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(54) **Title**: IMPROVED PROCESS FOR REDUCING ULTRA LOW SULFUR DIESEL COLOR

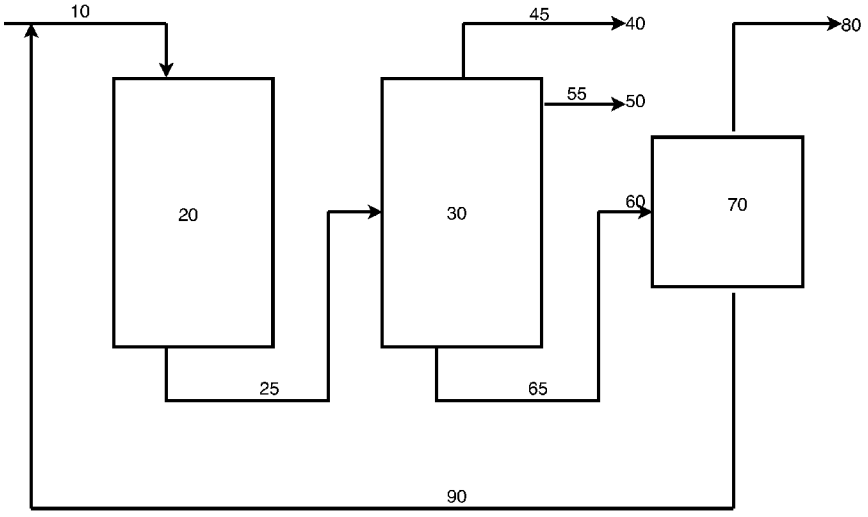


FIG. 1

(57) **Abstract**: The present invention is a process for preparing ultra low sulfur diesel. The steps include reacting a feedstock of petroleum crude oil with hydrogen in the presence of a hydrodesulfurization catalyst under hydrodesulfurization conditions, fractionating the reaction products, flash distilling the bottoms fraction, condensing the volatile distillate fraction as ultra low sulfur diesel, and recycling the distillation bottoms fraction for further reacting with hydrogen.

WO 2014/011967 A1

IMPROVED PROCESS FOR REDUCING ULTRA LOW SULFUR DIESEL COLOR

CROSS-REFERNCE TO RELATED APPLICATIONS

[0001] This application claims benefit and priority of United States Provisional Patent Application No. 61/671,484 filed on July 13, 2012, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to processing Ultra Low Sulfur Diesel (ULSD). In particular, the invention relates to hydrodesulfurizing ULSD and reducing the color of the ULSD.

DESCRIPTION OF RELATED ART

[0003] Ultra Low Sulfur Diesel must satisfy regulatory and industry standards. Some of those standards relate to impurities such as sulfur. Others relate to physical properties such as flash point. Yet, other standards relate to manufacturing controls.

[0004] With regard to sulfur impurities, hydrocarbon fractions such as diesel fuel produced in the petroleum industry are typically contaminated with various sulfur-based impurities. The presence of sulfur compounds is undesirable since they result in a serious pollution problem. Combustion of hydrocarbons containing these impurities results in the release of sulfur oxides which are noxious and corrosive.

[0005] Federal legislation, specifically the Clean Air Act of 1970 and its 1990 Amendments (42 U.S.C. § 7401 et seq. (2008)), has imposed increasingly more stringent requirements to reduce the amount of sulfur released to the atmosphere. Under its rule-making authority, the United States Environmental Protection Agency has lowered the sulfur standard for diesel fuel to 15 parts per million by weight (ppm or μg/g).

[0006] ASTM International, formerly known as the American Society for Testing and Materials (ASTM), has established test methods for measuring impurties such as sulfur and physical properties such as flash point. ASTM International sets forth a Standard Specification

for Diesel Fuel Oils in ASTM D975-08. Notably, the Specification covers seven grades of diesel fuel oils for various types of diesel engines.

[0007] With regard to Grade No. 1-D S15 and Grade No. 2-D S15 (both special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum)), ASTM D975 sets forth alternate test methods (i) ASTM D2622 "Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescense Spectrometry" for measuring sulfur in the range of 0.0003 to 5.3 mass %, (ii) ASTM D3120 "Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidate Microcoulometry" for measuring sulfur in the range of 3.0 to 100 mg/kg (wt ppm), and (iii) ASTM D5453 "Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence" for measuring sulfur in the range of 0.0001 to 0.8 mass % or 1.0 to 8000 mg/kg (wt ppm).

