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

(11) Publication number: **0 115 382**
A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **84300093.6**

(51) Int. Cl.³: **C 10 G 27/12**

(22) Date of filing: **06.01.84**

(30) Priority: **07.01.83 GB 8300443**
23.09.83 GB 8325601

(43) Date of publication of application:
08.08.84 Bulletin 84/32

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(71) Applicant: **The British Petroleum Company p.l.c.**
Britannic House Moor Lane
London EC2Y 9BU(GB)

(72) Inventor: **Lancaster, Michael**
The British Petroleum Co. p.l.c. Chertsey Road
Sunbury-on-Thames Middlesex, TW16 7LN(GB)

(72) Inventor: **Middleton, Anthony Robert**
The British Petroleum Co. p.l.c. Britannic House
Moor Lane London, EC2Y 9BU(GB)

(72) Inventor: **Smith, David John Harry**
The British Petroleum Co. p.l.c. Chertsey Road
Sunbury-on-Thames Middlesex, TW16 7LN(GB)

(72) Inventor: **Tinley, Edward John**
The British Petroleum Co. p.l.c. Chertsey Road
Sunbury-on-Thames Middlesex, TW16 7LN(GB)

(74) Representative: **Harry, John et al,**
c/o The British Petroleum Company plc Patents Division
Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN(GB)

(54) **Process for upgrading hydrocarbon fuels.**

(57) Hydrocarbon fuels, for example straight run gasoline and cat-cracked spirit, are up-graded by reacting the fuel with a hydrocarbyl hydroperoxide at a temperature greater than the decomposition temperature of the hydroperoxide and at a pressure sufficient to maintain the reactants in the liquid phase. The reaction may be carried out in the presence or absence of a metal catalyst for the decomposition of the hydroperoxide and optionally in the presence of a solid not generally regarded as a hydroperoxide decomposition catalyst, e.g. alumina, silica or silica-alumina.

Croydon Printing Company Ltd.

PROCESS FOR UPGRADING HYDROCARBON FUELS

The present invention relates to a process for upgrading hydrocarbon fuels for spark ignition internal combustion engines.

Internal combustion engines are so-called because they convert the latent chemical energy of their fuels to useful power by burning the fuels inside the engine. Both petrol engines and diesel engines are examples of internal combustion engines and are mechanically similar to the extent that both have cylinders and pistons connected to a flywheel by a crankshaft, which converts the reciprocating action of the piston caused by sequenced combustion of the fuel to the rotary action needed to power the driving wheels of the vehicle. The most significant difference between the petrol and the diesel engine is the way in which combustion is achieved. In the petrol engine, a mixture of petrol and air is drawn into the combustion chamber by the action of the piston, or the petrol can be injected directly. As the piston makes its return stroke, the mixture is compressed and then ignited by an electric spark. In the diesel engine only air is drawn into the combustion chamber. Once it has been compressed by the piston (to a much higher pressure than in the petrol engine), diesel fuel is injected into the combustion chamber, wherein it ignites spontaneously due to the heat that has been generated by compression in the cylinder. The present invention is concerned only with fuels for spark ignition internal combustion engines, as opposed to diesel engines. The term spark ignition engine includes not only the aforesaid reciprocating piston type engine but also the rotary piston engine, conventionally referred to as the Wankel engine, and any modifications or variations of such engines.

The combustion properties of the fuel are of prime importance to engine performance. Thus petrol must volatilise, ignite easily and burn progressively to ensure smooth combustion and efficient engine performance. Spontaneous or premature explosion, giving rise to a metallic knocking ("knock") sound and to a loss of power, is undesirable in petrol engines. A desirable property of a spark ignition fuel is therefore a high knock resistance, which is measured in terms of octane rating. The higher the octane rating, the higher is the fuel's knock resistance. Another desirable property for a spark ignition fuel is good volatility, the fuel must vapourise adequately to form a readily combustible mixture in the combustion chamber, but it must not be so volatile that it turns into a vapour in the fuel system, otherwise a phenomenon called vapour lock will occur, which manifests itself in the physical symptom of stalling.

US Patent No. 3,879,467 describes a method for the catalytic oxidation of either straight chain, branched chain or cyclic C_3 to C_{20} alkanes or mono-olefins to form alcohols and ketones using tertiary butyl hydroperoxide in the presence of a chromium catalyst at relatively low temperatures. Chromium catalysts are said to be superior to other metal catalysts known to decompose hydroperoxides, for example platinum, palladium, rhenium, thallium, thorium, manganese, cobalt, iron, zirconium, nickel, zinc, cesium, copper, antimony, bismuth, lead, arsenic, molybdenum, vanadium, tungsten and titanium.

