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(54) Process for hydrocracking and catalytic dewaxing.

(57) A method for selectively increasing production of jet fuel, distillate or heavy fuel oil in a fuels refinery involves combining hydrocracking and catalytic dewaxing.

PROCESS FOR HYDROCRACKING AND CATALYTIC DEWAXING

This invention relates to a hydrocarbon conversion process for the increased production of fuels in a refinery by combining hydrocracking and catalytic dewaxing steps, and more particularly, to a process to increase jet fuel, distillate or low pour heavy fuel oil yields.

The refining of petroleum crude oils to yield a variety of fuel products such as jet fuel, distillate and heavy fuel oil has been practiced for many years. Special uses for these products normally include a requirement that the freeze point or pour point may not exceed a certain maximum value. In some instances, it is necessary to subject these fuels to additional processing to reduce their pour points or their freeze points.

One such process is referred to as catalytic hydrodewaxing, in which gas oil is contacted with hydrogen and a shape-selective catalyst to selectively crack or hydrocrack the paraffinic molecules in the gas oil. Initially, the catalysts were those cracking zeolite catalysts which had pore openings that would admit and crack only normal paraffins and exclude all other gas oil components, for example, erionite-type zeolites. U.S. Patent Re. 28,398 describes an improvement to such a process by substituting a ZSM-5-type zeolite for the previously used erionite-type cracking zeolite catalysts. Using this addition, the normal paraffins and paraffins with slight branching, for example, those with a methyl side group, were also cracked so dewaxing was carried out to a greater extent. This permitted lowering of the gas oil pour point in a very efficient manner. The product of hydrodewaxing gas oil may be suitably fractionated to produce high yields of dewaxed gas oil boiling in the same range as the feed, some naphtha and some light (C_4^-)hydrocarbons.

Catalytic dewaxing with a ZSM-5-type zeolite may be employed to improve the quality of a variety of feedstocks. U.S. Patent Re. 28,398 describes in addition to gas oil other useful feedstocks including crude oil, full range dehydrated shale oil and lube oil stocks. U. S. Patents 3,893,906 and 3,894,939 teach that a mixture of gas oil and aromatic naphtha yield a lower pour point gas oil and a higher octane gasoline when subjected to such catalytic hydrodewaxing. U. S. Patent 3,989,617 describes an improved process for catalytically treating lubricating oil base stocks with ZSM-5-type zeolites. U. S. Patents 3,755,145, 3,852,189, 3,894,938 and 3,956,102 describe other improvements in this process when used alone or in combination with other processes.

One particularly effective combination process of catalytic cracking and catalytic dewaxing is described in U. S. Patent 3,891,540. That process is concerned with producing a light fuel oil with a low pour point, and involves catalytic cracking employing relatively mild conversion conditions. In the process, 45 volume percent of fresh gas oil and heavy cycle oil are cracked in one riser and intermediate cycle oil is cracked in a second riser. The light cycle oil recovered from the catalytic cracking fractionator is subjected to catalytic hydrodewaxing with a ZSM-5 type crystalline zeolite. The effluent from the hydrodewaxing reactor is condensed, the hydrogen recovered for recycle and the condensed effluent sent to the hydrodewaxing unit fractionator. Here the desired low pour point fuel oil is recovered as the bottoms with the tower overhead of about 400°F$^-$ hydrocarbons comprising C_4 and lighter gaseous products plus hydrocarbons in the gasoline boiling range. That combination process is practiced in two complete processing units: the catalytic cracker with all its usual attendant equipment including a fractionator, and a catalytic hydrodewaxer with its usual attendant equipment, including a fractionator. Thus, these units may be operated in combination or separately.

U. S. Patent 4,332,670 describes a process in which the fractionating and stripping equipment of a middle distillate catalytic dewaxing unit may be eliminated by integrating the catalytic dewaxing unit with a catalytic cracking unit.

U. S. Patent 4,283,271 describes another combination to upgrade lubricating oils comprising a combination process in which a hydrocarbon feed sequentially passes through a hydrocracking zone, a catalytic dewaxing zone, and a hydrotreating zone, all at high pressure. Hydrocracked product is separated from recycle hydrogen prior to dewaxing. U. S. Patents 4,347,121 and 4,325,805 describe other aspects of the combination process to produce lubricating oils by combining dewaxing and hydrocracking.

At present, non-hydrocracked heavy gas oil may be sold as fuel oil, sent to a coker to make gasoline, sent to a hydrocracker, sent to a fluid catalytic cracking unit or sent to thermofor catalytic cracking unit. If a heavy gas oil stream is hydrocracked, the resultant hydrocracked product may be unstable in the presence of air thus requiring some stabilization process such as hydrofinishing. Another disadvantage of hydrocracked heavy gas oil is that hydrocracking results in a high pour point hydrocracked product. Thus, if the hydrocracked product is distilled into its different cuts, the products tend to have high pour points thus reducing the amounts of useful products and reducing the selectivity to determine which products will be obtained.

The present invention is based on the observation that the selectivity of products from a heavy gas oil feedstock can be increased by combining hydrocracking and catalytic dewaxing. Hydrocracking is a process to convert a feedstock such as heavy fuel oil into naphtha, kerosene and distillate and remove heteroatoms such as oxygen, nitrogen or sulfur. In some hydrocracking operations, a heavy fuel oil product may be obtained if the hydrocracker effluent stream is not recycled to produce lighter products.

The Mobil distillate dewaxing (MDDW) process allows the refiner to improve specified product fluidity properties - (freeze point, pour point, cloud point and CFPP (cold filter plugging point)) of a jet fuel, distillate or heavy fuel oil. CFFP is a test procedure in which oil is put through filter paper and the temperature at which it plugs is measured. Usually, the CFFP temperature is between the cloud and pour points. In a typical application of the invention, a heavy gas oil feedstock is hydrocracked to yield a hydrocracked product which is distilled to produce a lighter boiling range stream and a relatively heavier boiling range stream. The lighter boiling range stream is the normal refinery product stream. By dewaxing the heavier boiling range stream, its fluid properties can be improved and its product value can be upgraded by blending it into the lower boiling point stream.

The process of the invention comprises selectively increasing the yield of a hydrocarbon product from a heavy gas oil hydrocarbon feedstock by:

hydrocracking the feedstock in a hydrocracking unit operating at a space velocity of about 0.25 to about 3 Liquid Hourly Space Velocity (LHSV), a temperature of about 500° to about 850°F (260° to 455°C), a hydrogen partial pressure of about 500 to about 3000 psig and a hydrogen feed rate of about 500 to about 20,000 SCF/bbl of the feedstock, thereby producing a hydrocracked product;

distilling the hydrocracked product to recover a first hydrocarbon stream having a selected range of boiling points, a naphtha stream, a jet fuel stream and a distillate stream; and

catalytically dewaxing the first stream at a space velocity of about 0.5 to about 10 LHSV, temperature of about 400° to about 850°F (205° to 455°C), hydrogen partial pressure of about 50 to about 2500 psig and hydrogen feed rate of about 500 to about 10,000 SCF/bbl of the first stream, thereby forming the product stream having a desired fluidity characteristic, such as freeze point, cloud point or pour point.