[0008] Other properties specified under ASTM D975 include flash point, water and sediment, distillation temperature, kinematic viscosity, and others.

[0009] While the Clean Air Act, its related rules, or the ASTM International Standard Specifications do not set forth a color requirement for ULSD, determination of the color of petroleum products has been used for manufacturing control purposes. Furthermore, it is an important quality characteristic because color is readily observed by the user of the product. ASTM D1500 "Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale) and ASTM D6045 "Standard Test Method for Color of Petroleum Products by the Automatic Tristimulus Method" are appropriate methods for measuring color of ULSD. A commonly-applied manufacturing control limit is 2.5 ASTM.

[0010] The manufacturing of ULSD presents challenges in satisfying regulatory and industry standards. Notably, the Clean Air Act and its related rules ensure that there is a continual need for more effective desulfurization methods. Moreover, the deterioration in ASTM Color does not correlate perfectly to the most common desulfurization method.

[0011] The most common method of desulfurization of fuels is hydrodesulfurization, in which the fuel is catalytically reacted with hydrogen gas at elevated temperature and high pressure in the presence of a costly catalyst. For example, United States Patent No. 5,985,136 describes a hydrodesulfurization process to reduce sulfur level in naptha feedstreams. Organic sulfur is reduced by this reaction to gaseous H_2S, which is then oxidized to elemental sulfur by the Claus process.

[0012] With this method, it is believed that the catalyst has several months of remaining life for reducing the sulfur level even though the ASTM Color begins to exceed 2.5. It is desirable to replace the catalyst only after it is fully exhausted in the process, not as prematurely required under the current process. There is a need to improve the process so that the ASTM Color does not exceed 2.5 until the catalyst is fully exhausted with regard to hydrodesulfurization.

[0013] To cause the decay in catalytic reduction of the sulfur level to correlate more closely to the deterioration in achieving the desired ASTM Color, the inventor in copending United States Patent Application Serial No. 13/156,487 teaches installation of a high-efficiency, flash tank at the end of the hydrotreating process. The flash tank's efficiency yields an overhead stream that 99+% ULSD and a small bottom stream containing the color bodies.

[0014] It remains desirable to provide a process that does not require a flash tank with a total stage efficiency of greater than 99%.

SUMMARY OF THE INVENTION

[0015] The present invention is a process for preparing ultra low sulfur diesel. The steps include reacting a feedstock of petroleum crude oil with hydrogen in the presence of a hydrodesulfurization catalyst under hydrodesulfurization conditions, fractionating the reaction products, flash distilling the bottoms fraction, condensing the volatile distillate fraction as ultra low sulfur diesel, and recycling the distillation bottoms fraction for further reacting with hydrogen.

[0016] The present invention provides an improved process for preparing ultra low sulfur diesel, wherein the hydrodesulfurization catalyst is more fully utilized while retaining suitable color.

DESCRIPTION OF THE DRAWINGS

[0017] Further details will be apparent from the following detailed description, with reference to the enclosed drawing, in which:

[0018] FIG. 1 is a block flow diagram of a process according to the present invention.

DETAILED DESCRIPTION

[0019] In an embodiment, the present invention is a process for preparing ultra low sulfur diesel which is diesel having a sulfur content of less than 15 parts per million. The process steps

include (a) reacting a feedstock of petroleum crude oil with hydrogen in the presence of a hydrodesulfurization catalyst under hydrodesulfurization conditions, (b) fractionating the reaction products into a naphtha fraction, a kerosene fraction, and a first bottoms fraction, (c) flash distilling the first bottoms fraction in a distillation column having at least one stage and a total stage efficiency of less than about 99%, thereby yielding a volatile distillate fraction and a second bottoms fraction, (d) condensing the volatile distillate fraction as ultra low sulfur diesel, and (e) recycling the second bottoms fraction into the feedstock of petroleum crude oil for further reacting of the second bottoms fraction with hydrogen in the presence of the hydrodesulfurization catalyst. The volatile distillate fraction should have an ASTM Color of less than or equal to 2.5 and a sulfur content less than 15 ppm. More preferably, the volatile distillate fraction will have an ASTM Color of less than or equal to 1.5.

