

PRODUCTION OF LOW COLOR MIDDLE DISTILLATE FUELS

FIELD OF THE INVENTION

[0001] This invention relates to a process for reducing the color level of middle distillate fuels, such as diesel fuel and kerosene.

BACKGROUND OF THE INVENTION

[0002] Color, sulfur level and cloud point are important product specifications for diesel fuel and kerosene. For example, changes in the U.S. regulatory system in 2006 reduced the maximum sulfur levels in diesel fuels from 500 wppm (S500) to 15 wppm (S15). Similarly, the color specification required for most refinery diesel pools is less than 2.5 ASTM color units, which means that many refineries limit the color for desulfurized diesel to less than about 2.0 ASTM color units. In addition, depending on season and geography, diesel fuels and kerosene may be required to have a cloud point of less than -27°C.

[0003] Generally, a multi-stage hydrotreating process is used to reduce the sulfur and color levels of diesel fuel to the required values. For example, U.S. Patent No. 6,103,104 discloses a process in which a middle distillate petroleum stream is hydroprocessed in two or more first temperature stages operated at a temperature from about 360°C to about 450°C. The reaction product of the first temperature stage(s) is(are) then quenched to a temperature from about 260°C to about 350°C, stripped of H₂S, NH₃ and other dissolved gases, then sent to the second temperature stage which is operated at the quenched temperature range, whereby color bodies produced in the higher temperature first stage are hydrogenated in the second stage.

[0004] Chinese Published Patent Application No. CN 1824736 discloses a method for preparing diesel oil with improved color property and ultra-low sulfur content by deep hydrodesulfurization and hydrotreating comprising (1) carrying out deep hydrodesulfurization to produce a hydrocarbon oil with a boiling point of 200-400°C in

- 2 -

the presence of a catalyst (including CoMo as active metal) at 330-380°C under 40-48 kg/cm² with a liquid hourly space velocity (LHSV) of 0.1-2.0 hr⁻¹, and (2) hydrotreating in the presence of catalyst (including NiMo as active metal) at 230-320°C under 40-80 kg/cm² with a LHSV of 4-10 hr⁻¹. The resultant diesel oil has a sulfur content not more than 10 ppm and a Saybolt color index not less than 10.

[0005] U.S. Patent No. 6,652,735 discloses a process for isomerization dewaxing of a hydrocarbon feed, such as a diesel oil, which includes contacting the hydrocarbon feed with a large pore size, small crystal size, crystalline molecular sieve, such as zeolite beta, and an intermediate pore size, small crystal size, crystalline molecular sieve, such as ZSM-23 or ZSM-48, to produce a dewaxed product with a reduced pour point and a reduced cloud point.

[0006] To date, the chemistry involved in the formation of color bodies in diesel fuels has not been well understood, although it is known to be generally related to prior desulfurization and/or isomerization at high temperature. As a result, the maximum operating temperature for many desulfurization and isomerization units is limited by the color specification of the product rather than by catalyst activity, thereby limiting cycle length.

SUMMARY OF THE INVENTION

[0007] It has been discovered that the color of diesel fuel and kerosene can be specifically dependent on the 3+ ring aromatic content of the fuel. Based on this knowledge, a new process for producing low color fuels has been developed in which an additional catalyst bed can be added to the desulfurization/isomerization reactor for color control or the last bed in the desulfurization/isomerization reactor is converted for color control. This final bed can be operated at a temperature close to, but lower than, that of the preceding catalyst beds in the reactor. Either a recycle gas or the liquid diesel product can be used to quench the effluent from the desulfurization/isomerization bed, so that the color control bed can be operated at the lower temperature. This color control catalyst bed can re-saturate at least some of the 3+ ring aromatics generated by

the desulfurization/isomerization catalyst beds. With such an arrangement, the main desulfurization/isomerization bed(s) can be operated over a broader temperature range as the catalyst ages, thereby prolonging the catalyst cycle length while simultaneously meeting the color specification.

[0008] One aspect of the invention relates to a process for producing a diesel and/or kerosene fuel of low color, the process comprising: (a) supplying a middle distillate feed having a first cloud point and hydrogen to a reactor having at least one first catalyst bed containing a first desulfurization and/or isomerization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and containing a decolorization catalyst; (b) reacting the feed with the hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 290°C to about 430°C to produce a first liquid effluent having a second cloud point; (c) cooling the first liquid effluent by about 10°C to about 40°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature of about 280°C to about 415°C to produce a second effluent having an ASTM color of less than 2.5 and a third cloud point.

