVENTION

(Technical Problem)

[0008] However, considering the use of a gas oil composition in cold climate areas such as the Arctic Circle or the Antarctic Circle, the FT synthetic gas oil composition obtained by the technique described in PTL 1 would not exhibit sufficient fluidity. Therefore, it has been required to improve the low temperature performance.

[0009] Further, when the aforesaid FT synthetic gas oil is used as fuel for a diesel engine, in order to keep favorable startability in engine combustion and stability in idling, the kinetic viscosity at 30 °C is required to be high. On the other hand, in order to improve the fluidity in a low temperature environment, the pour point is required to be low. In short, since there is a trade-off between the favorable kinetic viscosity and the favorable pour point, it has been difficult to achieve the both using conventional techniques. Therefore, it is desirable to develop a technique making it possible to improve the fluidity without reducing the kinetic viscosity even in a severe low temperature environment.

[0010] The present invention was made in view of the above circumstances, and an object thereof is to provide a gas oil composition that provides superior low temperature performance as compared with the conventional techniques even if it contains as a feedstock, an oil having a high normal paraffin content, such as an FT synthetic oil.

(Solution to Problem)

[0011] The inventors of the present invention made various studies on the above problem to find that excellent fluidity in a low temperature environment can be realized without reducing the kinetic viscosity, by optimizing the composition of a gas oil composition and also adding a certain amount of a cold flow improver to the gas oil composition.

[0012] The invention is made based on such findings, and the summary is as described in the claims.

(Advantageous Effect of Invention)

[0013] The present invention makes it possible to provide a gas oil composition providing superior low temperature performance as compared with the case of using the conventional techniques even if an oil having a high normal paraffin content is used as a feedstock.

DESCRIPTION OF EMBODIMENTS

[0014] The invention of the present application is described below in detail. A gas oil composition of the present invention is disclosed in claim 1.

(Sulfur content, Aromatic content)

[0015] The gas oil composition of the present invention has a sulfur content of 1 ppm by mass or less and an aromatic content of 1 % by mass or less. In order to further reduce particulates emitted from a diesel engine, and in terms of further improving the fuel efficiency, the sulfur content is 1 ppm by mass or less and the aromatic content is 1 % by mass or less.

(C5-C15 Paraffin content)

[0016] The gas oil composition of the present invention has a C5-C15 paraffin content of 40 % to 70 % by mass. The C5-C15 paraffin content is limited to 40 % by mass or more in terms of improving the startability of a diesel engine and the stability in idling, and is limited to 70 % by mass or less in terms of reducing the particulates emitted from the diesel engine.

(C20-C27 Paraffin content)

[0017] The gas oil composition of the present invention has a C20-C27 paraffin content of 7 % to 16 % by mass. The C20-C27 paraffin content needs to be 7 % by mass or more for favorable solubility of the cold flow improver, and needs to be 16 % by mass or less for favorable low temperature fluidity of the gas oil composition.

(Isoparaffin content)

[0018] The gas oil composition of the present invention has an isoparaffin content of 50 % to 75 % by mass, preferably 60 % to 70 % by mass. In order to improve the startability and operability at a low temperature, the isoparaffin content needs to be 50 % by mass or more, whereas in order to obtain a gas oil composition with high yield, the isoparaffin content needs to be 75 % by mass or less.

(Mass ratio between normal paraffin and isoparaffin)

[0019] Further, the mass ratio of the normal paraffin content with respect to the isoparaffin content (normal paraffin content / isoparaffin content) is preferably in the range of 0.3 to 1.0, more preferably in the range of 0.4 to 0.7. In terms of improving the startability in the combustion and the stability in idling of a diesel engine under very low temperature weather conditions, the mass ratio (normal paraffin content / isoparaffin content) is preferably 0.3 or more. Since a certain amount of isoparaffin is contained due to isomerization in order to achieve favorable startability and operability at low temperatures, the mass ratio is preferably 1.0 or less.

(Distillation properties)

[0020] The gas oil composition of the present invention preferably has a 5 % distillation temperature of 140 °C to 200 °C, more preferably 150 °C to 195 °C. In order to improve the startability of a diesel engine and the stability in idling, the 5 % distillation temperature is 140 °C or more, whereas in order to achieve favorable startability and operability at low temperatures, the 5 % distillation temperature is preferably 200 °C or less.