More particularly the process of this invention comprises the steps of:

hydrocracking a heavy gas oil hydrocarbon feedstock at a space velocity of about 0.5 to about 2 LHSV, a temperature of about 650° to about 800°F (343° to 427°C), a hydrogen partial pressure of about 1500 to about 2500 psig and a hydrogen feed rate of about 2000 to about 10,000 SCF/bbl of the feedstock, thereby producing a hydrocracked product;

distilling said hydrocracked product by atmospheric distillation to recover a heavy kerosene stream comprising about 450° to about 550°F b.p. (230° to 288°C) hydrocarbons and a jet fuel stream comprising about 380° to about 450°F b.p. (195° to 230°C) hydrocarbons and having a freeze point from about -40° to about -58°F (-40° to -50°C);

catalytically dewaxing the heavy kerosene stream with a catalyst comprising a zeolite having the structure of ZSM-5 and a nickel hydrogenation component at a space velocity of about 0.5 to about 5 LHSV, temperature of about 475° to about 800°F (246° to 427°C), hydrogen partial pressure of about 50 to about 1500 psig and hydrogen feed rate of about 500 to about 3000 SCF/bbl of the heavy kerosene stream, thereby forming a low freeze point heavy kerosene stream having a freeze point from about -40° to about -58°F (-40° to -50°C); and

blending the jet fuel and low freeze point heavy kerosene stream.

The process may employ any dewaxing catalyst, such as one comprising a large pore or medium pore zeolite. The most suitable catalyst is determined by feedstock characteristics and operating conditions. The process may be operated to selectively increase the yield of either jet fuel, distillate or heavy fuel oil. The process may catalytically dewax a feedstock, then hydrocrack, and subsequently distill the dewaxed feedstock to desired products. In addition, the process may include sequential hydrocracking, dewaxing, subsequent hydrocracking and distillation to produce the desired products. After dewaxing, the dewaxing effluent can be hydrotreated to remove sulfur and saturate aromatics and then blended with a normal product stream. For the purposes of this invention, the hydrocracking step may be distinguished from a hydrotreating step by the amount of hydrogen consumed. The hydrocracking step typically consuming about 1000 to about 2000 SCF/bbl, while the hydrotreating step consumes only about 100 to about 200 SCF/bbl.

In addition to selectively increasing the yields of jet fuel, distillate or heavy fuel oil, the process also increases the production of high octane MDDW gasoline by-product, increases the production of C_3/C_4 olefinic by-product streams from MDDW for possible use in alkylation or petrochemical processes, and increases the BTU/gallon content in both the jet fuel and distillate fuels which may increase product value. An advantage of the process in which catalytic dewaxing precedes hydrocracking is that it may allow use of a smaller hydrocracking unit. The advantage of the process in which hydrocracking precedes catalytic dewaxing is that the hydrocracking reduces the levels of nitrogen in the feedstock so the feedstock is relatively easy to dewax, and thus results in very long dewaxing cycles.

Fig. 1 is a schematic diagram of a process of the invention to selectively increase jet fuel yield;

Fig. 2 is a schematic diagram of a process of the invention to selectively increase distillate yield;

Fig. 3 is a schematic diagram of a process to selectively increase heavy fuel oil yield;

Fig. 4 is a schematic diagram of a process in which catalytic dewaxing precedes hydrocracking; and

Fig. 5 is a schematic diagram of a process of the invention with two-stage hydrocracking and catalytic dewaxing between the hydrocracking stages.

Referring to the drawings, Fig. 1 shows a hydrocracking/catalytic dewaxing flow scheme arrangement for selectively producing jet fuel. A heavy gas oil stream passes through conduit 10 to a hydrocracking unit 20 to produce a hydrocracked product 22. Typically, the heavy gas oil comes from a vacuum distillation tower (not shown). The hydrocracking unit 20 operates at a space velocity of 0.25 to 3 Liquid Hourly Space Velocity (LHSV), a temperature of about 500° to about 850°F (260° to 455°C), a hydrogen partial pressure of about 500 to about 3000 psig and a hydrogen feed rate of about 500 to about 20,000 SCF/bbl of the heavy gas oil feedstock in conduit 10. Liquid Hourly Space Velocity is a measure of unit volume per hour of reactant per unit volume of catalyst in a reactor. Preferably, the hydrocracking unit 20 operates at a space velocity of about 0.5 to about 2 LHSV, a temperature of about 650° to about 800°F (343° to 427°C), a hydrogen partial pressure of about 1500 to about 2500 psig and a hydrogen feed rate of about 2000 to about 10,000 SCF/bbl of the heavy gas oil feedstock in conduit 10.

The hydrocracked product 22 is distilled by a distillation unit 30 to produce a naphtha stream 32, a jet fuel stream 34, a heavy kerosene stream 36, a distillate stream 38 and a heavy fuel oil stream 39. The distillation unit 30 is preferably an atmospheric distillation unit. The boiling point of the hydrocracked jet fuel is cut by unit 30 to meet a desired fluidity characteristic, namely the refinery jet fuel freeze point specification. In addition, the boiling point of a virgin jet fuel stream 72 may also be cut by a fractionator (not shown) to meet the refinery jet fuel freeze point specification. Boiling points are related to freeze point, in that for a given stream the higher boiling point components have higher freeze points than the lower boiling point components. Cut points can be adjusted by adjusting distillation parameters, such as the temperature or pressure at which distillation unit 40 operates, or by adjusting other distillation parameters, as known in the art.

For jet fuel, the desired fluidity characteristic comprises a freeze point from about -40° to about -58°F (-40° to -50°C). Typically, the jet fuel stream 34 and virgin jet fuel stream 72 are cut to comprise hydrocarbons with a boiling point (b.p.) range from about 380° to about 450°F (195° to 230°C). The naphtha stream typically comprises hydrocarbons boiling from about 120° to about 380°F (50° to 195°C). Lighter components (120°F$^-$) may be in naphtha stream 32, or preferably form a light product stream (not shown) from the distillation unit 30. The heavy kerosene stream 36 and a virgin heavy kerosene stream 74 have boiling points adjacent that of the jet fuel streams 34, 72. Preferably, boiling points of the heavy kerosene streams 36, 74 are between about 450° to about 550°F (230° to 288°C). The actual cut point of the heavy kerosene streams 36, 74 is determined to be a cut point where the next jet fuel specification, such as distillation boiling points, or specific gravity become limiting.

