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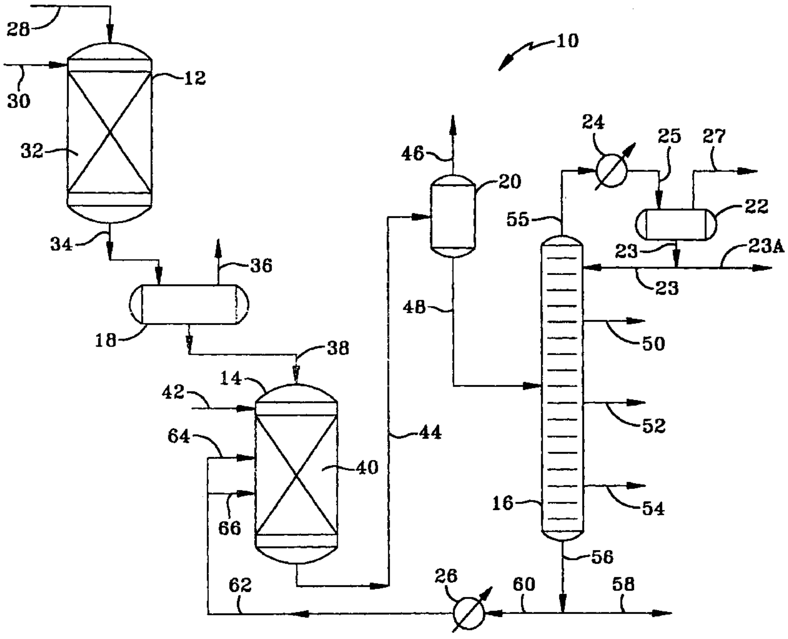
# (54) Title: QUENCHING DEWAXING REACTOR WITH HEAVY DEWAXATE RECYCLE



(57) Abstract: During catalytic dewaxing of paraffinic hydrocarbons, the exothermic catalytic dewaxing reaction is moderated by separating and cooling a heavy dewaxate having an initial boiling point of at least 800 °F+, and recycling it back into the dewaxing zone as quench liquid. The heavy dewaxate reacts very little, if at all, with the hydrogen in the dewaxing zone. This has been found to be particularly useful for dewaxing hydroisomerized, paraffinic Fischer-Tropsch synthesized, hydrocarbons.

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# QUENCHING DEWAXING REACTOR WITH HEAVY DEWAXATE RECYCLE

## BACKGROUND OF THE DISCLOSURE

### Field of the Invention

The invention relates to a process for quenching a dewaxing reactor with recycled heavy dewaxate. More particularly the invention relates to catalytically dewaxing a highly paraffinic, Fischer-Tropsch synthesized waxy hydrocarbon fraction, wherein the temperature of the exothermic dewaxing reaction is controlled by recycle of heavy dewaxate back into the reactor, as quench liquid.

### Background of the Invention

It has recently been found that premium, high quality fuels, solvents and lubricating oils can be produced from Fischer-Tropsch wax and hydrotreated slack wax. Fischer-Tropsch wax is a term used to describe waxy hydrocarbons produced by a Fischer-Tropsch hydrocarbon synthesis process, in which a synthesis gas feed comprising a mixture of $H_2$ and CO reacts in the presence of a Fischer-Tropsch catalyst, under conditions effective to form hydrocarbons. Typical processes for producing these high quality products from the wax include two or more of fractionation, hydroisomerization and dewaxing, particularly catalytic dewaxing. Sometimes hydrotreating is necessary before hydroisomerization, particularly with petroleum derived slack waxes. For example, U.S. patent 4,963,672 discloses a process for converting waxy Fischer-Tropsch hydrocarbons to a lubricant base stock having a high VI and a low pour point by sequentially hydrotreating, hydroisomerizing, and solvent dewaxing. European patent publication EP 0 668 342 A1 suggests a process for producing lubricating base oils by hydrogenating and then hydroisomerizing a waxy Fischer-Tropsch raffinate, followed by dewaxing. The hydrogenation is performed without cracking, to lower the hydroisomerization temperature and increase the catalyst life, both of which those skilled in the art know are adversely affected by the presence of oxygenates and heteroatoms in the waxy feed.

## SUMMARY OF THE INVENTION

The invention relates to catalytically dewaxing a waxy hydrocarbon feed (hereinafter “waxy feed”), wherein the temperature of the exothermic dewaxing reaction is controlled by recycling heavy dewaxate back into the reactor, as quench liquid. The waxy feed is catalytically dewaxed by reacting it with hydrogen in the presence of a dewaxing catalyst at elevated temperature and pressure. By waxy is meant including hydrocarbons that solidify at standard conditions of room temperature and pressure of 75$^{O}$F and 1 atm. The heavy dewaxate is that fraction of the dewaxed waxy feed having an initial boiling point in the range of from about 800 to 950$^{O}$F and preferably at least 850$^{O}$F (850$^{O}$F+). At least a portion of this heavy dewaxate is separated from the total dewaxate and cooled to a temperature sufficient to control the temperature in the catalytic dewaxing zone, but not lower than its cloud point. It has been found that the recycled heavy dewaxate reacts very little, if at all, with the hydrogen in the dewaxing zone and therefore does not contribute a significant amount of heat to the exothermic dewaxing reaction. The waxy feed will contain at least 15, preferably at least 25 and more preferably at least 35 wt. % of hydrocarbons having an initial boiling point of about 800 to 950$^{O}$F and preferably at least 850$^{O}$F. At least 50 wt. % and preferably at least 90 wt. % of the waxy feed fed into the dewaxing reactor will have an initial boiling point in the range of from 650-750$^{O}$F (a 650-750$^{O}$F+ fraction), with an end boiling point of at least 1050$^{O}$F and preferably greater than 1050$^{O}$F. A preferred waxy feed comprises highly paraffinic, Fischer-Tropsch synthesized hydrocarbons that have been hydroisomerized. Other, less preferred waxy hydrocarbons, such as those derived from slack wax and hydrocrackates, are treated by extraction and/or catalytic hydrorefining to remove non-paraffinic hydrocarbons such as aromatics and other unsaturates, along with heteroatom compounds, to form a waxy feed. The waxy feed resulting from these treatments is typically fed into the dewaxer, without an intervening hydroisomerization stage. The dewaxate is fractionated to separate and cool at least a portion of the heavy dewaxate for recycle as quench liquid, along with useful lubes and fuels product fractions.

