⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 236 021**
A2

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **87301467.4**

㉒ Date of filing: **20.02.87**

(51) Int. Cl.⁴: **C 10 G 53/10**, C 10 G 53/14

㉚ Priority: **24.02.86 US 832612**

(43) Date of publication of application: **09.09.87 Bulletin 87/37**

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

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(54) **Process for upgrading diesel oils.**

(57) A process for upgrading diesel oil to produce an upgraded diesel fuel comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, derived from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone wherein
  (1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number cf the diesel oil feed to step (a), and
  (2) (i) the reacting is such that when the oxidant is a nitrogeneous treating agent, the amount of oxidant, equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed to step (a); and
    (ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

b) contactig the diesel oil from step (a) above with an extracting solvent, the extracting solvent
  (1) having a dipole moment of about 2 or greater,
  (2) being substantially immiscible with the diesel oil obtained in step (a),
  (3) being a nonhalogenated solvent, and
  (4) excluding amines, which are reactive with the oxidant,

or a mixture of such solvents or a water mixture of such solvents comprising about 50% by weight or less water; and

(c) separating the diesel oil from step (b) above from the extracting solvent to recover upgraded diesel fuel.

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PROCESS FOR UPGRADING DIESEL OILS

FIELD OF THE INVENTION

This invention relates to a process for upgrading the cetane rating of diesel oils. More particularly, the invention relates to a process for upgrading the cetane rating of diesel fuels while also removing compounds containing heteroatomic sulfur impurities, and selectively removing instability-causing organic compounds from the oil. Specifically, this invention relates to a process for upgrading middle distillates containing such impurities by contacting the oils with ozone, nitrogen oxides, nitrous acid or nitric acid under conditions enhancing removal of impurities by solvents in solvent extraction, solvent extracting the oil using selected solvents to remove the organic impurities, and then separating the oil from the solvents employed for extraction.

BACKGROUND OF THE INVENTION

In refining petroleum distillates the removal of sulfur-containing compounds is generally required to meet product specifications. In the past various methods have been used to remove unwanted sulfur compounds, both by chemical treatment and by hydrodesulfurization. With increasing reliance on high-sulfur crude oil feedstocks, and the desire to divert hydrogen for other uses in the refining process than hydrodesulfurization, chemical desulfurization methods are of increased interest.

In addition to sulfur content, other important distillate fuel specifications are feedstock-dependent. For example, the important properties of diesel fuels include ignition quality, oxidation stability, and Ramsbottom carbon in addition to sulfur content. Particularly with respect to ignition quality, cetane number is a limiting specification for diesel fuels. In order to be suitable for automotive use, No. 1 diesel fuel is generally made from virgin stocks having cetane numbers of about 45. Railroad diesel fuels are similar to the automotive diesel fuels, but can have somewhat lower cetane numbers of about 40.

Many uncracked or virgin paraffinic stocks such as straight run atmosphere gas oil have good compression ignition properties, i.e., a cetane number of about 45 or higher. In contrast, thermally or catalytically cracked stocks such as cycle oils have unsatisfactory ignition properties, i.e., cetane numbers below about 35.

In the past, in most countries of the world, sufficient quantities of diesel fuel were obtained as a stable, virgin product from crude oil distillation. However, higher crude prices and poorer quality crude oils have increasingly become an economic reality in refining processes. This has significantly changed the properties of distillate fuels and diesel fuels, especially in the United States of America, Canada and Europe. As heavier crudes are being used, bottom products are no longer in demand, and streams from various heavy oil cracking processes have increasingly been used as supplemental blending components for middle distillates fuels. Cracked products generally have poorer qualities as fuels (unless hydrocracked) than straight-run products of equivalent boiling range. With respect to diesel fuels, blending with cracked products has resulted in declining cetane numbers, increasing aromaticity and stability problems in the distillate pool.

The changes discussed above have resulted in a steady decline of cetane number over the past decade. These factors have also led to a loss of distillate fuel stability, which in turn has created problems with diesel fuel handling and performance characteristics. Instability of middle distillates is a result of complex reactions which are not completely understood, but is believed to be the result of three separate reactions: (1) acid-base reactions in which an organic acid and basic nitrogen react to form a sediment (acid-base salt); (2) oxidative gum reactions in which alkenes and oxygen react to form gum and (3) esterification reactions, in which aromatic hydrocarbons, heterocyclic nitrogens and benzothiols combine in a multistep process to form sediment.

Higher levels of unsaturates have resulted from increased use of fluid catalytic cracking units, as well as from blending of streams from thermal processes to meet market demands. The shift to heavier feedstocks and to higher severity operations is significant since, for example, a major change in FCC use could increase the availability of light cycle oil, which is a poor diesel fuel feedstock. The recent emphasis on bottom-of-the-barrel conversion is also expected to increase both nitrogen and sulfur compounds, as well as to produce additional distillate products not well suited for diesel fuel blending.

With an increase in the demand for middle distillates, diesel fuel quality is expected to erode further due to poorer quality of crude oils, a lower demand for bottom products and the increasing use of heavy oil cracking processes.

Recently, treatment to improve distillate quality and stability has been concentrated in three areas: hydrotreating, caustic scrubbing and chemical additives. Although hydrotreating is effective in desulfurization and in improving stability, it is a costly method of improving cetane and stability, requiring a high capital investment, use of hydrogen which is expensive and a high utilities cost relative to other treatment methods.

The prior approaches involving high temperature, high pressure hydrodesulfurization to reduce the sulfur content of hydrocarbonaceous oils involve a number of major disadvantages. As indicated above, the high temperature, high pressure requirements make these processes quite expensive. The hydrogen required in the processes is expensive and requires water for its production. Further processing of the byproducts produced, such as hydrogen sulfide, which is highly toxic, and ammonia also contribute to the expense of the hydrodesulfurization process. Additionally, the catalyst used is often poisoned by materials contained in the hydrocarbonaceous oil, contributing to a further expense in the process. All of these factors result in economic disadvantage for the known processes.

Strong caustic scrubbing is often employed to remove sediment precursors such as benzenthiol, mercaptan sulfur, H_2S, acids and phenols from middle distillates. Although caustic scrubbing is often effective, it removes little sulfur, it does not improve cetane rating, and it cannot produce a stable product in all cases, and cannot, for example, remove pyrrolic nitrogen impurities. The disadvantages of caustic treating include cost of maintaining caustic strength, disposal of spent caustic and loss of product by extraction.

Many types of chemical additives are currently used to improve middle distillate fuel quality, alone or in combination with other treatment techniques. Stabilizers generally provide basicity without initially entering into an organic acid-base reaction to form a salt. Antioxidants perform the same function with thermally derived distillates as they do for gasolines. Unsaturates provide free radical precursors that can enter into any of several sediment forming reactions, but these reactions are interrupted by the presence of an antioxidant. Once sediment starts to form, however, stabilizers are less effective and dispersant type additives are used, which cause disassociation of agglomerated sediment particles as well as preventing agglomeration.

Because of the current economic requirement of cutting deeper into the barrel, and the desirability of blending uncracked with catalytically cracked stocks to produce diesel fuels, alternative methods of upgrading diesel fuel to meet the above specifications are now particularly important.

In the petroleum industry, solvent extractions have often been used to remove sulfur and/or nitrogen compounds from petroleum distillates and synfuels, the extract oil and solvent then being separated by distillation. In general, however, solvent extraction of petroleum products to remove sulfur involves a large loss of oil yield and high solvent-to-oil ratio, and provides only limited sulfur removal.

A method of increasing cetane number has long been sought in the art, and it is generally known that the cetane characteristics of a fuel composition containing both aromatic and paraffinic constituents can be improved by removing the aromatic component to increase the concentration of paraffins, e.g., by solvent extraction.

It has long been known that the cetane number of diesel fuels can be improved either by adding a nitrogen-containing fuel additive, or by nitrogenation with a nitrogenous oxidizing agent. Fuel oils in the diesel range having the proper physical characteristics such as pour point, cloud point, viscosity and volatility can be obtained by nitrogenating the diesel fraction in order to increase the cetane number. However, it is well known that the nitrogenation of such fuel oils tends to increase the Ramsbottom carbon content and to decrease the stability of the oils by forming an insoluble sediment, which produces a haze and eventually a deposit while the fuel oils are in storage. While many attempts to eliminate the disadvantage of poor stability characteristics have been made and solvent extraction, including caustic scrubbing, has been applied for stability improvement, conventional solvent extraction has proven insufficient to provide sufficient stability in the case of nitrogen-treated fuels and to achieve high yields, with sulfur removal, and without cetane loss.

The invention described and claimed herein is directed to a process for upgrading a diesel fuel by removing sulfur-containing organic compounds, increasing cetane rating, reducing Ramsbottom carbon and instability-causing compounds using an oxidation/extraction/separation approach in contrast to the generally used catalytic hydrogenation, caustic scrubbing and chemical additive approaches conventionally practiced.

Although various processes for treating petroleum fractions by oxidation or extraction are known, no satisfactory method has been discovered for upgrading a substandard diesel oil fuel stock and simultaneously removing sulfur, increasing cetane number and improving stability and Ramsbottom carbon of the resulting fuel.

Nitrogen treatment without extraction using nitric acids was investigated as early as 1893 (as disclosed in U.S. Patent No. 508,479) and a process is described in U.S. Patent No. 542,849, issued in 1895, which involves the oxidation of petroleum stocks using nitrous acid fumes. U.S. Patent No. 522,028 discloses removing sulfur from illuminating oils by contacting oil with oxidizing nitrogenous compounds and distilling in the presence of sulfuric acid. This process, however, leads to formation of carbonaceous deposits in the still, and is commercially uneconomical. Further, U.S. Patent No. 1,864,541, issued in 1925, discloses the oxidation of organic compounds by nitrogen oxides at 400° to 500°C with contact times on the order of seconds, the oxidation being either homogeneous or catalytic using copper and silver catalysts. U.S. Patent No. 1,933,748 describes using nitrogen oxides to remove sulfur compounds from cracked petroleum stocks at 150 to 350°F followed by the use of sulfuric acid for extraction, and U.S. Patent No. 1,935,207 discloses a similar process with improved results obtained by carrying out the oxidation using nitrogen oxides in the presence of sulfuric acid at a temperature below 30°C.

The use of nitric and acetic acid, followed by sulfuric acid, to improve color and odor and to remove sulfur from cracked distillate stocks is disclosed in U.S. Patent No. 2,027,648. Although nitric acid treatment followed by sulfuric acid will remove odor and sulfur and will improve color, it will not satisfactorily reduce Ramsbottom carbon without uneconomic levels of sulfuric acid usage and cetane loss. The desulfurization of petroleum fractions using sulfuric acid in combination with air and nitrosyl sulfuric acid is disclosed in U.S. Patent No. 3,294,677.

U.S. Patent No. 2,009,898 describes the treatment of cracked gasoline vapors with nitrogen oxides without significant olefin oxidation, followed by clay-treatment of the product to achieve a reduction in sulfur content. This process, however, requires the use of uneconomical quantities of clay to meet product specifications. U.S. Patent No. 2,825,744 discloses a similar process operated in the vapor phase at temperatures less than 200°C to produce low molecular weight sulfoxides. U.S. Patent No. 3,824,342 discloses oxidation of residue using a number of oxidants including nitrogen oxides, followed by thermal treating to reduce the sulfur content of the residue, in which both steps can be promoted with catalysts. When applied to diesel fuel, this process produces substantial carbonaceous deposits in the thermal treating still, and is unsatisfactory for commercial use. A process of deodorizing and desulfurizing light petroleum distillates by treatment with nitrogen dioxide followed by a caustic wash and water wash is disclosed in U.S. Patent No. 3,267,027. This process is unsuitable for producing diesel fuels of acceptable stability and Ramsbottom carbon content.

U.S. Patent No. 3,163,593 describes a process using a number of different oxidants, including nitrogen dioxides, to treat vacuum residues, residues from cracking processes, oil from tar sands and oil shale followed by thermal decomposition at 350°C to 400°C to produce volatile sulfur compounds and low sulfur oil. The disclosure in this patent is that an alkaline material such as dolomite or lime can be used to accelerate the process.

The use of air as an oxidizing agent for thermally decomposed residues, along with Group VA and Group VIII metal catalysts, as an alternative to nitrogen oxides, followed by hydrodesulfurization is disclosed in U.S. Patent No. 3,341,448. A disclosed advantage of this procedure is a higher degree of desulfurization at comparable conditions than that afforded with hydrotreating alone. U.S. Patent No. 3,244,618 discloses a process for sweetening petroleum hydrocarbons by treating the hydrocarbon fraction with molecular oxygen in the presence of a catalytic amount of a nitrogen oxide. Application of this process to diesel fuel results in a product of unacceptable stability and Ramsbottom carbon content.

U.S. Patent No. 2,004,849 discloses the use of an oxidant, hydrogen peroxide, in combination with sulfuric acid to effect sulfur removal from hydrocarbons, without substantial loss of aromatics. However, this process is ineffective for improving cetane of diesel fuel, and would not provide a yield enhancement upon extraction.

These methods have generally employed nitrogen or oxidation treatment for purification or desulfurization of oils, but it has also been known that the cetane number of diesel fuels can be increased by adding various nitrated hydrocarbon derivatives to the fuels, including amyl nitrate, octyl nitrate, and the nitric ester "dopes" disclosed in British Patent No. 491,648. Other nitrogen-containing additives for improving cetane are disclosed in U.S. Patent No. 4,398,505.

Regarding the use of nitration to improve the cetane number of diesel fuels, British Patent No. 491,648 teaches contacting a diesel fuel with a nitrating agent in order to increase its cetane number. Extraction with solvents including acetone, methyl and ethyl alcohols, ethylene dichloride and aniline is described for obtaining concentrates of nitrated petroleum components. However, by contacting a diesel fuel with a nitrating agent, stability is decreased and Ramsbottom carbon is increased, and poor process yields and loss of cetane rating are encountered when the product is extracted using the solvents disclosed.

U.S. Patent No. 3,135,680 discloses the use of oxidation by nitrogen dioxide followed by washing with water and alkali, to desulfurize diesel fuel oils and improve cetane. The product obtained, however, tends to have an objectionable color resulting from the nitrogen dioxide treatment, and subsequent sulfuric acid treatment, vacuum distillation or clay treating to completely remove materials formed during oxidation reduces or eliminates the increase in cetane number. Due to its high Ramsbottom carbon content, the product of this process forms substantial coke in the still upon distillation. In U.S. Patent No. 3,164,546 a process is described for producing diesel fuels having improved cetane number and odor, by treating the oil with nitrogen dioxide, washing with aqueous caustic and/or solvent extraction, followed by a water wash. Solvents disclosed as suitable for the solvent extraction step are nitromethane, dimethylformamide, pyridine, acetonitrile, glycolonitrile, ethylene glycol, ethanolamine and phenol. No reference is made, however, to the important stability and Ramsbottom carbon content specifications, which are by far the most difficult product specifications to meet when employing nitrogenous treating agents. The process is exemplified only at low cetane enhancement levels, which is disadvantageous.

