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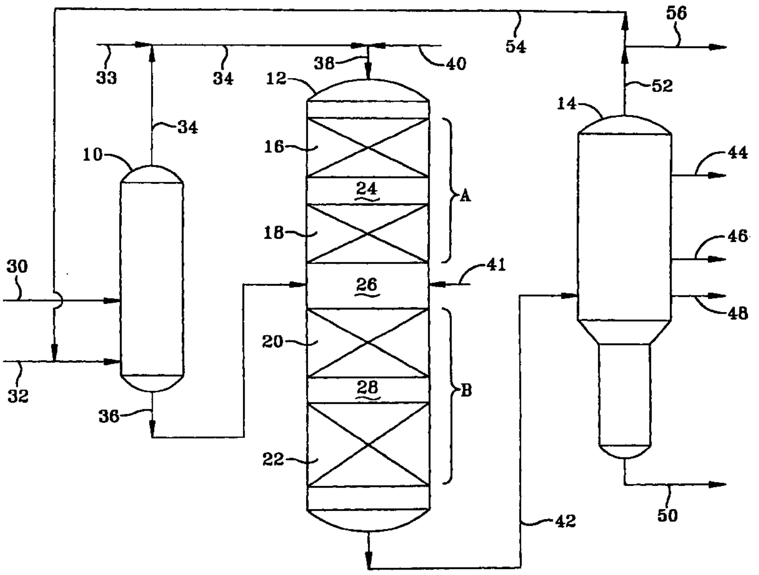
(54) Title: SINGLE STAGE MULTI-ZONE HYDROISOMERIZATION PROCESS



(57) Abstract: Fischer-Tropsch synthesized hydrocarbons comprising both a 500-750°F+ heavy fraction and a 500-750°F -light fraction are separately hydroisomerized by a single-stage, two-zone hydroisomerization process, in which at least a portion of the light fraction is hydroisomerized in the first zone, with the total first zone effluent containing unreacted hydrogen and a light hydroisomerate. The first zone effluent and the heavy fraction are passed into the second zone to form a second zone effluent comprising the hydroisomerized product. The product is fractionated into a plurality of product fractions, including a distillate fuels fraction containing a jet fuel fraction. The hydrogen treat gas is used to separate a portion of the light fraction from the heavy fraction, prior to the hydroisomerization.

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SINGLE STAGE MULTI-ZONE HYDROISOMERIZATION PROCESS

BACKGROUND OF THE DISCLOSURE

Field of the Invention

The invention relates to a process for hydroisomerizing Fischer-Tropsch synthesized hydrocarbons. More particularly the invention relates to a process for hydroisomerizing the Fischer-Tropsch synthesized hydrocarbon product of a hydrocarbon synthesis reactor, which comprises separately hydroisomerizing the lower and higher boiling synthesized hydrocarbons in separate zones in a single stage, wherein the total effluent from the lower boiling hydrocarbon hydroisomerizing zone is passed, with the higher boiling hydrocarbons, into the higher boiling hydroisomerizing zone. The effluent from the higher boiling hydroisomerizing zone comprises the hydroisomerized product.

Background of the Invention

Fischer-Tropsch hydrocarbon synthesis is well known and includes fixed bed, fluidized bed and slurry processes, in all of which a synthesis gas comprising a mixture of H_2 and CO is contacted with a Fischer-Tropsch hydrocarbon synthesis catalyst, at reaction conditions effective for the H_2 and CO to react and form hydrocarbons. Water vapor and CO_2 are major by-products of the synthesis reaction. Typically, at least a portion of the synthesized hydrocarbons are upgraded by fractionation and/or one or more conversion operations, in which the molecular structure of the hydrocarbon product is changed. One well known upgrading operation comprises hydroisomerization, in which the hydrocarbon product is hydroisomerized to increase branching of the linear paraffinic molecules and thereby reduce the pour point. Typical process schemes for hydroisomerizing the hydrocarbon product of a Fischer-Tropsch hydrocarbon synthesis reactor are disclosed, for example, in U.S. patents 4,832,819; 4,919,786; 5,378,348; 5,660.714; 5,689,031 and 5,766,274. In these schemes, the light and heavy fractions are hydroisomerized together, in separate stages or trains, or only the heavy fraction is hydroisomerized.