Thus the invention relates to a catalytic dewaxing process which comprises contacting a waxy, paraffinic hydrocarbon feed with hydrogen, in the presence of a dewaxing catalyst in a catalytic dewaxing zone, at conditions of elevated temperature and pressure effective for the hydrogen to react with said feed and produce a dewaxate of reduced pour point, which includes a heavy fraction, separating and cooling at least a portion of said heavy fraction, and passing it back into said dewaxing zone as a quench liquid for temperature control. More specifically, the invention comprises a catalytic dewaxing process in which a waxy feed, comprising hydrocarbons having an initial boiling point in the range of 650-750$^{O}$F, and which includes an 800$^{O}$F+ fraction, reacts with hydrogen in the presence of a dewaxing catalyst in a dewaxing zone at elevated temperature and pressure, to produce a dewaxate of reduced pour point which contains an 800$^{O}$F+ fraction, followed by separating at least a portion of the 800$^{O}$F+ fraction from the dewaxate and cooling to a temperature above its cloud point and below the dewaxing temperature, and recycling the cool dewaxate back into the dewaxing zone as quench fluid, to reduce the temperature in the dewaxing zone. In a preferred embodiment, the invention relates to a process for dewaxing Fischer-Tropsch synthesized waxy hydrocarbons by hydroisomerizing the hydrocarbons to form a hydroisomerate comprising a waxy feed containing an 800$^{O}$F+ fraction, catalytically dewaxing the feed to form a dewaxate of reduced pour point, separating at least a portion of a heavy, 800°F+ fraction from the dewaxate, cooling at least a portion of the heavy fraction and passing it back into the dewaxing zone as quench fluid. In a more detailed embodiment, the invention comprises an integrated process for synthesizing a waxy, paraffinic hydrocarbon fraction from a synthesis gas comprising a mixture of $H_2$ and CO, hydroisomerizing said waxy fraction to form a hydroisomerate and catalytically dewaxing said hydroisomerate in a dewaxing zone, to form a dewaxate of reduced pour point which contains a heavy dewaxate fraction, a portion of which is cooled and used as quench liquid in said dewaxing zone, said process comprising:

(a) reacting said mixture of $H_2$ and CO in the presence of a Fischer-Tropsch hydrocarbon synthesis catalyst containing a catalytic cobalt component, at reaction conditions effective to form high purity, paraffinic, waxy hydrocarbons, at least a portion of which are liquid at said reaction conditions;

(b) passing said waxy hydrocarbons it into a hydroisomerization reaction zone;

(c) reacting said waxy hydrocarbons with hydrogen in the presence of a dual functional hydroisomerization catalyst in said hydroisomerization reaction zone to form a hydroisomerate comprising hydrocarbons having an initial boiling point in the range of 650-750°F and an end boiling point of at least 1050°F;

(d) catalytically dewaxing said hydroisomerate in a catalytic dewaxing zone to reduce its pour point, by reacting it with hydrogen at elevated temperature and pressure, in the presence of a catalyst comprising a Group VIII catalytic metal component and a crystalline aluminosilicate component, to form a dewaxate comprising hydrocarbons having an initial boiling point above and below said 650-750$^{O}$F range, which includes heavy hydrocarbons having an initial boiling point in the range of 800-950$^{O}$F;

(e) separating at least a portion of said heavy hydrocarbon dewaxate from the rest of said dewaxate;

(f) cooling at least a portion of said separated heavy hydrocarbon dewaxate to a temperature below that in said catalytic dewaxing zone, and

(g) passing said cool dewaxate back into said dewaxing reaction zone as quench liquid.

In a preferred embodiment, the Fischer-Tropsch process is a slurry hydrocarbon synthesis process in which the $H_2$ and CO react in a slurry comprising a hydrocarbon slurry liquid, gas bubbles and a particulate hydrocarbon synthesis catalyst and the slurry liquid comprises synthesized hydrocarbons that are liquid at the reaction conditions. The slurry liquid is withdrawn from the Fischer-Tropsch hydrocarbon synthesis reactor and passed into the hydroisomerization reaction zone in step (b).

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow diagram of a dewaxing process useful in the practice of the invention.

Figure 2 is a schematic flow diagram of a slurry Fischer-Tropsch hydrocarbon synthesis process which includes a dewaxing process according to the practice of the invention.

## DETAILED DESCRIPTION

Hydroisomerization and other hydroconversion processes convert some of the 650-750$^{O}$F+ hydrocarbons to hydrocarbons boiling below the 650-750$^{O}$F range (650-750$^{O}$F-). While this lower boiling material may remain in the hydroconvertate (e.g., the hydroisomerate), it is preferred to remove it prior to dewaxing to minimize the size of the dewaxing reactor and the amount of dewaxing catalyst needed. Removal of the lower boiling components may be achieved, for example, by rough flashing and/or fractionation prior to the dewaxing. The choice is determined by the practitioner. The lower boiling components may be used for fuels. The dewaxate is separated into various desired fractions, as set forth above, and typically includes, in addition to the 850$^{O}$F+ fraction, more than one lubricant base stock (fraction). By lubricant base stock is meant all or a portion of the 650-750$^{O}$F+ dewaxate produced by the process of the invention. As those skilled in the art know, a lubricant base stock is an oil possessing lubricating qualities boiling in the general lubricating oil range and is useful for preparing various lubricants such as lubricating oils and greases.

The dewaxing is conducted to convert no more than 40 wt. % and preferably limited to no more than 30 wt. % of the 650-750$^{O}$F+ hydroisomerate to 650-750$^{O}$F- material. The extent of conversion will depend on the dewaxing catalyst, as well as the feed to the dewaxer. In contrast to the process disclosed in U.S. patent 4,963,672 referred to above, due to the very low or nil concentration of nitrogen and sulfur compounds and the very low oxygenates level in Fischer-Tropsch produced waxy hydrocarbons, hydrogenation or hydrotreating for heteroatom removal, aromatics and other unsaturates is not normally required prior to hydroisomerization to form the waxy feed. Further, the only heteroatom compounds present in any quantity in Fischer-Tropsch synthesized hydrocarbons comprise oxygenates. These oxygenates are present primarily and mostly in the 400$^{O}$F- hydrocarbons, which are easily separated from the heavier hydrocarbons. If the waxy, 650-750$^{O}$F+ Fischer-Tropsch hydrocarbons contain less than, e.g., 5 wt. % of the 400$^{O}$F- hydrocarbons, hydrotreating is not typically required prior to hydroisomerization to form the waxy feed. Such is not the case for a petroleum derived slack wax, which may contain appreciable quantities of heteroatom compounds, particularly those containing sulfur and nitrogen, as well as aromatics and other unsaturates. Typical hydrotreating catalysts include the well known hydrotreating catalysts such as Co/Mo or Ni/Mo on alumina. Other hydrotreating catalysts include combinations of Co and/or Ni and Mo and/or W on a silica/alumina base. Such catalysts are typically sulfided. The hydrotreated hydrocarbons are stripped to remove $H_2S$, water, nitrogen and other catalyst deactivating species, prior to dewaxing. Typical conditions for hydrotreating slack wax and hydrocrackate hydrocarbons to form a waxy feed for dewaxing include temperatures in the range of from about 450 to 800$^{O}$F, a hydrogen pressure between about 400 and 2500 psia, a space velocity between about 0.5 and 3 V/V/Hr (volume of feed/volume of catalyst per hour), and a hydrogen gas rate of between about 500 to 5000 scf/b.