With respect to improving product stability by oxidizing a petroleum stock, U.S. Patent No. 2,083,253 discloses the use of a bichromate oxidizing agent followed by a sulfuric acid treatment to remove polymers and gums. This process does not enhance cetane rating, and the product does not have the instability characteristics of nitrated products which are improved by the extraction step of the present invention. U.S. Patent No. 2,333,817 discloses oxidation of diesel fuel oils by nitrogenous compounds followed by hexane dilution and filtering to improve cetane and prevent sediment formation. Such a product does not pass present-day industry standards for stability (although haze formation is reduced) and it does not meet Ramsbottom carbon specifications.

Techniques including an extraction step for treatment of petroleum products, without a prior oxidation step as required in the present invention, are also known, e.g., for removal of sulfur impurities.

For example, U.S. Patent No. 2,114,852 discloses a process comprising heating high boiling hydrocarbon oils or shale containing objectionable sulfur compounds as an impurity to obtain hydrocarbon fractions, extracting the product obtained with solvents to remove high boiling sulfur compounds in the presence of unsaturated hydrocarbons, followed by oxidizing the extract.

With respect to such extracting solvents, U.S. Patent No. 2,114,852 discloses a preference for solvents with boiling points no more than 80°C below the boiling range of the initial hydrocarbonaceous oil mixture to improve fractionation. I.N. Diyarov, <u>Khim. Tekhnol. Topl. Masel</u>, (5), pages 14-16 (1978) discloses treatment of diesel fuel with ethylene chlorohydrin mixed with water, and Yu. E. Nikitin, <u>Neftekhimiya</u>, 16, (6), pages 917-920 (1976) describes a comparison of extraction of sulfoxides from diesel fuel using citric and tartaric acids with citric acid being found five times more efficient than tartaric acid in the extraction of sulfoxides. An aqueous solution of quarternary ammonium compounds is disclosed in Japanese Patent Application (OPI) No. 74-30401 as suitable for treating diesel fuel oil. Further, U.S. Patent No. 4,113,607 describes the use of ferric chloride and furfural as an effective solvent in reducing the nitrogen content in hydrogenated oils and U.S. Patent No. 3,804,749 discloses using a complex of boron trifluoride in a petroleum immiscible solvent to remove sulfur in oil. U.S. Patent No. 1,971,753 relates to the use of solvent extraction to reduce sulfur content of lubricating oils, employing an admixture of furfural and amyl amines. These solvents are either not effective in the process according to the present invention or the importance of an oxidation step and its effect on other important product properties are not disclosed. U.S. Patent No. 2,608,519 discloses dimethyl formamide (with less than 25% water) for extraction to remove sulfur and aromatics from highly olefinic naphthas, without extracting olefins.

Improvement of cetane by solvent extraction methods, without previous oxidation, is disclosed in U.S. Patent No. 2,361,080, which describes the use of nitromethane, nitroparaffin-SO_2, benzol-acetone, furfural, methyl ethyl ketone, liquified sulfur dioxide, benzol-SO_2 and chlorex as suitable solvents to extract aromatics from catalytic cycle stock, to thereby improve cetane rating. The yields from this process are uneconomically low, and there is no disclosure of the yield enhancement obtained by nitrogenous oxidation, coupled with specific solvents which also control other important properties, such as stability and Ramsbottom carbon, not normally controlled with nitrogenous oxidation.

Selective solvent extraction to remove aromatic components of petroleum distillates is well known.

U.S. Patent No. 3,317,423 discloses preparation of a carbon black feedstock by aromatics extraction of a heavy (500°F+) hydrocarbon using a dual solvent of furfural and a paraffinic hydrocarbon. Preparation of an aromatic carbon black feedstock in a two-stage solvent extraction process using furfural, phenol, liquid sulfur dioxide or glycol ethers is disclosed in U.S. Patent No. 3,349,028, in which Ramsbottom carbon is also extracted. U.S. Patent No. 3,415,743 discloses the extraction of heavy aromatics and heavy aliphatics from cycle oil in a two-stage process using dimethyl formamide (5 to 18% water) and xylene in the first stage. U.S. Patent No. 3,546,108 discloses a furfural/dimethyl formamide/water mixed solvent used for the extraction of aromatics from gas oils and U.S. Patent No. 2,137,206 also relates to a method for dewaxing oils using furfural. These patents all fail to appreciate the importance of treatment prior to solvent extraction, and the surprising yield enhancement obtained thereby, or the control of other important product properties, such as stability and Ramsbottom carbon, obtained by the combined use of nitrogen treatment and extraction with selected solvents in the present invention.

In U.S. Patent No. 3,169,998, the selective separation of aromatic hydrocarbons from olefinic hydrocarbons, and the extraction of olefinic hydrocarbons from mixtures of olefinic and saturated hydrocarbons is disclosed using liquid gamma-butyrolactone as a solvent. Amine sulfonate solvents for extraction of aromatic feedstocks are disclosed in U.S. Patent No. 2,522,618.

U.S. Patent No. 3,539,504 describes production of a middle distillate fuel such as kerosene with improved burning and color characteristics by a temperature graduated furfural extraction to remove aromatics and olefins.

Processes for treating petroleum stocks by oxidation followed by solvent extraction have been described for various purposes. For example, oxidation/extraction processes of hydrocarbonaceous oils to produce sulfoxides and sulfones are disclosed in U.S. Patent No. 2,825,744, British Patent

No. 442,524, U.S. Patent No. 2,702,824, and U.S. Patent No. 2,925,442.

Further, U.S. Patent Nos. 3,847,800 and 3,919,402 describe the use of nitrogen oxides followed by extraction by methanol to remove both sulfur and nitrogen compounds from petroleum stocks.

U.S. Patent No. 4,485,007 discloses a process for purifying hydrocarbonaceous oils containing both heteroatom sulfur and heteroatom nitrogen compound impurities, such as shale oils, by first reacting the hydrocarbonaceous oil with an oxidizing gas containing nitrogen oxides while limiting the molar ratio of the nitrogen oxide to the total sulfur heteroatom content and nitrogen heteroatom content and limiting the conversion of sulfur heteroatom content into gaseous sulfur oxides to about 60% or less on a weight basis, followed by extracting the oxidized oil in one step with an amine selected from the group consisting of ethylene diamine, monoethanolamine, diethanolamine and mixtures thereof, and a second extracting step using formic acid as an extracting solvent. It is disclosed that the amine extracting solvent acts to remove sulfur compound impurities and the formic acid extracting solvent acts to remove nitrogen impurities.

A process for producing a fuel composition by oxidizing a hydrocarbon oil with aqueous nitric acid, followed by extraction with acetone, methyl ethyl ketone, cyclohexanone, methanol, ethanol, normal propanol, isopropanol, ethyl acetate, tetrahydrofuran, dioxane, or a combination of an alcohol and a ketone, an alcohol and water, a ketone and water or a combination of alcohols is disclosed in U.S. Patent No. 4,280,818.

Although the methods described above have met with some success in desulfurizing petroleum fuels, the known approaches toward oxidation to remove a portion of the original sulfur content as gaseous sulfur oxides, and to convert a portion of the original sulfur content into sulfoxides and/or sulfones followed by extraction with appropriate solvents to achieve a desired low sulfur raffinate have not completely eliminated problems.

Similarly, direct extraction of hydrocarbonaceous oils with selected solvents to remove sulfur and nitrogen impurities to produce a raffinate which is low in sulfur content results in uneconomically low yields of the desired raffinate, along with reductions in the sulfur content of the hydrocarbonaceous oil. The methods described above basically have the disadvantages that (a) the solvents selected are suitable only for specific selected oils; (b) the solvents result in poor extraction yields or they do not provide sufficient phase separation to make solvent extraction possible; (c) unacceptably high solvent-to-oil ratios are required, decreasing oil yield and making the processes uneconomical; (d) they require expensive catalysts or extremely severe oxidizing conditions to provide sufficient sulfur removal; or (e) oxidative desulfurization methods involving nitrogenous oxidizing agents result in increased gum and sedimentation, and reduce the stability of the fuels produced.

For these reasons, the present technology for sulfur removal involving oxidation and subsequent extraction of hydrocarbonaceous oils needs great improvement.

Similarly, conventional methods of improving diesel cetane number by oxidation with nitrogenous oxidizing agents are inadequate to meet other product specifications. Particularly, diesel fuels produced by nitrogenous oxidation and solvent extraction can in some cases meet sulfur and cetane requirements for fuels, but are unsatisfactory with respect to the important specifications of yield, stability and Ramsbottom carbon content. Processes employing sulfuric acid in conjunction with nitrogenous oxidizing agents are ineffective to retain a high cetane rating. Distillative methods are commercially unfeasible due to the presence of substantial carbonaceous deposits in the still, and when thermal treating is applied to diesel fuel to reduce the sulfur content of the residue, this process also produces substantial carbonaceous deposits in the thermal treating still.

Apart from the failure of conventional oxidative cetane enhancement methods to provide diesel fuels of sufficient stability and Ramsbottom carbon content, these methods, like the oxidative desulfurization methods, employ solvents which result in poor yields, requiring unacceptably high solvent-to-oil ratios. Alternatively, the solvents used in some prior methods reduce or entirely eliminate the advantage of cetane enhancement obtained by oxidation.

Particularly because of the variety of sulfur-containing compounds and instability-causing compounds present in petroleum hydrocarbon feedstocks, and because of the selectivity of solvents for particular sulfur-containing compounds, nitrogen-containing compounds, aromatic compounds and olefinic compounds, previous attempts to upgrade middle distillate fuels by oxidation, solvent extraction or a combination of the two have concentrated on at most one or two product characteristics, and have generally required sacrificing product yield and stability in order to achieve products of acceptable sulfur content or ignition properties.

Although many diesel fuels having low cetane ratings and high sulfur content meet stability and Ramsbottom carbon specifications, if these fuels are oxidized to improve cetane rating or reduce sulfur, Ramsbottom carbon and stability become unacceptable.

Because of these significant disadvantages, conventional oxidation/extraction methods for upgrading middle distillates have largely been supplanted by hydrotreatment, or by chemical additive treatments for improving stability and cetane.

SUMMARY OF THE INVENTION

One object of the present invention is a process for improving the cetane number of diesel oil without decreasing stability or increasing Ramsbottom carbon content.

A second object of the present invention is a process for upgrading diesel oil by decreasing sulfur content and improving stability.

Another object of the present invention is a process for upgrading diesel oil employing solvent extraction with a high solvent extraction efficiency and correspondingly high yield.

An additional object of the present invention is a process for producing a blended diesel fuel from off-specification diesel oils meeting industrial specifications for cetane, sulfur content, Ramsbottom carbon, product stability and pour point.

It has now been discovered that a diesel oil can be improved, and the production of diesel fuels from substandard or blended stocks made possible, by a simple and economical process of first contacting the diesel oil with an oxidant selected from the group consisting of ozone, gaseous nitrogen oxides, nitric acid and nitrous acid, followed by selective solvent extraction. The process according to the invention permits the simultaneous desulfurization and cetane improvement of diesel fuels with remarkably improved stability on storage and enhanced handling characteristics.

Accordingly, one embodiment of the present invention provides a process for upgrading diesel oil to produce an upgraded diesel fuel comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone, wherein

  (1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed to step (a), and

  (2) (i) the reacting is such that when the oxidant is a nitrogenous oxidizing agent, the amount of oxidant,

equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed; and

(ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

(b) contacting the diesel oil from step (a) above with an extracting solvent, the extracting solvent

(1) having a dipole moment of about 2 or greater;

(2) being substantially immiscible with the diesel oil at the temperature of contacting with the diesel oil obtained in step (a),

(3) being a nonhalogenated solvent, and

(4) excluding amines, which are reactive with the oxidant

or a mixture of such solvents; or a water mixture of such solvent containing about 50% by weight or less water; and

(c) separating the diesel oil from step (b) above from the extracting solvent to recover upgraded diesel fuel.

Another embodiment of the process of this invention provides a process for upgrading diesel oil comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone, wherein
  (1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed, and
  (2) (i) the reacting is such that when the oxidant is a nitrogenous oxidizing agent, the amount of oxidant, equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed to step (a); and
    (ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

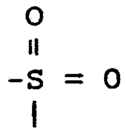
(b) contacting the diesel oil from step (a) above with an extracting solvent, the extracting solvent
  (1) having a dipole moment of about 2 or greater;
  (2) being substantially immiscible with the diesel oil at the temperature of

contacting with the diesel oil obtained in step (a),

(3) being a nonhalogenated solvent,

(4) excluding amines, which are reactive with the oxidant, and

(5) containing at least one of the following functional groups:



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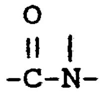

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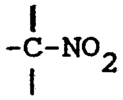

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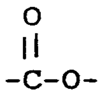

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or a mixture of such solvents; or a water mixture of such solvent containing about 50% by weight or less water; and

(c) separating the diesel oil from step (b) above from the extracting solvent to recover upgraded diesel fuel.

A further embodiment of the process of this invention provides a process for upgrading diesel oil comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, derived from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone, wherein

  (1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed to step (a), and

  (2) (i) the reacting is such that when the oxidant is a nitrogenous oxidizing agent, the amount of oxidant, equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed to step (a); and

    (ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

(b) contacting the diesel oil from step (a) above with an extracting solvent selected from the group consisting of furfural, butyrolactone, dimethyl formamide, methyl carbitol, tetrahydrofurfuryl alcohol, dimethyl sulfoxide, sulfolane, sulfolene, dimethyl acetamide, 1-methyl-2-pyrrolidone, acetonitrile, acetic anhydride, nitrobenzene, nitromethane, and mixtures thereof, or a water mixture thereof containing about 50% by weight or less water; and

(c) separating the diesel oil from step (b) above from the extracting solvent to recover upgraded diesel fuel.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

FIG. 1 is a schematic flow diagram of one embodiment of the process of this invention.

FIG. 2 shows the results of the extraction of atmospheric gas oil by gamma-butyrolactone.

FIG. 3 illustrates the effects of oxidation of atmospheric gas oil on gamma-butyrolactone extraction.

FIG. 4 shows the relationship between cetane enhancement and N content in oxidant reacted but solvent unextracted oil.

FIG. 5 shows graphically the results obtained on extraction of oxidant reacted diesel oil in terms of the sulfur content and extracting solvent content present.

FIG. 6 is a graphical presentation of equilibrium data obtained on extraction of oxidant reacted diesel oil.

DETAILED DESCRIPTION OF THE INVENTION

As indicated above, this invention provides a process for upgrading petroleum derived diesel fuel oils having a boiling point at normal pressure of about 300°F to about 700°F, including those containing heteroatom sulfur compounds, to produce a cetane number increase of at least about 5 of the reacted product of step (a) over the diesel oil feed to step (a) while meeting stability requirements. The process of this invention is applicable to the upgrading of diesel oil which can be derived from any source, for example, a conventional petroleum crude oil or crude oil fraction containing sulfur, aromatic, olefinic and napthenic compounds as impurities. The term "diesel oil" as used herein is broadly defined to include any hydrocarbon having a nominal boiling range of about 300°F to about 700°F of petroleum origin which can be upgraded by the process of this invention to meet commercial product specifications for a diesel fuel and the term "diesel fuel" is generally used to describe the upgraded product, although the terms can be used interchangeably. Preferred petroleum source of diesel oils which can be used in the process of this invention are those containing less than about 40% by weight aromatics content, those containing less than about 35% by weight olefins content and those containing both less than about 40% by weight aromatics and less than about 35% by weight olefinics content.