[0021] Further, the gas oil composition of the present invention preferably has a 95 % distillation temperature of 300 °C to 340 °C, more preferably 310 °C to 330 °C. In terms of improving the specific fuel consumption of a diesel engine, the 95 % distillation temperature is preferably 300 °C or more, whereas in terms of reducing particulates emitted from the diesel engine, the 95 % distillation temperature is preferably 340 °C or less.

(Density)

[0022] The gas oil composition of the present invention preferably has a density at 15 °C of 0.750 g/cm^3 to 0.780 g/cm^3, more preferably 0.760 g/cm^3 to 0.780 g/cm^3. The density at 15 °C is 0.750 g/cm^3 or more for favorable specific fuel consumption of a diesel engine, and is 0.780 g/cm^3 or less for favorable low temperature fluidity of the gas oil composition.

(Cloud point)

[0023] Further, the gas oil composition of the present invention preferably has a cloud point of -35 °C or less, more preferably -55 °C or less so as to withstand the use under very low temperature weather conditions. The cloud point used herein means the pour point measured based on JIS K 2269 "Testing method for pour point and cloud point of crude oil and petroleum products".

(Kinetic viscosity at 30 °C)

[0024] The gas oil composition of the present invention preferably has a kinetic viscosity at 30 °C of 1.5 mm^2/s to 4.0 mm^2/s, more preferably 2.0 mm^2/s to 3.5 mm^2/s. The kinetic viscosity at 30 °C is 1.5 mm^2/s or more in terms of improving the startability of a diesel engine or the stability in idling, and is preferably 4.0 mm^2/s or less in terms of reducing particulates emitted from the diesel engine.

(Pour point)

[0025] The pour point of the gas oil composition of the present invention is preferably °C or less. In order to achieve favorable low temperature fluidity under very low temperature weather conditions, the pour point is -55 °C or less.

[0026] The pour point need not be lower than necessary, and the pour point is preferably -70 °C or more, more preferably -66 °C or more in terms of the production cost of the gas oil composition.

(Cold flow improver)

[0027] The gas oil composition of the present invention is required to contain 150 ppm to 1000 ppm by mass of a cold flow improver, the content of the cold flow improver is preferably 150 ppm to 500 ppm by mass, more preferably 200 ppm to 300 ppm by mass. The content (addition amount) of the cold flow improver is 150 ppm by mass or more in order to prevent a filter of a diesel powered automobile from being plugged in a low temperature situation, and is 1000 ppm by mass or less in terms of the effectiveness of the cold flow improver and the economic efficiency.

[0028] As the cold flow improver, ethylene-vinyl acetate copolymer and/or a cold flow improver having a surfactant effect are/is used. Examples of the cold flow improver having a surfactant effect include one or more selected from copolymers of ethylene and methyl methacrylate, copolymers of ethylene and α-olefin, chlorinated methylene-vinyl acetate copolymers, alkyl ester copolymers of unsaturated carboxylic acids, eaters synthesized from nitrogen-containing compounds having a hydroxyl group and saturated fatty acids and salts of the esters, esters and amide derivatives synthesized from polyhydric alcohols and saturated fatty acids, esters synthesized from polyoxyalkylene glycol and saturated fatty acid, esters synthesized from alkyleneoxide adducts of polyhydric alcohols or partial esters thereof and saturated fatty acids, chlorinated paraffin/naphthalene condensates, alkenyl succinamides, and amine salts of sulfobenzoic acids.

(Lubricity improver)

[0029] The gas oil composition of the present invention preferably contains a lubricity improver at a concentration of 20 mg/L to 300 mg/L, more preferably 50 mg/L to 200 mg/L. With the addition amount of the lubricity improver being within the range of 20 mg/L to 300 mg/L, the efficacy of the added lubricity improver can be effectively exerted. For example, for a diesel engine equipped with a distributor injection pump, increase in the driving torque of the pump in operation can be suppressed and the wear of the pump can be reduced.

