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2,877,749

COMPRESSION-IGNITION ENGINE OPERATION

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22 Claims. (Cl. 123—1)

This invention relates to compression-ignition engine operation. In one of its more specific aspects, it relates to the operation of a diesel engine with a fuel having improved ignition characteristics. In another of its more specific aspects, it relates to the operation of a diesel engine with a fuel containing a minor proportion of an organic sulfenamide.

For compression-ignition engines, of which the well-known diesel engine is representative, it is desirable to have a fuel which has a high cetane number in order to prevent knocking, smoking, and other harmful results which usually attend the use of low cetane number fuels.

In engines operating on the diesel cycle, where the fuel charge is injected into compressed air in a combustion space, it is important to the attainment of maximum efficiency that the delay period between injection and ignition be short. Enhanced speed of ignition in a diesel fuel is, therefore, a highly desirable characteristic. Improperly delayed ignition in a diesel engine gives rise to the phenomena known as "knocking," due to improper coordination of combustion and cylinder conditions. By properly adjusting the ignition delay period of the fuel, through acceleration of the ignition, it is possible to lower the compression pressure which will insure spontaneous ignition without combustion shock, thereby increasing the ease of starting and the smoothness with which combustion takes place. The low compression pressure permits a lower weight in the engine and a lower cost per unit power output.

It is a well-known fact that many petroleum oil fractions have a suitable boiling range and other characteristics which, in general, would make them suitable as diesel fuels, but which unfortunately are not sufficiently high in cetane number to give satisfactory performance. This is particularly true in regard to diesel engines operating at very high speeds such as over one thousand R. P. M. It has, therefore, been proposed in the past to incorporate in the petroleum oil fraction to be used as diesel fuel, a small amount of an addition agent, usually called an ignition promoter or diesel dope, which is adapted to cause a substantial increase in the cetane number of the fuel base stock. A large number of such ignition promoters have been proposed in the past, but many such promoters possess inherent disadvantages which more than offset the value in raising the cetane number. For instance, ethyl nitrate is very effective for improving the cetane number but is such a volatile liquid that, when added in substantial quantities to a diesel fuel base stock, it causes an undesirable lowering of the flash point of the fuel. On the other hand, some other types of ignition promoters which are very effective in raising the cetane number of the fuel have very harmful characteristics such as causing corrosion of the fuel tank.

The following objects of this invention will be attained by the various aspects of this invention.

An object of the invention is to provide improved compression-ignition engine operation. Another object of the invention is to provide improved diesel engine operation with a fuel having improved ignition characteristics. Another object of the invention is to provide an improved diesel engine fuel. Another object of the invention is to provide improved diesel engine operation with a fuel combustion in which the ignition delay characteristic is shortened by the incorporation therein of an organic sulfenamide. Other and further objects of this invention will be apparent to those skilled in the art upon study of the accompanying disclosure.

This invention resides broadly in the discovery that the cetane value of a compression ignition engine fuel is improved by the incorporation therein of a minor amount of an organic sulfenamide. The efficiency of operation of a diesel engine is materially improved when a fuel containing a minor amount of an organic sulfenamide is burned in a combustion chamber of the engine. The sulfenamide, either individual organic sulfenamides or mixtures thereof, is incorporated in the diesel fuel, at some time prior to injection into the combustion zone, in an amount within the range of between 0.1 and 10 volume percent, generally within the range of between 0.5 and 5 volume percent.

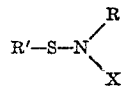
The ignition quality or the ease with which a diesel fuel is ignited after it is injected into the cylinders of a diesel engine is measured in terms of cetane number. Cetane number is defined as the percentage of n-cetane in a mixture of α-methylnaphthalene and n-cetane which has an ignition quality comparable to the fuel in question. The use of fuels of poor quality results in starting difficulty and detonation, knocking, or rough running. Many additives have been developed for blending with a diesel fuel in a comparatively small amount to impart a high cetane value to the fuel. Compounds which have been proposed as additives for such fuels include peroxides, nitrates of glycols, and lower molecular weight alkyl nitrates and nitrites.

The fuel base stock to be used is preferably a gas oil boiling from about 400° F. to 750° F. In a broader aspect, the fuel is one which has a suitable boiling range and viscosity for use as a fuel in a diesel type engine. Under some circumstances, a more normally cut fraction, such as one distilling from 400° F. to 600° F. or from 500° F. to 700° F., may be used.

Although oil of the paraffinic type or hydrogenated oils are preferred for fueling compression-ignition engines, such fuels are generally more expensive and are not always available or practical. Diesel fuels giving satisfactory engine performance are formed from crude oils, gas oil, and residual fuels having low pour point, low A. P. I. gravity and high heat value, such as are procured from naphthenic base, asphaltic base, or mixed base stock. Heavier and lower grades of petroleum oil, such as residual oils, are made suitable for a slow-speed engine. On the other hand, for high-speed engines, such as those operating at speeds above 1,000 R. P. M., it is probably best to use a fuel base stock rich in paraffinic hydrocarbons or hydrogenated oil and still further improve the cetane number thereof.