US Patent No. 4,104,036 describes an improved fuel composition, e.g. for fueling an internal combustion engine, comprising a major amount of hydrocarbons boiling in the gasoline boiling range; a minor amount of at least one hydrocarbon soluble compound of a metal selected from the group consisting of Group VIII metals and mixtures thereof capable of improving the octane number rating of the composition; a minor amount of at least one aliphatic alcohol containing from about 1 to about 8 carbon atoms per molecule; and a minor amount of at least one organic peroxy component containing from 1 to about 20 carbon atoms per molecule, wherein the compound and the combination of alcohol and peroxy component are present in mutually activating amounts to improve the octane number rating of the fuel composition.

We have now found that hydrocarbon fuels for spark ignition internal combustion engines can be upgraded, that is to say that one or more of the aforesaid desirable characteristics can be improved, by reacting the fuel with a hydrocarbyl hydroperoxide.

Accordingly the present invention provides a process for upgrading a hydrocarbon fuel for a spark ignition internal combustion engine which process comprises reacting the hydrocarbon fuel with a hydrocarbyl hydroperoxide at a temperature greater than the decomposition temperature of the hydrocarbyl hydroperoxide and at a pressure sufficient to maintain the reactants in the liquid phase.

As the hydrocarbon fuel there may be used a gasoline, i.e. a petroleum distillate, normally boiling up to 200°C. Suitably the gasoline may be, for example, a straight run gasoline, that is a gasoline fraction produced directly from crude oil by distillation but not cracked or reformed, or a cat-cracked spirit, that is a gasoline fraction obtained by catalytic cracking of a heavy hydrocarbon fraction. Generally, a straight-run gasoline principally comprises paraffins, aromatics and naphthenes. On the other hand, a cat-cracked spirit generally comprises olefins, paraffins and aromatic hydrocarbons, the paraffins principally comprising isoparaffins. The detailed compositions of the aforesaid gasolines will depend on the relative amounts of the principal components of the crude oil from which the gasolines are derived.

The hydrocarbyl group of the hydrocarbyl hydroperoxide may suitably be an alkyl, cycloalkyl, aryl or alkaryl group. Examples of suitable hydrocarbyl hydroperoxides include t-butyl hydroperoxide, cumyl hydroperoxide, cyclohexyl hydroperoxide and phenyl ethyl hydroperoxide, of which t-butyl hydroperoxide is preferred. Hydrocarbyl hydroperoxides may be prepared in known manner by oxidation of the corresponding hydrocarbon, for example t-butyl hydroperoxide may be prepared by the oxidation of isobutane. The molar ratio of hydrocarbyl hydroperoxide to the hydrocarbon fuel reactant may be varied over a wide range. For high utilisation of the hydroperoxide reactant, low standing concentrations of the hydroperoxide are preferred.

In a preferred embodiment the process of the invention is operated in the absence of a metal catalyst active for the decomposition of hydrocarbyl hydroperoxides. Problems associated with the separation and recovery of a catalyst are thereby avoided.

It can be advantageous in certain circumstances to effect the reaction of the hydrocarbon fuel with the hydrocarbyl hydroperoxide in the presence of solids generally regarded as inert as catalysts for the decomposition of hydrocarbyl hydroperoxides. Suitable solids include clays and aluminosilicate zeolites, which may be natural or synthetic, active carbons and refractory oxides, for example silica, alumina or silica-alumina.

In another embodiment, the process of the present invention is operated in the presence of a catalyst active for the decomposition of hydrocarbyl hydroperoxides. The catalyst for the decomposition of hydrocarbyl hydroperoxides may suitably be one or more of the metals rhodium, ruthenium, chromium, platinum, palladium, rhenium, thallium, thorium, manganese, cobalt, iron, zirconium, nickel, zinc, caesium, copper, antimony bismuth, lead, arsenic, molybdenum, vanadium, tungsten and titanium in elemental or compound form. Preferred metals include rhodium, ruthenium, chromium, cobalt, iron and manganese. Although the metal in finely divided form may be employed, it is preferred to use a compound, suitably a salt or a complex, of the metal. Suitable compounds of the metals include the carbonyls, acetates, acetyl-acetonates, porphyrin complexes, phthalocyanine complexes and the 1,3-bis(pyridylamino) isoindolines. The process may suitably be operated in the liquid phase using a catalyst soluble in the reaction mixture or in the liquid phase using an insoluble catalyst suspended therein or in the liquid phase using a supported catalyst. Suitable supports include refractory oxides, such as silica, alumina and silica-alumina, aluminosilicate zeolites, clays and active carbon. The supported catalyst may be prepared by any suitable conventional technique, such as by impregnation from an aqueous or organic solution, ion-exchange, precipitation and co-precipitation. It is preferred to use a supported catalyst in the form for example of a fixed bed, a moving bed or a fluidised bed. The amount of catalyst added in a batch process may suitably be in the range from 0.001 to 10%, preferably from 0.01 to 5% by weight, based on the total weight of the reactants.