The waxy feed preferably comprises the entire 650-750$^{O}$F+ fraction of either (i) a hydrotreated slack wax or hydrocrackate from which heteroatom compounds, aromatics and other unsaturates have been removed and, preferably hydroisomerized prior to dewaxing and (ii) hydroisomerized waxy hydrocarbons formed by a hydrocarbon synthesis process, with the initial cut point between 650$^{O}$F and 750$^{O}$F being determined by the practitioner and the exact end point preferably above 1050$^{O}$F, determined by the feed, catalyst and process variables used for the synthesis. The waxy feed may also contain lower boiling material (650-750$^{O}$F-), if desired. While this lower boiling material is not useful for a lubricant base stock, when processed according to the process of the invention it is useful for fuels. The waxy feed also comprises more than 90 % and typically more than 95 % paraffinic hydrocarbons and this is what is meant by "paraffinic" in the context of the invention. Most of the hydrocarbons in Fischer-Tropsch wax are normal paraffins. Waxy feeds derived by hydroisomerizing a Fischer-Tropsch waxy fraction have negligible amounts of sulfur and nitrogen compounds (e.g., less than 1 wppm). Fischer-Tropsch waxy feeds having these properties and useful in the process of the invention have been derived from the waxy fraction made from a slurry Fischer-Tropsch process, with a catalyst having a catalytic cobalt component. In the practice of the invention, it is preferred that a slurry Fischer-Tropsch hydrocarbon synthesis process be used for synthesizing the waxy feed and particularly one employing a Fischer-Tropsch catalyst comprising a catalytic cobalt component, to provide a high alpha for producing the more desirable higher molecular weight paraffins.

The practice of the invention is not limited to the use of any particular dewaxing catalyst, but may be practiced with any dewaxing catalyst which will reduce the pour point of the waxy feed, and preferably a catalyst which produces a reasonable yield of the desired dewaxate fractions. Such catalysts comprise at least one metal catalytic component and an acidic, refractory metal oxide component. The catalytic metal component may comprise one or more compounds or metals of Group VIII of the periodic table of the elements and preferably at least one noble metal component, such as, but not limited to, platinum. The Groups referred to herein refer to Groups as found in the Sargent-Welch Periodic Table of the Elements copyrighted in 1968 by the Sargent-Welch Scientific Company. The refractory metal oxide component preferably comprises at least one crystalline aluminosilicate and preferably at least one zeolite. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as being useful for dewaxing Fischer-Tropsch and slack waxes and include, for example, mordenite, ZSM-5, ferrierite, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or TON, and the silicoaluminophosphates known as SAPO's

(5,135,638). The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from about 400-600$^{O}$F, a pressure of 500-2500 psig, $H_2$ treat rate of 1000-5000 SCF/B for flow-through reactors and LHSV of 0.1-10, preferably 0.2-2.0. The dewaxing is typically conducted to convert no more than 40 wt. % and preferably no more than 30 wt. % of the 650-750$^{O}$F+ hydroisomerate to lower boiling material.

A dewaxing catalyst comprising a catalytic platinum component and a component comprising the hydrogen form of mordenite (Pt/H-mordenite) is preferred, particularly for dewaxing a Fischer-Tropsch derived waxy feed. This is because it has been found that not all dewaxing catalysts and conditions are equivalent, when used to dewax these very pure and highly paraffinic hydroisomerates, due to cracking reactions which occur during the dewaxing. These cracking reactions produce lower boiling material. For example, US patent 3,539,498 discloses that by using 0.5 wt. % platinum on H-mordenite for dewaxing a light lube oil distillate feed (600-700$^{O}$F) down to a pour point of -10$^{O}$F, the product yield was only 68 volume %. US patent 4,057,488 discloses a 65.5 volume % yield, by using platinum on H-mordenite, to dewax a de-nitrogenated raffinate boiling between 740-950$^{O}$F. It has been surprisingly and unexpectedly found that by using Pt/H-mordenite to dewax a hydroisomerized Fischer-Tropsch waxy feed boiling in the lube oil range (e.g., 650-750$^{O}$F+), these high conversion levels to lower boiling hydrocarbons do not occur. When a noble metal is used, the noble metal loading, based on the combined weight of the mordenite and noble metal, will range from about 0.1-1.0 wt. % and preferably from 0.3-0.7 wt. %, with the noble metal preferably comprising Pt. Another noble metal Pd, may be used, in combination with the Pt. It has been found that a combination of a Pt/H-mordenite dewaxing catalyst with a hydroisomerized waxy feed derived from a slurry Fischer-Tropsch process employing a catalyst comprising a cobalt catalytic component, resulted in a lower pour point at a given conversion level, than the same catalyst with a waxy raffinate derived from a petroleum oil. This is unexpected.

During hydroisomerization of the waxy hydrocarbons to obtain the waxy feed, conversion of the 650-750$^{O}$F+ hydrocarbons to 650-750$^{O}$F- hydrocarbons, may range from about 20-80 wt. %, preferably 30-70 % and more preferably from about 30- 60 %, based on a once-through pass of the feed through the reaction zone. The waxy feed may contain minor amounts of 650-750$^{O}$F- material prior to the hydroconversion and at least a portion of this lower boiling material will also be converted into even lower boiling components. Typical hydroisomerization reaction conditions include a temperature and pressure typically ranging from 300-900$^{O}$F and 0-2500 psig, with preferred ranges of 550-750$^{O}$F and 300-1200 psig, respectively. Hydrogen treat rates are 500-5000 SCF/B, with a preferred range of 2000-4000 SCF/B. The hydroisomerization catalyst comprises one or more Group VIII catalytic metal components, and preferably one or more non-noble metals, such as Co, Ni and Fe, which will typically also include a Group VIB metal (e.g., Mo or W) oxide promoter, supported on an acidic metal oxide support to give the catalyst both a hydrogenation function for hydroisomerizing the hydrocarbons and an acid hydrocracking function. The catalyst may also have a Group IB metal, such as copper, as a hydrogenolysis suppressant. The cracking and hydrogenating activity of the catalyst is determined by its specific composition, as is known. In a preferred embodiment the catalytically active metal comprises cobalt and molybdenum. The acidic oxide support or carrier may include silica, alumina, silica-alumina, silica-alumina-phosphates, titania, zirconia, vanadia, and other Group II, IV, V or VI oxides, as well as Y sieves, such as ultra stable Y sieves. Preferred supports include silica, alumina and silica-alumina and, more preferably silica-alumina in which the silica concentration in the bulk support (as opposed to surface silica) is less than about 50 wt. %, preferably less than 35 wt. % and more preferably 15-30 wt. %. As is known, if the support is alumina, small amounts of fluorine or chlorine may be incorporated into it to increase the acid functionality. The surface area of the support will be in the range of from about 180-400 $m^2/g$, preferably 230-350 $m^2/g$, with a respective pore volume, bulk density and side crushing strength in the ranges of 0.3 to 1.0 mL/g and preferably 0.35-0.75 mL/g; 0.5-1.0 g/mL, and 0.8-3.5 kg/mm. A particularly preferred hydroisomerization catalyst comprises cobalt, molybdenum and optionally, copper, on an amorphous silica-alumina support containing about 20-30 wt. % silica. The preparation of these catalysts is well known and documented. Illustrative, but non-limiting examples of such catalysts, their preparation and use may be found, for example, in U.S. patents 5,370,788 and 5,378,348.