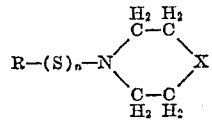
I have discovered that organic sulfenamides, when added to a diesel fuel in relatively minor amounts, have the effect of materially increasing the cetane value of such a fuel. The organic sulfenamides are made up of atoms selected from the group consisting of carbon, hydrogen, sulfur, nitrogen and oxygen. More specifically, I have discovered that organic sulfenamides, particularly sulfenamides having more than five and not more than 24, preferably not more than 17, carbon atoms per molecule, are suitable for use as the ignition improver of this invention.

These sulfenamides comprise compounds which are characterized by the structural formula



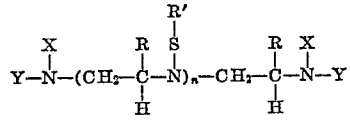
wherein X is selected from the group consisting of a hydrogen atom and an SR′ group, wherein R is an alkyl or cycloalkyl group containing from 1 to 8 carbon atoms and wherein R′ is an alkyl group containing from 1 to 7 carbon atoms. Typical compounds within this group include N-normal butyl—S-tertitary-butyl sulfenamide, N-cyclohexyl-S-tert-butyl sulfenamide and the like.

Another group of sulfenamides which are suitable for use as ignition improvers are characterized by the structural formula



wherein R is an alkyl group containing from 2 to 12 carbon atoms and wherein X is a methylene group, a nitrogen atom, a sulfur atom or an oxygen atom and wherein *n* is a whole integer selected from a group of 1 or 2 and wherein when X is an oxygen atom, *n* is 2. Typical compounds within this group include tert-butyl thiosulfenylpiperidine, isopropylsulfenylpiperidine, tert-butyl thiosulfenylmorpholine, and the like.

Still another group of organic sulfenamides which are suitable for use as ignition improvers include those sulfenamides characterized by the formula



wherein X is a hydrogen atom or an SR′ group, at least one of which is an SR′ group, wherein Y is a hydrogen atom or an alkyl group containing not more than 6 carbon atoms, wherein R is a hydrogen atom or a methyl radical and *n* is a numeral selected from the group of 0 through 5, inclusive, and wherein R′ is an alkyl group containing from 2 to 12 carbon atoms. Typical compounds within this group include ethylene di(tertiary-butyl sulfenamide), propylene di-(tertiary-butyl sulfenamide), triethylene tetra (tertiary-butyl sulfenamide), tetraethylene penta (tertiary-butyl sulfenamide), and the like.

The sulfenamides used in the fuel of the present invention are known in the art. U. S. Patent 2,520,400 to C. M. Himel et al. describes the production of sulfenamides by the interaction of sulfenyl halides wtih amines in the presence of an alkaline material, such as sodium hydroxide, or the like. U. S. Patent 2,520,401 to C. M. Himel et al. describes the production of thiosulfenamides by the interaction of thiosulfenyl halides with amines in the presence of an alkaline material, such as sodium hydroxide. The compounds of the above-described type, such as ethylene di(tertiary-butyl sulfenamides), and the like, are prepared by the interaction of alkylene polyamines and polyalkylene polyamines with alkyl sulfenyl chlorides. A further discussion of the methods of preparing sulfenamides may be found in Chemical Reviews 39, 304–323 (1946).

It is, of course, understood that other known addition agents may be used, such as oiliness agents, sludge dispersers, colloidal suspension dispersers, stabilizers, dyes, anti-oxidants, viscosity improvers, pour point depressors, solubilizers, gum solvents, and corrosion inhibitors.

This invention is exemplified by the following example which is not intended to unduly limit the invention.

Example

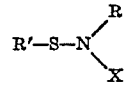
The effectiveness of different organic sulfenamides in increasing the cetane number of a diesel fuel is illustrated by comparing the cetane numbers of a base diesel fuel and an organic sulfenamide-diesel fuel admixture. The cetane number was determined by the procedure of the ASTM Committee D–2 on Petroleum Products and Lubricants entitled, "Tentative Method of Tests for Ignition Quality of Diesel Fuels by the Cetane Method," and designated as Method D613–48T. The base fuel used comprised a blend of ASTM secondary reference fuels T–12 and U–5, described in the "ASTM Manual of Engine Test Methods for Rating Fuels," and had a cetane number of 40. The improvement of cetane number of this base fuel containing two volume percent of several organic sulfenamides is shown in the table below.