The distillate stream 38, produced by distillation unit 30, preferably has hydrocarbons with a boiling point ranging from about 550° to about 650°F (288° to 345°C). The heavy fuel oil stream 39, produced by distillation unit 30, preferably comprises hydrocarbons having a boiling point range of 650°F$^+$ (345°C). However, actual cut points of the distillate stream 38 are determined to meet the desired fluidity characteristics of pour point or cloud point specifications required by the refinery, as discussed below. Boiling points are related to pour point or cloud point, in that for a given stream the higher boiling point components have higher pour points or cloud points than the lower boiling point components. Cut points may be adjusted by adjusting distillation parameters, as outlined above. In addition, a portion of the heavy fuel oil stream 39 may be recycled through conduit 24 to the hydrocracking unit 20. Conduit 24 and conduit 10 are attached so the recycled heavy fuel oil may combine with the heavy gas oil prior to feeding into the hydrocracking unit 20.

Both heavy kerosene streams 36, 74 may be combined and then catalytically dewaxed by catalytic dewaxing unit 50 to lower their freeze point and produce low freeze heavy kerosene stream 54. It is desired that the freeze point of stream 54 range between about -40° to about - -58°F (-40° to -50°C). The dewaxing unit 50 operates at a space velocity of about 0.5 to about 10 LHSV, a temperature of about 400° to about 850°F (205° to 455°C), a hydrogen partial pressure of about 500 to about 2500 psig and a hydrogen feed rate of about 500 to about 10,000 SCF/bbl of liquid feed, namely streams 36, 74 in this embodiment. Preferably, the dewaxing unit 50 operates at a space velocity of about 0.5 to about 5 LHSV, a temperature of about 475° to about 800°F (246° to 427°C), a hydrogen partial pressure of about 50 to about 1500 psig and a hydrogen feed rate of about 500 to about 3000 SCF/bbl of liquid feed, namely streams 36, 74 in this embodiment.

After dewaxing the hydrotreated jet fuel stream 34, the low freeze heavy kerosene stream 54 and the virgin jet fuel stream 72 may be hydrotreated (not shown) to remove sulfur and saturate aromatics and then be blended into the refinery jet fuel pool stream 70. Also, the low freeze point heavy kerosene stream 54 may pass into a separation means (not shown) to form a high octane MDDW gasoline by-product stream, comprising C_5 to 380°F b.p. hydrocarbons, a C_3/C_4 olefinic by-product stream, and a heavier hydrocarbon stream comprising 380° to 550°F b.p. hydrocarbons. These heavier hydrocarbons may be blended into the jet fuel pool 70. A pool generally consists of storage facilities for intermediate or final products.

The advantages of the embodiment of Fig. 1 include increased production of jet fuel having a low freeze point. However, there are also other advantages. The catalytic dewaxing unit 50, using shape selective catalysts, such as a ZSM-5 type zeolite-containing catalyst, cracks the waxy components particularly the n-paraffins into lighter products, such as paraffins, olefins and aromatics, which remain in the jet fuel boiling range. These lighter products also include C_3/C_4 olefinic streams which may be used in alkylation or petrochemical processes. These light olefins may be recovered from the low pour heavy distillate stream 52 by separation means (not shown), such as flash drums or a distillation unit. In addition, higher BTU/gallon content may result because the low freeze heavy kerosene stream 54 is heavier and has more BTU's/lb and is denser than the hydrocracked jet fuel stream 34, yet it meets the freeze point specifications.

Fig. 2 illustrates a process of the invention for selectively increasing distillate yields in a manner similar to the embodiment of Fig. 1 which increases jet fuel yields. As shown by Fig. 2, heavy gas oil passes through a conduit 10 to a hydrocracking unit 20 operating at the conditions outlined for the embodiment of Fig. 1, to produce a hydrocracked product stream 22. The hydro-cracked product stream 22 is separated by a distillation unit 40 to form a naphtha stream 42, a jet fuel stream 44, a distillate stream 46, a heavy distillate stream 48, and a heavy fuel oil stream 49. Unit 40 preferably operates as an atmospheric distillation unit. A portion of the heavy fuel oil stream 49 may recycle through conduit 24 to the hydrocracking unit 20.

In the embodiment of Fig. 2, the naphtha stream 42 comprises hydrocarbons with a boiling point (b.p.) ranging from about 120° to about 380°F (50° to 195°C), while lighter components (120°$^-$F) may be contained in the naphtha stream 42 or form a separate light product stream (not shown) from the distillation unit 40. The jet fuel stream 44 is optional and comprises hydrocarbons having a boiling point ranging from about 380° to about 450°F (195° to 230°C). The distillate stream 46 comprises hydrocarbons ranging from about 450° to about 650°F (230° to 345°C). If the jet fuel stream 44 is not produced, the distillate stream 46 preferably comprises about 380° to about 650°F b.p. hydrocarbons (195° to 345°C). A virgin distillate stream 64 may also be cut by a fractionator (not shown) to meet pour point (cloud point) specifications and comprise hydrocarbons boiling from about 450° to about 650°F (230° to 345°C), or preferably about 380° to about 650°F b.p. (195° to 345°C). However, the virgin and hydrocracked distillate streams 64, 46 are both cut to suitable boiling points by the fractionator (not shown) and unit 40, respectively, to meet the refinery's desired specifications for pour point and cloud point. Boiling points are related to pour point or cloud point, in that for a given stream the higher boiling point components have higher pour points or cloud points than the lower boiling point components. Cut points may be adjusted by adjusting distillation parameters, as outlined above. The desired fluidity specifications of pour point range from about -10° to about 25°F (-23° to -4°C), while the desired cloud point ranges from about 0° to about 35°F (-17° to 2°C). The heavy fuel oil stream 49 comprises hydrocarbons with a boiling range of about 750°F$^+$ (418°C).

A hydrocracked heavy distillate stream 48 is also produced by distillation unit 40 and a virgin heavy distillate stream 62 is produced to meet distillation specifications by a fractionator (not shown). These streams 48, 62 have boiling point ranges adjacent that of the distillate streams 46, 64 and are distilled to a cut point where the next distillate specification becomes limiting, such as boiling point or specific gravity, preferably the streams 48, 62 comprise about 650° to about 750°F b.p. (345° to 418°C) hydrocarbons. Both heavy distillate streams 48, 62 are then combined and catalytically dewaxed by catalytic dewaxing unit 80, at conditions disclosed above, to form a low pour point heavy distillate stream 52. Preferably, stream 52 has a desired fluidity specification, namely a pour point ranging from about -10° to about 25°F (-23° to -4°C) and a cloud point ranging from about 0° to about 35°F (-17° to 2°C). After dewaxing, stream 52 may be hydrotreated (not shown) to remove sulfur and to saturate aromatics, and then blended with virgin distillate stream 64 and hydrotreated distillate stream 46 into the refinery distillate pool 82. A pool generally consists of storage facilities for intermediate or final products.