A hydroisomerization catalyst that is particularly preferred in the practice of the invention comprises both cobalt and molybdenum catalytic components supported on an amorphous, low silica alumina-silica support, and most preferably one in which the cobalt component is deposited on the support and calcined before the molybdenum component is added. This catalyst will contain from 10-20 wt. % $MoO_3$ and 2-5 wt. % CoO on an amorphous alumina-silica support in which the silica content ranges from 20-30 wt. % of the support. This catalyst has been found to have good selectivity retention and resistance to deactivation by oxygenates found in Fischer-Tropsch produced waxy feeds. The addition of a copper component suppresses hydrogenolysis. The preparation of this catalyst is disclosed in, for example, U.S. patents 5,757, 920 and 5,750,819, the disclosures of which are incorporated herein by reference.

Referring to Figure 1, there is shown a simple schematic flow diagram of a dewaxing unit 10 and process useful in the practice of the invention. Thus, there is shown a hydroconversion reactor 12, a catalytic dewaxing reactor 14 and a vacuum distillation tower 16. Associated with these are three flash drums 18, 20 and 22, and two heat exchangers 24 and 26. A waxy, paraffinic hydrocarbon fraction is fed, via line 28, into a hydroconversion reactor 12. The waxy fraction has an initial boiling point in the 650-750°F range and continuously boils up to an end boiling point greater than 1050°F. Reactor 12 may be a hydrogenator, a hydrotreater or a hydroisomerizer. In the hydroconversion reactor, the downflowing waxy feed reacts with downflowing hydrogen entering the reactor via line 30, in the presence of a suitable catalyst in a fixed catalyst bed 32. For the sake of illustration, the waxy fraction will be that produced by a slurry Fischer-Tropsch hydrocarbon synthesis process and reactor 12 a hydroisomerizing unit. The hydroisomerization catalyst in reactor 12 comprises 10-20 wt. % $MoO_3$ and 2-5 wt. % CoO on an amorphous alumina-silica support component in which the silica content ranges from 10-30 wt %. The reaction conditions include a temperature and a hydrogen pressure of 713°F and 725 psig. During the hydroisomerization, about 40 wt. % of the feed is converted to a lighter hydrocarbon fraction boiling below the initial boiling point of the waxy fraction, with the remaining 60 wt. % comprising the heavier, hydroisomerized feed for the dewaxing operation. The hydroisomerized hydrocarbons are removed from the bottom of the reactor via line 34 and pass into a simple separation drum 18, in which the lighter hydrocarbon are removed as vapor overhead, via line 36. This separation may also include a fractionation column (not shown) for the separated liquid, before it passes into the downstream dewaxing unit. The heavier, waxy feed is withdrawn from drum 18 as liquid and passed, via line 38, into catalytic dewaxing reactor 14. Reactor 14 contains a fixed bed 40 of dewaxing catalyst comprising 0.5 wt. % Pt on H-mordenite. Hydrogen or a hydrogen containing treat gas is passed into the reactor via line 42. The dewaxing conditions in the reactor include a temperature of about 550°F and hydrogen pressure of about 725 psig. The waxy feed reacts with the hydrogen in the presence of the dewaxing catalyst, which reduces its pour point and converts some of the feed to lower boiling material. About 20 volume % of the waxy feed is converted to lower boiling material during the dewaxing. The dewaxed hydrocarbons are removed from the dewaxing reactor via line 44 and passed into a flash evaporator 20, which operates at a lower pressure than the dewaxing reactor. The flash evaporator is also a simple drum type of separator. The lighter material is removed as vapor overhead, via line 46. The remaining 650-750°F+ dewaxate is removed via line 48 and passed into distillation tower 16, in which it is fractionated into the desired number of lubricant and fuels fractions, as shown. The vapor overheads are passed, via line 55, through a heat exchanger 24, in which a portion of the hydrocarbon vapors are condensed and the resulting liquid and vapor mixture passed, via line 25, into separation drum 22. The vapor and liquid separate, with the vapor removed overhead, via line 27, and the condensate returned, via line 23, back into the top of the tower as reflux. A portion of the overhead liquid (23A) is withdrawn as a light product stream. Which can be used as a light lubricant basestock or a fuel. Less than 10 vol. % of the feed passed into the distillation tower via line 48 is converted into a light vacuum gas oil fraction, suitable for use in diesel fuel. This is withdrawn from the tower via line 50. About 25 vol. % is withdrawn, via line 52, as an automatic transmission fluid basestock. About 50 vol. % of the dewaxed distillate is withdrawn via line 54, as a lubricant fraction useful as a basestock for passenger car motor oils (crankcase motor oil). The remaining 25 vol. % is a heavy lubricant basestock fraction, which is removed from the bottom of the tower, via line 56. This has an initial boiling point in the range of 800-850°F and an end point of about 1142°F. About 75 vol. % of this heavy dewaxate is passed, via line 58, to further processing into a heavy lubricant for industrial oil applications and/or heavy engine oils. The remaining 25 vol. % is passed, via line 60, into and through heat exchanger 26, in which it is cooled to a temperature of below 550°F, and then via lines 62, 64 and 66 into reactor 14 as quench fluid. As is demonstrated in the example below, this quench fluid does not seem to react with the hydrogen in the presence of the dewaxing catalyst to any significant extent, for reasons that are not well understood. The use of this cool, recycled dewaxate maintains the dewaxing reactor at the desired temperature of 550°F, without the need for using cool feed, a cool gas, another cool hydrocarbon fluid which would dilute the dewaxate and feed, or an indirect heat exchange system.