[0020] The hydrodesulfurization catalyst can include, but is not limited to, at least a first metal component selected from Groups 8-10 (IUPAC) metals such as iron, cobalt, and/or nickel, and at least a second metal component selected from Group 6 (IUPAC) metals such as molybdenum and/or tungsten, on a high surface area support material such as alumina. Other suitable desulfurization catalysts include zeolitic catalyts as well as nobel metal catalyts where the noble metal is palladium or platinum. More than one type of hydrodesulfurization catalyst can be used in the same reaction vessel or zone to remove sulfur. In a preferred embodiment, the hydrodesulfurization catalyst is a nickel molybdenum catalyst.

[0021] In a preferred embodiment, the hydrodesulfurization conditions are the following operation conditions:

Temperature:	200-485 degrees Celsius
Pressure:	8-200 bar
Liquid Hourly Space Velocity:	0.1-10 hr^{-1}

[0022] With consideration of FIG. 1, the flow of a process according to the present invention includes providing a feedstock of petroleum crude oil via a line 10 into a main reactor 20 wherein hydrogen and a hydrodesulfurization catalyst are provided. The main reactor 20 may be a hydrotreater or other reactor as known in the art. Under hydrodesulfurization conditions, the sulfur-containing components of the feedstock and the hydrogen react.

[0023] The reaction products flow through line 25 into the product fractionator 30, wherein products are fractionated into a naptha fraction 40 , a kerosene fraction 50, and a first bottoms

fraction 60. The naptha fraction 40 is collected via line 45. The kerosene fraction is collected via line 55. For convenience, line 45 and line 55 may be a single line.

[0024] The first bottoms fraction 60 flows through line 65 into a flash distillation column or flash tank 70 to separate the volatile distillate fraction 80 from a second bottoms fraction 90 containing heavy diesel, sulfur, colorants, and other impurities. Depending upon the stage efficiency of flash distillation column 70, the volatile distillate fraction 80 may contain at least about 80% of the first bottoms stream's diesel having an ASTM Color of less than or equal to 2.5 and a sulfur content of less than 15 ppm. The corresponding second bottoms fraction 90 may contain up to about 20% of the first bottoms stream's heavy diesel.

[0025] Preferably, the the distillation column for the flash distilling step will have a stage efficiency in the range of about 80% to about 99%. More preferably, the distillation column for the flash distilling step will have a stage efficiency of about 95%.

Examples

[0026] The following non-limiting examples illustrate the invention.

[0027] Samples of a first bottoms fraction were collected from a hydrodesulfurizing manufacturing plant. Each sample was evaluated for initial ASTM Color and post-treatment ASTM Color according to ASTM D6045, the contents of which are incorporated herein by reference in its entirety.

[0028] The post-treatment methods were either (a) flash distilling the sample with a single-stage flash distillation column to 99% efficiency (i.e., 99% volatile distillate fraction and 1% bottoms fraction) or (b) reacting the sample with hydrogen in the presence of a hydrodesulfurization catalyst under hydrodesulfurization conditions in a pilot plant hydrotreater. The flash distillation method demonstrated that the volatile distillate fraction satisfies the ASTM Color requirement, and the additional hydrotreatment method showed conversion of the sample into ULSD that satisfies the ASTM Color specification.

Flash Distillation

(Comparative Examples 1 and 2)

Example No.	Initial ASTM Color	Post-Treatment ASTM Color
1	5.2	1.1
2	3.9	0.3

Additional Hydrotreatment

(Examples 3 and 4)

Example No.	Initial ASTM Color	Post-Treatment ASTM Color
3	3.3	1.7
4	4.8	1.9

[0029] Although the invention has been described in considerable detail by the preceding specification, this detail is for the purpose of illustration and is not to be construed as a limitation upon the following appended claims. All cited ASTM standards, reports, references, U.S. patents, allowed U.S. patent applications, and U.S. Patent Applications Publications are incorporated herein by reference.