The process must be operated at a temperature above the decomposition temperature of the hydrocarbyl hydroperoxide. The particular temperature employed will depend on the nature of the hydrocarbyl hydroperoxide to be used. Generally, in the absence of a catalyst for the decomposition of hydrocarbyl hydroperoxides the temperature will be greater than 125°C. Using t-butyl hydroperoxide, for example, the temperature may suitably be in the range from 125 to 250°C, preferably from 150 to 225°C. It will be appreciated by those skilled in the art that the presence of a catalyst for the decomposition of a hydrocarbyl hydroperoxide may considerably lower the decomposition temperature. Although it may be possible to employ atmospheric pressure using higher boiling hydrocarbon fuels and lower reaction temperatures, it will usually be necessary to use elevated pressures in order to maintain the reactants in the liquid phase.

Since it is possible that not all the hydrocarbyl hydroperoxide added will be consumed in the process of the invention, particularly when the process is operated in the presence of a catalyst for the decomposition of hydrocarbyl hydroperoxides, in a final step the temperature may be raised above the reaction temperature for a period such as to effect decomposition of the hydroperoxide.

The invention may be operated batchwise or continuously, preferably continuously.

Oxygenated hydrocarbons, particularly hydroxylated and ketonised paraffins, can result fom participation of the alkanes component of the fuel in the decomposition of the hydroperoxide to the corresponding alcohol. Oxygenated hydrocarbons, as is well-known, can increase the octane rating of fuels in which they are present. Furthermore, the alcohol formed by decomposition of the hydroperoxide can boost the octane rating. For example, t-butanol, formed by can boost the octane rating. For example, t-butanol, formed by decomposition of t-butyl hydroperoxide, is a known fuels supplement. The olefins component of the fuel, too, can participate in the reaction to give oxygenated products.

The invention will now be illustrated by reference to the following Examples. In the Examples the abbreviations "TBA" and "TBHP" represent tertiary-butyl alcohol and tertiary-butyl hydroperoxide respectively.

Octane Ratings were determined by the CFR engine test method according to ASTM D2699 and D2700 on 10% vol. blends in an aromatic basestock.

Example 1

100ml of a mixture of a straight-run gasoline and TBHP (65% w/w solution in TBA) were mixed in a weight ratio of 3.5:1 and heated together for 2 hours at 200°C in a 200ml stainless steel autoclave. Thereafter the bomb was allowed to cool and the RON and MON of the resulting product were measured. The values of the RON and MON obtained are given in the Table.

Example 2

The procedure of Example 1 was repeated except that the weight ratio of straight-run gasoline to TBHP was reduced to 2:1.

Comparison Test 1

The straight-run gasoline as used in Example 1 was mixed with TBA in an amount equivalent to the amount that would be formed by complete decomposition of TBHP in the proportion as used in Example 1 into TBA. The mixture was heated at 200°C for 2 hours in a 200ml stainless steel autoclave. The bomb was then allowed to cool and the RON and MON of the resulting mixture determined.

Example 3

100ml of a mixture of the straight-run gasoline as used in Example 1 and TBHP (65% solution in TBA) were mixed in a weight ratio of 3.5:1 and heated together for 16 hours at 80°C in the presence of a 5% platinum on alumina catalyst (0.5g). The catalyst was filtered off and the mixture was heated in a 200ml stainless steel autoclave for 2 hours at 200°C to decompose any residual dialkyl peroxides. The product were measured.

Example 4

The procedure of Example 3 was repeated using a 5% ruthenium on alumina catalyst (0.5g) in place of the platinum on alumina catalyst.

The RON and MON results for Examples 2 to 4 and Comparison Test 1 together with the RON and MON figures for the untreated straight-run gasoline are given in the following Table 1.

TABLE 1

Example	Research Octane No (RON)	Motor Octane No (MON)	Improvement*
1	78.4	77.9	7.95
2	80.5	81.9	11.0
Comp. Test 1	76.3	72.2	4.05
3	75.7	76.5	5.9
4	75.7	79.7	7.5
Straight-run gasoline (SRG)	70.9	69.5	-

*Improvement = $(RON_{measured}-RON_{SRG}) + (MON_{measured}-MON_{SRG})/2$

The improvements in octane ratings obtained in the absence of a catalyst for the decomposition of the hydroperoxide (cf Examples 1 and 2) are comparable with or better than those obtained using a catalyst at lower temperatures (cf Examples 3 and 4). Moreover these improvements are obtained over considerably shorter reaction periods. All the Examples demonstrate an improvement in octane rating over Comparison Test 1.