Fig. 3 shows another embodiment of the invention in which yields of heavy fuel oil having a low pour point are increased. The heavy gas oil passes through a conduit 10 into a hydrocracking unit 20 to produce a hydrocracked product 22. The unit 20 operates as above. The hydrocracked product stream 22 is separated by distillation unit 60 into a naphtha stream 92, a jet fuel stream 94, a distillate stream 96 and a heavy fuel oil stream 98. Unit 60 is preferably an atmospheric distillation apparatus. A portion of the heavy fuel oil stream 98 may be recycled through recycle conduit 24 to the hydrocracking unit 20. The naphtha stream 92 comprises hydrocarbons with a boiling point ranging from 120° to about 380°F (50° to 195°C). The jet fuel stream 94 is optional and comprises hydrocarbons ranging from about 380° to about 450°F b.p. (195° to 230°C). The distillate stream 96 comprises hydrocarbons ranging from about 450° to about 650°F (230° to 345°C). If the jet fuel stream 94 is not included, the distillate stream 96 comprises about 380° to about 650°F (195° to 345°C). The heavy fuel oil stream comprises hydrocarbons with a boiling point ranging from about 650°F$^+$ (345°C$^+$).

The heavy fuel oil stream 98 is catalytically dewaxed by catalytic dewaxing unit 90 to produce a dewaxed heavy fuel oil stream 56. The catalytic dewaxing unit 90 operates at the dewaxing conditions outlined above. The dewaxed heavy fuel oil stream 56 has a desired fluidity specification, namely a pour point less than 100°F, and preferably ranging from about -10° to about 70°F. The desired pour point is determined by intended use of the product and the season during which the product is used. For example, lower pour points are more necessary in winter than in summer. The third embodiment is particularly useful to produce a specialty low pour point (less than 100°F) heavy fuel oil. In certain countries (e.g., Japan and Austria), there is a demand for a domestic low pour point heavy fuel oil which has no distillation end point specification. Part or all of the hydrocracked heavy fuel oil stream 22 can be dewaxed to produce this specialty product. Generally, a virgin heavy fuel oil of the same boiling range would be difficult to dewax and would result in a very short dewaxing operating cycle. The hydrocracked heavy fuel oil 22, however, because of its low levels of nitrogen, is a relatively easy stock to dewax and can result in very long dewaxing cycles.

Fig. 4 illustrates a scheme in which dewaxing of a heavy gas oil is followed by hydrocracking. In Fig. 4, heavy gas oil passes through a conduit 10, which is attached to a catalytic dewaxing unit 110, to produce a dewaxed heavy gas oil stream 112. Stream 112 is then dewaxed by a post-dewaxing hydrocracking unit 120 to produce a hydrocracked product stream 122. Both the catalytic dewaxing unit 110 and the post-dewaxing hydrocracking unit 120 operate at the conditions outlined for the hydrocracking unit 20 above.

The hydrocracked product stream 122 passes into a distillation unit 130 where it is separated to form a naphtha stream 132, a jet fuel stream 134, a distillate stream 136 and a heavy fuel oil stream 138. This produces a high yield of low freeze jet fuel and low pour point distillate. Preferably, the naphtha stream will include hydrocarbons having boiling points (b.p.) ranging from about 120° to about 380°F (50°to 195°C), jet fuel ranging from about 380° to about 450°F (195° to 230°C), distillate ranging from about 450° to about 650°F (230° to 345°C), and heavy fuel oil ranging from about 650°F$^+$ (345°C$^+$). Also, preferably the jet fuel stream 134 will have a freeze point ranging from about -40° to about -58°F (-40° to -50°C) and the distillate stream 136 and heavy fuel oil stream 138 will have pour points ranging from about -10° to about 25°F (-23° to -4°C). However, the cut points and required product specifications may be changed to accommodate refinery customers. Cut points may be adjusted by adjusting distillation parameters, as outlined above. For example, the distillate b.p. range may be extended during the winter to accommodate increased demand for distillate fuels. Other product specifications, such as pour point or freeze point, may be adjusted by adjusting cut point of the product or adjusting operating conditions, such as temperature or pressure, in the catalytic dewaxing unit or hydrocracking unit.

Another embodiment of the invention is shown by Fig. 5, which adds a pre-dewaxing hydrocracking unit 100 to the embodiment of Fig. 4. Unit 100 operates in the same range of conditions outlined above for the hydrocracking unit 20. Heavy gas oil is fed through a conduit 10 to the pre-dewaxing hydrocracking unit 100 to increase cycle length above that obtainable by the apparatus for the method of Fig. 4. The pre-dewaxing unit 100 produces a pre-dewaxing hydrocrackate which passes through conduit 102 to the catalytic dewaxing unit 110. Dewaxing by the pre-dewaxing hydrocracking unit 100 removes the paraffins from the catalytic dewaxing effluent stream 112, which otherwise feed the post-dewaxing hydrocracking unit 120. The hydrocracking units 100, 120 and dewaxing unit 110 operate at conditions as described above. Removal of the paraffins from pre-dewaxing hydrocrackate stream 102 may result in improved post-dewaxing hydrocracking catalyst performance because paraffins are the most difficult molecules to hydrocrack. After post-dewaxing hydrocracking unit 120, a high yield of low freeze point jet fuel and low pour point distillate will result because the wax molecules have been removed. MDDW catalyst performance is also enhanced because many of the catalyst poisons have been removed by the pre-dewaxing hydrocracking unit 100.

All of the above embodiments have the advantage of selectively increasing yields of jet fuel, distillate or heavy fuel oil. The system of Fig. 1 allows increased production of jet fuel and the system of Fig. 2 allows increased production of distillate fuel. The systems of Figs. 1 and 2 allow higher BTU/gallon content in the jet fuel and distillate fuels respectively, thus resulting in higher value products. There are higher BTU's/gallon in the jet fuel or distillate fuels, because the catalytic dewaxing allows denser hydrocarbons to be blended into the jet fuel or distillate fuel respectively. The hydrocracking unit also enhances the operation of the catalytic dewaxing unit because hydrocracking removes materials, such as nitrogen, which are poisonous to catalytic dewaxing catalysts.

The system of Fig. 3 allows for enhanced production of a heavy fuel oil having a low pour point. Generally, a virgin heavy fuel oil of the same boiling range would be difficult to dewax and would result in a very short dewaxing operating cycle. The hydrocracked heavy fuel oil, however, because of its low levels of nitrogen is a relatively easy stock to dewax and can result in very long dewaxing cycles. Additionally, the embodiments of Figs. 1-3 can result in production of high octane MDDW gasoline and C_3/C_4 olefinic streams as by-products of the catalytic dewaxing unit.

The systems of Figs. 4 and 5 allow for the use of smaller hydrocracker reactors, possible reduction of hydrogen consumption in hydrocracking, production of high octane MDDW gasoline and C_3/C_4 streams from MDDW, higher BTU/gallon content in both the jet fuel and distillate streams and increased yields of low freeze/pour point jet fuel and distillate. The system of Fig. 4 allows for a simple processing scheme requiring relatively few unit operations, while the system of Fig. 5 allows for longer cycle-lengths than from the system of Fig. 4 because materials which are poisonous to dewaxing catalysts are removed by the pre-dewaxing hydrocracking unit.