Additive Agent in 40 Cetane Number Secondary Reference Fuel Blend	Cetane No.	Cetane No. Increase
N-methyl-S-tert-butylsulfenamide, crude	51.7	11.7
N-methyl-S-ethylsulfenamide, crude	49.4	9.4
Propylene di(tert-butylsulfenamide) crude	47.8	7.8

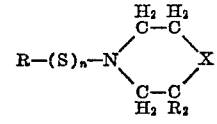
Various modifications of this invention will be apparent to those skilled in the art upon study of the accompanying disclosure and are believed to be within the spirit and the scope of this invention.

I claim:

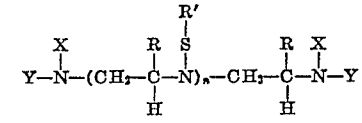
1. The method of operating a compression-ignition engine, which method comprises: compressing a charge comprising air in a cylinder of said engine; and injecting a liquid hydrocarbon fuel having an organic sulfenamide in an amount within the range of 0.1 to 10 percent by volume admixed therewith into said compressed charge, said amount being sufficient to accelerate the ignition of said fuel, and said sulfenamide being selected from the group of sulfenamides consisting of compounds having the formulae



wherein X is selected from the group consisting of a hydrogen atom and an —S—R′ group, R is selected from the group consisting of alkyl and cycloalkyl groups containing from 1 to 8 carbon atoms and R′ is an alkyl group containing from 1 to 7 carbon atoms and



wherein R is an alkyl group containing from 2 to 12 carbon atoms, X is selected from the group consisting of an oxygen atom, a methylene group, a nitrogen atom and a sulfur atom, *n* is an integer selected from the group of 1 and 2 and when X is an oxygen atom, *n* is 2 and



wherein X is selected from the group consisting of a hydrogen atom and an —SR′ group, at least one of which is an —SR′ group, Y is selected from the group consisting of a hydrogen atom and an alkyl group containing not more than 5 carbon atoms, R is selected from the group consisting of a hydrogen atom and a methyl group, and *n* is a numeral selected from the group of from 0 to 5 and wherein R′ is an alkyl group containing from 2 to 12 carbon atoms.

2. The method of claim 1, wherein said organic sulfenamide is tert-butyl thiosulfenylmorpholine.

3. A method according to claim 1, wherein said organic sulfenamide is ethylene di(tert-butylsulfenamide).

4. A method according to claim 1, wherein said organic sulfenamide is propylene di(tert-butyl sulfenamide).

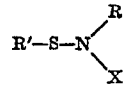
5. A method according to claim 1, wherein said organic sulfenamide is N-methyl-S-tert-butylsulfenamide.

6. A method according to claim 1, wherein said organic sulfenamide is N-methyl-S-ethylsulfenamide.

7. The method of claim 1 wherein said organic sulfenamide is admixed with the fuel in an amount within the range of between 0.5 and 5 volume percent.

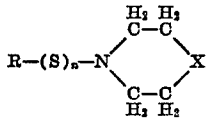
8. The method of claim 1 wherein said liquid hydrocarbon fuel is a gas oil boiling within the range of about 400° F. to about 750° F.

9. The method of operating a compression-ignition engine, which method comprises: compressing a charge comprising air in a cylinder of said engine; and injecting a liquid hydrocarbon fuel having an organic sulfenamide in an amount within the range of 0.1 to 10 percent by volume admixed therewith into said compressed charge, said amount being sufficient to accelerate the ignition of said fuel, and said sulfenamide being characterized by the formula



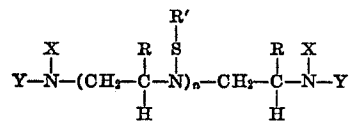
wherein X is selected from the group consisting of hydrogen atom and an —SR′ group, R is selected from the group consisting of alkyl and cycloalkyl groups containing from 1 to 8 carbon atoms, and wherein R′ is an alkyl group containing from 1 to 7 carbon atoms.

10. The method of operating a compression-ignition engine, which method comprises: compressing a charge comprising air in a cylinder of said engine; and injecting a liquid hydrocarbon fuel having an organic sulfenamide in an amount within the range of 0.1 to 10 percent by volume admixed therewith into said compressed charge, said amount being sufficient to accelerate the igition of said fuel, and said sulfenamide being characterized by the formula



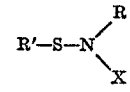
wherein R is an alkyl group containing from 2 to 12 carbon atoms, X is selected from the group consisting of an oxygen atom, a methylene group and a sulfur atom, *n* is an integer selected from the group of 1 and 2, and when X is an oxygen atom, *n* is two.