[0030] As for the type of the lubricity improver, a lubricity improver containing a compound which comprises a fatty acid and/or a fatty acid ester and has a polar group is used. There is no particular restriction on the specific name of the compounds and so on. For example, any one or more selected from carboxylic acid-, ester-, alcohol- and phenol-based lubricity improvers can be used. Out of those, carboxylic acid- and ester-based lubricity improvers are preferred. Examples of the carboxylic acid-based lubricity improver include linoleic acid, oleic acid, salicylic acid, palmitic acid, myristic acid or hexadecenoic acid or a mixture of two or more of these carboxylic acids. Carboxylic acid esters of glycerin can be given as an example of the ester-based lubricity improver. The carboxylic acid ester may include one or more carboxylic acids. Specific examples of the carboxylic acids include linoleic acid, oleic acid, salicylic acid, palmitic acid, myristic acid, and hexadecenoic acid. The weight-average molecular weight of the active component of the lubricity improver is preferably 200 or more and 1000 or less in order to enhance the solubility to the gas oil composition.

(Other additives)

[0031] In order to further enhance the properties of the gas oil compositions of the present invention, other known fuel oil additives mentioned later (hereinafter referred to as "other additives" for convenience) may be used alone or in combination. Examples of the other additives include phenolic- and aminic- antioxidants; metal deactivators such as salicyliden derivatives; anti-corrosion agents such as aliphatic amines and alkenyl succinic acid esters; anti-static additives such as anionic, cationic, and amphoteric surfactants; coloring agents such as azo dye; silicone-based antifoaming agents and antifreezing agents such as 2-methoxyethanol, isopropyl alcohol, and polyglycol ethers.

[0032] The amounts of the other additives may be set to any value. Especially, the amount of each of the other additives is preferably 0.5 % by mass or less, more preferably 0.2 % by mass or less, on the basis of the total amount of the gas oil composition.

[0033] There is no particular restriction on the other specifications of a diesel engine in which the gas oil composition of the present invention is used, the applications thereof, and the environment where the gas oil composition is used.

(FT Synthetic oil)

[0034] The gas oil composition of the present invention preferably further contains Fischer Tropsch synthetic oil (FT synthetic oil). As described above, the FT synthetic oil contains a relatively large amount of straight-chain saturated hydrocarbon (normal paraffin) compounds and accordingly, a gas oil derived from an FT synthetic oil cannot be used in a low temperature environment, which has been a problem. Thus, the advantageous effect of the present invention can be exerted most significantly.

[0035] Further, in order to suppress the consumption of oil base blendstock by using an FT synthetic oil in terms of alternative fuels for petroleum, the gas oil composition preferably contains an FT synthetic oil.

[0036] For example, the FT synthetic oil can be obtained by a production method including the steps of fractionating an FT synthesis oil into a light fraction and a wax fraction, hydroisomerizing the light fraction to obtain a hydroisomerized oil, hydrocracking the wax fraction to obtain a hydrocracked oil, mixing the hydroisomerized oil and the hydrocracked oil and then supplying it to a product fractionator, and adjusting the cutting temperature at the product fractionator so as to obtain a kerosene composition of the invention. Moreover, it is preferable to recycle a bottom oil of the product fractionator and mix it with the wax fraction and then hydrocrack it thereby obtaining the hydrocracked oil.

[0037] Furthermore, the light gas oil blendstock and a heavy gas oil blendstock obtained from the product fractionator may be mixed at a predetermined ratio, thereby producing a gas oil composition of the present invention. The light gas oil blendstock and the heavy gas oil blendstock have a sulfur content of 1 ppm by mass or less and an aromatic content of 1 % by mass or less. The light gas oil blendstock preferably has a density of 0.740 to 0.760, a 5 % distillation temperature of 155 °C to 175 °C, a 95 % distillation temperature of 230 °C to 250 °C, a C5-C15 paraffin content of 90 % to 99.9 % by mass, and an isoparaffin content of 40 % to 55 % by mass. The heavy gas oil blendstock preferably has a density of 0.770 to 0.790, a 5 % distillation temperature of 240 °C to 260 °C, a 95 % distillation temperature of 330 °C to 350 °C, a C5-C15 paraffin content of 15 % to 35% by mass, and an isoparaffin content of 70 % to 85 % by mass.

[0038] In addition, it can also be prepared by being blended with a solvent or a blendstock obtained from each unit of a petroleum refinery plant as appropriate to meet the composition of the gas oil composition of the present invention.

EXAMPLES

[0039] The present invention will now be described in more detail with Examples; however, the invention is not limited to any of the following Examples.

[0040] It should be noted that analysis methods for each property in Examples are as follows.