[0009] Another aspect of the invention relates to a process for producing a low color and low sulfur diesel and/or kerosene fuel, the process comprising: (a) supplying a hydrogen and middle distillate feed having a first cloud point and containing at least 0.03 wt% sulfur to a reactor having at least one first catalyst bed comprising a first desulfurization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and comprising a decolorization catalyst; (b) reacting the feed with hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 315°C to about 430°C to produce a first liquid effluent comprising 15 wppm or less sulfur and having a second cloud point; (c) cooling the first liquid effluent by about 15°C to about 35°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature from about 300°C to about 415°C to produce a

- 4 -

second effluent comprising 15 wppm or less sulfur, having a third cloud point, and having an ASTM color of less than 2.5.

[0010] Still another aspect of the invention relates to a process for producing a low color diesel and/or kerosene fuel having a low cloud point, the process comprising: (a) supplying a middle distillate feed having a first cloud point and hydrogen to a reactor having at least one first catalyst bed comprising a first isomerization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and comprising a decolorization catalyst; (b) reacting the feed with hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 285°C to about 420°C to produce a first liquid effluent having a second cloud point that is at least 10 °C less than that of the first cloud point; (c) cooling the first liquid effluent by about 10°C to about 20°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature from about 275°C to about 400°C to produce a second effluent having a third cloud point that is at least 10 °C less than that of the first cloud point and having an ASTM color of less than 2.5.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a graph of diesel color against average reaction bed temperature for the desulfurization process of Example 1 with and without a final decolorization bed.

[0012] Figure 2 is a graph of diesel color against average reaction bed temperature for the combined desulfurization/isomerization process of Example 2 with and without a final decolorization bed.

[0013] Figure 3 is a graph of diesel color against average reaction bed temperature for the isomerization process of Example 3 with and without a final decolorization bed.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0014] Described herein is a simplified process for lowering the sulfur content and/or the cloud point of a middle distillate feed and for simultaneously removing color components produced in the desulfurization and/or isomerization step. The product can be a fuel composition having a boiling range in the diesel and/or kerosene temperature range, and which fuel composition can exhibit a low sulfur content and/or a low cloud point and can exhibit a low color value. As used herein, the term “low color” refers to a (diesel and/or kerosene) fuel product having a color value of less than 2.5, for example less than 2, as measured according to ASTM D-6045. Also as used herein, the term “low sulfur” refers to a (diesel and/or kerosene) fuel product containing less than 15 wppm sulfur, as measured according to ASTM D-5453. Further as used herein, the term “low cloud point” refers to a (diesel and/or kerosene) fuel product having a cloud point of less than 10°C, as measured according to ASTM D-2500.

[0015] The middle distillate feed suitable for use in the present processes can include any refinery hydrocarbon feedstream boiling in the range from about 300°F (about 149°C) to about 775°F (about 413°C), for example from about 350°F (about 177°C) to about 750°F (about 399°C), from about 400°F (about 204°C) to about 700°F (about 371°C), or from about 450°F (about 232°C) to about 650°F (about 343°C). Such middle distillate feeds can include hydrotreated feedstreams, feedstreams that have not previously been hydrotreated, and combinations thereof.

[0016] The middle distillate feeds employed herein can generally contain significant quantities of nitrogen and sulfur impurities, in which case the process can be employed to lower the nitrogen and/or sulfur level of the feed to that required for the final (diesel and/or kerosene) fuel. The feeds according to the invention can contain nitrogen-containing compounds, abbreviated as “nitrogen”, “nitrogen level”, or “nitrogen content”, and/or sulfur-containing compounds, abbreviated as “sulfur”, “sulfur level”, or “sulfur content”. Typically, the nitrogen content of such feeds can be from about 50 wppm to about 6000 wppm, preferably from about 50 wppm to about 2000 wppm, for example from about 50 wppm to about 1500 wppm, from about 50

- 6 -

wppm to about 1000 wppm, from about 75 wppm to about 1000 wppm, from about 75 wppm to about 800 wppm, or from about 100 wppm to about 500 wppm. The nitrogen may be present as both basic nitrogen and/or non-basic nitrogen species. Non-limiting examples of basic nitrogen species can include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles. Additionally or alternately, the sulfur content of such feeds can be from about 50 wppm to about 40000 wppm, for example from about 50 wppm to about 15000 wppm, from about 100 wppm to about 30000 wppm, from about 100 wppm to about 10000 wppm, from about 200 wppm to about 20000 wppm, from about 200 wppm to about 10000 wppm, from about 200 wppm to about 5000 wppm, from about 500 wppm to about 5000 wppm, or from about 350 wppm to about 2500 wppm sulfur. The sulfur can typically be present as organically bound sulfur, *e.g.*, including simple aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and poly- sulfides, and the like, and combinations thereof. Other organically bound sulfur compounds can include thiophenes, tetrahydrothiophenes, benzothiophenes, and their higher homologs and analogs, as well as combinations thereof.