The process of this invention is basically not limited in terms of the source of the diesel oil, but is applicable to any diesel oil with the above described boiling point range from petroleum sources, including conventional crude oil, heavy crude oil and tar sands.

In the process for upgrading diesel oils according to the invention, particular product specifications may vary over a wide range. With the disclosure given herein, the present process may be readily applied and modified by one skilled in the art to produce a diesel fuel by blending and having particular desired specifications, particularly with respect to the basic criteria of cetane, sulfur content, Ramsbottom carbon and stability, density and boiling range. Furthermore, the process of this invention can be employed in combination with conventional techniques for meeting product specifications as desired, e.g., by addition of chemical additives such as corrosion inhibitors, stabilizers and the like.

Fuel stability is measured by a number of accelerated tests, one of which is the Nalco 300°F test. For satisfactory stability in commercial storage and use, a transportation fuel must exhibit a Nalco rating of about 7.0 or lower. A rating of about 7.0 is the upper limit of acceptability for commercial use, although a lower level is desirable. The applicable Nalco test is well known in the art, and can be simply performed, for example, by placing 50 ml of oil to be tested in a tube 3 cm in diameter, heating the tube in a 300°F bath for 90 minutes, and then cooling the oil. The oil is then filtered using a micropore filter with a number 1 filter paper, the paper and the filter are washed with heptane, and the residue remaining is compared with standard samples to determine the stability rating.

Desulfurization is a second generally important aspect of purification or upgrading of diesel oils. Sulfur compounds present as impurities may include, for example, thiophenic sulfur, mercaptan sulfur, sulfides, thiols and disulfides. Because of the differing selectivities of various solvents in extracting different sulfur-containing impurity compounds, which can be enhanced or depressed by oxidation, depending on the particular solvent and feed characteristics, selection of an appropriate solvent for desulfurization is empirical and selection generally is not possible on the basis of theory.

Although cetane number is an important quality characteristic of diesel fuels, cetane enhancement obtained by oxidation is poorly understood. In particular, although it is known that increasing oxidizer nitrogen is related to increased cetane and it is known that aromatics extraction contributes to cetane improvement, raffinate nitrogen is not well correlated with cetane improvement, and aromatics removal alone cannot account for the cetane response obtained at the high yields observed in this invention. Oxidation with non-nitrogen containing oxidants such as ozone as in this invention increases cetane although nitrogen is not added by the oxidant.

In addition to management of the above criteria of stability, sulfur content and cetane number, Ramsbottom carbon content is an important quality specification for diesel fuels, since fuels high in Ramsbottom carbon cause fouling problems when used in diesel engines. In an acceptable diesel fuel, the Ramsbottom carbon content is preferably less than about 0.3 weight percent, as determined by the method disclosed in ASTM D 524.

While not desiring to be bound by theory, it is currently believed that the complex process according to the present invention for upgrading diesel oils by oxidation and extraction probably involves nitrogen addition to paraffins, olefins, naphthenes and aromatics to form nitrates, esters, amines, azides, indoles and the like. The choice of an appropriate extracting solvent with a high selectivity for the compounds formed with oxidation permits selective removal of cetane-neutral or cetane-depressing compounds in extraction. In addition, sulfur-containing and instability-causing compounds can be simultaneously extracted by the choice of an appropriate solvent. The choice of an appropriate solvent is critical, and is made difficult by the circumstance that solvents which are capable of extracting some of the above-mentioned components will nonetheless be ineffective for use in the present invention because they will (a) not remove appreciable sulfur; (b) remove so much nitrogen to improve stability that an undesirably low cetane results; (c) not remove nitrogen, resulting in acceptable cetane but unacceptable stability and Ramsbottom carbon; or (d) result in poor yield.

Typically, the process of this invention can be employed on atmospheric gas oils and cycle oils. Atmospheric gas oil is a fraction derived from petroleum crude sources. Atmospheric gas oil is one component used in diesel oil blending, and may contain an off-specification sulfur content for use as a diesel fuel. Typically, sulfur as a heteroatom is present as thiols, disulfides, sulfides, thiophenes, mercaptans, and nitrogen is present as substituted pyridines and pyrroles, and other compounds. Typical analyses of diesel oils which can be used in this invention are set forth in Table 1 below.

Table 1

Properties of Diesel Oils

	X	C	CC	K1	K2	K3	K4	K5	K6	KD	TD	KG	KH	CB	TS	TH	G
Sulfur (Y.) wt	1.07	1.19	0.72	2.60	1.08	0.4	0.6	0.09	0	0.43	0.39	3.02	1.2	0.02	1.32	0.31	0.69
Nitrogen, ppm	200	60	150	750	93	61	191	96	87	295	6	1353	83	33	100	7	700
Density, g/cc	0.85	0.828	.840	0.870	0.863	0.850	0.843	0.856	0.872	0.854	0.821	0.892	0.839	0.828	0.87	0.82	0.855
Gravit, API	35.0	39.4	36.9	31.1	32.5	35	36.3	33.8	30.8	34.2	40.8	27.1	37.1	39.4	31.1	41.1	34.0
Ramsbottom C	0.13	--	0.14	0.34	0.139	--	0.111	0.122	0.107	0.247	--	0.519	--	--	--	--	0.519
Nalco	--	--	--	2	2	2	1	4	2	--	--	--	--	--	--	--	--
Cetane	58.2	54.3	52.7	37.3	46.0	42	41	39.7	40.5	40.3	--	40.1	--	57.552	43.1	52.2	44
Distribution; °F																	
5%	490		--	370	440	420	380	418	410	--	--	--	368	376	--	--	--
10%	506		446	402	468	435	395	440	426	323	326	490	448	452	--	--	432
30%	536		501	468	520	--	450	485	480	480	438	547	510	512	--	--	482
50%	560		529	515	550	525	490	508	519	521	482	588	544	536	--	--	510
70%	585		562	568	580	568	540	558	550	566	536	626	590	561	--	--	539
90%	620		619	620	640	642	600	619	610	630	602	668	650	600	--	--	589

FIG. 1 describes schematically an embodiment of the process of this invention comprising mixing diesel oil feed at 1 and nitric acid through inlet 2 into a reactor 3. After reaction in the reactor, the oxidized product 4 may be separated from a byproduct residue 5 and is passed into a solvent extractor 6, where it is contacted with an extracting solvent 7 and after solvent/oxidized oil separation to remove an extract phase containing solvent with impurities 8, the oxidized raffinate phase with residual solvent 9 is subjected to recovery at 10 to remove residual solvents 11 and to obtain upgraded diesel fuel 12 in accordance with this invention.

In the first step of the process of this invention, a diesel oil, such as an atmospheric gas oil fraction, is reacted by contacting the oil with an oxidant. If desired, the feed oil can first be subjected to pretreatment, such as by washing to remove phenols or other corrosive components of the oil, filtering to remove gum or sediment, heating or treatment with H_2SO_4 as conventionally used. In the first step of the process of the invention, the oxidant can be a nitrogenous oxidizing agent or a non-nitrogenous oxidizing agent such as ozone. The term "nitrogenous oxidizing agent" is used herein to mean any nitrogen-containing oxidizing compound including, e.g., an oxidizing gas containing at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom, a liquid containing at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom, nitrous acid and nitric acid.

The oxidizing gas used can be a gas containing only such a nitrogen oxide or can be one which contains mixtures of such nitrogen oxides. Furthermore, the oxidizing gas can be one which also contains other components such as oxygen, nitrogen, lower nitrogen oxides, i.e., nitrogen oxides containing only one oxygen atom or less than one oxygen atom per nitrogen atom in the oxide. For efficiency, preferably the oxidizing gas will be one which contains only nitrogen oxides with more than one oxygen atom for each nitrogen atom but mixtures with other gases such as oxygen, nitrogen, as well as inert gases such as air, helium and helium with air can be employed if desired. Suitably the oxidizing gas will contain at least 0.5% by volume of at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom, but the concentration can be reduced if the flow rate of oxidant is increased for a longer time. Nitrogen dioxide or its dimer N_2O_4 can be advantageously employed, alone or in admixture with air.

The nitrogenous oxidizing liquid used can be a liquid nitrogen oxide as defined above, nitrous acid, or nitric acid, either acid concentrated or in a mixture with about 0 to 90% water by weight. Preferably, the liquid nitrogenous oxidizing agent is an aqueous solution of nitric acid containing about 50 to 90% nitric acid by weight.

When nitric acid is used as a nitrogenous oxidizing agent in the present invention, it may advantageously be used in combination with other organic or inorganic acids. Suitable inorganic acids include sulfuric and phosphoric acids, and suitable organic acids include, e.g., acetic and formic acids. The organic and inorganic acid may be used alone or in combination. Typically, an inorganic acid can be added to the aqueous nitric acid solution used as an oxidizing agent in an amount of from about 5 to 200% by weight of the nitric acid solution, and an organic acid can be added in an amount from about 5 to 200% by weight of the nitric acid solution. Preferred combinations of nitric and auxiliary acids include nitric and sulfuric, nitric and acetic, and nitric and formic acids.

When ozone is used as an oxidizing agent in the present invention, it is typically used as an oxidizing gas containing either ozone alone or a mixture which contains other components such as oxygen, nitrogen, as well as inert gases such as helium or helium with air. Suitably, the oxidizing gas will contain at least about 1% volume of ozone. If desired, ozone can be used in the process according to the present invention in combination with a nitrogenous oxidizing agent as described above.

In the first step of the process of this invention, a diesel oil such as atmospheric gas oil is reacted with the oxidant in the form of a liquid or gas. The contacting of the diesel oil with the oxidant as a liquid can be accomplished by any means conventional in the art for contacting two liquid reactants, e.g., by injecting the oxidant under the surface of agitated oil contained in a reactor. When an oxidant as a gas is employed, the oxidant gas can be contacted with the diesel oil using any conventional means for contacting a gaseous reactant with a liquid reactant. Suitable examples of such means for contacting a gaseous reactant with a liquid reactant include dispersing the gas as bubbles in the liquid, trickling the liquid over an inert solid bed with gas passing also over the bed co-currently with or countercurrently to the liquid flow, the latter type flow being preferred.

It is important in the first step of the process of this invention to control the operating parameters during the reacting of the diesel oil with the oxidant to insure sufficient reaction to improve cetane and to improve the extraction efficiency in the second step of sulfur compound containing impurities and impurities contributing to instability. However, the reaction step should be limited so that detrimental effects on the diesel oil substrate ultimately obtained and recovered after the process for upgrading of this invention do not occur. These important processing controls as to the reaction of the diesel oil with the oxidant are described in more detail below.

As used herein, the term "acid-to-oil ratio" (acid-to-oil nitric acid, A/O) refers to the weight of water-free acid (or its nitrogen equivalent based on 100% concentration nitric acid when a nitrogenous oxidizing agent such as NO_2 or N_2O_4 is used) to the weight of diesel oil feedstock, and is from about 0.0001 to about 0.1, preferably from about 0.0005 to about 0.05. The control of the treatment with a nitrogenous oxidizing agent in the first step of the process of this invention may be achieved by controlling the water content of the acid used in the reactor. Treatment with a nitrogenous oxidizing agent in the first step can also be controlled and improved by the copresence of sulfuric acid or other auxiliary acid mixed with the oxidizing agent. In the case of using ozone as the oxidant, the amount of ozone is that amount sufficient to achieve about 10% or greater reduction up to about 50% reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a).

This control of the amount of nitrogenous oxidizing agent or ozone to the total amount of the diesel oil feed can be easily maintained.

As a result of the control of the parameters of step (a) of the process of this invention, a cetane number increase of the reacted diesel oil over the diesel oil feed to step (a) of at least about 5 is achieved.

For example, with the knowledge of the concentration of the nitrogenous oxidizing agent/ozone and from a knowledge of the sulfur heteroatom content, and cetane number of the feed, attained using conventional chemical analysis, the amount of oxidizing agent can be determined. Conventional means for metering gaseous and liquid reactants can be employed.

The reaction of the first step of the present invention can be performed at any temperature from about -40 to about 200°C, but is preferably conducted at a temperature of about 90°C or less, most preferably about 25 to 90°C. The reaction time is not particularly limited, and may include, for example, any time from about 1 minute to about 3 weeks. The first step of the present invention may be conducted at atmospheric pressure or at greater or lower pressures as desired. Advantageously, the reaction step is conducted using conventional agitation means, such as a stirrer. In the process of this invention, step (a) above is conducted to the extent that an increase in cetane number of at least five cetane numbers, generally seven cetane numbers and more generally nine cetane numbers, over the diesel oil feed to step (a) is achieved.

When a nitrogenous oxidizing agent is used in the first step of the present invention, typically an increase in nitrogen compound content over that originally present in the diesel oil will be observed. While not desiring to be bound by theory, the reason for the increase in observed nitrogen compound content is believed to be that nitration of the diesel oil substrate can occur resulting in an increase in the heteroatom nitrogen compound content. Contact times on the order of less than about 120 minutes and weight ratios of nitrogenous oxidizing agent to total feed of less than about 0.1 are desirable not only from the standpoint of efficiency but also from the standpoint of economics. Particularly preferably, a contact time of about 30 minutes in combination with a weight ratio of nitrogenous oxidizing agent to diesel oil of about 0.05 or less can be advantageously employed with maximum yield of diesel oil having reduced sulfur content and improved stability.

However, because of the known relationship of nitrogenous oxidant to cetane number, it is also advantageous when using a nitrogenous oxidizing agent to carefully control the minimum amount of nitrogen compounds added to the diesel oil feed in order to insure a sufficient cetane number in the diesel fuel produced.

In the process of the invention, in order to improve Ramsbottom carbon and stability while retaining high cetane, a preferred level of nitrogen in the diesel oil following the first step of contacting the oil with a nitrogenous oxidizing agent is from about

1500 to 2000 ppm of nitrogen. If desired, oil can be subjected to acid separation step, such as decanting, alkali treatment, water wash or clay treatment.

A diesel oil, after being subjected to the reaction described above for step (a) of the process of this invention, is then subjected to an extraction step (b) with an appropriate extracting solvent. As will be seen from the examples to be given hereinafter, processing conditions set forth for the reaction step (a) above are controlled to improve the ability of the specific and selected extracting solvents used in the extracting step (b) of the process of this invention to enhance removal by extraction of sulfur-containing impurities, instability-causing compounds, Ramsbottom carbon, cetane-depressing compounds present originally in the diesel oil to be upgraded, and thereby to reduce their level in the ultimate diesel oil recovered and upgrading as a result of the process of this invention.