Figure 2 is a schematic flow diagram of an integrated hydrocarbon synthesis process useful in the practice of the invention, which includes hydroisomerizing and dewaxing a Fischer-Tropsch synthesized waxy fraction. The same numbers in Figure 2 refer to the same reactors, heat exchangers, separators, lines and distillation tower as in Figure 1. Referring to Figure 2, integrated unit 100 comprises a slurry hydrocarbon synthesis reactor 110 containing a three phase slurry 112 inside, has a gas distribution plate 114 at the bottom of the slurry for injecting synthesis gas from the plenum area below, and liquid filtration means indicated as box 116, immersed in the slurry. The synthesis gas, which comprises a mixture of $H_2$ and CO in a mole ratio of 2.1:1, is passed into the reactor via line 118, with the slurry liquid, which comprises the synthesized hydrocarbons that are liquid at the reaction conditions, continuously withdrawn as filtrate via line 120 and the gaseous reactor effluent removed overhead as tail gas via line 122. The filtrate, which comprises the synthesized hydrocarbons which are liquid at the reaction conditions, and which contains the 650-750$^{O}$F+ boiling fraction, is passed into a hydroisomerization reactor 12, which is the same as that in Figure 1 and has the same catalyst within. In the hydrocarbon synthesis reactor 110, the $H_2$ and CO of the synthesis gas react in the presence of the particulate catalyst to form the desired hydrocarbons, most of which comprise the slurry liquid, along with gas reaction products, much of which is water vapor and $CO_2$. The circles in 112 represent the bubbles of synthesis gas and gas products, while the solid dots represent the particulate Fischer-Tropsch hydrocarbon synthesis catalyst. The gaseous overhead comprises water vapor, $CO_2$, gaseous hydrocarbon products, unreacted synthesis gas and minor amounts of oxygenates. The overhead is passed through respective hot and cold heat exchangers 124 and 126, in which it is cooled to condense a portion of the water and hydrocarbons, and into respective hot and cold separators 128 and 130, to recover condensed hydrocarbon liquids. Thus, the gas overhead is passed via line 122 through a hot heat exchanger 124 to condense out some of the water vapor and heavier hydrocarbons as liquid, with the gas and liquid mixture then passed via line 132 into separator 128, in which the water and liquid hydrocarbons separate from the remaining gas as separate liquid layers. The water layer is removed via line 134 and the hydrocarbon liquids removed via line 136 and passed into the hydroisomerization unit 12, along with the filtrate from filter 116. The separated hydrocarbon liquid from the hot separator 128 contains hydrocarbons which solidify at standard conditions of room temperature and pressure, and are useful as part of the waxy feed to the hydroisomerization unit 12. The uncondensed gas is removed from separator 128 and passed via line 140 through cold heat exchanger 126, to condense more water and lighter hydrocarbons as liquid, with the gas and liquid mixture then passed via line 142 into cold separator 130, in which the liquid separates from the uncondensed gas as two separate layers. The water is removed via line 144 and the hydrocarbon liquid via line 146 and into line 34. The uncondensed vapors are removed overhead via line 150. Hydrogen or a hydrogen-containing treat gas is passed into the top of the hydroisomerization unit via line 30. The hydrocarbons are hydroisomerized and the mixture of hydroisomerized hydrocarbons and gas is removed from the reactor via line 34 and passed, along with the lighter hydrocarbons from line 146, into a fractionator 156, operating at atmospheric pressure or above, in which the lighter components are separated as fuel fractions, such as a naphtha fraction removed via line 158, and a jet/diesel fuel fraction removed via line 160, with the unreacted hydrogen from 138 and light hydrocarbon gas removed as tail gas via line 162. The heavier hydroisomerate, comprising the desired hydrocarbons boiling in the lube oil range which have an initial boiling point in the range of from 650-750$^{0}$F, is removed from the bottom of the fractionator via line 164. Thus, in this embodiment, the lighter portion of the hydroisomerate is separated from the lube oil material before dewaxing. This greatly reduces the load on both the dewaxing unit and subsequent vacuum pipe still. The lube oil fraction having an initial boiling point of about 700$^{O}$F and an end point above 1050$^{O}$F, is passed via line 164 into a catalytic dewaxing unit 14, which contains a fixed bed 40 of a dewaxing catalyst comprising Pt/H-mordenite. Hydrogen or a hydrogen-containing treat gas is passed into the top of the dewaxing reactor 14, via line 42, and reacts with the hydroisomerate to reduce its pour point and produce a dewaxate comprising a lubricant base stock, which is removed, along with unreacted hydrogen and gas products of the dewaxing reaction, via line 44, passed through a simple flash fractionator 20 to remove vapor and gas as overheads, and then to vacuum distillation tower 16, via line 48. As is the case with the hydroisomerization, the catalytic dewaxing also results in some of the base stock material being cracked into lower boiling material, to form a light fraction. In the vacuum pipe still, the light fraction is separated from the dewaxed base stock and removed from the unit via line 158, with the dewaxed lubricant base stock removed from the unit via line 56. While only a single stream of base stock is shown for convenience, more typically a plurality of base stocks of different viscosity are produced by the vacuum fractionation. Light hydrocarbon gases and any remaining unreacted hydrogen are removed overhead via line 80. Most (e.g., more than 50 %) of the heavy base stock is removed via line 58 and sent to further processing into various lubricants. The rest is passed, via line 60, into and through heat exchanger 26, in which it is cooled to a temperature sufficiently below the temperature in the dewaxing reactor to be used as quench fluid. This cool quench fluid is passed, via lines 62, 64 and 66, back into the dewaxing reactor, in which it does not react with the hydrogen in the reactor to an extent that will impair its efficacy as a quench fluid.

While suitable Fischer-Tropsch reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re, it is preferred in the process of the invention that the catalyst comprise a cobalt catalytic component. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania, particularly. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674. In a slurry hydrocarbon synthesis process, which is a preferred Fischer-Tropsch type of hydrocarbon synthesis process in the practice of the invention, a synthesis gas comprising a mixture of $H_2$ and CO is bubbled up as a third phase through a slurry in a reactor which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. The stoichiometric mole ratio for a Fischer-Tropsch hydrocarbon synthesis reaction is generally about 2.0, but in a slurry hydrocarbon synthesis process it is typically about 2.1/1 and may be increased to obtain the amount of hydrogen desired from the synthesis gas for other than the synthesis reaction. Slurry process conditions vary somewhat, depending on the catalyst and desired products. In the practice of the invention, it is preferred that the hydrocarbon synthesis reaction be conducted under conditions in which little or no water gas shift reaction occurs and more preferably with no water gas shift reaction occurring during the hydrocarbon synthesis. It is also preferred to conduct the reaction under conditions to achieve an alpha of at least 0.85, preferably at least 0.9 and more preferably at least 0.92, so as to synthesize more of the more desirable higher molecular weight hydrocarbons. This has been achieved in a slurry process using a catalyst containing a catalytic cobalt component. Those skilled in the art know that by alpha is meant the Schultz-Flory kinetic alpha. Typical conditions effective to form hydrocarbons comprising mostly $C_{5+}$

paraffins, (e.g., $C_{5+}$-$C_{200}$) and preferably $C_{10+}$ paraffins (and more preferably $C_{20+}$) in a slurry hydrocarbon synthesis process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-600$^{o}$F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and $H_2$ mixture (0$^{o}$C, 1 atm) per hour per volume of catalyst, respectively. The hydrocarbons which are liquid at the reaction conditions are removed from the reactor using filtration means.

