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(54) **LOW SULFUR DISTILLATE FUELS**

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**Related U.S. Application Data**

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(60) Provisional application No. 60/111,346, filed on Dec. 8, 1998.

(51) **Int. Cl.<sup>7</sup>** ..... **C10L 1/08**

(52) **U.S. Cl.** ..... **44/300; 208/15; 585/14**

(58) **Field of Search** ..... 44/300; 208/15; 585/14

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

- 5,389,111 A \* 2/1995 Nikanjam et al.
- 5,389,112 A \* 2/1995 Nikanjam et al.
- 5,792,339 A \* 8/1998 Russell
- 5,976,201 A \* 11/1999 Barry et al.
- 6,004,361 A \* 12/1999 Barry et al.
- 6,150,575 A \* 11/2000 Angevine et al.

\* cited by examiner

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(57) **ABSTRACT**

A distillate fuel composition boiling in the range of about 190° C. to 400° C. with a T10 point greater than 205° C., and having a sulfur level of less than about 100 wppm, a total aromatics content of about 15 to 35 wt. %, a polynuclear aromatics content of less than about 3 wt. %, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.

**23 Claims, 2 Drawing Sheets**

FIGURE 1

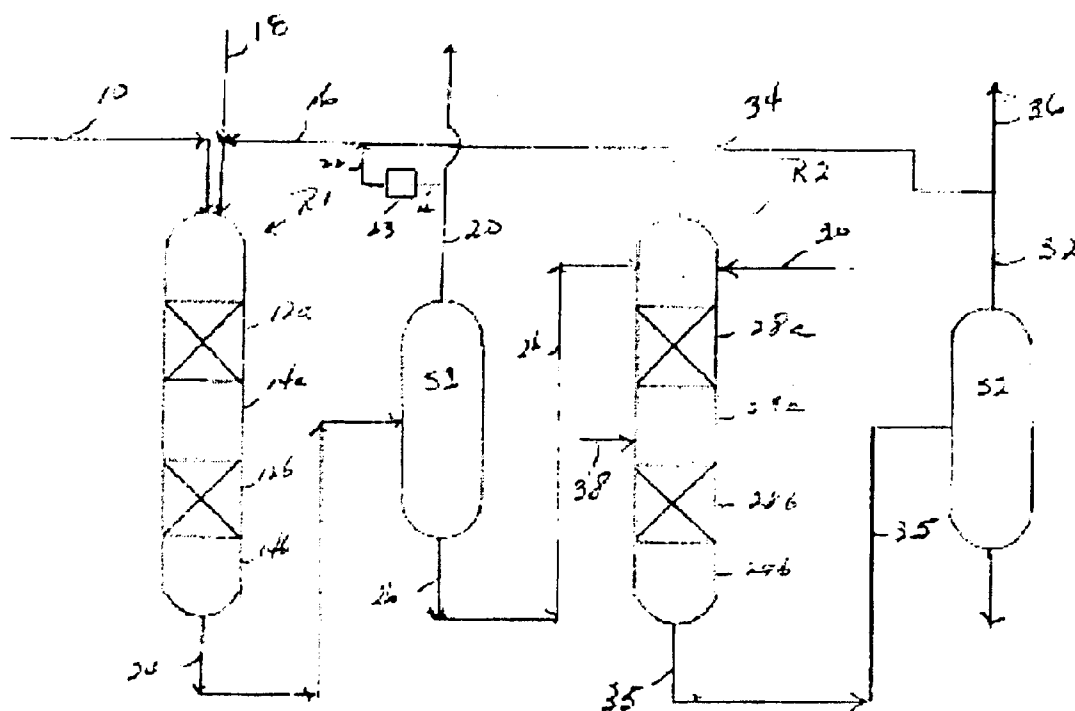
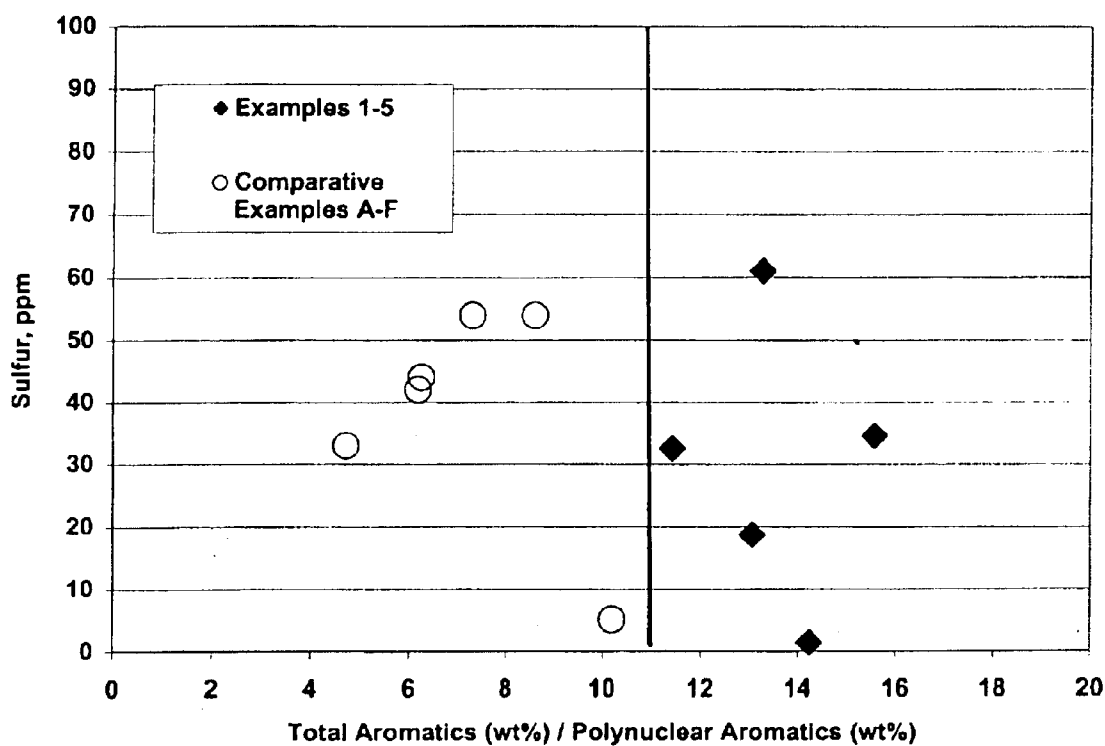