In extraction step (b) of the process of this invention, the diesel oil obtained from step (a) of the process of this invention is contacted with an extracting solvent

(a) having a dipole moment about 2 or greater,

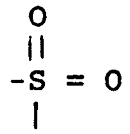
(b) being substantially immiscible with the diesel oil at the temperature of contacting with the diesel oil obtained in step (a),

(c) being a nonhalogenated solvent, and

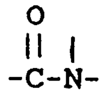
(d) excluding amines, which are reactive with the oxidant,

or mixtures of such solvents or in a water mixture of a single solvent or a mixture of solvents containing about 50% by weight or less water. The term "dipole moment" as used in the present invention means the dipole moment measured in benzene at 25°C, and it is considered that substantially all solvents having a dipole moment of 2 or greater, more generally 3 or greater, and having the other characteristics as described above will exhibit sufficient selectivity towards sulfur-containing and instability-causing impurities contained in the reacted diesel oil feed.

In particular, appropriate extracting solvents having the above-described characteristics as to dipole moment, immiscibility, non-halogenation and oxidant-non-reactivity include solvents having the following functional groups therein



$-\overset{\overset{O}{\|}}{\underset{|}{S}}=O$



$-\overset{\overset{O}{\|}}{C}-\overset{|}{N}-$

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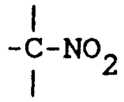
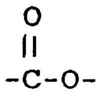


$-\overset{|}{\underset{|}{C}}-NO_2$

and



$-\overset{\overset{O}{\|}}{C}-O-$.

Exemplary immiscible, nonhalogenated organic solvents having a dipole moment of 2.0 or greater and excluding oxidant reactive amine solvents which are useful in the present invention are set forth in Table 2 below:

Table 2

Solvent	Dipole Moment In Benzene at 25°C
gamma-Butyrolactone	4.00
Furfural	3.60
Dimethyl Formamide (DMF)	3.86
Acetic Anhydride	3.15
Dimethyl Sulfoxide (DMSO)	3.90
Sulfolane	4.70
1-Methyl-2-pyrrolidone	4.09
Acetonitrile	3.40
Nitromethane	3.13
Tetrahydrofurfuryl Alcohol	2.12, (neat)

In contrast, commonly used extracting solvents having a dipole moment of less than about 2 are generally considered unsuitable for use in step (b) of the present invention, including those set forth in Table 3 below:

Table 3

Solvent	Dipole Moment In Benzene at 25°C
Formic Acid (88% Aqueous Solution)	1.20
Acetic Acid	1.60
Methanol	1.70
Ethanol	1.75
Ethylene Glycol	1.50
Phenol	1.45
Diethylamine	1.17
Aniline	1.55
Hexamethylene Diamine (70% Aqueous Solution)	1.94
Ethylene Diamine	1.92

In particular, solvents useful in the extraction step (b) of the present invention which have the required dipole moment and immiscibility and are nonhalogenated and non-amine include furfural, butyrolactone, dimethyl formamide, methyl carbitol, tetrahydrofurfuryl alcohol, dimethyl sulfoxide, sulfolane, sulfolene, acetic anhydride, dimethylacetamide, acetonitrile, 1-methyl-2-pyrrolidone, nitrobenzene, and nitromethane. These extracting solvents can be used alone or in combination, and further each of the extracting solvents used can be used alone in admixture with or as mixture in admixture with water to the extent of up to about 50% by weight of water. Water in combination with these extracting solvents can be advantageously used to increase phase separation and yields of oil recovered in extraction step (b). The amount of water which can be used with any particular extracting solvent can be appropriately determined by running routine screening tests to determine for a particular diesel oil feedstock to be upgraded and under the reaction conditions employed in step (a), which of the extracting solvents, alone or in admixture with water and to what extent in admixture with water can be advantageously used. These routine screening tests can be simply a consideration of yield, reduction in sulfur content present, stability and cetane number, determined by routine chemical analysis, to determine which of the extracting solvents or water/extracting solvent mixtures can be most advantageously used with a given diesel oil feed.

In the extracting step (b) of the present invention, conventional extraction procedures are employed. Generally, the extracting solvent is simply added to and mixed with the diesel oil processed as in step (a). The length of time for contact of the extracting solvent is only that time necessary to permit a simple mass transfer of the sulfur compound impurities, instability-causing compound impurities, or Ramsbottom carbon containing components from the diesel oil phase into the extracting solvent phase, and is typically from about 1 to 30 minutes. Generally, a suitable extraction time ranges from about 1 to about 10 minutes.

The temperature of the extracting step is controllable over wide ranges, and can be, for instance, any temperature from about 40°F to about 300°F and preferably is at room temperature, e.g., about 70°F to 90°F. The solvent can be added in substantially pure form, e.g., as obtained directly from commercial sources, or can be a used solvent which is recovered and purified or a recycle stream rich solvent, with any deficiency in amount of solvent desired for extraction being made up by the addition of additional solvent. Although the present invention is illustrated in the examples using a single solvent extraction step, the solvent extraction step (b) can be conducted, if desired, in a sequence of separate solvent extraction zones, varying, e.g., time, temperature, or solvent-to-oil ratio as desired.

It should be recognized that in the extraction step (b) of the present invention, the extracting solvent is immiscible with the diesel oil and is nonhalogenated. The lack of miscibility thus permits an easy phase separation after the extraction is completed. If an emulsion is formed, it can be easily broken, e.g., by warming, for phase separation. Further, oxidant reactive amine solvents are not employed as extracting solvents in extraction step (b) of the process of this invention.

The extraction in step (b) of the process of this invention can be generally conducted by simply adding the extracting solvent to the diesel oil, mixing such with the diesel oil, allowing phase separation of the mixture to occur and then separating the extracting solvent phase containing the sulfur impurity content or instability-causing content removed from the diesel oil substrate phase. Conventional chemical engineering techniques can be employed to achieve this extraction conducted in step (b) of the process of this invention.

Generally, a suitable extracting solvent-to-oil ratio (S/O) by weight can range from about 0.05:1 to about 5:1, preferably 0.1:1 to 0.5:1, but these ratios are not considered to be limiting.

In a preferred embodiment of the present present invention, the solvent-to-oil ratio in the solvent extraction step (b) is reduced to much smaller values than those conventionally used in order to increase the overall efficiency of the reaction/extraction process of this invention. As shown in FIG. 2, the efficiency of solvent extraction of sulfur impurities can be improved by increasing the solvent-to-oil ratio in extraction even without reaction with an oxidant. FIG. 2 shows the results of the extraction of an atmospheric gas oil of Table 1 by gamma-butyrolactone. For an unreacted AGO, at a solvent-to-oil ratio (S/O) of 1.0:1 by weight, the raffinate had a yield of 91% by weight but with only 22% sulfur reduction (0.93% S). About 60% sulfur removal (0.48% S) was achieved by using a very high S/O ratio, 9.0:1, but the oil yield was very low (only 76%). Thus, a higher S/O ratio in extraction involves higher costs due to solvent recovery, coupled with greater loss of oil, one factor that has made solvent extraction of hydrocarbon oils such as diesel oils for sulfur removal uneconomical.

As is seen from FIG. 3, which illustrates the effects of reaction of an atmospheric gas oil of Table 1 on gamma-butyrolactone extraction, an increase in solvent-to-oil ratio decreases oil yield even with reacted oils. However, the loss in oil yield can be offset by an increase in severity of reaction. Thus, a 55% sulfur removal by extraction requires a S/O ratio of about 6.0:1 for unreacted oil, an S/O ratio of more than 1.0:1 for mildly reacted AGO, a S/O ratio of less than 1.0:1 for moderately severely reacted AGO and a

S/O ratio of less than 0.5:1 for severely reacted AGO, when the severity of reaction is here expressed in terms of sulfur content remaining after reaction. The oil is defined as "severely reacted" when the sulfur reduction is more than about 50%. In each case, the decrease in solvent-to-oil ratio is accompanied by a significant increase in oil yield, i.e., from about 75 weight percent extracted oil yield for unreacted oil to more than 90% extracted oil yield for severely reacted oil. Accordingly, one aspect of the present invention is that surprisingly low solvent-to-oil ratios are required to obtain a desired degree of sulfur reduction for reacted as opposed to unreacted stocks.

With increased severity of reaction in the first step of the present invention, increased cetane and sulfur reduction are obtained; however, stability decreases and Ramsbottom carbon is undesirably increased. Extraction in the second step of the present invention further reduces sulfur content, while significantly improving stability and Ramsbottom carbon. The degree of stability and Ramsbottom carbon content improvement obtained is directly related to the solvent-to-oil ratios used in extraction.

Generally, even mild treatment by nitric acid or ozone will significantly deteriorate stability and Ramsbottom carbon. For example, a weight ratio of only 0.0025 of 90% nitric acid to oil will increase Ramsbottom carbon to levels of over 1.5% and will deteriorate Nalco stability to about 20.

Solvent extraction by the solvents of the present invention can be used to bring stability and Ramsbottom carbon into commercially acceptable specifications, while removing sulfur, retaining cetane, and achieving high raffinate yields. As in any extraction process, the results achieved depend upon solvent to oil ratio, the extracting solvent chosen, extractor stage efficiency, number of stages, and co-current or counter-current operation. With an efficient extractor, an oxidant treated diesel oil with a Ramsbottom carbon of 7% and a Nalco stability of 20 can be extracted to produce an upgraded diesel fuel with a Nalco stability of 7 and a Ramsbottom carbon of 0.2% at a solvent-to-oil ratio of 0.56. At solvent-to-oil ratios of 0.24 and 0.86, Ramsbottom carbon contents of 0.62% and 0.14% can be achieved.

It should be noted that one skilled in the art utilizes product blending or stabilizers to bring diesel oils, even though upgraded yet are still outside commercially acceptable specifications, into a blend which meets all commercially required specifications. This approach can be employed with the upgraded diesel fuel obtained in the process of this invention.

Furthermore, the remarkably low solvent-to-oil ratios required for reacted feedstocks are accompanied by surprisingly increased oil yields. Accordingly, the process according to the present invention provides substantially improved yields with substantially lower and more economic solvent-to-oil ratios than heretofore achieved.

The extracting solvents employed in the present invention can be used in their commercially available forms as described above or can be upgraded to remove any undesired components which might be present in the commercially available forms.

Step (c) of the process of this invention comprises recovery of the diesel oil substrate purified as a result of the reaction step (a) and extraction step (b) of the process of this invention. Conventional purification procedures for removal of an extracting solvent from a diesel oil can be employed. These extraction procedures include distillation, fractional crystallization, water washing followed by distillation and any other appropriate conventional procedures for removing an extracting solvent from an oil substrate. The process of this invention is not to be construed as limited in any way to selection of a specific diesel oil recovery and separation procedure.

The process of this invention described above can be advantageously used to upgrade various types of petroleum derived diesel oils containing heteroatom sulfur compound impurities and organic compounds causing instability in the diesel oil products. Generally, diesel oils having a heteroatom sulfur content ranging up to about 4% by weight can be subjected to and purified in accordance with the process of this invention to yield from the process of this invention an upgraded diesel fuel having on the order of at least about 30%, preferably about 75%, sulfur impurity content removal, while simultaneously improving product stability. Alternatively, diesel oils of relatively low initial sulfur content can be upgraded and purified in accordance with the process of this invention to yield a upgraded diesel oil having improved cetane and meeting stability, Ramsbottom carbon and sulfur product specifications with somewhat reduced sulfur content removal at higher yield, by conducting the extraction step (b) of this invention using a low solvent-to-oil ratio.

Diesel oils which are not of petroleum origin generally contain high levels of aromatics, olefins, or both. The solvents employed in the present invention are generally ineffective for such oils, and are less effective for petroleum oils with high aromatics or olefin levels, due to the strong affinity of the solvent employed in this invention for these compounds. In general, such diesel oils will exhibit inferior yields at all solvent-to-oil ratios employed, and many of such solvents become miscible with the oil at low solvent-to-oil ratios of about 0.2 or lower.

It can be seen from an examination of the essential steps in the process of this invention that because of the mild reaction conditions employed in step (a) of the process of this invention, the simple control of the essential parameters which need to be controlled, the efficiency and selectivity of the extracting solvents employed, and the low pressure, low temperature and reduced complexity involved, the present invention results in a remarkably economical and advantageous process. This is particularly true when it is compared with the high temperature and high pressure hydrodesulfurization treatments employed conventionally in the past. Further, the advantages of the process of this invention can be seen in comparison with similar upgrading processing using catalysts conventionally employed in the art since an expensive catalyst is not needed and no steps are required to separate catalyst or regenerate catalyst. Thus, the process of this invention is considered to be a marked advance over current technology for cetane improvement and upgrading diesel oils containing sulfur impurities or instability-causing impurities, and is believed to be of particular commercial significance.

As indicated above, the process of this invention can be used to purify and upgrade diesel fuel oils, to reduce sulfur content, improve stability, increase cetane number and reduce Ramsbottom carbon content. In general, diesel oils after reaction in step (a) of the present invention and having a sulfur content up to about 4% by weight, a stability as determined by the Nalco test of up to about 20 or higher, and a Ramsbottom carbon content of up to about 15% or higher can be purified and upgraded according to the process of this invention to obtain a diesel fuel having on the order of about 5-70% sulfur impurity content removal, a Nalco stability improvement including improvements to about 7 or less, a cetane number improvement for the product of the process of this invention of about 5 to about 20 cetane numbers above feed and a significant reduction in Ramsbottom carbon content including the ability to achieve a Ramsbottom carbon content of less than about 0.3%.

In addition, the diesel oil upgraded in accordance with the process of this invention can be used *per se* or as a blending stock to produce desired products, such as a diesel fuel having an improved cetane number. For example, the high-cetane, low-sulfur raffinate obtained in the process according to the invention can be blended with other diesel fuels or cycle oils which may have adequate stabilities but low cetane, or in some cases high sulfur, to obtain a diesel fuel meeting standard commercial product specifications.

Further, each of the embodiments of the process of this invention described above can be advantageously conducted in a batchwise, semi-continuous or continuous manner.

The following examples are given to illustrate the process of the present invention in greater detail. These specific examples are given for the purpose of exemplification, and are not to be construed as in any way limiting the practice of the the process of the present invention. In the examples to follow, unless otherwise indicated, the reacting of the diesel oil with an oxidant comprising an oxidizing gas was conducted using a semi-batch reactor system consisting of a jacketed cylindrical vessel capable of accommodating a one-liter charge. The reactor was fitted with an impeller shaft terminating with a Teflon or stainless steel impeller. The reactor was further equipped with a thermometer, a sample withdrawal tube and a glass condenser. A gas inlet tube passing into the bottom of the reactor was used to introduce the oxidizing gas through a sparger to the oil previously charged to the reactor. In the examples to follow, the diesel oil used was one having the properties shown in Table 1 above.

The procedure employed, unless otherwise indicated, for reacting the oxidizing gas with the diesel oil was to charge a weighed amount of the oil, approximately 400 grams, into the reactor. From the weight of the oil charged and the chemical analysis thereof, the total moles of sulfur heteroatom compounds, nitrogen heteroatom compounds, cetane number and Ramsbottom carbon content were known.

The oxidant gas flow rate into the reactor was set by considering the weight ratio of oxidant to diesel gas oil and the contact time. The weight ratio set forth in the examples to follow is the ratio of total weight of oxidant used for a particular contact time to the total weight of the oil charged. Control of the flow rate was achieved using a rotameter, appropriately calibrated. Various contact times for reaction of 5, 15, 30 and 60 minutes, various weight ratios of oxidant to total feed weight of 0.01 to 0.14 were employed at an initial reactor temperature of 25°C unless otherwise indicated. When nitrogen dioxide was used as an oxidant, it was mixed with air at a volume ratio of one part nitrogen dioxide to four parts air. When ozone was used as an oxidant, the ozone was generated with oxygen at a volume ratio of about one part by volume ozone to ten parts by volume oxygen before being introduced into the reactor.