The invention will be further understood with reference to the example below.

## EXAMPLE

### Fischer-Tropsch Synthesis

Fischer-Tropsch synthesized waxy hydrocarbons were formed in a slurry reactor from a synthesis gas feed comprising a mixture of $H_2$ and CO having an $H_2$ to CO mole ratio of between 2.11-2.16. The slurry comprised particles of a Fischer-Tropsch hydrocarbon synthesis catalyst comprising cobalt and rhenium supported on titania dispersed in a hydrocarbon slurry liquid, with the synthesis gas bubbled up through the slurry. The slurry liquid comprised hydrocarbon products of the synthesis reaction which were liquid at the reaction conditions. These included a temperature of 425$^{o}$F, a pressure of 290 psig and a gas feed linear velocity of from 12 to 18 cm/sec. The alpha of the synthesis step was greater than 0.9. The waxy hydrocarbons, which are liquid at the reaction conditions and which comprise the slurry ,were withdrawn from the reactor by filtration. The boiling point distribution of this waxy hydrocarbon liquid is given in Table 1.

Table 1

| Wt. % Boiling Point Distribution of Fischer-Tropsch Reactor Product | |
|---|---|
| IBP-500$^{O}$F | 1.0 |
| 500-700$^{O}$F | 28.1 |
| 700$^{O}$F+ | 70.9 |
| 1050$^{O}$F+ | 6.8 |

Hydroisomerization

The waxy liquid was hydroisomerized without fractionation and therefore included the 29 wt. % of material boiling below 700$^{O}$F shown in Table 1. The waxy liquid was hydroisomerized by reacting with hydrogen in the presence of a dual function hydroisomerization catalyst which consisted of cobalt (CoO, 3.2 wt. %) and molybdenum ($MoO_3$, 15.2 wt. %) supported on an amorphous silica-alumina cogel acidic component, 15.5 wt. % of which was silica. The catalyst had a surface area of 266 $m^2/g$ and a pore volume ($P.V._{H2O}$) of 0.64 mL/g. This catalyst was prepared by depositing and calcining the cobalt component on the support prior to the deposition and calcining of the molybdenum component. The conditions for the hydroisomerization are set forth in Table 2 and were selected for a target of 50 wt. % conversion of the 700$^{O}$F+ fraction, which is defined as:

700$^{O}$F+ Conv. = [1-(wt. % 700$^{O}$F+ in product)/(wt. % 700$^{O}$F+ in feed)] x 100

Table 2

| Hydroisomerization Reaction Conditions | |
|---|---|
| Temperature, °F (°C) | 713 (378) |
| $H_2$ Pressure, psig (pure) | 725 |
| $H_2$ Treat Gas Rate, SCF/B | 2500 |
| LHSV, v/v/h | 1.1 |
| Target 700°F+ Conversion, wt. % | 50 |

As indicated in the Table, 50 wt. % of the 700°F+ waxy feed was converted to 700°F- boiling products. The hydroisomerate was fractionated to separate the 700°F+ and 700°F- fractions, with the separated 700°F- hydroisomerate fractionated to recover fuel products of reduced cloud point and freeze point.

Table 3 shows the properties of the 700°F+ hydroisomerate which comprises 86.8 wt. % hydrocarbons boiling in the range of 700-950°F and 11.6 wt. % of 950°F+ hydrocarbons.

Table 3

| °F, Wt. % Boiling Point Distribution by GCD and Pour Point of the 700°F+ Hydroisomerate Fraction | |
|---|---|
| IBP-320 | 0 |
| 320-500 | 0 |
| 500-700 | 1.6 |
| 700-950 | 86.8 |
| (730°F+) | (78.3) |
| 950+ | 11.6 |
| Pour Point, °C | 2 |
| KV @ 40°C, cSt | 26.25 |
| KV @ 100°C, cSt | 5.07 |
| VI | 148 |

## Catalytic Dewaxing

The 700°F+ hydroisomerate shown in Table 3 was catalytically dewaxed using a 0.5 wt. % Pt/H-mordenite catalyst to reduce the pour point and form a high VI lubricating base stock. In this experiment, a small up-flow pilot plant unit was used. The dewaxing conditions included a 750 psig $H_2$ pressure, with a nominal treat gas rate of 2500 SCF/B at 1 LHSV and a temperature of 550°F. The dewaxate product exiting the reactor was fractionated using the standard 15/5 distillation to remove the lower boiling fuel components produced in the dewaxing reactor and the 700°F+ product subjected to Hivac distillation to obtain narrow cuts, with low temperature properties measured on the 730-950°F and 950°F+ portions. The results are summarized in Table 4.

Table 4

| F-T Waxy Hydroisomerate Catalytic Dewaxing Results | |
|---|---|
| Reactor Temperature, °F | 550 |
| Yields, wt. % | |
| $C_1$-$C_4$ | 11.3 |
| $C_5$-320°F | 9.1 |
| 320-730°F | 1.3 |
| 730-950°F | 59.9 |
| 950°F+ | 18.4 |
| Total Yield | 78.3 |
| | |
| 730-950°F | |
| Pour Point, °C | 26 |
| KV at 40°C, cSt | 17.27 |
| KV at 100°C, cSt | 3.96 |
| VI | 127.3 |
| 950°F+ | |
| Pour Point, °C | 7 |
| KV at 40°C, cSt | 80.19 |
| KV at 100°C, cSt | 11.90 |
| VI | 142.5 |
| | |
| Total 700°F+ Base Stock (dewaxate) | |
| Pour Point, °C | 15 |
| KV at 40°C, cSt | 22.76 |
| KV at 100°C, cSt | 4.83 |
| VI | 138.1 |

The data in Table 3 show respective yields of 86.8 wt. % hydroisomerate boiling in the range of 700-950°F and 11.6 wt. % of the 950°F+ hydroisomerate. Thus, of the 700°F+ hydroisomerate, the 700°F+ material is 88.2 wt. % and the 950°F+ material is 11.8 wt. %. After dewaxing, of the about 700°F+ dewaxate, Table 4 shows only 59.9 wt. % is 700°F+, while 23.5 wt. % comprises 950°F+ dewaxate. This thus indicates significant conversion of the 700-950°F hydroisomerate feed in the dewaxer to lower boiling hydrocarbons, with essentially no conversion of the 950°F+ dewaxate to lower boiling hydrocarbons.