CLAIMS

What is claimed is:

1. A process for preparing ultra low sulfur diesel comprising the steps of:
   (a) reacting a feedstock of petroleum crude oil with hydrogen in the presence of a hydrodesulfurization catalyst under hydrodesulfurization conditions;
   (b) fractionating the reaction products into a naphtha fraction, a kerosene fraction, and a first bottoms fraction;
   (c) flash distilling the first bottoms fraction in a distillation column having at least one stage and a total stage efficiency of less than about 99%, thereby yielding
      (i) a volatile distillate fraction having an ASTM Color of less than or equal to 2.5 and a sulfur content less than 15 ppm and
      (ii) a second bottoms fraction;
   (d) condensing the volatile distillate fraction as ultra low sulfur diesel; and
   (e) recycling the second bottoms fraction into the feedstock of petroleum crude oil for further reacting of the second bottoms fraction with hydrogen in the presence of the hydrodesulfurization catalyst.

2. The process of claim 1 wherein the reacting step occurs in a hydrotreater.

3. The process of claim 1 wherein the distillation column for the flash distilling step has a stage efficiency of at least about 80%.

4. The process of claim 3 wherein the distillation column for the flash distilling step has a stage efficiency in the range of about 80% to about 99%.

5. The process of claim 4 wherein the distillation column for the flash distilling step has a stage efficiency of about 95%.

6. The process of claim 1 wherein the hydrodesulfurization catalyst is a zeolite catalyst.

7. The process of claim 1 wherein the hydrodesulfurization catalyst is a nickel molybdenum catalyst.

8. The process of claim 1 wherein the hydrodesulfurization catalyst consists of more than one hydrodesulfurization catalyst.

9. The process of claim 1 wherein the hydrodesulfurization catalyst comprises palladium.

10. The process of claim 1 wherein the hydrodesulfurization catalyst comprises platinum.

11. The process of claim 1 wherein the hydrodesulfurization catalyst comprises at least a first metal component selected from Group 8, 9, and 10 (IUPAC) metals and at least a second metal component selected from Group 6 (IUPAC) metals, on a high surface area support material.

12. The process of claim 11 wherein the first metal component is selected from the group consisting of iron, cobalt, and nickel.

13. The process of claim 11 wherein the second metal component is selected from the group consisting of molybdenum and tungsten.

14. The process of claim 11 wherein the high surface area support material is alumina.

15. The process of claim 11 wherein the reacting step occurs at a temperature of 200-485 degrees Celsius.

16. The process of claim 11 wherein the reacting step occurs at a pressure of 8-200 bar.

17. The process of claim 11 wherein the reaction has a liquid hourly space velocity of 0.1-10 hr^{-1}.

18. A process for preparing ultra low sulfur diesel comprising the steps of:
    (a) reacting a feedstock of petroleum crude oil with hydrogen in a hydrotreater in the presence of a nickel molybdenum hydrodesulfurization catalyst under hydrodesulfurization conditions of
        (i) a temperature of 200-485 degrees Celsius,
        (ii) a pressure of 8-200 bar, and
        (iii) a liquid hourly space velocity of 0.1-10 hr^{-1};

(b) fractionating the reaction products into a naphtha fraction, a kerosene fraction, and a first bottoms fraction;

(c) flash distilling the first bottoms fraction in a distillation column having at least one stage and a total stage efficiency of less than about 99%, thereby yielding

(i) a volatile distillate fraction having an ASTM Color of less than or equal to 2.5 and a sulfur content less than 15 ppm and

(ii) a second bottoms fraction;

(d) condensing the volatile distillate fraction as ultra low sulfur diesel; and

(e) recycling the second bottoms fraction into the feedstock of petroleum crude oil for further reacting of the second bottoms fraction with hydrogen in the presence of the nickel molybdenum hydrodesulfurization catalyst.