[0017] Further additionally or alternately, the total aromatic content of such feeds can be between about 5 vol% and about 30 vol%, with the 3+ ring aromatic content generally ranging from about 0.5 wt% to about 5 wt%. Still further additionally or alternately, the middle distillate feeds may contain significant quantities of straight chain and/or lightly branched paraffins that can solidify at relatively high temperatures. In such circumstances, the present process can be employed to hydroisomerize those materials into more highly branched paraffins, *e.g.*, thereby reducing the cloud point and/or pour point of the feed.

[0018] In the present process the middle distillate feed and hydrogen can be supplied to a reactor comprising one or more first catalyst beds, each containing a first catalyst effective to desulfurize and/or isomerize the feed, and at least one second catalyst bed downstream of the first catalyst bed(s) and containing a second catalyst effective to remove color components in the feed. Depending on the composition of the feed, the first catalyst bed can be operated at a temperature from about 290°C to about 430°C, for example from about 315°C to about 400°C, such that the feed can

- 7 -

react with the hydrogen in the presence of the first catalyst to produce a first liquid effluent having a lower sulfur content and/or a lower cloud point than the feed.

[0019] On exiting the first catalyst bed(s), the first liquid effluent can be cooled by about 10°C to about 40°C, for example about 15°C to about 35°C, with a quench medium, and then the entire cooled first liquid effluent can be cascaded to the at least one second catalyst bed. The second catalyst bed can be operated at a temperature from about 280°C to about 415°C, for example from about 300°C to about 400°C, such that the first effluent can react with the hydrogen in the presence of the second catalyst to remove color components produced in the first catalyst bed(s) and can produce a second liquid effluent having an ASTM color of less than 2.5, for example less than 2.0. As indicated above, without being bound by theory, it is believed that the color in the first liquid effluent can be the result of 3+ ring aromatics present in the feed and/or generated during the desulfurization and/or isomerization step. Such 3+ ring aromatics can be at least partially saturated (in this context, "saturated" is meant chemically by hydrogen, not having hydrogen physically dissolved therein) during the decolorization reaction such that the second liquid effluent can advantageously contain less than 3 vol%, for example less than 2.0 vol%, of 3+ ring aromatic compounds. The term "3+ ring aromatic compounds" as used herein means a compound that has at least 3 aromatic rings in its structure.

[0020] Generally, the quench medium used to cool the first liquid effluent can be the second effluent and/or unreacted hydrogen gas from the decolorization reaction, though one or more other refinery streams can be additionally or alternately used. Typically, the hydrogen partial pressure in either or both of the first and second catalyst beds (and/or in a reactor containing same) can be between about 400 psig (about 2.8 MPag) and about 1500 psig (about 10.3 MPag), for example between about 500 psig (about 3.5 MPag) and about 1300 psig (about 9.0 MPag).

[0021] In a first embodiment, in which the sulfur level of the feed is at least 0.03 wt%, for example at least 0.05 wt% or at least 0.5 wt%, the/each first catalyst bed can contain a desulfurization catalyst. Suitable desulfurization catalysts can comprise at

least one metal/compound from Groups 8-10 of the Periodic Table of the Elements (such as iron, cobalt, and/or nickel, preferably cobalt and/or nickel) and at least one metal/compound from Group 6 (such as molybdenum and/or tungsten, preferably including molybdenum), optionally but preferably on a high surface area support material (such as alumina, silica, alumina-silica, titania, zirconia, or a combination thereof). Typically, the reactor can contain a plurality, for example from 2 to 5, of the first catalyst beds, which can be operated at a temperature from about 315°C to about 430°C and at an LHSV from about 0.3 hr⁻¹ to about 1.5 hr⁻¹ to produce a first liquid effluent containing 15 wppm sulfur or less, for example 10 wppm sulfur or less.

[0022] In the first embodiment, the quenching step can be controlled to lower the temperature of the first liquid effluent by about 17°C to about 40°C, and the entire cooled first liquid effluent can be cascaded to a decolorization catalyst, which can optionally but preferably be the same as the desulfurization catalyst. The second catalyst bed can typically be operated at a temperature from about 300°C to about 415°C and at an LHSV from about 4 hr⁻¹ to about 10 hr⁻¹ to produce a second effluent having an ASTM color of less than 2.5, preferably less than 2.0, in addition to a sulfur content of 15 wppm or less.