In operation, when using a gaseous oxidant, after calculation of an appropriate rotameter setting, diesel oil feed was charged to the reactor, the reactor was heated to the prescribed temperature, the rotameter valve was opened to achieve appropriate oxidant gas flow into the reactor, and the timer was started. The reaction mixture was agitated by a stirrer. Temperature measurements were made at appropriate intervals and at the conclusion, flow of the oxidant gas was stopped and a sample of the oxidized diesel oil was obtained for analysis. The remainder of the reacted oil was then employed in extraction.

All solvent extractions performed, unless otherwise indicated, were single-stage batch extractions. In the extraction set forth in the examples below, approximately 20 ml of oil was poured into a 60 ml separatory funnel. The solvent employed was then added to the oil in the separatory funnel in an appropriate ratio by weight to the oil. The separatory funnel was then shaken and allowed to stand from one to thirty minutes at room temperature to achieve complete separation. After the system was stabilized, an extract phase (containing solvent, sulfur-containing compounds, instability-causing compounds, nitrogen-containing compounds and cetane-inhibiting compounds) was collected and the yield of raffinate (oil plus minor amount of dissolved solvent) was determined. Also, after each extraction the raffinate was washed twice with water, using a water-to-raffinate ratio of 1.0 by weight for each wash, before measuring the raffinate oil yield. After washing, the final oil obtained (from which the solvent had been removed) was collected and weighed.

Sulfur analysis was conducted using a Princeton Gamma-Tech Model 100 chemical analyzer. Stability analysis was conducted by a standard Nalco test, i.e., by heating a tube containing the sample of oil for 90 minutes and then filtering the heated oil using a micropore filter and No. 1 filter paper, followed by washing the filter and the filter paper with heptane and comparing the residue to a standard. Determination of the cetane number of the resulting diesel fuel was determined using a diesel test engine (ASTM D613). Ramsbottom carbon content (ASTM D524) was evaluated by distilling 90% overhead and taking a portion of the bottom 10% which was burned in a Ramsbottom oven, after which the residue was weighed.

Unless otherwise indicated herein, all parts, percent ratios and the like are by weight.

COMPARATIVE EXAMPLE 1

Samples of virgin atmospheric gas oil (Stock C, as described in Table 1) were individually contacted with each solvent shown in Table 4 below. This stock had not reacted prior to extraction. Each 20 milliliter oil sample was contacted with the extracting solvent for one minute by shaking with 20 ml of each solvent. After phase separation had occurred, the yield of raffinate was determined and each sample was evaluated for sulfur content.

Table 4

Extraction of Atmospheric Gas Oil
(Sulfur Content, 1.19%; S/O 1:1)

Extracting Solvent	Oil Yield (%)	Sulfur Content (%)	Sulfur Removal (%)
Furfural	88.3	0.84	29.4
gamma-Butyrolactone	90.0	0.88	26.1
Dimethyl Formamide (DMF)	85.4	0.70	41.2
Ethylene Diamine (EDA)	94.5	0.96	19.3
Methyl Carbitol	87.6	0.88	26.1
Phenol	89.3	0.88	26.1
Tetrahydrofurfuryl Alcohol	89.7	0.93	21.9
Aniline	85.1	0.95	20.2
Dimethyl Sulfoxide (DMSO)	93.0	1.00	16.0
Sulfolane	96.5	1.00	16.0
Nitromethane	96.2	1.00	16.0
Ethyl Cyanoacetate	98.6	1.06	10.9
Ethylene Chlorohydrin	91.7	1.02	14.3
Acetic Acid	92.6	1.14	4.2
Acetonitrile	89.6	1.04	12.6
Monoethanolamine	98.0	1.08	9.2
Ethylene Glycol	95.1	1.19	0
1-Methyl-2-Pyrrolidone	79.8	0.72	39.5
Methanol	87.8	1.14	4.2

The results shown in Table 4 demonstrate that a high yield of oil (greater than about 90%) could not be achieved simultaneously with a high degree (greater than about 40%) of sulfur hetero compound removal employing a wide range of solvents which have been conventionally used in prior methods for extraction and impurity removal, when the oil had not previously been oxidized. Additional solvents were tested at this solvent-to-oil ratio but were found unsuitable for extraction because of miscibility. These solvents were acetone, hexane, 2-butanone, 2-octanone, nitrobenzene, isobutylamine, diethylamine, ethyl acetate, pyridine, methylene chloride, diethyl ether, 2-propanol, trichloroethane, and trichloroethene.

COMPARATIVE EXAMPLE 2

A 0.5 liter sample of atmospheric gas oil, Stock C as described in Table 1, was oxidant reacted at 10°C, one atmosphere pressure, using a stream of 25% by weight nitrogen dioxide in air, for a contact time of 60 minutes. The reaction severity was measured by the weight ratio of NO_2/oil, which is defined as the ratio of weight of NO_2 added within the given contact time to the weight of oil charged. For this reaction, the NO_2/oil ratio was about 0.04. A 20 milliliter sample of this oxidized oil was then extracted using 20 ml of each solvent shown in Table 5 below, using the same procedures as described above in Comparative Example 1.

From Figure 3, comparisons of extraction yields must be made at equal levels of oxidation severity, taken as the degree of sulfur reduction over the treating reactor. All severities in Table 5 are approximately equal. The yields of Table 5 for phenol and aniline are at least 10% too high, due to the inability to remove these solvents by water washing. Also, ethylene diamine is unsuitable due to its reactivity, as discussed in Comparative Example 7 hereinafter.

All solvents of Table 5 having a low dipole moment give low yields, low sulfur removal, or both.

Table 5

Extraction of NO_2 Reacted Atmospheric Gas Oil Using Comparison Solvents1/

Extracting Solvent	Extraction Feed S (%)	Oil Yield (%)	Sulfur Content (%)	Sulfur Removal (%)	Dipole Moment2/
Monoethanolamine	0.63	94.2	0.46	27.0	-- 3/
Diethylamine	0.63	99.0	0.60	4.8	1.17
Ethylene Glycol	0.63	99.0	0.61	3.2	1.50
Methanol	0.60	84.1	0.37	37.3	1.70
Hexamethylene diamine (70% aqueous solution)	0.63	92.3	0.51	19.0	-- 3/
Ethylene Diamine	0.60	89.4	0.31	47.5	1.92
Phenol	0.60	83.7 4/	0.13	78.3	1.45
Aniline	0.63	83.0 4/	0.14	77.8	1.55
Formic Acid	0.63	97.0	0.63	0	1.20

1/ Water washed to remove residual solvent.

2/ In benzene at 25°C.

3/ Not available.

4/ Solvent insoluble in water; estimated solvent content of raffinate expected to reduce yields by at least 10%.

Additional solvents tested at this solvent-to-oil ratio and found unsuitable because of miscibility were acetone, hexane, 2-butanone, 2-octanone, nitrobenzene, isobutylamine, diethylamine, ethyl acetate, pyridine, methylene chloride, diethyl ether, 2-propanol, tricholoroethane, and trichloroethene.

COMPARATIVE EXAMPLE 3

A one liter sample of atmospheric gas oil, Stock C, as described in Table 1, was oxidant reacted at 10°C, and one atmosphere pressure, using a stream of 15% by weight nitrogen dioxide in air, for contact times of 15, 30, 60, and 80 minutes. The reaction severity was measured by the weight ratio of NO_2/oil, which is defined as the ratio of grams of NO_2 added within the given contact time to the grams of oil charged. Each oxidized oil was water-washed at a water/oil weight ratio of 1.0. Sulfur removal and higher cetane number improvement in the oil were accomplished, as shown in Table 6, both increasing as the weight ratio of NO_2/oil was increased. There is an unavoidable and undesirable increase of Nalco stability rating and Ramsbottom carbon to unacceptable levels. Oxidation improves the cetane number and removes sulfur from the oil but results in oxidized oil being unacceptably unstable and having poor Ramsbottom carbon content.

This comparative example clearly shows that the prior art teaching of nitrogen oxide reaction does improve the cetane rating of diesel fuel, but with unacceptable deterioration of stability and Ramsbottom carbon which are commercially important specifications for diesel fuel. Contacting this product with alkali, even at uneconomically high levels, is insufficient to effect sufficient improvement thereof.

Table 6

Oxidation of Diesel Oil with NO_2

Weight Ratio (NO_2/Oil)	S in Oil (%)	N in Oil (ppm)	Cetane Number	Nalco Stability	Ramsbottom Carbon (%)
0	1.19	60	54.3	3	0.15
0.007	1.09	1113	61.9	>>20[1/]	--
0.015	1.05	2713	68.1	>>20	--
0.030	0.87	6365	72.4	>>20	--
0.040	0.70	7150	72.0	>>20	18.73
0.040[2/]	0.66	5000	67.0	15	5.64

COMPARATIVE EXAMPLE 4

Samples of virgin, untreated atmospheric gas oil, Stock CC, as described in Table 1, were individually contacted with each solvent shown in Table 7 below. Each 20 millimeter oil sample was contacted for one minute by shaking the oil with each solvent at the indicated solvent-to-oil ratio. After phase separation had occurred, the yield of diesel oil separated (raffinate) was determined and each sample was analyzed for sulfur content and cetane number. The results show that a high yield of oil greater than 90% could not be

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1/ The symbol >> means "much greater than".

2/ Alkali washed with sodium hydroxide aqueous solution (5M) at 1:1 weight ratio to oil.

achieved simultaneously with a high sulfur removal of greater than 40%, and a substantial cetane number improvement. In addition, uneconomically high solvent-to-oil ratios with associated low raffinate yields are required for substantial sulfur removal and even moderate cetane improvement, for the Table 7 data without prior treatment with nitrogen oxidizing agents or ozone.

Table 7

Solvent Extraction of Diesel Oil[1/]

Extracting Solvent	Solvent-to-Oil Ratio	Extraction Oil Yield (%)	S in Oil (%)	Sulfur Removal (%)	Cetane Number
gamma-Butyro-lactone	0.55	93.6	0.57	21.9	55.8
gamma-Butryo-lactone	2.00	87.4	0.33	54.8	52.7
Furfural	0.70	91.2	0.51	30.1	53.9
DMF	0.25	94.1	0.62	15.1	55.0
DMF	0.50	89.7	0.51	30.1	55.2
DMSO	2.50	86.7	0.34	53.4	62.9
Sulfolane	9.00	88.7	0.38	47.9	60.7
1-Methyl-2-Pyrrolidone	0.25	93.1	0.58	20.5	56.4
1-Methyl-2-Pyrrolidone	0.38	88.9	0.51	30.1	57.3

[1/] Diesel Oil: Cetane No. 52.7, 0.73% S.

COMPARATIVE EXAMPLE 5

In an attempt to control the Ramsbottom carbon and stability by reducing the acid/oil ratio in reaction, atmospheric gas oil, Stock K2, as described in Table 1 was reacted with 90% HNO_3 at an 0.0025 acid/oil weight ratio. The cetane rating of the reacted diesel oil was only 48 and the nitrogen content was 350 ppm.

The Ramsbottom carbon content of the reacted diesel oil was 1.52%, considerably above the commercial specification level of 0.3% for a diesel fuel. Although the Nalco stability was not measured, significant deposits formed upon storage for 20 days, indicating the stability rating would exceed 15.

It does not appear to be possible to achieve significant cetane improvements by reaction with a nitrogenous oxidizing agent without encountering simultaneous reaction selectivity problems which are harmful to Ramsbottom carbon and stability specifications.

COMPARATIVE EXAMPLE 6

Nitrogen is known to contribute Ramsbottom carbon and stability problems in diesel fuels. Therefore, a nitrogen removal solvent, formic acid, disclosed in U.S. Patent No. 4,485,007 as being an excellent nitrogen removal solvent, was tested.

Stock CC, as described in Table 1, was reacted with gaseous nitrogen dioxide and extracted with formic acid at a 1.0 solvent-to-oil ratio using the procedures of U.S. Patent No. 4,485,007. The raffinate product obtained still had a Ramsbottom carbon content of 1.5% and a stability of 17. These poor results demonstrate that control of Ramsbottom carbon and stability requires more than a good nitrogen removal solvent. As taught by the present invention, formic acid with a dipole moment of 1.2 does not meet the dipole criteria of the present invention and is not a suitable solvent.

It is concluded that the nitrogenous oxidizing agent reaction is very complex, the individual compounds removed during extraction are unknown, and the specific characteristics influencing Ramsbottom carbon and stability are unpredictable. The result is that reaction-extraction results are poor while, based upon the prior art, they would have been expected to be excellent. The cetane-Ramsbottom carbon-stability characteristics of reacted diesel fuel are thus heretofore difficult to predict and are not achieved with the teachings of the prior art.

COMPARATIVE EXAMPLE 7

With the procedures discussed above, similarly, ethylene diamine disclosed in U.S. Patent No. 4,485,007 was used to extract reacted diesel oil, Stock X as described in Table 1. The oil diesel had been reacted with a nitro- genous oxidizing agent, nitric acid, at a nitric acid-to- oil weight ratio of 0.01. Substantial heat and fumes were released, probably as a result of an acid-base reaction associated with an active base amine group. This amine solvent was not usable in the process of the present invention because of oxidant reactivity.

COMPARATIVE EXAMPLE 8

Gaseous nitrogen dioxide, liquid nitrogen dioxide and 90% nitric acid were added as oxidants to a well mixed sample of diesel oil, a cycle oil, Stock V, having the characteristics as shown in Table 1 in proportions sufficient to provide the nitrogen content shown in Figure 3. The cetane rating of each oil sample was measured. The results are also shown in Figure 4, after water washing with a 1:1 weight ratio of oil to water.

It is apparent that all three nitrogenous oxidants provide equivalent cetane rating of the oil product produced. However, all products exhibited a poor stability and Ramsbottom carbon content, since solvent extraction was not conducted, similar to the results obtained in Comparative Example 1. Indeed, within the few minutes required to conduct cetane engine testing, the oil injectors in the engine foiled substantially, illustrating that the product of Comparative Example 8 is unsuitable as a diesel fuel in spite of high cetane ratings of Figure 4.

EXAMPLE 1

Samples of atmospheric gas oil, Stock C, as shown in Table 1, were reacted with oxidant in accordance with the procedures described in Comparative Example 2 above using a weight ratio of nitrogen dioxide to the total weight of feed diesel oil of about 0.014.

Following the reaction, samples of the oxidant reacted oil were extracted with the solvents set forth in Table 8 below using the extraction procedures as described above in Comparative Example 1. The results obtained are shown in Table 8 below.

By comparison of the results of the present invention shown in Table 8 with the comparison results shown in Table 4 without oxidant treatment and the comparison results in Table 5 for inferior solvents, substantial improvements in both yields and sulfur removal are achieved.