This therefore demonstrates that essentially little or none of the recycled heavy, 950°F+ dewaxate used as quench fluid reacts with the dewaxing catalyst.

It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those skilled in the art without departing from the scope and spirit of the invention described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all the features and embodiments which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

CLAIMS:

1. A catalytic dewaxing process comprises contacting a waxy, paraffinic hydrocarbon feed with hydrogen, in the presence of a dewaxing catalyst in a catalytic dewaxing zone, at conditions of elevated temperature and pressure effective for the hydrogen to react with said feed and produce a dewaxate of reduced pour point, which includes a heavy fraction, separating and cooling at least a portion of said heavy fraction, and passing it back into said dewaxing zone as a quench liquid for temperature control.

2. A process according to claim 1 wherein said heavy dewaxate fraction has an initial boiling point in the range of from 800-950$^{O}$F.

3. A process according to claim 2 wherein said waxy feed comprises hydrocarbons having an initial boiling point in the range of 650-750$^{O}$F.

4. A process according to claim 3 wherein said waxy feed has an end boiling point of at least 1050$^{O}$F.

5. A process according to claim 4 wherein said waxy feed comprises a hydroisomerate.

6. A process according to claim 5 wherein said dewaxing catalyst comprises at least one catalytic metal component and at least one acidic, microcrystalline aluminosilicate component.

7. A process according to claim 7 wherein said catalytic metal component comprises at least one metal from Group VIII.

8. A process according to claim 7 wherein said metal component comprises a noble metal component.

9. A process according to claim 8 wherein said waxy feed is derived from Fischer-Tropsch synthesized hydrocarbons.

10. A process according to claim 8 wherein said waxy feed is derived from a slack wax or a hydrocrackate which has been treated to remove non-paraffinic hydrocarbons and heteroatom compounds.

11. A process according to claim 10 wherein said waxy feed has been hydroisomerized.

12. A process according to claim 8 wherein said catalyst comprises Pt and H-mordenite.

13. An integrated process for synthesizing a waxy, paraffinic hydrocarbon fraction from a synthesis gas comprising a mixture of $H_2$ and CO, hydroisomerizing said waxy fraction to form a hydroisomerate and catalytically dewaxing said hydroisomerate in a dewaxing zone, to form a dewaxate of reduced pour point which contains a heavy dewaxate fraction, a portion of which is cooled and used as quench liquid in said dewaxing zone, said process comprising:

(a) reacting said mixture of $H_2$ and CO in the presence of a Fischer-Tropsch hydrocarbon synthesis catalyst containing a catalytic cobalt component, at reaction conditions effective to form high purity, paraffinic, waxy hydrocarbons, at least a portion of which are liquid at said reaction conditions;

(b) passing said waxy hydrocarbons it into a hydroisomerization reaction zone;

(c) reacting said waxy hydrocarbons with hydrogen in the presence of a dual functional
hydroisomerization catalyst in said hydroisomerization reaction zone to form a hydroisomerate comprising hydrocarbons having an initial boiling point in the range of 650-750$^{O}$F and an end boiling point of at least 1050$^{O}$F;

(d) catalytically dewaxing said hydroisomerate in a catalytic dewaxing zone to reduce its pour point, by reacting it with hydrogen at elevated temperature and pressure, in the presence of a catalyst comprising a Group VIII catalytic metal component and a crystalline aluminosilicate component, to form a dewaxate comprising hydrocarbons having an initial boiling point above and below said 650-750$^{O}$F range, which includes heavy hydrocarbons having an initial boiling point in the range of 800-950$^{O}$F;

(e) separating at least a portion of said heavy hydrocarbon dewaxate from the rest of said dewaxate;

(f) cooling at least a portion of said separated heavy hydrocarbon dewaxate to a temperature below that in said catalytic dewaxing zone, and

(g) passing said cool dewaxate back into said dewaxing reaction zone as quench liquid.

14. A slurry hydrocarbon synthesis process according to claim 13, wherein said $H_2$ and CO react in a slurry comprising a hydrocarbon slurry liquid, gas bubbles and a particulate hydrocarbon synthesis catalyst and wherein said slurry liquid comprises synthesized hydrocarbons that are liquid at the reaction conditions, and wherein said slurry liquid is withdrawn from said slurry, and passed into said hydroisomerization reaction zone in step (b).

15. A process according to claim 14 wherein said quench liquid reduces the temperature in said dewaxing zone.

16. A process according too claim 15 wherein said waxy synthesized hydrocarbon fraction comprises hydrocarbons having an initial boiling point in said 650-750$^{O}$F range and an end point of at least 1050$^{O}$F.

17. A process according to claim 16 wherein said hydroisomerization catalyst comprises a Group VIII non-noble metal catalytic component and an acid support.

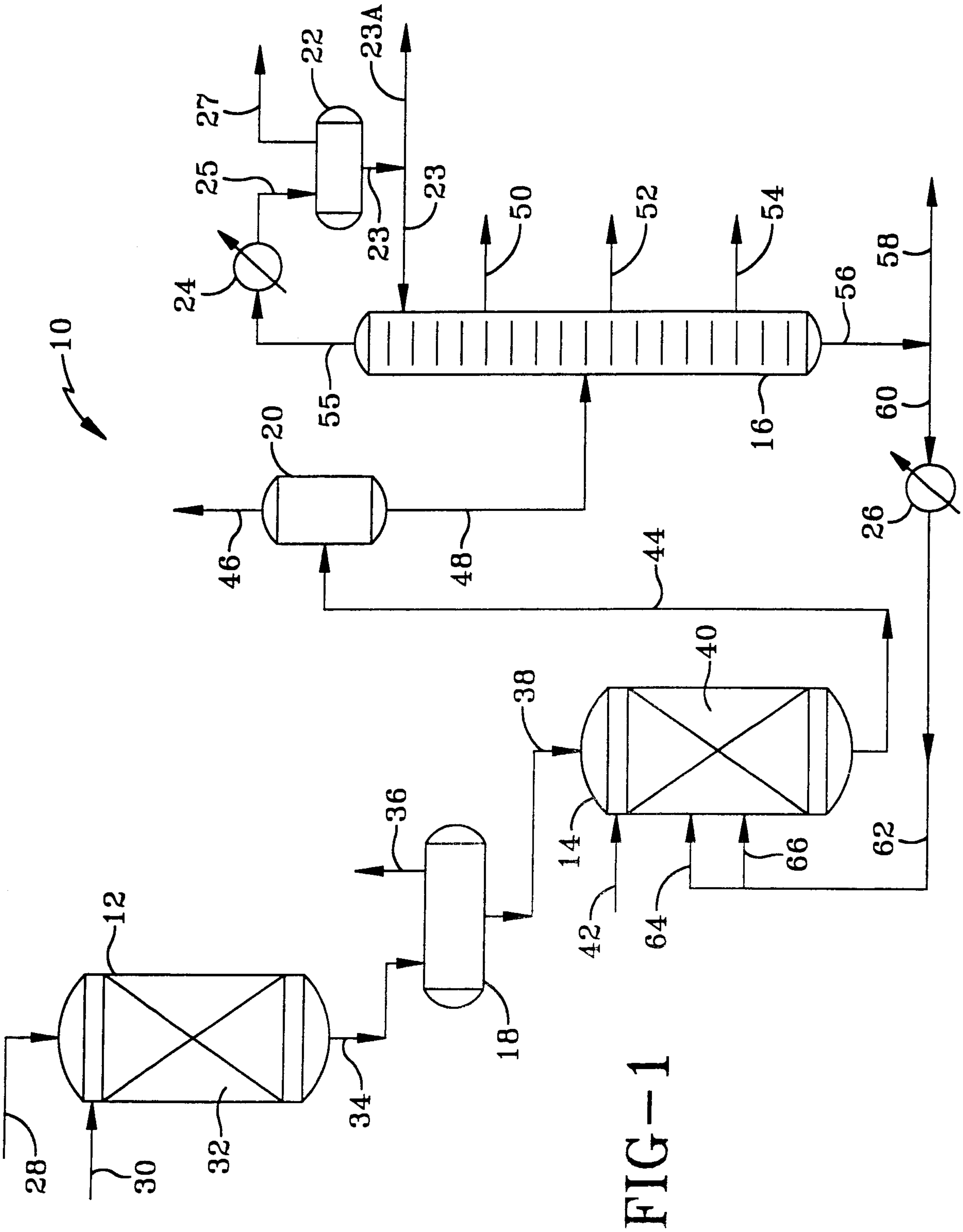
18. A process according to claim 17 wherein said dewaxing catalyst comprises a zeolite component and a noble metal component..