[0023] In a modification to the first embodiment, in which the feed can have a cloud point of at least 5°C in addition to a sulfur level of at least 0.03 wt%, the reactor can include a plurality of first catalyst beds connected in series, and the final first catalyst bed in the series can contain an isomerization catalyst. Suitable isomerization catalysts for use in this modification can include, but are not limited to, shape selective zeolites selected from zeolite beta, ZSM-23, ZSM-48, and mixtures thereof. The isomerization catalyst bed can typically be operated at a temperature from about 343°C to about 430°C and at an LHSV from about 1 hr⁻¹ to about 4 hr⁻¹ to produce a first liquid effluent containing 15 wppm sulfur or less and typically having a cloud point from about 10°C to about 30°C less the feed. The quenching step can then be arranged to lower the temperature of the first liquid effluent by about 10°C to about 28°C, and the entire cooled first liquid effluent can be cascaded to a decolorization catalyst, which can optionally but preferably be the same as the isomerization catalyst. The second

catalyst bed can typically be operated at a temperature from about 300°C to about 421°C and at an LHSV from about 4 hr⁻¹ to about 10 hr⁻¹ to produce a second effluent having a relatively low color (*e.g.*, an ASTM color of less than 2.5, preferably less than 2.0), a relatively low sulfur content (*e.g.*, 15 wppm or less, such as 10 wppm or less) and a lower cloud point than the feed.

[0024] In another embodiment, the sulfur level of the feed can be less than 0.03 wt%, but the cloud point of the feed can be in excess of 0°C. In this embodiment, the/each first catalyst bed can contain an isomerization catalyst, typically at least one shape selective zeolite, *e.g.*, selected from zeolite beta, ZSM-23, ZSM-48, and mixtures thereof. Generally, the reactor can contain a plurality, for example from 2 to 5, of the first catalyst beds, which can be operated at a temperature from about 285°C to about 420°C and at an LHSV from about 1 hr⁻¹ to about 4 hr⁻¹ to produce a first liquid effluent having a cloud point at least 10°C, for example from about 10°C to about 30°C, less than that of the feed.

[0025] Additionally or alternately in such an embodiment, the quenching step can be controlled to lower the temperature of the first liquid effluent by about 10°C to about 22°C, and the entire cooled first liquid effluent can be cascaded to a second catalyst bed containing a decolorization catalyst. Suitable decolorization catalyst can include, but are not limited to, (a) a noble metal (*e.g.*, platinum, palladium, rhodium, or the like, or a combination thereof, preferably containing platinum) with MCM-41, and/or (b) at least one Group 8-10 metal or metal compound (*e.g.*, cobalt and/or nickel) and at least one Group 6 metal or metal compound (*e.g.*, molybdenum and/or tungsten) on a relatively high surface area support material (*e.g.*, having a BET surface area of at least 60 m²/g, at least 75 m²/g, at least 90 m²/g, at least 100 m²/g, or at least 110 m²/g), such as alumina, silica, alumina-silica, titania, zirconia, or a combination thereof, for example comprising alumina. In one preferred embodiment, the decolorization catalyst can be the same as the isomerization catalyst. The second catalyst bed can typically be operated at a temperature from about 275°C to about 400°C and at an LHSV from about 5 hr⁻¹ to about 15 hr⁻¹ to produce a second effluent having a cloud point at least 10°C less than that of the feed and an ASTM color of less than 2.5.

[0026] Additionally or alternately, the present invention can include one or more of the following embodiments.

[0027] Embodiment 1. A process for producing a diesel and/or kerosene fuel of low color, the process comprising: (a) supplying a middle distillate feed having a first cloud point and hydrogen to a reactor having at least one first catalyst bed containing a first desulfurization and/or isomerization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and containing a decolorization catalyst; (b) reacting the feed with the hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 290°C to about 430°C to produce a first liquid effluent having a second cloud point; (c) cooling the first liquid effluent by about 10°C to about 40°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature of about 280°C to about 415°C to produce a second effluent having an ASTM color of less than 2.5 and a third cloud point.

[0028] Embodiment 2. A process for producing a low color and low sulfur diesel and/or kerosene fuel, the process comprising: (a) supplying a hydrogen and middle distillate feed having a first cloud point and containing at least 0.03 wt% sulfur to a reactor having at least one first catalyst bed comprising a first desulfurization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and comprising a decolorization catalyst; (b) reacting the feed with hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 315°C to about 430°C to produce a first liquid effluent comprising 15 wppm or less sulfur and having a second cloud point; (c) cooling the first liquid effluent by about 15°C to about 35°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature from about 300°C to about 415°C to produce a second effluent comprising

15 wppm or less sulfur, having a third cloud point, and having an ASTM color of less than 2.5.

[0029] Embodiment 2a. The process of Embodiment 1 for producing a low color and low sulfur diesel and/or kerosene fuel, wherein the process further comprises: in step (a) the middle distillate feed contains at least 0.03 wt% sulfur; in step (b) the first catalyst bed is operated at a temperature from about 315°C to about 430°C thereby producing the first liquid effluent comprising 15 wppm or less sulfur; in step (c) the first liquid effluent is cooled by about 15°C to about 35°C with the quench medium; and in step (e) the cooled first liquid effluent is contacted with hydrogen in the presence of said decolorization catalyst at a temperature from about 300°C to about 415°C to produce a second effluent having 15 wppm or less sulfur and having an ASTM color of less than 2.5.