11. The method of operating a compression-ignition engine, which method comprises: compressing a charge comprising air in a cylinder of said engine; and injecting a liquid hydrocarbon fuel having an organic sulfenamide in an amount within the range of 0.1 to 10 percent by volume admixed therewith into said compressed charge, said amount being sufficient to accelerate the ignition of said fuel, and said sulfenamide being characterized by the formula

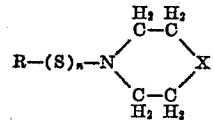


wherein X is selected from the group consisting of a hydrogen atom and an —SR′ group, at least one of which is an —SR′ group, wherein Y is selected from the group consisting of a hydrogen atom and an alkyl group containing not more than 6 carbon atoms, wherein R is selected from the group consisting of a hydrogen atom and a methyl group, and *n* is a numeral selected from the group consisting of 0 through 5, and wherein R′ is an alkyl group containing from 2 to 12 carbon atoms.

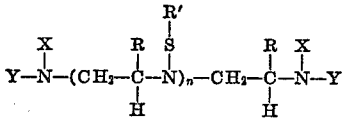
12. A compression-ignition engine fuel which comprises a liquid hydrocarbon fuel containing from 0.1 to 10 percent by volume of an organic sulfenamide selected from the group of sulfenamides consisting of compounds having the formulae



wherein X is selected from the group consisting of a hydrogen atom and an SR′ group, R is selected from the group consisting of alkyl and cycloalkyl groups containing from 1 to 8 carbon atoms and R′ is an alkyl group containing from 1 to 7 carbon atoms and



wherein R is an alkyl group containing from 2 to 12 carbon atoms, X is selected from the group consisting of an oxygen atom, a methylene group, a nitrogen atom and a sulfur atom, *n* is an integer selected from a group of 1 and 2 and when X is an oxygen atom, *n* is 2 and



wherein X is selected from the group consisting of a hydrogen atom and an SR′ group, at least one of which is an SR′ group, Y is selected from the group consisting of a hydrogen atom and an alkyl group containing not more than 5 carbon atoms, R is selected from the group consisting of a hydrogen atom and a methyl group and *n* is a numeral selected from the group of from 0 to 5 and wherein R′ is an alkyl group containing from 2 to 12 carbon atoms.

13. A compression-ignition engine fuel according to claim 12 wherein said liquid hydrocarbon fuel contains from 0.5 to 5 volume percent of said organic sulfenamide.

14. A compression-ignition engine fuel according to claim 12 wherein said liquid hydrocarbon fuel is a gas oil boiling within the range of about 400° to about 750° F.

15. The compression-ignition engine fuel of claim 12 wherein said organic sulfenamide is tert-butyl thiosulfenylmorpholine.

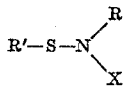
16. The compression-ignition engine fuel of claim 12 wherein said organic sulfenamide is ethylene di(tert-butylsulfenamide).

17. The compression-ignition engine fuel of claim 12 wherein said organic sulfenamide is propylene di (tert-butyl sulfenamide).

18. The compression-ignition engine fuel of claim 12 wherein said organic sulfenamide is N-methyl-S-tert-butyl-sulfenamide.

19. The compression-ignition engine fuel of claim 12 wherein said organic sulfenamide is N-methyl-S-ethyl-sulfenamide.

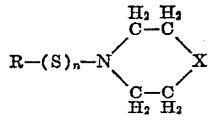
20. A compression-ignition engine fuel which comprises a liquid hydrocarbon fuel containing from 0.1 to 10 percent by volume of a compound characterized by the formula



wherein X is selected from the group consisting of hydrogen atom and an SR′ group, R is selected from the group consisting of alkyl and cycloalkyl groups containing from 1 to 8 carbon atoms and wherein R′ is an alkyl group containing from 1 to 7 carbon atoms.

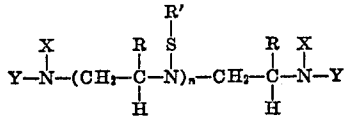
21. A compression-ignition engine fuel which com-

prises a liquid hydrocarbon fuel containing from 0.1 to 10 percent by volume of a compound characterized by the formula



wherein R is an alkyl group containing from 2 to 12 carbon atoms, X is selected from the group consisting of an oxygen atom, a methylene group and a sulfur atom, *n* is an integer selected from the group of 1 and 2 and when X is an oxygen atom, *n* is two.

22. A compression-ignition engine fuel which comprises a liquid hydrocarbon fuel containing from 0.1 to 10 percent by volume of a compound characterized by the formula



wherein X is selected from the group consisting of a hydrogen atom or an SR′ group, at least one of which is an SR′ group, wherein Y is selected from the group consisting of a hydrogen atom and an alkyl group containing not more than 6 carbon atoms, wherein R is selected from a group consisting of a hydrogen atom and a methyl group and *n* is a numeral selected from the group consisting of 0 through 5 and wherein R′ is an alkyl group containing from 2 to 12 carbon atoms.

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