Table 8

Extraction of NO_2 Reacted Atmospheric Gas Oil

Extracting Solvent	Feed S (%)	Oil Yield (%)	Sulfur Content (%)	Sulfur Removal (%)	Dipole Moment[1]
Furfural	0.63	82.4	0.11	82.5	3.60
gamma-Butyrolactone	0.63	83.9	0.16	74.6	4.00
Dimethyl Formamide	0.63	79.1	0.13	79.4	3.86
Methyl Carbitol	0.63	81.5	0.17	73.0	--[2]
Tetrahydrofurfuryl Alcohol	0.60	84.9	0.21	65.0	2.12[3]
Nitromethane	0.60	91.5	0.28	53.3	3.13
Dimethyl Sulfoxide	0.45	87.5	0.20	55.6	3.90
Sulfolane	0.45	90.4	0.26	42.2	4.70
Acetic Anhydride	0.45	85.5	0.18	60.0	3.15
Ethylene Cyanoacetate	0.60	90.0	0.23	61.7	--[2]

1/ In benzene at 25°C.

2/ Not available; functional analysis suggests greater than 2.

3/ Measured neat as a liquid.

It can be seen that the oxidant reacted and extracted reaction product exhibited a superior yield, and sulfur removal compared to the extracted unreacted oil produced in Comparative Example 1.

EXAMPLE 2

Samples of atmospheric gas oil, Stock C, as described in Table 1, were reacted, except for using a stream of 6.5% by weight ozone and oxygen for a contact time of 240 minutes. The weight ratio of ozone to the total weight of atmospheric gas oil feed was about 0.029.

Following the reaction, samples of the oxidant reacted oil were extracted using the solvents set forth in Table 9 below using the extraction procedures as described above in Example 1. The results obtained are shown in Table 9 below, showing substantial improvements in oil yield or sulfur removal compared to Table 4. As shown in Figure 3, sulfur removal and oil yield are interrelated through adjustments in solvent-to-oil ratio. Hence, one skilled in the art can adjust the conditions used to produce the results in Table 9 to achieve superior results in both yield and sulfur removal compared to the results in Table 4.

Table 9

Extraction of Ozone Reacted Atmospheric Gas Oil

Extracting Solvent	Extraction Feed S (%)	Oil Yield (%)	Sulfur Content (%)	Sulfur Removal (%)
Furfural	0.68	80.0	0.17	75.0
gamma-Butyrolactone	0.68	86.0	0.23	66.2
Dimethyl Formamide	0.68	77.0	0.16	76.5
Dimethyl Sulfoxide	0.96	93.7	0.71	26.0

Further, a three-liter sample of atmospheric gas oil, Stock X, as described in Table 1, was reacted at 25°C with 10% by weight ozone in air, for reaction times of 6, 15, and 22 hours. The cetane number of the oxidant reacted oil and sulfur removal increased with increasing oxidant/oil contact time, as shown in Table 10 below.

Although the prior art would suggest that nitration is necessary to improve cetane rating, the results of Table 10 below demonstrate that ozonation also improves cetane rating. Measurements of stability of the oxidant reacted oil prior to extraction were also attempted, but the stability was so bad that the filter was plugged, rendering stability measurements impossible.

Table 10

Reaction of Diesel Oil With Ozone

Time (hr)	S in Oil (%)	Cetane Number
0	1.07	58.0
6	0.95	63.0
15	0.75	71.4
22	0.50	75.0

Extraction of the Table 10 product which had been subjected to a 15-hour oxidation as in Example 2 with one of the preferred solvents of the present invention, gamma-butyrolactone, showed excellent stability as demonstrated by the results in Table 11 below.

Table 11

Reaction of Diesel Oil With Ozone Plus gamma-butyrolactone Extraction

S/O Ratio	Yield (%)	Sulfur Content (%)	Nalco Stability	Sulfur Removal (%)
0.25	90.0	0.35	4	53.3
0.50	88.0	0.28	5	62.7
1.00	87.0	0.18	3	76.0

From the results presented in Table 11 above, it can be further seen that ozone is a suitable oxidant for use in the process according to the present invention. In addition, in Table 10 these results demonstrate that the improvement obtained in cetane number is not solely due to nitration of the feedstock, since in this case a non-nitrogenous oxidant, ozone, was used.

EXAMPLE 3

Reaction of samples of atmospheric gas oil, Stock C, as described in Comparative Example 1, with oxidant was carried out under varying oxidation conditions varying from mild to severe. Each of the oxidant reacted atmospheric gas oil charges was then extracted using gamma-butyrolactone at four different solvent-to-oil ratios of 0.1, 0.2, 0.5 and 1.0 from left to right in Figure 3. The results shown in Figure 2 are reproduced in Figure 3 and again the S/O ratio for extraction of untreated oil is shown at the data points. The results obtained are shown in Table 12 below and in FIG. 3, which illustrates the effect of oxidant reaction conditions on extraction with gamma-butyrolactone in terms of raffinate yield and sulfur content.

It is apparent from the results shown in Table 12 and FIG. 3 that good yields of raffinate can be achieved, along with substantial improvement in sulfur removal. Specifically, the extraction of sulfur was much more effective in oil after oxidant reaction, and for the same percent sulfur removal (in the extraction step only), the extraction oil yields were higher for reacted oil than for unreacted oil, even using a very mild oxidant treatment (1.1% S in product oil). This enhancement was further improved with increasing severity in the oxidation reaction. In addition, a great saving in solvent recovery was observed. For example, a solvent-to-oil (S/O) ratio of 5.0 was required to remove 50% of the sulfur from unoxidized oil (1.19% S), while a S/O ratio of only 1.0 was sufficient to obtain the same percent sulfur reduction in the oxidized oil with 1.1% sulfur, with a higher oil yield. Table 12 describes the effect of oxidation conditions on these important product characteristics for other oxidation severity levels.

As is evident from Figure 3, the comparative effects of various solvents must take into account the oxidation severity, and various yields can be achieved with differing levels of sulfur removal. Further, the diesel oil feedstock used affects the results obtained. In the examples herein, these complexities have been taken into account, but care must be taken in making comparisons beyond those contained within each individual table herein.

Table 12

gamma-Butyrolactone Extraction of Unoxidized and Oxidized AGO

Sulfur In Oil for Extraction (%)	S/O Ratio	Sulfur In Extracted Oil (%)	Yield (%)
Not Oxidized			
1.19	0.2	1.11	97.0
1.19	0.5	1.02	95.0
1.19	1.0	0.92	90.3
1.19	2.0	0.79	88.2
1.19	3.0	0.72	83.9
1.19	5.0	0.59	81.0
1.19	9.2	0.46	73.9
Oxidized			
1.10	0.1	0.81	95.5
1.10	0.2	0.77	92.8
1.10	0.5	0.63	89.2
1.10	1.0	0.53	85.0
0.88	0.1	0.69	95.4
0.88	0.2	0.61	92.9
0.88	0.5	0.50	89.3
0.88	1.0	0.49	85.8
0.56	0.1	0.37	93.3
0.56	0.2	0.36	91.5
0.56	0.5	0.26	88.0
0.56	1.0	0.18	82.8
0.31	0.1	0.24	95.0
0.31	0.2	0.19	94.0
0.31	0.5	0.14	90.5
0.31	1.0	0.10	88.0

EXAMPLE 4

A one-liter sample of atmospheric gas oil, Stock CC, as described in Table 1 was oxidized for 30 minutes using 90% HNO_3 at a weight ratio of HNO_3/diesel oil feed of 0.01 at a temperature of 25°C in accordance with the process of the present invention. The oxidant reacted oil obtained was then extracted with mixtures of dimethylformamide and water, as set forth in Table 13 below, using the extraction procedures described above for Comparative Example 1. The results obtained are set forth in Table 13 below. The results show that the water content of the solvent can be adjusted to further improve the yield of the product of the present invention.

Still further, selected solvents of the present invention are compared to comparison solvents in Table 14. The raffinates from the high dipole moment solvents have an improved sulfur level, yield, and Ramsbottom carbon, and stability compared to the raffinates obtained using comparison solvents.

Still further, another solvent of the present invention, furfural, is shown in Table 15 to have improved sulfur removal compared to methanol, even when operated at a significantly lower solvent-to-oil ratio.

Table 13

Extraction of Reacted Stock CC

A/O = 0.01
Extraction Feed Sulfur = 0.73%

	Raffinate Yield, %	
Raffinate Sulfur Removal	100% DMF	90% DMF [1/]
30%	91.5	93.5
40%	88.0	90.5

[1/] With 10% water.

Table 14

Extraction of Reacted Stock CC

A/O = 0.01
Extraction Feed Sulfur = 0.73%

Solvent		Raffinate Properties			
		Sulfur Content (%)	Yield (%)	Ramsbottom Carbon (%)	Stability
Nitromethane[1]	(Present Invention)	0.52	97.7	1.22	7
Dimethylformamide[2]	(Present Invention)	0.31	82.8	0.36	9
Methanol[3]	(Comparison)	0.61	90.95	1.74	16
Acetic Acid[4]	(Comparison)	0.52	87.2	1.97	6

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[1] Dipole moment = 3.13.

[2] Dipole moment = 3.86.

[3] Dipole moment = 1.70.

[4] Dipole moment = 1.60.

Table 15

Extraction of Reacted Stock CC

A/O = 0.01

Extraction Feed Sulfur = 0.66

Solvent	Yield (%)	Sulfur Removal (%)	Solvent-to-Oil Ratio
Furfural[1] (Present Invention)	90	40	0.6
Methanol[2] (Comparison)	90	22	1.2

---

[1] Dipole moment = 3.6.

[2] Dipole moment = 1.7.

EXAMPLE 5

A one-liter sample of atmospheric gas oil, Stock CC, as described in Table 1, was oxidized for 30 minutes using 90% HNO_3 at a weight ratio of HNO_3/oil feed of 0.01 at a temperature of 28°C in accordance with the process of the present invention. Before introducing the oxidant into the reactor, H_2SO_4 in the three concentrations set forth in Table 16 below was added to the 90% nitric acid. The oxidized oil obtained was then extracted with gamma-butyrolactone using the extraction procedures described above in Comparative Example 1 at a solvent-to-oil ratio of 0.5. The results obtained were set forth in Table 14 below. With the present invention, excellent cetane, Ramsbottom carbon, stability and yields were achieved where with H_2SO_4 only (see Table 16), an inferior cetane rating was obtained.

Table 16

Effect of Reaction In Presence of Co-Acid Followed by Extraction By gamma-Butyrolactone
(Stock CC With 0.73% S) (0.5 S/O)

Oxidant(s)	A/O Ratio (%)	Total Oil Yield (%)	Raffinate Sulfur Content (%)	Sulfur Removal (%)	Nalco Stability	Cetane Number	Ramsbottom Carbon (%)	Nitrogen (ppm)
HNO_3	0.01	92.5	0.55	24.7	19	62	0.89	392
H_2SO_4	0.02	93.2	0.45	38.4	--	56	--	0
HNO_3/H_2SO_4	0.01/0.005	93.0	0.45	38.4	--	67	1.07	330
HNO_3/H_2SO_4	0.01/0.01	92.2	0.43	41.1	--	66	0.60	293
HNO_3/H_2SO_4	0.01/0.02	89.0	0.33	54.8	4	61	0.42	14

Cetane accuracy ±3 (estimated).

EXAMPLE 6

Several diesel oils (stocks with characteristics as described in Table 1) as described in Table 17 below were reacted with 90% HNO_3 at an 0.01 acid/oil weight ratio to produce reacted diesel oils of about 1400 ppm nitrogen. The reacted oils were extracted with selected solvents of the present invention, under a variety of extraction conditions.

The results are summarized in Table 17 below, displaying the ratio of the raffinate cetane to the reacted diesel oil cetane. Over a wide range of conditions over 95% of the cetane of the reactor products was retained. The Ramsbottom carbon content and the stability were greatly improved. These data illustrate that the cetane can be controlled in the reactor, and was not lost upon extraction with the solvents of the present invention. In contrast, as disclosed in British Patent No. 491,648, cetane was lost upon use of the solvents disclosed therein. Table 17 shows that extraction does not contribute to the cetane rating achieved, in contrast to the prior art effects shown in Table 7.

Table 17

Diesel Stock	Solvent	S/O	Yield (%)	% CN Retained
K1	90% DMF	.25	95.9	102.2
K2	90% DMF	.25	97.8	96.9
K4	90% DMF	.5	91.5	97.2
K4	90% DMF	.25	97.1	102.3
K5	90% DMF	.25	97.1	98.3
K5	90% DMF	.75	95.1	94.8
K6	90% DMF	.26	98.3	96.1
K6	90% DMF	.75	96.4	92.2
CC	Furfural	.3	93.4	93.3
CC	Furfural	.6	90.1	88.6
CC	Furfural	1	86.5	89.5
CC	Furfural	2	80.4	96.4
CC	DMSO	.2	97.0	93.1
CC	DMSO	.4	95.6	93.8

Table 17 (Continued)

Diesel Stock	Solvent	S/O	Yield (%)	% CN Retained
CC	DMSO	1	93.4	98.6
CC	gamma-Butyrolactone	.36	94.0	98.0
CC	Furfural	.36	95.1	98.0
CC	DMF	.25	92.8	98.0
CC	1-Methyl-2-pyrrolidone	.3	90.8	98.6
CC	Sulfolane	2.03	93.6	95.4
CC	Furfural	.23	95.7	100.8
CC	Furfural	.35	92.0	85.4
CC	Furfural	.5	93.2	94.5

Table 17 (Continued)

Diesel Stock	Solvent	S/O	Yield (%)	% CN Retained
CC	Furfural	.25	92.3	98.1
CC	Furfural	.99	87.5	84.2
CC	Furfural	.25	95.5	95.5
CC	DMF	.5	83.6	99.1
CC	DMF	.5	86.1	95.1
CC	DMF	.5	85.0	100.6
CC	gamma-Butyrolactone	.5	92.3	97.6
CC	gamma-Butyrolactone	.5	91.9	101.6
CC	gamma-Butyrolactone	.5	93.0	106.8
CC	gamma-Butyrolactone	.5	88.7	97.6
CC	gamma-Butyrolactone	.5	92.2	107.3
CC	DMF	.5	86.1	95.1
CC	DMF	.5	83.6	99.8

Table 17 (Continued)

Diesel Stock	Solvent	S/O	Yield (%)	% CN Retained
CC	DMF	.29	93.4	97.0
CC	90% DMF	.25	97.3	89.1
CC	DMF	.151	94.5	90.9
CC	90% DMF	.5	95.4	90.3
CC	DMF	.25	92.4	88.5
CC	90% DMF	.1	97.2	91.8
CC	DMF	.25	92.3	97.5
CC	DMF	.5	87.7	99.8
CC	DMF	1	81.6	100.6
CC	DMF	2	73.8	104.1
CC	DMF	.5	88.45	92.0
CC	DMF	.5	87.4	102.2
CC	DMF	.5	85.7	95.1

Table 17 (Continued)

Number	N_{RA} (ppm)	Solvent	S/O	Yield (%)	% CN Retained
KD	2363	DMF	.3	85.9	97.6
TD	1492	DMF	.3	90.1	95.0
KG	2992	DMF	.3	77.0	89.5
KW	1788	DMF	.3	87.2	98.5
CB	1682	DMF	.3	89.3	96.8
TS	2371	DMF	.3	84.3	100.5
TH	1553	DMF	.3	89.7	95.8
G	1818	DMF	.3	84.5	100.0

CN Retained = raffinate cetane based on reacted oil cetane.