[0030] Embodiment 3. A process for producing a low color diesel and/or kerosene fuel having a low cloud point, the process comprising: (a) supplying a middle distillate feed having a first cloud point and hydrogen to a reactor having at least one first catalyst bed comprising a first isomerization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and comprising a decolorization catalyst; (b) reacting the feed with hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 285°C to about 420°C to produce a first liquid effluent having a second cloud point that is at least 10 °C less than that of the first cloud point; (c) cooling the first liquid effluent by about 10°C to about 20°C with a quench medium; (d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and (e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature from about 275°C to about 400°C to produce a second effluent having a third cloud point that is at least 10 °C less than that of the first cloud point and having an ASTM color of less than 2.5.

[0031] Embodiment 3a. The process of Embodiment 1 for producing a low color diesel and/or kerosene fuel having a low cloud point, wherein the process further

- 12 -

comprises: in step (a) the middle distillate has a first cloud point; in step (b) the first liquid effluent has a second cloud point that is at least 10 °C less than that of the first cloud point; in step (c) the first liquid effluent is cooled by about 10°C to about 20°C with the quench medium; and in step (e) the second effluent is produced having a third cloud point that is at least 10 °C less than that of the first cloud point and has an ASTM color of less than 2.5.

[0032] Embodiment 4. The process of any one of the previous embodiments, wherein said reacting step (b) is conducted at a temperature from about 315°C to about 400°C and/or wherein said contacting step (e) is conducted at a temperature from about 300°C to about 400°C.

[0033] Embodiment 5. The process of any one of the previous embodiments, wherein the hydrogen partial pressure in the reactor is between about 400 psig (about 2.8 MPag) and about 1500 psig (about 10.3 MPag).

[0034] Embodiment 6. The process of any one of the previous embodiments, wherein the first liquid effluent is cooled in step (c) by about 15°C to about 35°C, and/or wherein the quench medium is the second effluent and/or unreacted hydrogen gas from said contacting step (e).

[0035] Embodiment 7. The process of any one of the previous embodiments, wherein said second effluent has an ASTM color of less than 2.0 and/or comprises less than 2 vol% of 3+ ring aromatic compounds.

[0036] Embodiment 8. The process of any one of the previous embodiments, wherein the desulfurization catalyst, the decolorization catalyst, or both comprises nickel and molybdenum.

[0037] Embodiment 9. The process of any one of the previous embodiments, wherein the reactor includes a plurality of first catalyst beds, and wherein at least one of

- 13 -

said first catalyst beds comprises an isomerization catalyst, such as selected from zeolite beta, ZSM-23, ZSM-48, and mixtures thereof.

[0038] Embodiment 10. The process of any one of the previous embodiments, wherein said reacting step (b) is conducted at an LHSV from about 0.3 hr^{-1} to about 1.5 hr^{-1} or from about 1 hr^{-1} to about 4 hr^{-1} , and/or wherein said contacting step (e) is conducted at an LHSV from about 5 hr^{-1} to about 15 hr^{-1} or from about 4 hr^{-1} to about 10 hr^{-1} .

[0039] Embodiment 11. The process of any one of the previous embodiments, wherein the decolorization catalyst comprises a noble metal, such as platinum, and MCM-41.

[0040] Embodiment 12. The process of any one of the previous embodiments, wherein the second cloud point is about 10°C to about 30°C less than the first cloud point.

EXAMPLES

[0041] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

Example 1

[0042] Example 1 was based on pilot plant data which simulated the operation of a ~30,000 barrel/day reactor with a total of 3 catalyst beds in series in the case of “without color control” operation. For the “color control” operation, a 4th bed can be added to the reactor as the “color control” bed.

[0043] A conventional NiMo/Al₂O₃ desulfurization catalyst was employed in each of the first three catalyst beds using the conditions summarized in Table 2. The same catalyst was employed in the 4th bed in each of the runs (Runs 6 to 10 in Table 2) with

- 14 -

color control operation. In each of the color control runs, the effluent from the third desulfurization bed was quenched by about 63°F (about 35°C) before entering the inlet of the color control bed. For these simulations, recycled hydrogen gas was used to quench the color control bed.

[0044] The feed used for the simulation in this Example had the properties listed in Table 1 below.