SUMMARY OF THE INVENTION

The invention relates to a process for hydroisomerizing the higher and lower boiling hydrocarbons (hereinafter "feed") produced by a Fischer-Tropsch hydrocarbon synthesis reactor, wherein at least a portion of the lower boiling hydrocarbons are hydroisomerized in the first zone of two, sequential hydroisomerization zones in a single reaction stage, to form a first zone effluent comprising a light hydroisomerate and unreacted hydrogen, followed by combining the first zone effluent with the higher boiling hydrocarbons and passing them into the second zone, to form a second zone effluent comprising a hydroisomerized hydrocarbon product. The higher boiling material is waxy, which means that it contains hydrocarbons that are solid at standard conditions of room temperature and pressure. By single stage is meant that the total first zone effluent is passed directly into the second zone. The first and second zones may be in the same or separate reaction vessels and preferably in the same vessel. The second zone effluent comprises the hydroisomerized product and is fractionated into the desired liquid product fractions. The hydroisomerate product fractions have a pour and freeze point lower than the corresponding feed fractions boiling in the same range. By lower boiling hydrocarbons is generally meant synthesized hydrocarbons boiling in the range of below about 500-750°F and preferably below 550-700°F (550-700°F-). The higher boiling hydrocarbons will therefore be those that boil above about 500-750°F and preferably above about 550-700°F (550-700°F+). The exact feed cut point used to define and separate the lower and higher boiling hydrocarbons, will depend on the intended end use of the hydroisomerized product. The lower boiling hydrocarbons include distillate fuels and, optionally light oils and the like. The lower and higher boiling hydrocarbons are commonly referred to as respective light and heavy fractions. These terms are used synonymously herein and by light fraction is meant to include at least distillate fuels.

At least a portion of the lower boiling hydrocarbons are hydroisomerized in the first zone and preferably comprising at least those boiling in the jet fuels range (e.g., about 350-500°F). Separation of most of the lower and higher boiling feed hydrocarbons occurs as a consequence of the hydrocarbon synthesis process, in which lower boiling hydrocarbons are in the vapor state and higher boiling hydrocarbons are in the liquid state, at the reaction conditions. However, in some cases, such as in a slurry Fischer-Tropsch process, at least some 500-750°F- hydrocarbons will be present in the higher boiling 500-750°F+ fraction. These lower boiling hydrocarbons may be separated from the 500-750°F+ hydrocarbons by fractionation. However, in the process of the invention it is preferred to separate them from the 500-750°F+ fraction by stripping, using the hydroisomerization hydrogen or hydrogen treat gas fed into the first hydroisomerization zone as the stripping gas. It is also preferred that all or most of the hydrogen or hydrogen treat gas used for the hydroisomerization will be introduced into the first hydroisomerization zone with the light fraction. Additional hydrogen may be introduced into the second zone, if required.