FIGURE 2



1

**LOW SULFUR DISTILLATE FUELS****CROSS REFERENCE TO RELATED APPLICATIONS**

This is a Continuation-in-Part of U.S. Ser. No. 09/457,434 filed Dec. 7, 1999, which claims priority from U.S. Provisional Patent Application No. 60/111,346, filed Dec. 8, 1998.

**FIELD OF THE INVENTION**

The present invention relates to a distillate fuel composition boiling in the range of about 190° C. to 400° C. with a T10 point greater than 205° C., and having a sulfur level of less than about 100 wppm, a total aromatics content of about 15 to 35 wt. %, a polynuclear aromatics content of less than about 3 wt. %, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.

**BACKGROUND OF THE INVENTION**

Diesel fuels are used widely in automotive transport largely due to their high fuel economy. However, one of the problems when such fuels are burned in internal combustion engines is the pollutants in the exhaust gases that are emitted into the environment. For instance, some of the most common pollutants in diesel exhausts are oxides of nitrogen (hereafter abbreviated as "NOx"), particulate matter (including inter alia soot, adsorbed hydrocarbons and sulfates), unburned hydrocarbons, and to a lesser extent carbon monoxide. Also, sulfur dioxide emissions from diesel fuel exhaust gases are becoming increasingly a problem due to their affinity with after-treatment devices designed to reduce NOx and particulate emissions, thereby adversely affecting the functioning efficiency. The oxides of sulfur have been reduced considerably by reducing the sulfur levels in the diesel itself through refining operations such as by hydrodesulfurization. However, further advances are required to meet increasingly demanding worldwide legislation for progressively lower diesel powered vehicle exhaust emissions, especially NOx and particulate matter. An established trade-off exists between the two pollutants, i.e. NOx and particulate matter, whereby an increase in one leads to a decrease in the other, for a given engine and operating conditions.

A typical example of such a scenario is U.S. Pat. No. 5,792,339 in which a diesel oil composition comprising 250–495 wppm sulfur, 5–8.6 wt. % of polynuclear aromatics (PNAs) and 10–23.9 wt. % total aromatics is disclosed. At the same time, further advances in sulfur-sensitive after-treatment technology have led to increasing demand for lower levels of sulfur in diesel fuels.