Sulfur content: Measured according to JIS K 2541 "Crude oil and petroleum products -- Determination of sulfur content"
Aromatic content: Measured according to JIS K 2536-3 "Determination of aromatic components by gas chromatography"
Distillation property: Measured according to JIS K 2254 "Petroleum products -- Determination of distillation characteristics"
Density: Measured according to JIS K 2249 "Crude petroleum and petroleum products -- Determination of density and petroleum measurement tables based on a reference temperature"
Kinetic viscosity: Measured according to JIS K 2283 " Crude petroleum and petroleum products -- Determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity"
Flash point: Measured according to JIS K 2265 "Crude oil and petroleum products -- Determination of flash point"
Cetane index: Measured according to JIS K 2280 "8. Calculation of cetane index by the four-variable equation"
Cloud point: Measured according to JIS K 2269 "Testing methods for pour point and cloud point of crude oil and petroleum products"
Cold Filter Plugging point: Measured according to JIS K 2288 "Petroleum products -- Diesel fuel -- Determination of cold filter plugging point"
Pour point: Measured according to JIS K 2269 "Testing methods for pour point and cloud point of crude oil and petroleum products"

[0041] Paraffin content, Isoparaffin content: the paraffin content and isoparaffin content per carbon atom were measured using GC-FID. The calculation was performed using values measured using a temperature program (column oven temperature: heated at 8 °C/min from 140 °C to 355 °C, sample injection temperature: 360 °C, detector temperature: 360 °C) at a carrier gas (helium) flow rate of 1.0 mL/min using a nonpolar column (stainless steel capillary column ULTRA ALLOY-1) and an FID (flame ionization detector).

(Light gas oil blendstock, Heavy gas oil blendstock)

[0042] A light gas oil blendstock and a heavy gas oil blendstock were prepared in accordance with the following procedure.

[0043] An FT synthetic oil obtained by FT synthesis was used and a light fraction of the FT synthetic oil was subjected to hydroisomerization (LHSV: 1.8 h^{-1}, hydrogen partial pressure: 3.0 MPa, reaction temperature: 320 °C). After that, the resultant hydroisomerized oil and a hydrocracked oil obtained by performing hydrocracking (LHSV: 1.8 h^{-1}, hydrogen partial pressure: 4.0 MPa, reaction temperature: 310 °C) on a wax fraction of the FT synthetic oil were mixed while recycling (recycling rate: 50 vol%) a bottom oil (fraction at the cutting temperature: not less than 360 °C) of a product fractionator, and the mixture was then supplied to the product fractionator. Subsequently, the mixture was fractionated by the product fractionator, thereby obtaining the light gas oil blendstock and the heavy gas oil blendstock. The cutting temperature of the light gas oil blendstock and the heavy gas oil blendstock was 250 °C.

[0044] The composition of the obtained light gas oil blendstock 1 and the heavy gas oil blendstock 1 is shown in Table 1.

(Examples 1 to 3, Comparative Examples 1, 2 and 4)

[0045] Light gas oil blendstocks and heavy gas oil blendstocks were mixed based on the mixing ratios shown in Table 1. A cold flow improver (Infineum R240 manufactured by Infineum Japan Ltd.) was added at 200 ppm by mass to the mixture, thereby obtaining gas oil compositions used as samples.

[0046] For the gas oil compositions obtained in Examples and Comparative Examples above, after the properties were measured (note that the distillation temperature, cloud point, flash point, and cetane index were measured only with respect to Example 2, Comparative Example 1, and Comparative Example 2), the pour point and kinetic viscosity were evaluated. The results are shown in Table 1.

[0047] As for the conditions suitable for use under very low temperature weather conditions, cases where the requirements for the pour point of - 70 °C to -35 °C and the kinetic viscosity at 30 °C of 1.5 mm^2/s to 4.0 mm^2/s were met were evaluated as "preferable (+)", whereas cases where the requirements for the pour point of - 66 °C to - 55 °C and the kinetic viscosity at 30 °C of 2.0 mm^2/s to 3.5 mm^2/s were met were evaluated as "particularly preferable (++)". On the other hand, cases where none of the above conditions were met were evaluated as "poor (-)".