Although the hydrocracking catalysts per se individually are not regarded as part of this invention, it is noted that a wide variety of hydrocracking catalysts are suitable for use in the process of the invention. Such catalysts in general possess an acid function and a hydrogenation function, exemplified by a porous acidic oxide, such as a silica alumina or silica zirconia, associated with a nickel-tungsten or palladium or platinum, or cobalt-moly or nickel-moly component. In general, a Group VIII metal or a combination of a Group VI and a Group VIII metal, as the oxides or sulfides thereof, deposited on silica alumina or silica or zirconia, may serve as hydrocracking catalyst.

The process is effective for improving the dewaxing performance of intermediate pore or large pore zeolites, which are described below, because the hydrocracking of the invention removes nitrogen compounds which are believed to inhibit the dewaxing activity of most dewaxing catalysts.

The catalysts employed in the dewaxing units described above may be the same type or different. However, they will possess shape-selective paraffin cracking ability. Catalysts that have shape-selective qualities include crystalline zeolites and crystalline silica alumina phosphates - (SAPO). These materials may be bound in a variety of matrices, such as those containing silica alumina or silica and alumina alone. The catalysts may contain up to 15% metals that are known to possess a hydrogenation ability. The preferred hydrogenation components are the noble metals of Group VIII, especially platinum and palladium, but other noble metals, such as iridium, ruthenium or rhodium, may also be used. Combinations of noble metals with non-noble metals, such as nickel, rhenium, tungsten, chromium and molybdenum are of interest. Combinations of Group VIB and Group VIII are also of interest. Base metal hydrogenation components may also be used especially nickel, cobalt, molybdenum, tungsten, copper or zinc.

The metal may be incorporated into the catalyst by any suitable method, such as impregnation or exchange onto the zeolite. The metal may be incorporated in the form of a cationic, anionic or a neutral complex, such as $Pt(NH_3)_4^{2+}$, and cationic complexes of this type will be found convenient for exchanging metals onto a zeolite. Anionic complexes are also useful for impregnating metals into the zeolites.

The zeolites useful for dewaxing are termed medium or intermediate pore zeolites and are characterized by an effective pore size of generally less than about 7 Angstroms, and/or pore windows in a crystal formed by 10-membered rings. The medium or intermediate pore zeolites are represented by those zeolites having the structure of ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and TMA (tetra methyl ammonium) Offretite.

By "intermediate pore size zeolite", as used herein, is meant zeolites having the unique characteristic of being able to differentiate between large molecules and molecules containing quaternary carbon atoms on the one hand, and smaller molecules on the other hand. Thus, the intermediate pore size materials have surprising catalytic selectivities by reason of their effective pore apertures, as well as highly desirable and surprising catalytic activity and stability, when compared to most of the larger pore size crystalline zeolites.

By "intermediate pore size", as used herein, is meant an effective pore aperture probably in the range of about 5 to 6.5 Angstroms when the zeolite is in the H-form. Zeolites having pore apertures in this range tend to have unique zeolite characteristics and to be particularly useful in dewaxing. Unlike small pore size zeolites, such as erionite and chabazite, they will allow hydrocarbons having some branching into the zeolite void spaces. Unlike larger pore size zeolites, such as the faujasites, they can differentiate between n-alkalines and slightly branched alkanes having, for example, quaternary carbon atoms.

The effective pore size of zeolites can be measured using standard adsorption techniques and compounds of known minimum kinetic diameters. The preferred effective pore size range is from about 5.3 to 6.2 Angstroms. See Breck, Zeolite Molecular Sieves, 1974 (especially Chapter 8) and Anderson et al, J. Catalysis 58, 114 (1979), both of which are incorporated by reference.

Intermediate pore size zeolites in the H-form will typically admit molecules having kinetic diameters of 5.0 to 6.5 Angstroms with little hindrance. Examples of such compounds (and their kinetic diameters in Angstroms) are: n-hexane (4.3), 3 methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds having kinetic diameters of about 6 to 6.5 Angstroms can be admitted into the pores, depending on the particular zeolite, but do not penetrate as quickly and, in some cases, are effectively excluded. Compounds having kinetic diameters in the range of 6 to 6.5 Angstroms include: cyclohexane (6.0), 2,3 dimethylbutane (6.1), m-xylene (6.1), and 1,2,3,4 tetramethylbenzene (6.4). Generally compounds having kinetic diameters of greater than about 6.5 Angstroms do not penetrate the pore apertures, and thus are not absorbed into the interior of the zeolite lattice. Examples of such larger compounds include: hexamethylbenzene (7.1), 1,3,5-trimethyl-benzene (7.5), and tributylamine (8.1).

In performing adsorption measurements to determine effective pore size, standard techniques are used. It is convenient to consider a particular molecule as excluded if it does not fill at least 80% of the zeolite pore volume in less than about one hour (p/po = 0.5; 25°C).

The acid activity of zeolite catalysts is conveniently defined by the alpha scale described in an article published in Journal of Catalysis, Vol. VI, 278-287 (1966). In this text, the zeolite catalyst is contacted with hexane under conditions prescribed in the publication, and the amount of hexane which is cracked is measured. From this measurement is computed an "alpha" value, which characterizes the catalyst for its cracking activity for hexane. The entire article above referred to is incorporated herein by reference. The alpha scale so described will be used herein to define activity levels for cracking n-hexane. And, in particular, for purposes of this invention, a catalyst with an alpha value of not greater than about 1.0, and preferably not greater than about 0.5, will be considered to have substantially no activity for cracking hexane.

Another class of zeolites useful for hydrodewaxing are termed large pore zeolites and have a pore size larger than the medium pore zeolites and sufficiently large to admit the vast majority of components normally found in a feedstock. These zeolites generally are stated to have a pore size in excess of 7.5 Angstroms and/or formed by 12-membered rings. The large pore zeolites are represented by ZSM-4, ZSM-12, ZSM-20, Zeolie Beta, Mordenite, TEA (tetra ethyl ammonium) Mordenite, Dealuminized Y, and Rare Earth Y. Additionally, the large pore component may include a low sodium Ultrastable Y molecular sieve (USY). Generally, with the exception of Zeolite Beta, the large pore zeolites have less hydrodewaxing effectiveness than the intermediate pore zeolites.

ZSM-4 is described in U. S. Patent 3,923,639. ZSM-5 is described in U. S. Patents 3,702,886 and Re. 29,948. ZSM-11 is described in U. S. Patent 3,709,976. ZSM-12 is described in U. S. Patent 3,832,449. ZSM-20 is described in U. S. Patent 3,972,983. ZSM-23 is described in U. S. Patent 4,076,842. ZSM-35 is described in U. S. Patent 4,016,245. ZSM-38 is described in U. S. Patent 4,046,859. ZSM-48 is described in U. S. Patent 4,397,827. Zeolite Beta is described in U. S. Patents 3,308,069 and Re. 28,341. USY is described in U. S. Patents 3,293,192 and 3,449,070.