Table 1 : Feed		
Volumetric Flow Rate, BBD	BBL/D	30000
API Gravity		32.5
Total Sulfur	wt%	0.33
Total Nitrogen	ppm	212
Cetane Index D976-80		47.5
Cetane Index D4737		46.4
3+Ring Aromatics	vol%	2.63
Color	ASTM	2.6
Cloud Point	deg F	32
D86 IBP	deg F	346
D86 5%	deg F	394
D86 10%	deg F	446
D86 30%	deg F	524
D86 50%	deg F	554
D86 70%	deg F	591
D86 90%	deg F	636

[0045] The results of the simulation were provided in Table 2 and Figure 1, from which it can be seen that the use of color control bed produced diesel products with lower color ASTM values at the equivalent WABT (weight average bed temperature) for the main desulfurization catalyst beds (beds 1, 2 and 3). For example, without the color control bed, the WABT was limited to about 780°F (about 416°C) to meet the 2.0 ASTM color specification. However, using the color control bed, the WABT could be extended to above about 800°F (about 427°C), which can result in significantly longer cycle length.

Example 2

[0046] The same feed shown in Table 1 and the same reactor employed in Example 1 were used for the pilot plant simulations of Example 2. However, the

desulfurization catalyst in Bed-3 was replaced by an isomerization catalyst comprising a Pt-promoted ZSM-48/ Al_2O_3 catalyst that had a relatively high isomerization activity for converting normal paraffins to branched paraffins, such that a reduced cloud point of the diesel fuels resulted. The simulations were based on a cloud point reduction of about 32°F (about 18°C) between the feed and the diesel product.

[0047] The results are summarized in Table 3 and Figure 2. Again, the inclusion of the color control bed can produce lower color diesel and/or can prolong the cycle length by allowing operation of the main desulfurization catalysts and the isomerization catalyst at higher relative temperatures. The color control bed in this Example was the same as the isomerization catalyst in Bed-3.

Example 3

[0048] In this example, in the pilot plant simulations, the properties of the feed used in this Example are shown in Table 4. For the conditions without color control, the reactor had only one bed filled with the same isomerization catalyst as used in Example 2. For the color control conditions, the reactor had two catalyst beds, namely an isomerization bed and a color control bed, both filled with the same isomerization catalyst used in Example 2.

Table 4 : Feed Properties For Case 3 Simulations

API Gravity		35.4
Specific Gravity @ 60F		0.848
Total Sulfur	wt%	0.0002
Total Nitrogen	ppm	1.0
Cloud Point	deg F	16
Total Aromatic	vol%	17.46
3+Ring Aromatics	vol%	2.38
D86 IBP	deg F	451
D86 5%	deg F	457
D86 10%	deg F	463
D86 30%	deg F	503
D86 50%	deg F	554
D86 70%	deg F	612
D86 90%	deg F	677
D86 95%	deg F	689
D86 FBP	deg F	699

[0049] The results are summarized in Table 5 and Figure 3. Again, the results demonstrate that the inclusion of the color control concept can produce very low cloud point ULSD at relatively high temperature, with the ULSD still meeting the color specification. This approach also allowed the unit to achieve longer cycle length without encountering color issues.

[0050] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

- 17 -

Table 2 : Simulation Summary for the Case 1: Desulfurization only

Run #	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Color Control	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes
Inlet Pressure										
Bed-1	1125	1125	1125	1125	1125	1125	1125	1125	1125	1125
Bed-2	1115	1115	1115	1115	1115	1115	1115	1115	1115	1115
Bed-3	1105	1105	1105	1105	1105	1105	1105	1105	1105	1105
Bed-4	1105	1105	1105	1105	1105	1090	1090	1090	1090	1090
Catalyst Volume										
Bed-1 (HDS)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-2 (HDS)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-3 (HDS)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-4 (Color Control)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Make-Up Gas										
Flow Rate	653	548	439	354	304	410	441	502	581	650
H2 Purity	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00	85.00
Recycle Gas										
Flow Rate	2400	2400	2400	2400	2400	2400	2400	2400	2400	2400
H2 Purity	67.2	70.5	73.6	76.1	77.3	73.5	72.4	70.7	68.5	66.3
Temperature Profile										
Bed-1 Inlet	570	650	718	760	780	780	760	718	650	565
Bed-1 Outlet	628	697	752	788	807	797	782	749	701	627
Bed-2 Inlet	620	690	748	775	790	790	775	743	690	620
Bed-2 Outlet	648	709	760	788	800	793	780	753	709	649
Bed-3 Inlet	640	705	758	778	790	790	778	748	705	640
Bed-3 Outlet	668	719	766	787	798	792	781	754	717	668
WABT for bed-1, 2 and 3	635	700	753	782	797	791	778	747	700	635
Bed-4 Inlet						730	718	688	655	605
Bed-4 Outlet						758	743	709	669	612
Bed-4 Inlet Quench						62	63	66	62	63
Product Diesel										
Sulfur	6	9	6	8	9	8	7	7	6	7
3+Ring Aromatics	0.66	0.94	1.45	1.83	2.08	1.52	1.38	1.12	0.86	0.67
Color	0.77	1.07	1.59	1.95	2.17	1.66	1.53	1.26	0.99	0.78