Example 5

t-Butyl hydroperoxide (20 cm^3 of 8.5 M t-butyl hydroperoxide in t-butanol) was added dropwise over 0.5 hour to a stirred flask containing a straight-run gasoline (100 cm^3) and Fe(II)(Tpp).2THF (0.2g) under an inert atmosphere of nitrogen. The resulting solution was stirred for 16 hours and transferred to an autoclave. The autoclave was heated for 16 hours at 200°C and cooled. The resulting solution was filtered to remove the decomposed catalyst. The filtrate gasoline was analysed by GLC and its octane ratings determined. The results of the octane rating determinations are given in the Table.

The treated gasoline was shown to contain numerous oxygenates corresponding to the oxidation products of the initial constituents of the gasoline. Principal amongst these were:-

pentan-2-one
2-methyl butan-2-ol
various C_6 alcohols
cyclohexanol
cycloheptanol
3-methyl cyclopentanone
methyl phenyl ketone

Example 6

The procedure of Example 5 was repeated except that Fe(II)(Tpp).2THF was replaced by Fe(III)(Tpp)Cl (0.2g).

Example 7

The procedure of Example 5 was repeated except that Fe(II)(Tpp).2THF was replaced by 10% ruthenium supported on carbon (0.1g).

Comparison Test 2

The Research Octane No (RON) and Motor Octane No (MON) of the straight-run gasoline (SRG) as used in Examples 5 to 7 were determined. The RON was 65.6 and the MON was 64.4.

Comparison Test 3

t-Butanol (20 cm^3) was added dropwise to a solution of the straight-run gasoline as used in Examples 5 to 7 (100 cm^3) containing Fe(III)(Tpp)Cl (0.2g). The solution was stirred for 16 hours and thereafter the procedure of Example 5 was employed.

This is not an example according to the present invention because hydrocarbyl hydroperoxide was not added. It is included for the purpose of comparison only.

The results of the octane rating determinations for Examples 5 to 7 and Comparison Tests 2 and 3 are given in Table 2.

Table 2

Example	Research Octane No (RON)	Motor Octane No (MON)	Improvement*
5	79.8	74.1	11.95
6	75.4	72.0	8.70
7	76.4	70.8	8.60
Comp Test 2	65.6	64.4	-
Comp Test 3	74.9	68.0	6.45

*Improvement =
$(RON_{measured} - RON_{SRG}) + (MON_{measured} - MON_{SRG})/2$

It can be seen from the results in Table 2 that addition of t-butanol alone leads to an improvement in octane rating. The improvement in octane rating resulting from catalytically decomposing t-butyl hydroperoxide in the gasoline is in excess of that ascribable to the formation of t-butanol.

Claims:

1. A process for up-grading a hydrocarbon fuel for a spark ignition internal combustion engine which process comprises reacting the hydrocarbon fuel with a hydrocarbyl hydroperoxide at a temperature greater than the decomposition temperature of the hydrocarbyl hydroperoxide and at a pressure sufficient to maintain the reactants in the liquid phase.

2. A process according to claim 1 wherein the hydrocarbon fuel is a straight run gasoline.

3. A process according to claim 1 wherein the hydrocarbon fuel is a cat-cracked spirit.

4. A process according to any one of the preceding claims wherein the hydrocarbyl hydroperoxide is t-butyl hydroperoxide.

5. A process according to any one of the preceding claims wherein the hydrocarbyl hydroperoxide is reacted with the hydrocarbon fuel in the absence of a metal catalyst active for the decomposition of hydrocarbyl hydroperoxides.

6. A process according to any one of the preceding claims wherein the hydrocarbyl hydroperoxide is reacted with the hydrocarbon fuel in the presence of one or more solids selected from clays, aluminosilicate zeolites, active carbons and refractory oxides.

7. A process according to claim 6 wherein the solid is a refractory oxide which is either silica, alumina or silica-alumina.

8. A process according to any one of claims 1 to 4, 6 and 7 wherein the hydrocarbyl hydroperoxide is reacted with the hydrocarbon fuel in the presence of a catalyst active for the decomposition of hydrocarbyl hydroperoxides.

9. A process according to claim 8 wherein the catalyst is one or more of the metals rhodium, ruthenium, chromium, cobalt, iron and manganese in elemental or compound form.

10. A process according to either claim 8 or claim 9 wherein the catalyst is supported on either a clay, an aluminosilicate zeolite, an active carbon or a refractory oxide.

European Patent
Office

EUROPEAN SEARCH REPORT

0115382
Application number

EP 84 30 0093

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. ^{3})
A	US-A-2 593 761 (JOHNSTONE) * Claims 1,7,8; column 3, lines 43-52; examples II,III * -----	1-6,8, 9	C 10 G 27/12
			TECHNICAL FIELDS SEARCHED (Int. Cl. ^{3})
			C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-04-1984	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

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
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
& : member of the same patent family, corresponding document

EPO Form 1503. 03.82