EXAMPLE 7

Oxidized oil products from Example 3 were subjected to more extensive phase equilibria analysis. Without being limited by theory, it appears that heteroatoms are being added to the substrate material which enhance the affinity of the solvent in the extraction stage, thereby improving yields. The preferential addition of heteroatoms to molecules which also contain sulfur atoms, which thereby permits the selective extraction of sulfur compounds, is a particularly surprising aspect of the process of the present invention.

The fundamental shift in the extraction equilibrium is dramatically evident from the ternary equilibrium diagrams shown in Figures 5 and 6 where in Figures 5 and 6 percent solvent (gamma-butyrolactone), percent sulfur, and percent oil are shown. The equilibrium composition of the raffinate and extract phases from an extraction are connected by the solid lines. Several lines are shown at several different solvent-to-oil ratios.

As is evident from Figure 5, equilibrium data on oxidant unreacted diesel fuel (1.19% sulfur used in Example 3) do not provide a basis for improvement. In particular, the phase lines illustrate a negative slope, showing poor selectivity in the removal of sulfur from the oxidant unreacted diesel oil. For example, the point R_1 shows that the raffinate phase contained 2% gamma-butyrolactone and 0.97% sulfur whereas the corresponding extract phase E_1 contained 91% gamma-butyrolactone and 0.48% sulfur. In an extraction process for the purpose of sulfur removal, a much higher extract phase sulfur content would be desirable. These poor results account for the performance of the variety of solvents in Table 4.

By contrast, when operating in accordance with the present invention, the diesel fuel is first oxidant reacted prior to extraction as discussed in Example 3. The equilibrium data for the oxidant reacted diesel oil is shown in Figure 6. These data exhibit the desirable positive slope. The point R_1 shows that the raffinate contained 0.36% sulfur, with about 2% gamma-butyrolactone. The corresponding extract phase contained 1.24% sulfur with about 46% gamma-butyrolactone. This oxidized oil now exhibits excellent extraction efficiency, unlike the oxidant unreacted diesel oil for comparison as shown in Figure 5. These excellent results account for the performance of the variety of solvents of the present invention as shown in Table 8.

EXAMPLE 8

A one liter sample of atmospheric gas oil, Stock CC as described in Table 1, was reacted with 10°C, one atmospheric pressure, using 90% HNO by weight, for a contact time of 60 minutes, at an acid/oil (A/O) ratio of 0.01. The A/O ratio is defined as the ratio of weight of HNO_3 (calculated as 100% HNO_3) added within the contact time to the weight of oil charged. After reaction, each 20 milliliter sample of the oxidant reacted diesel oil sample was contacted with each solvent shown in Table 18 below using the procedures set forth in Comparative Example 2. As can be seen from the results, extraction of oxidant reacted diesel oil with selective solvents of this invention improves the Nalco stability and Ramsbottom carbon of the diesel oil while retaining its cetane number enhancement.

In addition, in Table 18, one solvent was tested with countercurrent extraction, which exhibits efficiencies similar to those practiced commercially. The yield, sulfur removal, stability and Ramsbottom carbon are all further improved relative to the excellent results shown in Tables 8 through 16 herein.

Table 18

Extraction of Oxidized Diesel Oil

Unoxidized Oil; 0.73% S, 52.7 Cetane
Oxidized Oil From 0.01 A/O Ratio With 90% HNO_3
100% Yield, 0.70% S, 62 Cetane Number,
7% Ramsbottom Carbon, and Greater Than
20 Nalco Stability

Solvent	S/O Ratio	Extraction Oil Yield (%)	S In Oil (%)	Nalco Stability	Cetane Number	Ramsbottom Carbon (%)
gamma-Butyrolactone	0.50	92.8	0.51	12	---	0.90
DMF	0.25	92.8	0.50	11	62.3	1.21
DMF	0.50	88.0	0.46	11	67.7	---
DMF	1.00	81.6	0.29	5	63.9	0.22
DMSO	1.0	93.4	0.49	8	62.7	0.89
Nitromethane	0.5	97.7	0.52	7	---	1.22
Sulfolane	2.0	92.1	0.39	--	---	---
1-Methyl-2-pyrrolidone	0.23	91.3	0.42	--	---	---
1-Methyl-2-pyrrolidone	0.38	87.2	0.33	--	---	---
Furfural[1]	0.24	94.6	0.49	8	---	0.62
Furfural[1]	0.56	92.3	0.38	7	---	0.21
Furfural[1]	0.86	90.3	0.29	9	---	0.14

---

[1] Continuous Extraction.

EXAMPLE 9

Five samples of diesel oil, Stock X, as described in Table 1, were oxidized using 90% HNO_3 at the following A/O ratios: 0.0012, 0.0025, 0.0050, 0.010 and 0.05. These oxidant reacted oils were further extracted with DMF to determine the relationship between oxidation condition and raffinate yield.

Table 19 below shows the results obtained for the five semi-batch oxidations with the cetane number of the oxidant reacted oil.

The effect of cetane number increase as a result of oxidation on total raffinate yields on oxidation-extraction are shown in Table 20 below. A 50% total sulfur removal was used as a reference point and the total yields are listed corresponding to the cetane number increase of the oxidant reacted diesel oil due to oxidation. The data show that a cetane number increase of 5 in step (a) as in this invention is required to produce an oil yield enhancement in the subsequent extraction step (b), and the raffinate yield enhancement increases with increasing cetane number. A similar relationship exists for gamma-butyrolactone.

Table 19

Oxidation of Stock X With 90% HNO_3

A/O	Yield (%)	S Content (%)	N Content (ppm)	Cetane Number
0	100	1.07	200	51.9
0.0012	99.7	1.07	234	51.7
0.0025	99.6	1.06	353	51.9
0.0050	99.5	1.03	686	53.0
0.0100	99.8	1.02	1375	61.1
0.0500	98.5	0.79	4960	62.5

Table 20

Effect of Cetane Number Increase In Oxidation on Total Raffinate Yield

Cetane Number Increase Due to Oxidation	Total Yield of Oxidation-Extraction (with DMF) for 50% Sulfur Removal (%)
	DMF
0	79.5
1	79.5
2	79.5
5	82.5
10	85.0
11	90.0

While the invention has been described in detail with respect to specific embodiments thereof, it will be apparent to one skilled in the art that modifications and changes can be made therein without departing from the spirit and scope thereof.

CLAIMS:

1. A process for upgrading diesel oil to produce an upgraded diesel fuel comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, derived from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone wherein

(1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed to step (a), and

(2) (i) the reacting is such that when the oxidant is a nitrogenous treating agent, the amount of oxidant, equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed to step (a); and

(ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

(b) contacting the diesel oil from step (a) above with an extracting solvent, the extracting solvent

(1) having a dipole moment of about 2 or greater.

(2) being substantially immiscible with the diesel oil at the temperature of contacting with the diesel oil obtained in step (a),

(3) being a nonhalogenated solvent, and

(4) excluding amines, which are reactive with the oxidant,

or a mixture of such solvents or a water mixture of such solvents comprising about 50% by weight or less water; and

(c) separating said diesel oil from step (b) above from said extracting solvent to recover upgraded diesel fuel.

2. The process of claim 1, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing gas comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

3. The process of claim 1, wherein said oxidizing agent is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

4. The process of claim 1, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid comprising nitric acid or nitrous acid and from about 0 to 90% by weight water.

5. The process of claim 1, wherein said oxidant is ozone.

6. The process of claim 1, wherein said reacting step (a) is conducted in the presence of at least one acid selected from the group consisting of organic acids, inorganic acids and mixtures thereof.

7. The process of claim 1, wherein said nitrogen oxidizing agent is employed, on a nitrogen equivalent basis to 100% nitric acid, in a weight ratio of about 0.0001 to about 0.1 to said diesel oil.

8. The process of claim 1, wherein the weight ratio of said extracting solvent to said diesel oil is from about 0.01 to about 5.

9. The process of claim 1, wherein said diesel oil contains less than about 40% by weight aromatics.

10. The process of claim 1, wherein said diesel oil contains less than about 35% by weight olefinics.

11. The process of claim 1, wherein said diesel oil contains less than about 40% by weight aromatics and less than about 35% by weight olefinics.

12. A process for upgrading diesel oil to produce an upgraded diesel fuel comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F, derived from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozone wherein

(1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed to step (a), and

(2) (i) the reacting is such that when the oxidant is a nitrogenous treating agent, the amount of oxidant, equivalent on a 100% nitric acid basis, is about 10% or less by weight of the diesel oil feed to step (a); and

(ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

(b) contacting the diesel oil from step (a) above with an extracting solvent, the extracting solvent

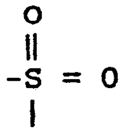
(1) having a dipole moment of about 2 or greater.

(2) being substantially immiscible with the diesel oil at the temperature of contacting with the diesel oil obtained in step (a),

(3) being a nonhalogenated solvent,

(4) excluding amines, which are reactive with the oxidant, and

(5) containing at least one of the following functional groups: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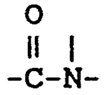
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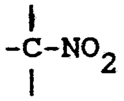
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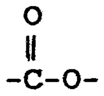
and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or a mixture of such solvents or a water mixture of such solvents comprising about 50% by weight or less water; and

(c) separating said diesel oil from step (b) above from said extracting solvent to recover upgraded diesel fuel.

13. The process of claim 12, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing gas comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

14. The process of claim 12, wherein said oxidizing agent is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid

comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

15. The process of claim 12, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid comprising nitric acid or nitrous acid and from about 0 to 90% by weight water.

16. The process of claim 12, wherein said oxidant is ozone.

17. The process of claim 12, wherein said reacting step (a) is conducted in the presence of at least one acid selected from the group consisting of organic acids, inorganic acids and mixtures thereof.

18. The process of claim 12, wherein said nitrogen oxidizing agent is employed, on a nitrogen equivalent basis to 100% nitric acid, in a weight ratio of about 0.0001 to about 0.1 to said diesel oil.

19. The process of claim 12, wherein the weight ratio of said extracting solvent to said diesel oil is from about 0.01 to about 5.

20. The process of claim 12, wherein said diesel oil contains less than about 40% by weight aromatics.

21. The process of claim 12, wherein said diesel oil contains less than about 35% by weight olefinics.

22. The process of claim 12, wherein said diesel oil contains less than about 40% by weight aromatics and less than about 35% by weight olefinics.

23. A process for upgrading diesel oil to produce an upgraded diesel fuel comprising the steps of:

(a) reacting a diesel oil, having a boiling point at normal pressure of about 300°F to about 700°F , derived from a petroleum source with an oxidant selected from the group consisting of nitrogenous oxidizing agents and ozones, wherein

(1) the reacting is to an extent sufficient to increase the cetane number of the diesel oil obtained in step (a) by at least 5 cetane numbers over the cetane number of the diesel oil feed to step (a), and

(2) (i) the reacting is such that when the oxidant is a nitrogenous treating agent, the amount of oxidant, equivalent on a 100% nitric acid bases, is about 10% or less by weight of the diesel oil feed to step (a); and

(ii) the reacting is such that when the oxidant is ozone, the amount of oxidant is sufficient to achieve an about 10% or greater reduction in the sulfur content of the reacted diesel oil obtained in step (a) over the diesel oil feed to step (a);

(b) contacting the diesel oil from step (a) above with an extracting solvent selected from the group consisting of furfural, butyrolactone, dimethyl formamide, methyl carbitol, tetrahydrofurfuryl alcohol, dimethyl sulfoxide, sulfolane, sulfolene, dimethyl acetamide, 1-methyl-2-pyrrolidone, acetonitrile, acetic anhydride, nitrobenzene, nitromethane and mixtures thereof, or a water mixture thereof comprising about 50% by weight or less water; and

(c) separating said diesel oil from step (b) above from said extracting solvent to recover upgraded diesel fuel.

24. The process of claim 23, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing gas comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

25. The process of claim 23, wherein said oxidizing agent is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid comprising at least one nitrogen oxide with more than one oxygen atom for each nitrogen atom.

26. The process of claim 23, wherein said oxidant is a nitrogenous oxidizing agent and said nitrogenous oxidizing agent is an oxidizing liquid comprising nitric acid or nitrous acid and from about 0 to 90% by weight water.

27. The process of claim 23, wherein said oxidant is ozone.

28. The process of claim 23, wherein said reacting step (a) is conducted in the presence of at least one acid selected from the group consisting of organic acids, inorganic acids and mixtures thereof.

29. The process of claim 23, wherein said nitrogenous oxidizing agent is employed, on a nitrogen equivalent basis to 100% nitric acid, in a weight ratio of about 0.0001 to about 0.1 to said diesel oil.

30. The process of claim 23, wherein said weight ratio of said extracting solvent to said diesel oil is from about 0.01 to about 5.

31. The process of claim 23, wherein said diesel oil is a diesel oil of petroleum origin.

32. The process of claim 23, wherein said diesel oil contains less than about 40% by weight aromatics.

33. The process of claim 23, wherein said diesel oil contains less than about 35% by weight olefinics.

34. The process of claim 23, wherein said diesel oil contains less than about 40% by weight aromatics and less than about 35% by weight olefinics.