[Table 1]

		Example 1	Example 2	Example 3	Comparative Example 4	Comparative Example 1	Comparative Example 2
Light gas oil blnedstock	vol%	20	40	60	80	0	100
Heavy gas oil blnedstock	vol%	80	60	40	20	100	0
CFI Addition amount	mass ppm	200	200	200	200	200	200
5 % Distillation temperature	°C		187,5			252	165
50 % Distillation temperature	°C		251			293,5	197
95 % Distillation temperature	°C		322			339	238
97 % Distillation temperature	°C		329			346	242
Sulfur content	ppm	< 1	< 1	< 1	< 1	< 1	< 1
Aromatic content	mass%	<1	< 1	< 1	< 1	< 1	< 1
Density	g/cm^3	0,776	0,769	0,762	0,755	0,783	0,749
Cloud point	°C		-56			-6	≤ -25 °C
Pour point	°C	-56	-58	-57	-53	-54	-53
Flash point	°C		59			88	48
Cetane index			84			94,4	73,1
Paraffin content	mass%	≥ 99.5	≥ 99.5	≥ 99.5	≥ 99.5	≥ 99.5	≥ 99.5
C5-15 Paraffin content	mass%	40	55	69	84	26	99,7
C20-27 Paraffin content	mass%	14	11	7	4	17	0
Isoparaffin content	mass%	71	66	59	54	76	48
Normal paraffin content	mass%	29	34	41	46	24	52
Normal paraffin content/Isoparaffin content	mass%	0,4	0,5	0,7	0,9	0,3	1,1
Pour point	°C	-56	-58	-57	-53	-54	-53
Kinetic viscosity (30 °C)	mm^2/s	3,2	2,5	2,1	1,7	4,1	1,4
Evaluation		++	++	++	+	-	-

[0048] The results in Table 1 show that the gas oil compositions obtained in Examples had good quality even if they were used under very low temperature weather conditions, and in particular, Examples to 3 that met the preferred ranges of the present invention achieved better quality.

[0049] On the other hand, for the gas oil compositions obtained in Comparative Examples, it was found that they deposited in the form of wax under very low temperature weather conditions or their kinetic viscosity was insufficient.

INDUSTRIAL APPLICABILITY

[0050] The present invention has particularly advantageous effects in that a gas oil composition providing superior low temperature performance as compared with the case of using the conventional techniques can be provided and an oil having a high normal paraffin content, such as FT synthetic oil can easily be used as a feedstock of the gas oil composition.

Claims

1. A gas oil composition, wherein a sulfur content is 1 ppm by mass or less, an aromatic content is 1 % by mass or less, a C5-C15 paraffin content is 40 % to 70 % by mass, a C20-C27 paraffin content is 7 % to 16 % by mass, and a isoparaffin content is 50 % to 75 % by mass,
characterized in that the gas oil composition comprise a cold flow improver at 150 ppm to 1000 ppm by mass.

2. The gas oil composition according to Claim 1, wherein a pour point is -70 °C to -55 °C and a kinetic viscosity at 30 °C is 1.5 mm^2/s to 4.0 mm^2/s.

Patentansprüche

1. Gas-Öl-Zusammensetzung, wobei ein Schwefelgehalt 1 Massen-ppm oder weniger beträgt, ein Aromatengehalt 1 Massen-% oder weniger beträgt, ein C5-C15-Paraffingehalt 40 bis 70 Massen-% beträgt, ein C20-C27-Paraffingehalt 7 bis 16 Massen-% beträgt und ein Isoparaffingehalt 50 bis 75 Massen-% beträgt, **gekennzeichnet dadurch, dass** die Gas-Öl-Zusammensetzung 150 bis 1000 Massen-ppm eines Kälteflußverbesserers umfasst.

2. Gas-Öl-Zusammensetzung nach Anspruch 1, wobei ein Pourpoint -70 °C bis -55 °C beträgt und eine kinematische Viskosität bei 30 °C 1,5 mm^2/s bis 4,0 mm^2/s beträgt.

Revendications

1. Composition de gasoil, où une teneur en soufre est de 1 ppm en masse ou moins, une teneur en aromatique est de 1% en masse ou moins, une teneur en paraffine C5-C15 est de 40% à 70% en masse, une teneur en paraffine C20-C27 est de 7% à 16% en masse, et une teneur en isoparaffine est de 50% à 75% en masse,
caractérisée en ce que la composition de gasoil comprend un agent améliorant l'écoulement à froid entre 150 ppm à 1000 ppm en masse.

2. Composition de gasoil selon la revendication 1, où un point d'écoulement est de -70°C à -55°C et une viscosité cinétique à 30°C est de 1,5 mm^2/s à 4,0 mm^2/s.

REFERENCES CITED IN THE DESCRIPTION

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