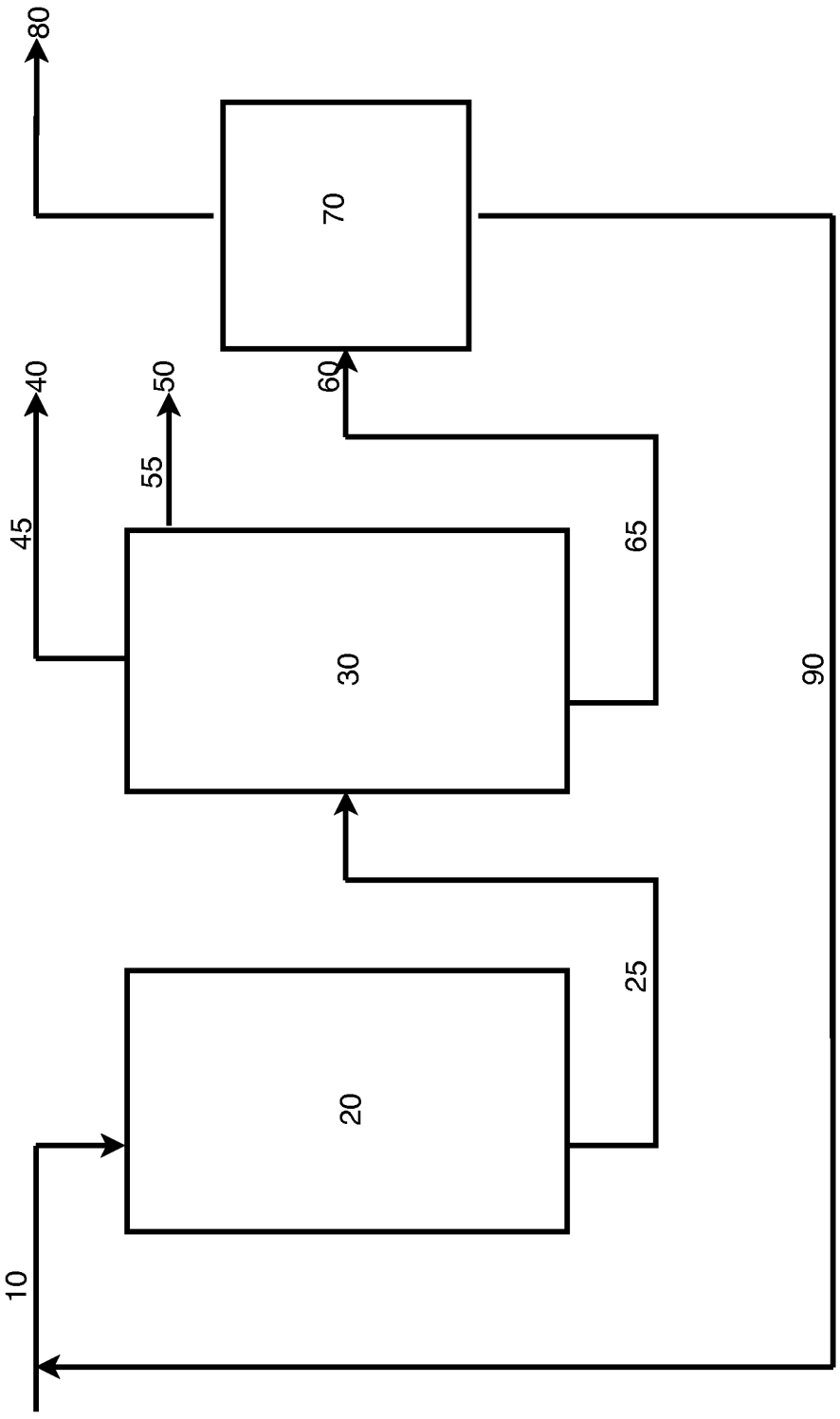


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/050227

A. CLASSIFICATION OF SUBJECT MATTER

C10G 45/04(2006.01)i, C10G 45/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G 45/04; C10G 45/06; C10G 69/02; C10G 69/00; C10G 45/00; B01J 23/30; C10G 45/08; B01J 8/00; C10G 47/00; C10G 65/12; C10G 45/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: ultra low sulfur diesel, petroleum, crude oil, hydrogen, hydrodesulfurization catalyst, naphtha, kerosene, recycling heavy distillate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6447673 B1 (CORDERA, M. H. G. et al.) 10 September 2002 See abstract; figure 1; column 3, lines 62-65; column 4, lines 5-8, 22-29; column 5, lines 16-26; and claims 1-6, 13-14.	1-18
A	US 2009-0145808 A1 (CHOI, K. H. et al.) 11 June 2009 See abstract; figure 1; paragraph [0042]; and claims 1, 20.	1-18
A	WO 2008-010799 A1 (UOP LLC) 24 January 2008 See abstract; figure 1; and claims 1-7.	1-18
A	US 7005057 B1 (KALINES, T. N.) 28 February 2008 See abstract; figure 1; and claims 1, 2, 8, 9, 13.	1-18
A	US 2011-0163010 A1 (LEE, I. S. et al.) 7 July 2011 See abstract; figure 2; and claims 1, 5, 10.	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
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