Table 3 : Case 2 Cascaded Desulfurization/Isomerization Summary

Run #	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20
Color Control	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes
Inlet Pressure										
Bed-1	1125	1125	1125	1125	1125	1125	1125	1125	1125	1125
Bed-2	1115	1115	1115	1115	1115	1115	1115	1115	1115	1115
Bed-3	1105	1105	1105	1105	1105	1105	1105	1105	1105	1105
Bed-4						1090	1090	1090	1090	1090
Catalyst Volume										
Bed-1 (HDS)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-2 (HDS)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-3 (Isomerization)	2750	2750	2750	2750	2750	2750	2750	2750	2750	2750
Bed-4 (Color Control)						1000	1000	1000	1000	1000
Make-Up Gas										
Flow Rate	SCF/BBL	742	719	635	510	432	490	594	670	704
H2 Purity	%	85	85	85	85	85	85	85	85	85
Recycle Gas										
Flow Rate	SCF/BBL	2400	2400	2400	2400	2400	2400	2400	2400	2400
H2 Purity	%	63.3	63.9	66.8	70.5	73.8	70.6	67.1	64.4	64.0
Temperature Profile										
Bed-1 Inlet	deg F	600	645	680	720	765	720	680	645	600
Bed-1 Outlet	deg F	664	703	728	759	797	759	729	707	672
Bed-2 Inlet	deg F	660	695	720	750	785	750	720	695	660
Bed-2 Outlet	deg F	694	717	737	764	795	761	736	716	694
Bed-3 Inlet	deg F	690	710	730	760	790	760	730	710	690
Bed-3 Outlet	deg F	699	729	744	770	796	763	741	726	699
WABT for Bed-1,2, and 3	deg F	674	705	728	757	791	755	727	705	675
Bed-4 Inlet	deg F					750	720	690	670	650
Bed-4 Outlet	deg F					779	727	698	678	660
Bed-4 Inlet Quench	deg F					41	43	51	56	49
Product Diesel										
Sulfur	ppm	0.8	1.5	2.1	2.0	2.6	4.7	5.0	3.9	2.1
Cloud Point	deg F	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3+Ring Aromatics	vol%	0.72	0.93	1.19	1.61	2.15	1.51	1.17	0.95	0.72
Color	ASTM	0.84	1.06	1.34	1.75	2.23	1.65	1.32	1.09	0.84

Table 5 : Simulation Summary for Case 3

	Run 21	Run 22	Run 23	Run 24	Run 25	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
Color Control	No	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Pressure												
Bed-1 Inlet Pressure	700	700	700	700	700	700	700	700	700	700	700	700
Bed-2 Inlet Pressure							675	675	675	675	675	675
Catalyst Volume												
Bed-1 (Isomerization)	ft3											
Bed-2 (Color Control)	ft3	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Make-Up Gas												
Flow Rate	357.4	300.1	246.3	192.7	181.4	163.8	294.8	306.1	267.2	240.6	216.3	186.5
H2 Purity	92.7	92.7	92.7	92.7	92.7	92.7	92.7	92.7	92.7	92.7	92.7	92.7
Recycle Gas rate	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
Reactor Temperature Profile												
Bed-1 Inlet	580	630	680	720	760	790	580	630	680	720	760	790
Bed-1 Outlet	627	659	694	724	764	790	631	662	694	723	758	787
Bed-1 WABT	611	650	690	723	763	790	614	651	690	722	759	
Bed-2 Inlet							560	610	650	680	710	740
Bed-2 Outlet							561	613	655	687	717	745
Bed-2 Inlet Quench							71	52	44	43	48	47
Product Diesel												
Cloud Point	-38	-38	-38	-38	-38	-38	-38	-38	-38	-38	-38	-38
2+Ring Aromatics	0.59	0.85	1.38	2.00	2.59	2.85	0.62	0.81	1.14	1.50	1.90	2.28
Color	0.7	1.0	1.5	2.1	2.6	2.8	0.7	0.9	1.3	1.6	2.0	2.3

- 20 -

CLAIMS:

1. A process for producing a diesel and/or kerosene fuel of low color, the process comprising:

(a) supplying a middle distillate feed and hydrogen to a reactor having at least one first catalyst bed containing a first desulfurization and/or isomerization catalyst and at least one second catalyst bed downstream of the first catalyst bed(s) and containing a decolorization catalyst;

(b) reacting the feed with the hydrogen in the presence of the first catalyst in said at least one first catalyst bed at a temperature from about 290°C to about 430°C to produce a first liquid effluent;

(c) cooling the first liquid effluent by about 10°C to about 40°C with a quench medium;

(d) cascading the entire cooled first liquid effluent to said at least one second catalyst bed; and

(e) contacting the cooled first liquid effluent with hydrogen in the presence of said decolorization catalyst at a temperature of about 280°C to about 415°C to produce a second effluent having an ASTM color of less than 2.5.