The catalysts preferred for use herein include crystalline alumina silicate zeolites having a silica-to-alumina ratio of at least 12, a Constraint Index of about 0.5 to 12 and acid cracking activity of about 160-200. A suitable shape selective catalyst for a fixed bed reactor is an HZSM-5 zeolite with alumina binder in the form of cylindrical extrudates of about 1-5 millimeters. HZSM-5 is a ZSM-5 type catalyst with only hydrogen on the active catalyst sites and no metals on these sites. Other catalysts which may be used in one or more reactor stages include siliceous materials with pore size in the range of 5 to 9 Angstroms. These include borosilicates, ferrosilicates and/or aluminosilicates, disclosed in U. S. Patent Nos. 4,414,143 and 4,417,088.

The following Examples illustrate the invention.

Example 1

Example 1 demonstrates the operability of a configuration as in Fig. 3 in which a hydrocracked heavy hydrocarbon stream is catalytically dewaxed. The properties of the feed are listed in Table 1 and the feed represents stream 98, as in Fig. 3. The dewaxing unit feed is taken from a moderate pressure (about 800 psig hydrogen partial pressure) hydrocracker product and comprises hydrocarbons having a boiling point from about 650° to about 1050°F. The hydrocarbons were dewaxed over a fresh, steamed, 1/16 inch Ni-ZSM-5 catalyst containing about 1% nickel. A test reactor was employed to represent catalytic dewaxing unit 90 of Fig. 3 and contained about 50 cubic centimeters of catalyst sample. The test reactor had an inside diameter of 7/8 inch and a 3/16 inch thermal well at its center and was operated isothermally. The dewaxing reactor operated for 20 days at a hydrogen partial pressure of 400 psig, a space velocity of 1.5 LHSV, a hydrogen treat rate of 2000 SCF H_2/bbl of feed and a start-of-cycle temperature of 500°F and a line out temperature of 550°F. The line out temperature is the temperature at which catalysts can be run without substantial aging, for example, less than 5°F per month. It is expected that a commercial unit for dewaxing of effluent from a moderate pressure hydrocracker would achieve an end-of-cycle temperature of 800°F after two years operation to produce a 20°F pour point product.

Table 2 shows the product yields from the dewaxing reactor. The dewaxed product is representative of stream 56 of Fig. 3. Over 90% of the hydrocracked feed was converted to 330°F+ boiling point (b.p.) hydrocarbon product, hydrocarbons in the naphtha/gasoline boiling range of C_6-330°F b.p. and lighter hydrocarbons comprising C_5^-. Table 1 lists the product properties of the gasoline range products and the 330°F$^+$ b.p. products.

Table 3 shows the product properties of the 330°F$^+$ b.p. product stream which has been separated into a 330° to 725°F b.p. distillate stream and a 725° to 1050°F b.p. dewaxed heavy fuel oil stream. The results shown by Tables 1-3 indicate a heavy fuel oil product having a low pour point can be produced by hydrocracking a stream prior to dewaxing.

Table 1

	Hydrocracked Feed	Product	
	$650°F^+$ b.p.	C_6-330°F b.p.	$330°F^+$ b.p.
API°	31.3	70	30
KV at 40°C (cs)	40.2	--	29.4
Pour Point (°F)	95	--	20
N (wppm)	10	--	15
S (wppm)	40	20	20
Octane, Research Clear	--	68	--
Octane, Motor	--	58	--
Distillation Type	D-1160-1	D-86	D-1160-1
Distillation Pressure	1 mm Hg	1 ATM	1 mm Hg
IBP, °F	655	120	497
10	760	130	712
50	879	170	844
90	1017	265	992
End Point	1062	315	1053
Paraffins (wt%)	36.2	60	--
Olefins	--	29	--
Naphthenes	37.2	8	--
Aromatics	26.6	3	--

Table 2

Yields	
C_5 - (wt %)	7.2
C_6 - 330°F b.p.	1.6
$330°F^+$ b.p.	91.2

Table 3

Product, b.p. °F	330 - 725	725 - 1050
Volume %	23.3	76.7
API°	30.6	29.7
KV at 40°C (cs)	9	45
Pour Point, °F	- 42	29
Cetane	49	--

Example 2

Example 2 demonstrates the results of dewaxing a virgin heavy gas oil having the properties listed in Table 4. The virgin feed had boiling points comparable to those of the hydrocracked feed of Example 1. The dewaxing was conducted in the same isothermal test reactor as in Example 1, having an inside diameter of 7/8 inch and a 3/16 inch thermal well at its center. The test reactor contained 50 cc of catalyst. The catalyst was the same type as in Example 1, namely, fresh, steamed, 1/16 inch Ni-ZSM-5 catalyst containing about 1 wt % nickel. Dewaxing occurred at a hydrogen partial pressure of 400 psig, a space velocity of 1 LHSV, a hydrogen feed rate of 2000 SCF H_2/bbl feedstock, a start-of-cycle temperature of 500°F and end-of-run temperature of 760°F. This test ran for 41 days to make a 20°F pour point product. Although the test was ended at 760°F, it is estimated that the test could have been run to an end-of-cycle temperature of 800°F after two months total operation.

Table 4 lists the product properties for the naphtha/gasoline range components containing C_6-330°F boiling point (b.p.) hydrocarbons and a heavier hydrocarbon stream containing 330°F$^+$ b.p. hydrocarbons. The distillation data shown for the C_6-330°F b.p. gasoline product consists of estimated values. Table 4 shows that although a 20°F pour point heavier hydrocarbon product can be produced by dewaxing of a heavy hydrocarbon stream alone, this causes a high catalyst aging rate which results in only a two month cycle time. Comparing the results of Example 1 and Example 2 shows that hydrocracking a feed prior to dewaxing reduces aging rates. Thus, hydrocracking a heavy hydrocarbon feedstock prior to dewaxing results in a cycle time estimated to be two years, as opposed to dewaxing without prior hydrocracking, which results in a cycle time estimated to be two months.