19. A process according to claim 18 wherein said dewaxing catalyst comprises Pt and H-mordenite.

20. A process according to claim 18 wherein said hydroisomerization catalyst comprises a cobalt and a molybdenum catalytic metal component and said support comprises alumina-silica having no more than 30 wt. % silica.

21. A process according to claim 14 wherein said slurry liquid comprises 650-750$^{O}$F- hydrocarbons, at least a portion of which are removed before said liquid is hydroisomerized.

22. A process according to claim 13 wherein said heavy dewaxate fraction has an end boiling point above 1050$^{O}$F.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FIG—1

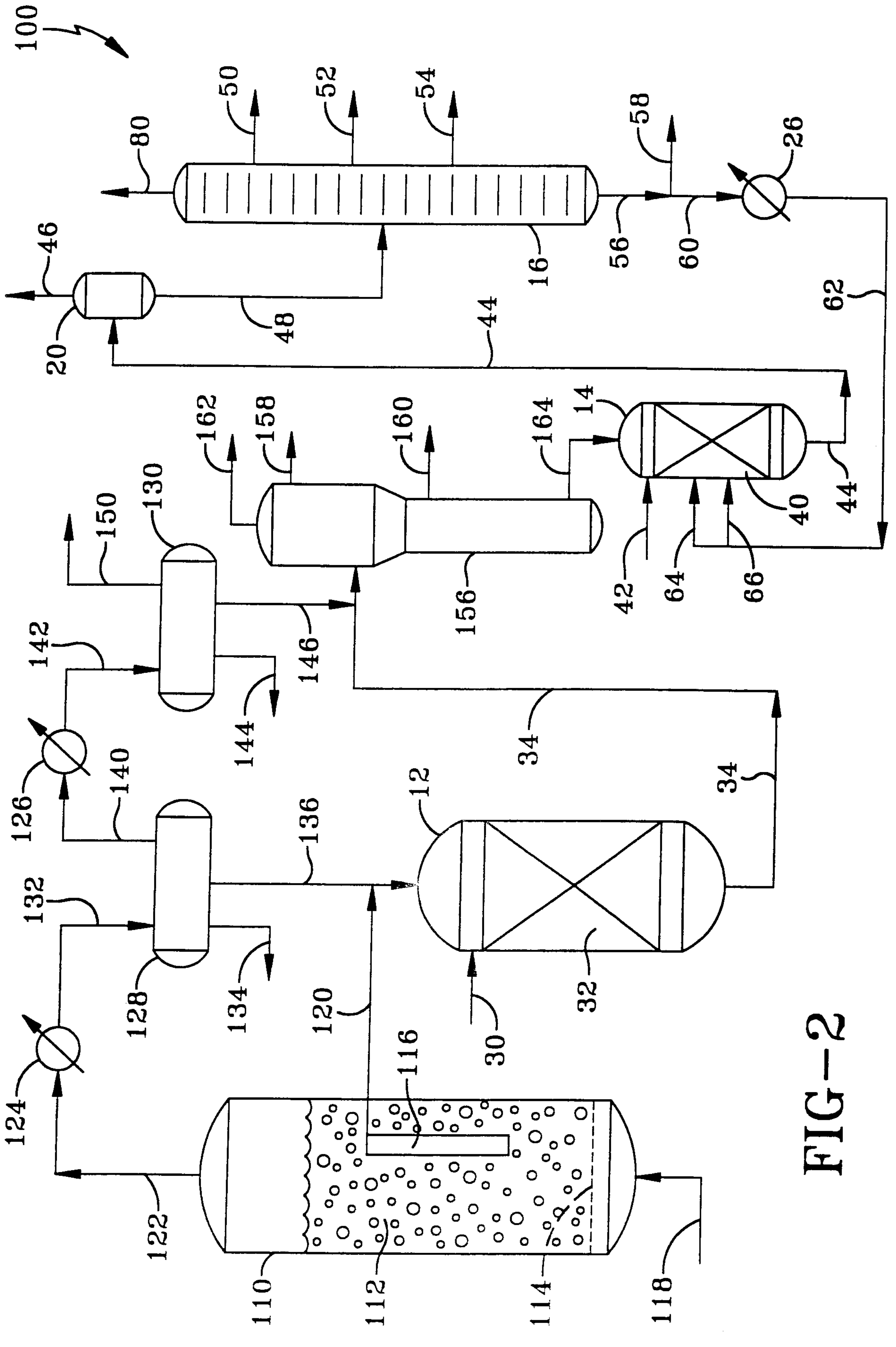
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FIG-2

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/01703

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C10G45/58 C10G65/04

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | US 5 246 568 A (FORBUS THOMAS R ET AL)<br>21 September 1993 (1993-09-21)<br>the whole document | 1-22 |
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| | |
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| Date of the actual completion of the international search<br>19 April 2001 | Date of mailing of the international search report<br>26/04/2001 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Michiels, P |

# INTERNATIONAL SEARCH REPORT

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