2. The process of claim 1, wherein said reacting step (b) is conducted at a temperature from about 315°C to about 400°C.

3. The process of claim 1, wherein the hydrogen partial pressure in the reactor is between about 400 psig (about 2.8 MPag) and about 1500 psig (about 10.3 MPag).

4. The process of claim 1, wherein the first liquid effluent is cooled in step (c) by about 15°C to about 35°C.

5. The process of claim 1, wherein the quench medium is the second effluent and/or unreacted hydrogen gas from said contacting step (e).

- 21 -

6. The process of claim 1, wherein said contacting step (e) is conducted at a temperature from about 300°C to about 400°C.

7. The process of claim 1, wherein said second effluent has an ASTM color of less than 2.0.

8. The process of claim 1, wherein said second effluent contains less than 2 vol% of 3+ ring aromatic compounds.

9. The process of claim 1, wherein the process further comprises:
in step (a) the middle distillate feed contains at least 0.03 wt% sulfur;
in step (b) the first catalyst bed is operated at a temperature from about 315°C to about 430°C thereby producing the first liquid effluent comprising 15 wppm or less sulfur;

in step (c) the first liquid effluent is cooled by about 15°C to about 35°C with the quench medium; and

in step (e) the cooled first liquid effluent is contacted with hydrogen in the presence of said decolorization catalyst at a temperature from about 300°C to about 415°C to produce a second effluent having 15 wppm or less sulfur and having an ASTM color of less than 2.5.

10. The process of claim 9, wherein the desulfurization catalyst comprises nickel and molybdenum.

11. The process of claim 9, wherein the hydrogen partial pressure in the reactor is between about 400 psig (about 2.8 MPag) and about 1500 psig (about 10.3 MPag).

12. The process of claim 9, wherein said reacting step (b) is conducted at an LHSV from about 0.3 hr⁻¹ to about 1.5 hr⁻¹.

- 22 -

13. The process of claim 9, wherein the quench medium is the second effluent and/or unreacted hydrogen gas from said contacting step (e).

14. The process of claim 9, wherein said contacting step (e) is conducted at an LHSV from about 4 hr^{-1} to about 10 hr^{-1} .

15. The process of claim 9, wherein the decolorization catalyst comprises nickel and molybdenum.

16. The process of claim 9, wherein the reactor includes a plurality of first catalyst beds, and wherein at least one of said first catalyst beds comprises an isomerization catalyst.

17. The process of claim 16, wherein the isomerization catalyst is selected from the group consisting of zeolite beta, ZSM-23, ZSM-48, and mixtures thereof.

18. The process of claim 9, wherein said second effluent has an ASTM color of less than 2.0.

19. The process of claim 9, wherein said second effluent contains less than 2 vol% of 3+ ring aromatic compounds.

20. The process of claim 1, wherein the process further comprises:
in step (a) the middle distillate has a first cloud point;
in step (b) the first liquid effluent has a second cloud point that is at least 10°C less than that of the first cloud point;
in step (c) the first liquid effluent is cooled by about 10°C to about 20°C with the quench medium; and
in step (e) the second effluent is produced having a third cloud point that is at least 10°C less than that of the first cloud point and has an ASTM color of less than 2.5.

- 23 -

21. The process of claim 20, wherein the isomerization catalyst is selected from the group consisting of zeolite beta, ZSM-23, ZSM-48, and mixtures thereof.

22. The process of claim 20, wherein the hydrogen partial pressure in the reactor is between about 500 psig (about 3.4 MPag) and about 1300 psig (about 9.0 MPag).

23. The process of claim 20, wherein said reacting step (b) is conducted at an LHSV from about 1 hr⁻¹ to about 4 hr⁻¹.

24. The process of claim 20, wherein the quench medium is the second effluent and/or unreacted hydrogen gas from said contacting step (e).

25. The process of claim 20, wherein said contacting step (e) is conducted at an LHSV from about 5 hr⁻¹ to about 15 hr⁻¹.

26. The process of claim 20, wherein the decolorization catalyst comprises a noble metal and MCM-41.

27. The process of claim 26, wherein the noble metal comprises platinum.

28. The process of claim 20, wherein the second cloud point is about 10°C to about 30°C less than the first cloud point.