Table 4

	Virgin Feed	Product	
	650°F$^+$ b.p.	C$_6$-330°F b.p.	330°F$^+$ b.p.
API°	21.8	65	19.1
KV at 40°C, cs	40.1*	--	70.1
Pour Point, °F	100	--	20
N, wppm	1480	--	1400
S, wt %	0.38	460 wppm	0.66
Octane, Research Clear	--	85	--
Distillation Type	D-1160	D - 86	D-1160
Distillation Pressure	10 mm Hg	1 ATM	10 mm Hg
IBP, °F	348	120	372
10	637	130	604
30	770	--	752
50	807	170	799
70	836	--	832
90	886	265	877
End Point	942	315	--
Paraffins, wt %	20.8	--	--
Olefins	--	--	--
Naphthenes	36.6	--	--
Aromatics	42.6	--	--

* At 130°F

Claims

1. A process for selectively increasing the yield of a hydrocarbon product from a heavy gas oil hydrocarbon feedstock comprising the steps of:

hydrocracking the feedstock in a hydrocracking unit operating at a space velocity of about 0.25 to about 3 LHSV, a temperature of about 500° to about 850°F, a hydrogen partial pressure of about 500 to about 3000 psig and a hydrogen feed rate of about 500 to about 20,000 SCF/bbl of said feedstock, thereby producing a hydrocracked product;

distilling the hydrocracked product to recover a first hydrocarbon stream having a selected range of boiling points, a naphtha stream and a distillate stream; and

catalytically dewaxing the first hydrocarbon stream at a space velocity of about 0.5 to about 10 LHSV, temperature of about 400 to about 850°F, hydrogen partial pressure of about 50 to about 2500 psig and hydrogen feed rate of about 500 to about 10,000 SCF/bbl of the first stream, thereby forming a product stream having a desired fluidity specification.

2. A process according to Claim 1, wherein hydrocracking is carried out at a space velocity of about 0.5 to about 2 LHSV, a temperature of about 650° to about 800°F, a hydrogen partial pressure of about 1500 to about 2500 psig, and a hydrogen feed rate of about 2000 to about 10,000 SCF/bbl of said feedstock, thereby producing a hydrocracked product; and catalytic dewaxing is carried out at a space velocity of about 0.5 to about 5 LHSV, a temperature of about 475° to about 800°F, hydrogen partial pressure of about 500 to about 3000 SCF/bbl of said first stream, thereby forming said product stream having said desired fluidity specification.

3. A process according to Claim 1 or Claim 2, wherein the distilling step produces a second hydrocarbon stream having the desired specification of the product stream.

4. A process according to Claim 3, wherein the first hydrocarbon stream comprises a heavy kerosene comprising about 450° to about 550°F b.p. hydrocarbons, the second hydrocarbon stream comprises a jet fuel, and the product stream comprises a low freeze point heavy kerosene.

5. A process according to Claim 4, wherein the desired

fluidity specification comprises a freeze point from about --40° to about -58°F.

6. A process according to Claim 5, wherein the distilling step produces a heavy fuel oil stream comprising about 650^{+}°F b.p. hydrocarbons and a portion of the heavy fuel oil is combined with the feedstock and recycled to the hydrocracking step.

7. A process according to Claim 3, wherein the distillate stream comprises about 380° to about 650°F b.p. hydrocarbons, the first hydrocarbon stream comprises a hydrocracked heavy distillate comprising about 650° to about 750°F b.p. hydrocarbons, the second hydrocarbon stream comprises the distillate stream, and the product stream comprises a heavy distillate.

8. A process according to Claim 7, wherein the desired fluidity specification comprises a pour point from about -10° to about 25°F.

9. A process according to Claim 8, wherein the distilling step produces a heavy fuel oil comprising about 750°F^{+} hydrocarbons and a portion of the heavy fuel oil is combined with the feedstock and recycled to the hydrocracking step.