There are a variety of analytical techniques that have been reported for measurement of total aromatics and polynuclear aromatics. In the discussion and claims that follow, aromatics and PNAs are measured by high performance liquid chromatography (HPLC) as defined by test number IP 391/95, unless otherwise indicated. IP391/95 is described in "IP Standard Methods for Analysis and Testing of Petroleum & Related Products, and British Standard 2000 Parts, 58th edition, February, 1999. This publication is incorporated

2

ASTM D2887 providing the temperature at which 10% of the fuel was recovered (T10) and the temperature at which 95% of the fuel was recovered (T95).

Hydrodesulfurization processes that reduce PNAs typically reduce monocyclic aromatics as well as resulting in higher than desired hydrogen consumption. Legislation requiring reduced sulfur content is also anticipated. For example, proposed sulfur limits for distillate fuels to be marketed in the European Union for the year 2005 is 50 wppm or less. Further, the maximum allowable total aromatics level for California Air Resources Board (CARB) reference diesel and Swedish Class I diesel are 10 and 5 vol. %, respectively. Further, the CARB reference fuels allows no more than 1.4 vol. % polyaromatics (PNAs). In Europe, from the year 2000, a limit of polynuclear aromatic content in diesel fuel has been set at 11% by weight but no limit has been set for the total aromatic content (including monocyclic aromatics) of the fuel. Consequently, much work is presently being done in the hydrotreating art because of these proposed regulations.

Hydrotreating, or in the case of sulfur removal, hydrodesulfurization, is well known in the art and typically requires treating the petroleum streams with hydrogen in the presence of a supported catalyst at hydrotreating conditions. The catalyst is usually comprised of a Group VI metal with one or more Group VIII metals as promoters on a refractory support. Hydrotreating catalysts that are particularly suitable for hydrodesulfurization, as well as hydrodenitrogenation, generally contain molybdenum or tungsten as the Group VI metal on alumina support promoted with cobalt, nickel, iron, or a combination thereof as the Group VIII metal. Cobalt promoted molybdenum on alumina catalysts are most widely used when the limiting specifications are hydrodesulfurization, while nickel promoted molybdenum on alumina catalysts are the most widely used for hydrodenitrogenation, partial aromatic saturation, as well as hydrodesulfurization.

Much work is also being done to develop more active catalysts and to improve reaction vessel designs in order to meet the demand for more effective hydroprocessing processes. Various improved hardware configurations have been suggested. One such configuration is a co-current design where feedstock flows downwardly through successive catalyst beds and treat gas, which is typically a hydrogen-containing treat gas, also flows downwardly, co-current with the feedstock. Another configuration is a countercurrent design wherein the feedstock flows downwardly through successive catalyst beds counter to upflowing treat gas, which is typically a hydrogen-containing treat-gas. The downstream catalyst beds, relative to the flow of feed, can contain high performance, but otherwise more sulfur sensitive catalysts because the upflowing treat gas carries away heteroatom components, such as H<sub>2</sub>S and NH<sub>3</sub>, that are deleterious to sulfur and nitrogen sensitive catalysts.

Other process configurations include the use of multiple reaction stages, either in a single reaction vessel, or in separate reaction vessels. More sulfur sensitive catalysts can be used in the downstream stages as the level of heteroatom components becomes successively lower. European Patent

3

Distillate fuel compositions are taught that meet some of the low emissions requirements. For example, U.S. Pat. No. 5,389,111 teaches a diesel fuel composition having an aromatics content in the range from about 13 to 20 wt. %, a cetane number from about 54 to 60, which cetane number and aromatics content being within a certain area defined in FIG. 1 of that patent. U.S. Pat. No. 5,389,112 teaches a low emissions diesel fuel composition having an aromatics content in the range of about 14.3 to 19.7 wt. %, a cetane number from about 53.4 to 60.8, which cetane number and aromatics content falls within a certain area of FIG. 1 of their patent.

While distillate fuel compositions exist that produce lower levels of emissions than years past, there is still a need in the art for fuels with ever lower emissions levels that are needed to meet the ever stricter environmental regulations.

It has now been found that by controlling the amount of sulfur, PNAs and total aromatics in the diesel fuel within specific limits, the amount of NOx and particulates emitted from exhausts can be synergistically reduced.

#### SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a distillate fuel composition boiling in the range of about 190° C. to 400° C. with a T10 point greater than 205° C., and having a sulfur level of less than about 100 wppm, a total aromatics content of about 15 to 35 wt. %, a polynuclear aromatics content of less than about 3 wt. %, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.

In a preferred embodiment of the present invention the sulfur level is less than about 50 wppm.

In another preferred embodiment of the present invention the total aromatics content is from about 20 to 35 wt. %.

In still another preferred embodiment of the present invention the ratio of total aromatics to polynuclear aromatics is at least 15.

In yet another embodiment, the invention is a fuel composition comprising

a distillate boiling in the range of about 190° C. to 400° C. with a T10 point greater than 205° C., and having a sulfur level of less than about 100 wppm, a total aromatics content of about 15 to 35 wt. %, a polynuclear aromatics content of less than about 3 wt. %, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11, to which is added at least one of (i) one or more lubricity aid, (ii) one or more viscosity modifier, (iii) one or more antioxidant, (iv) one or more cetane improver, (v) one or more dispersant, (vi) one or more cold flow improver, (vii) one or more metals deactivator, (viii) one or more corrosion inhibitor, (ix) one or more detergent, and (x) one or more distillate or upgraded distillate.

In still another preferred embodiment, the fuel is employed in a compression ignition (e.g. diesel) engine, preferably in order to abate NOx and particulate emissions therefrom. More preferably, the fuel is employed in an automotive diesel engine.

#### BRIEF DESCRIPTION OF THE FIGURE

4

This process scheme includes two co-current hydrodesulfurization stages with once through hydrogen-containing treat gas in the second hydrodesulfurization stage.

FIG. 2 hereof shows a plot that defines the composition of distillate products of the present invention where the sulfur content is less than 100 ppm and the ratio of total aromatics to polynuclear aromatics is greater than about 11.

#### DETAILED DESCRIPTION OF THE INVENTION

Feedstreams suitable for producing the low emissions distillate fuel compositions of this invention are those petroleum based feedstreams boiling in the distillate range and above. Such feedstreams typically have a boiling range from about 190 to about 400° C., preferably from about 200 to about 370° C. These feedstreams typically contain greater than about 3,000 wppm sulfur. Non-limiting examples of such feedstreams include virgin distillates, light cat cycle oils, light coker oils, etc. It is highly desirable for the refiner to upgrade these types of feedstreams by removing as much of the sulfur as possible, as well as to saturate aromatic compounds.

It is not critical how the distillate fuel compositions are produced. One preferred process for producing the fuel products of the present invention is illustrated in FIG. 1 hereof. The preferred process uses once-through hydrogen treat gas in a second hydrodesulfurization stage and optionally in a first hydrodesulfurization stage as well. Relatively low amounts of hydrogen are utilized in the second hydrodesulfurization stage in such a way that very low levels of sulfur in the liquid product can be achieved while minimizing the amount of hydrogen consumed via saturation of the aromatics. The first hydrodesulfurization stage will reduce the levels of both sulfur and nitrogen, with sulfur levels being less than about 1,000 wppm, preferably less than about 500 wppm. The second hydrodesulfurization stage will reduce sulfur levels to less than about 100 wppm, preferably to less than about 50 wppm. In the practice of this invention the hydrogen in the treat gas reacts with impurities to convert them to H<sub>2</sub>S, NH<sub>3</sub>, and water vapor, which are removed as part of the vapor effluent, and it also saturates olefins and aromatics.

Miscellaneous reaction vessel internals, valves, pumps, thermocouples, and heat transfer devices etc. are not shown for simplicity. FIG. 1 shows hydrodesulfurization reaction vessel R1 which contains reaction zones 12a and 12b, each of which is comprised of a bed of hydrodesulfurization catalyst. It will be understood that this reaction stage can contain only one reaction zone or two or more reaction zones. It is preferred that the catalyst be in the reactor as a fixed bed, although other types of catalyst arrangements can be used, such as slurry or ebullating beds. Downstream of each reaction zone is a non-reaction zone, 14a and 14b. The non-reaction zone is typically void of catalyst, that is, it will be an empty section in the vessel with respect to catalyst. Although not shown, there may also be provided a liquid distribution means upstream of each reaction stage or catalyst bed. The type of liquid distribution means is believed not to limit the practice of the present invention, but a tray

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