FIG. 1

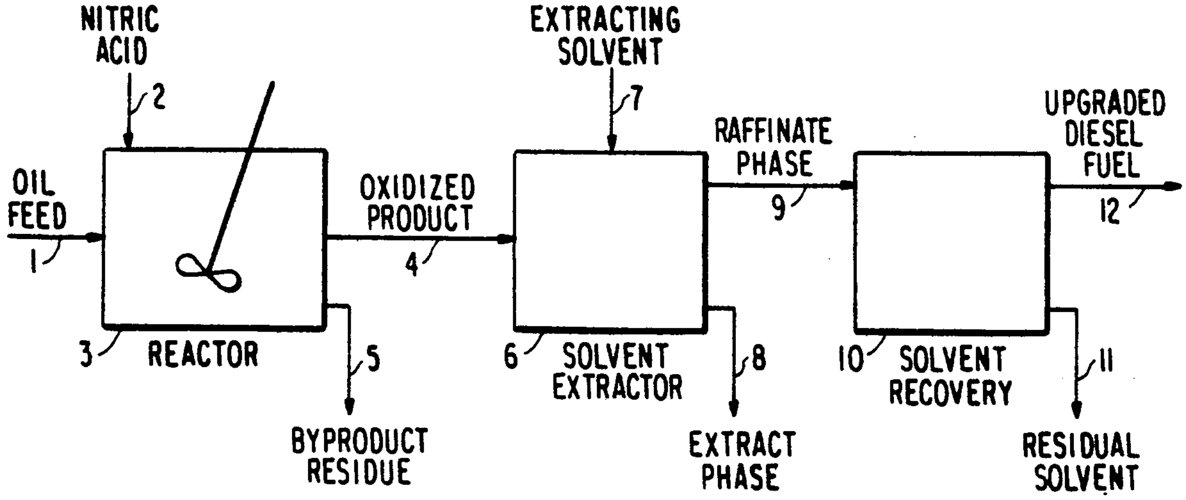

FIG. 2 SOLVENT EXTRACTION OF UNTREATED AGO BY γ-BUTYROLACTONE

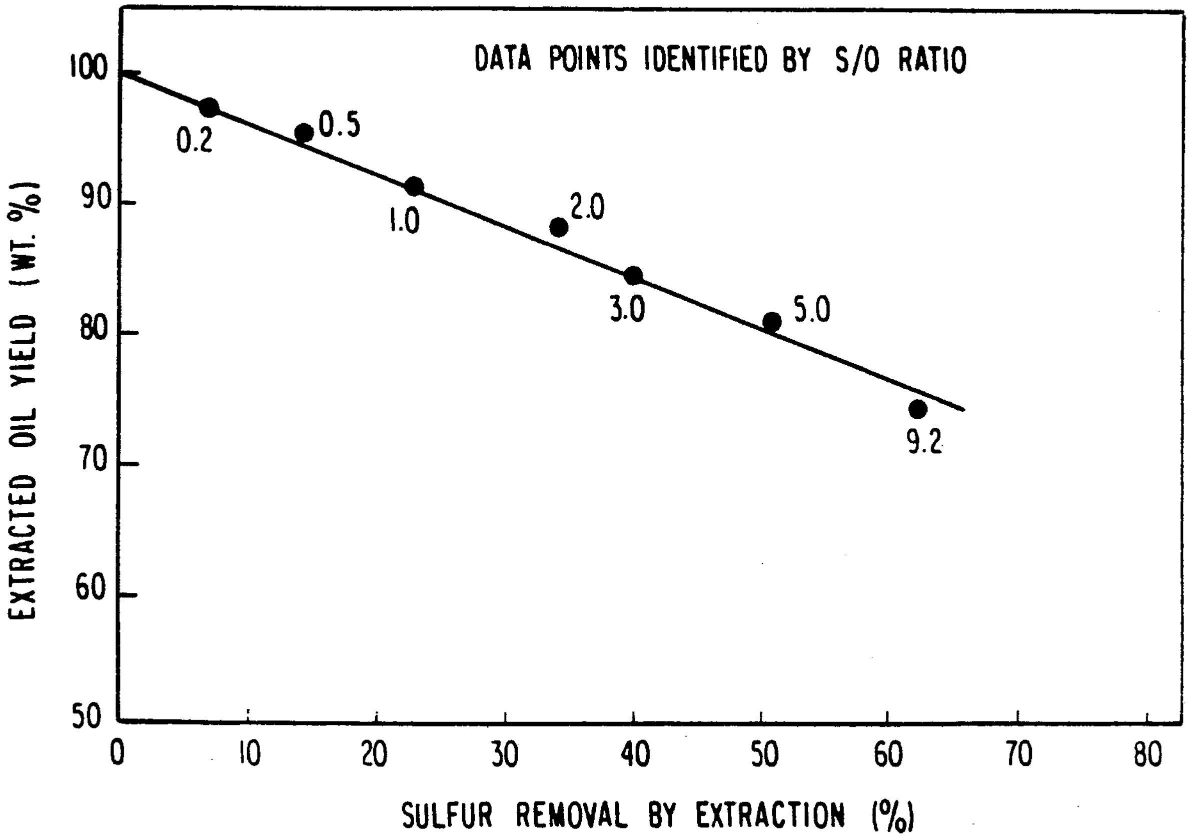

FIG.3 EFFECT OF OXIDATION OF AGO ON γ-BUTYROLACTONE EXTRACTION

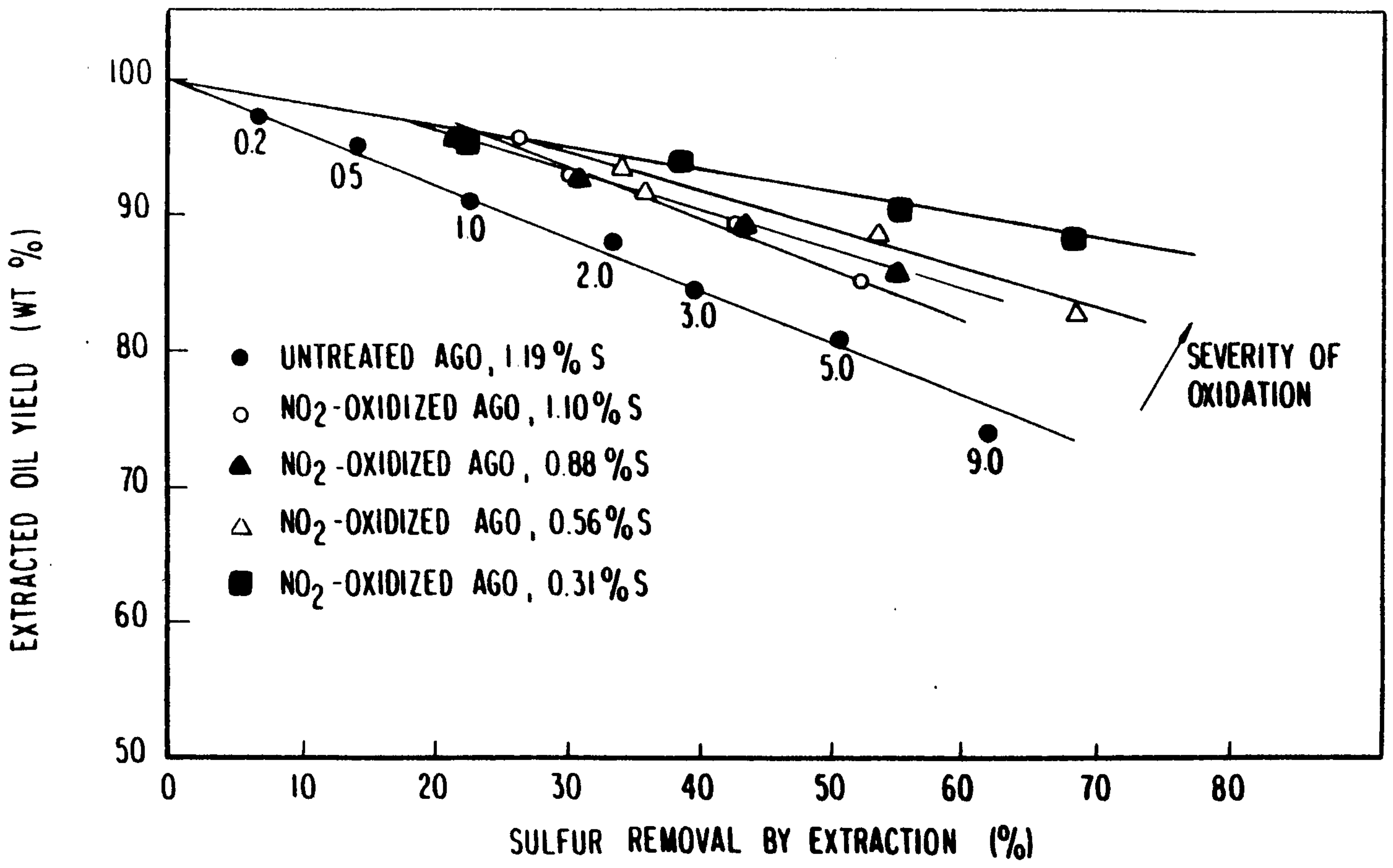

FIG.4 CETANE ENHANCEMENT OF STOCK V

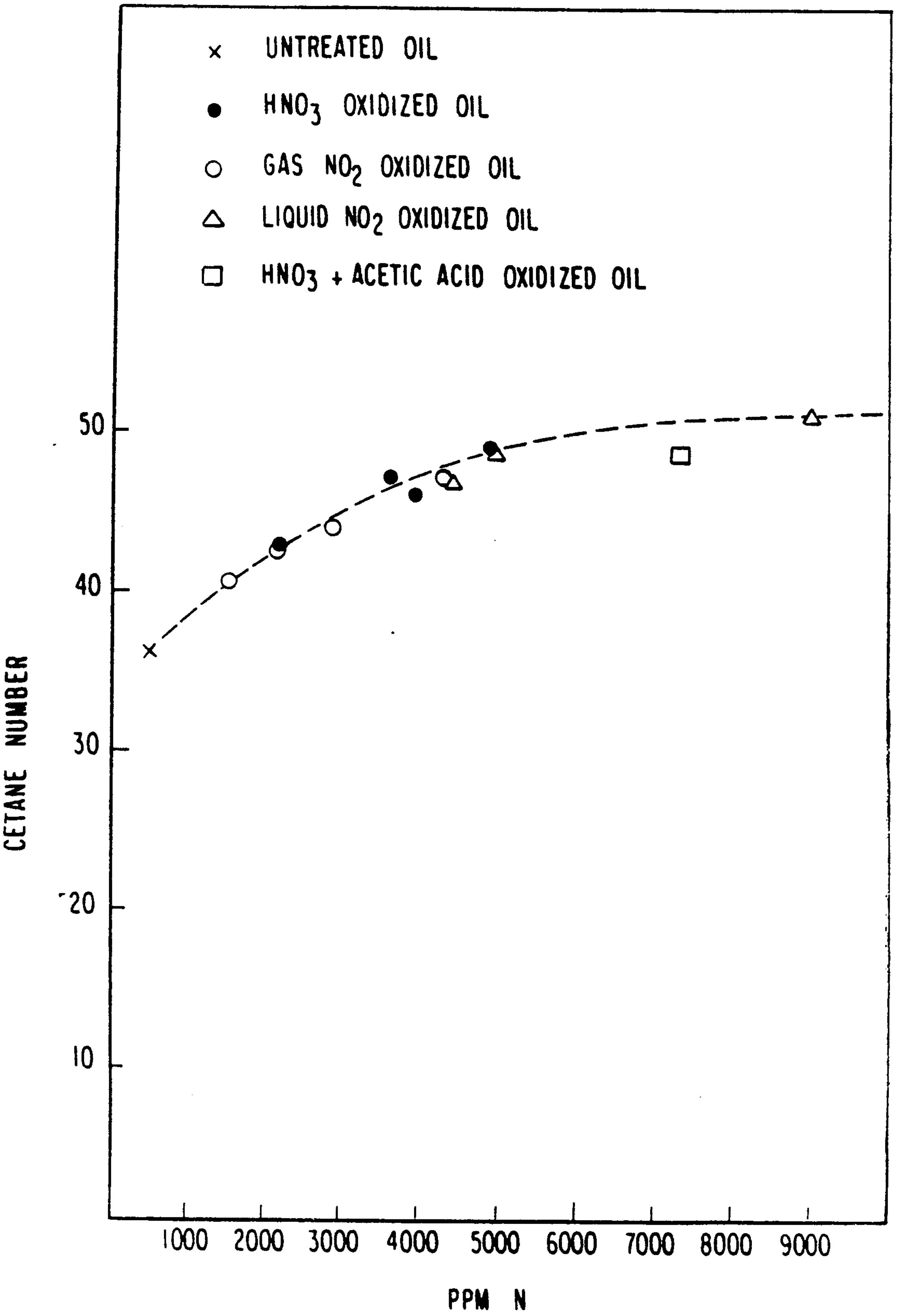

FIG. 5 CONTINUOUS EXTRACTION OF STOCK C

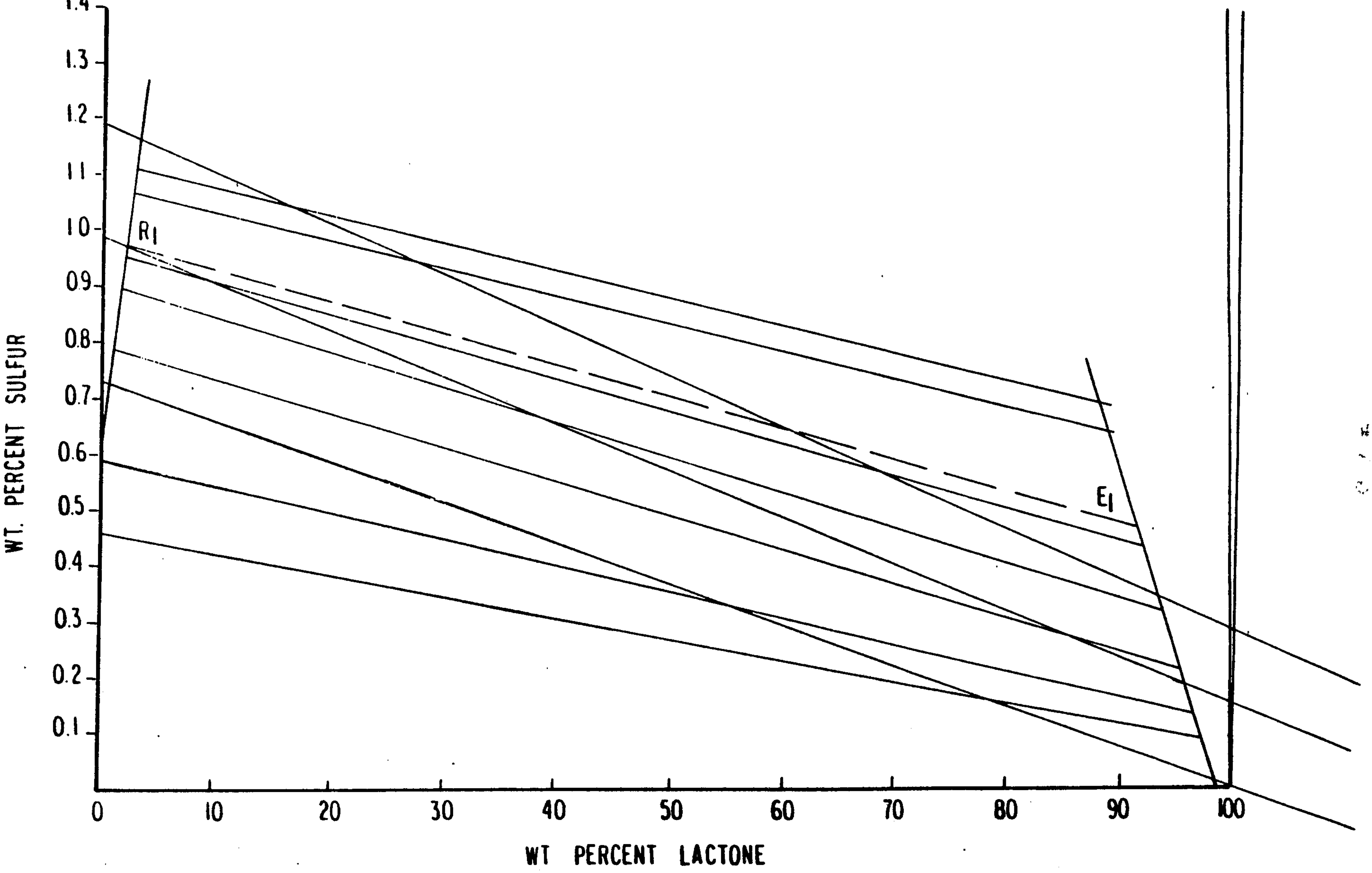

FIG.6 EQUILIBRIUM DATA FOR OXIDIZED STOCK C