FIG. 1

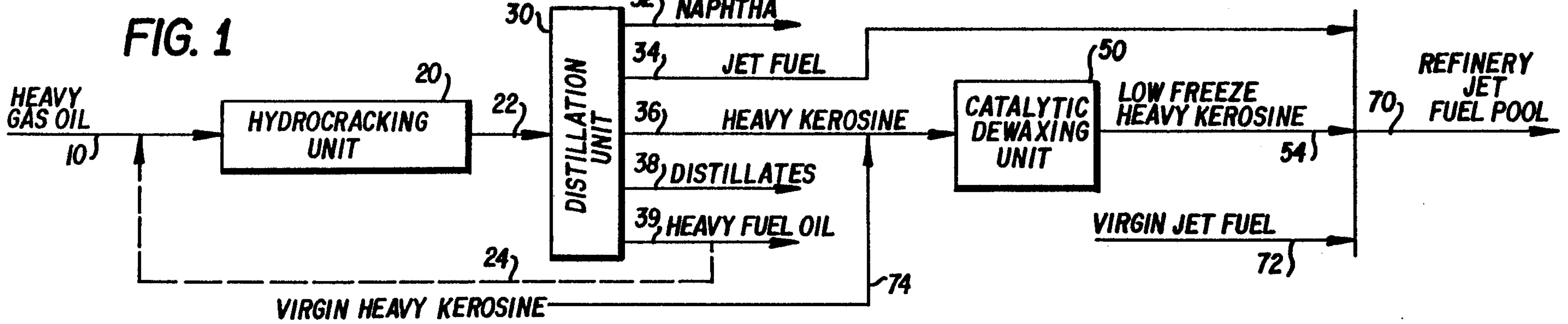


FIG. 2

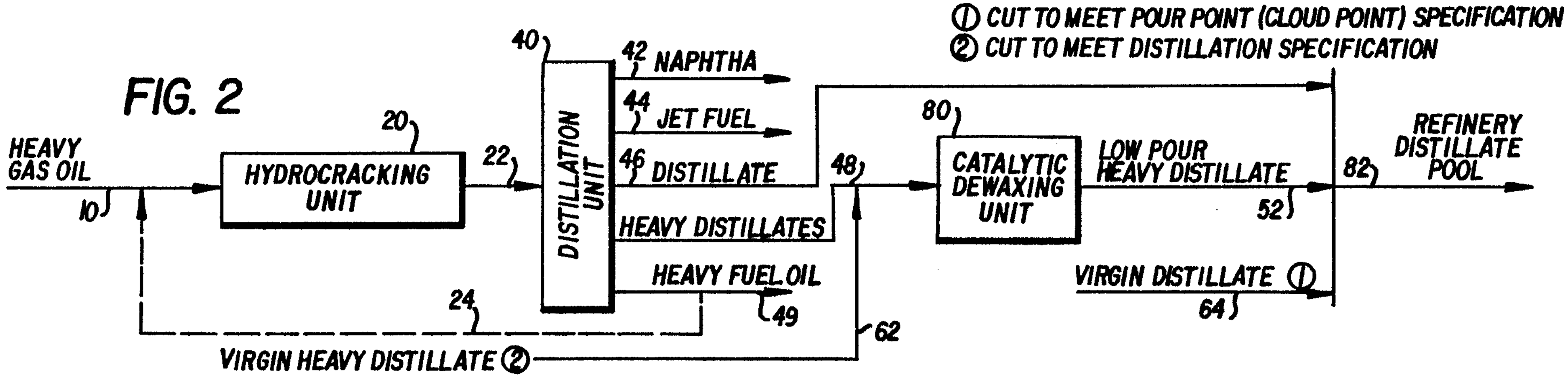


FIG. 5

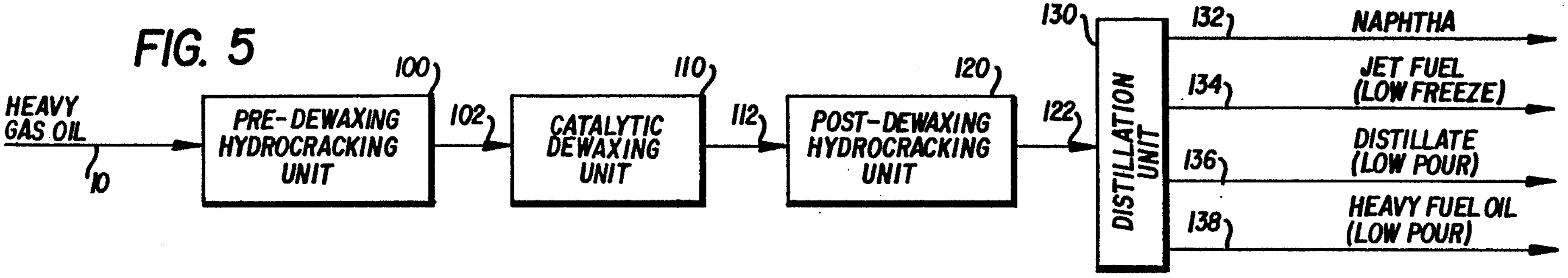
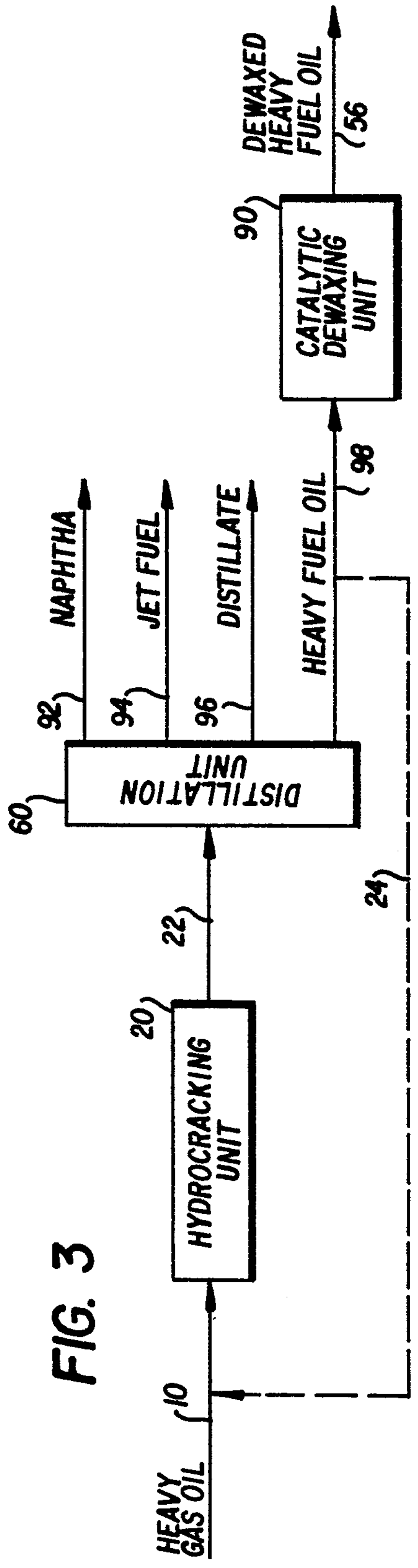


FIG. 3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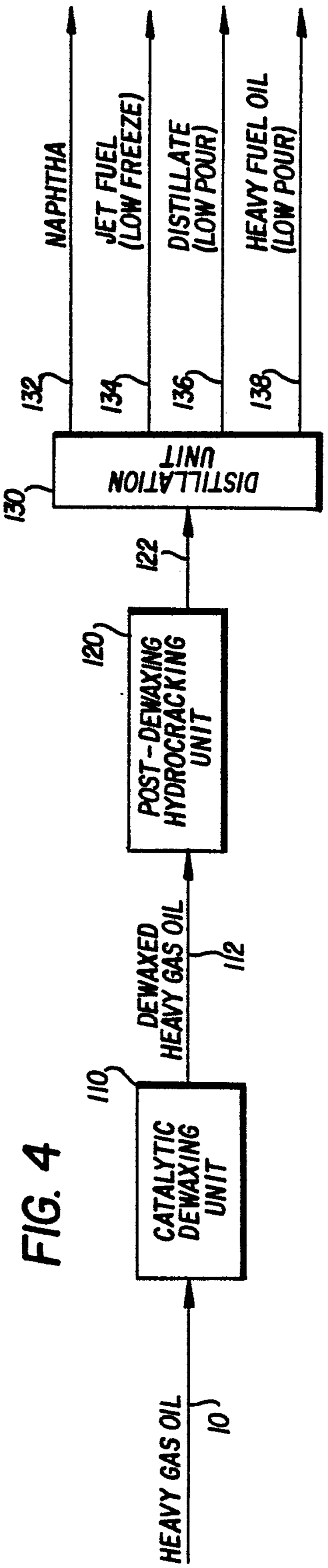
10
HYDROCRACKING UNIT
20
22
DISTILLATION UNIT
60
24
92
NAPHTHA
94
JET FUEL
96
DISTILLATE
HEAVY FUEL OIL
98
CATALYTIC DEWAXING UNIT
90
56
DEWAXED HEAVY FUEL OIL

FIG. 4


HEAVY GAS OIL
10
CATALYTIC DEWAXING UNIT
110
DEWAXED HEAVY GAS OIL
112
POST-DEWAXING HYDROCRACKING UNIT
120
122
DISTILLATION UNIT
130
132
NAPHTHA
134
JET FUEL (LOW FREEZE)
136
DISTILLATE (LOW POUR)
138
HEAVY FUEL OIL (LOW POUR)

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 85308595.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US - A - 4 257 872 (LA PIERRE et al.) * Claims; column 2, line 63 - column 7, line 27 * --	1,2	C 10 G 47/16
A	US - A - 4 283 271 (GARWOOD et al.) * Claims; column 3, line 20 - column 5, line 25 * --	1,2	
A	US - A - 4 210 521 (GORRING et al.) * Claims; column 2, line 65 - column 7, line 54 * --	1,2	
A	EP - A1 - 0 094 827 (MOBIL OIL CORPORATION) * Claims; page 4 - page 14, line 21 * --	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP - A1 - 0 062 985 (MOBIL OIL CORPORATION) * Claims; page 2, line 3 - page 14, line 3 * ----	1,2	C 10 G 47/00 C 10 G 49/00 C 10 G 65/00
	The present search report has been drawn up for all claims		

Place of search	Date of completion of the search	Examiner
VIENNA	14-04-1986	STÖCKLMAYER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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