In one embodiment therefore, the invention comprises a process for hydroisomerizing the light and heavy hydrocarbon fractions produced by a hydrocarbon synthesis reactor in a single stage, wherein hydrogen or a hydrogen treat gas and at least a portion of the light fraction only is passed into a first hydroisomerization zone, in which the light hydrocarbons react with the hydrogen in the presence of a hydroisomerization catalyst to form a first zone effluent comprising unreacted hydrogen and hydroisomerized hydrocarbons which are both passed, along with the heavy fraction, into a second hydroisomerization zone in which the heavy hydrocarbons react with the hydrogen to form a second zone effluent comprising a hydroisomerized hydrocarbon product. In another embodiment, the invention comprises a Fischer-Tropsch hydrocarbon synthesis process, in which the H_2 and CO in a synthesis gas comprising a mixture of H_2 and CO react in the presence of a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, to form a hydrocarbon product comprising 500-750^{o}F- lower boiling hydrocarbons and waxy, 500-750^{o}F+ higher boiling hydrocarbons, wherein hydrogen or a hydrogen treat gas and at least a portion of the lower boiling or light fraction is passed into a first hydroisomerization zone in which the light hydrocarbons react with the hydrogen in the presence of a hydroisomerization catalyst to form a first zone effluent comprising unreacted hydrogen and hydroisomerized hydrocarbons which are both passed, along with the higher boiling or heavy fraction, into a second hydroisomerization zone in which the heavy hydrocarbons react with the hydrogen to form a second zone effluent comprising a hydroisomerized hydrocarbon product. In both embodiments, the hydroisomerized hydrocarbon product is fractionated into the desired product fractions, including at least one distillate fuel fraction. The hydroisomerized fuel fraction product preferably comprises at least a jet fuel fraction.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow diagram of a hydroisomerization process of the invention in which stripping is used for separating the light and heavy synthesized hydrocarbon fractions.

Figure 2 is a schematic flow diagram of a slurry hydrocarbon synthesis process using the hydroisomerization process of the invention for product upgrading.

DETAILED DESCRIPTION

Fischer-Tropsch synthesized hydrocarbons may comprise more than 80 wt. % and even more than 90 wt. % paraffins, the majority of which are normal paraffins. Since normal paraffins tend to be waxy, with high pour and freeze points, hydroisomerization is used to impart branching and reduce the pour and cold flow properties of the various product fractions ultimately recovered from the synthesized hydrocarbons. However, it has been found that if prior to hydroisomerization the light and heavy fractions which comprise the Fischer-Tropsch synthesized waxy feed are not separated, but are passed into the same hydroisomerization zone together, the lighter hydrocarbons tend not to be hydroisomerized as much as the heavier fractions. While not wishing to be held to any particular theory, it is believed that the heavier hydrocarbons block off access to the active sites on the catalyst particles, thereby preventing them from contacting the lighter fractions. Whatever the mechanism, more catalyst volume, a larger reactor, more recycle back into the reactor, a lower space velocity, and generally more severe conditions are typically required to achieve hydroisomerization of the lighter fraction, in the presence of the heavier fraction.

Because of the cracking function of a hydroisomerization catalyst, this means more cracking of the lighter products into less valuable C_{4-} hydrocarbons and often unacceptably high heavy fraction conversion into lower boiling hydrocarbons. The process of the present invention avoids this by hydroisomerizing only the light fraction in a first hydroisomerizing zone to form a first zone effluent comprising unreacted hydrogen and a light fraction hydroisomerate, and then passing both the first zone effluent and the heavy fraction into a second hydroisomerizing zone, in which the heavy fraction is hydroisomerized, with the second zone effluent comprising the total hydroisomerized product. The use of a single stage reduces product loss and avoids the need for two parallel reaction stages. The use of the hydrogen treat gas for separating light hydrocarbons from the heavy fraction in a simple stripper, instead of using a more expensive fractionater, further reduces costs. In the context of the invention, the terms “hydrogen” and “hydrogen treat gas” are synonymous and may be either pure hydrogen or a hydrogen-containing treat gas which is a treat gas stream containing hydrogen in an amount at least sufficient for the intended reaction, plus other gas or gasses (e.g., nitrogen and light hydrocarbons such as methane and C_{4-} gasses) which will not adversely affect either the reactions or the products.

The distillate fuels hydrocarbons that make up the light fraction or lower boiling feed hydrocarbons, typically comprise from about C_{4+}-C_{6+} hydrocarbons up to an end boiling point of about $700^{O}F$ and include naphtha, jet, diesel and kerosene fractions. In some cases it will also include hydrocarbons useful as a light oil. In some cases the feed naphtha will not be hydroisomerized, in order to preserve any olefins present in the naphtha for octane. In a typical application, one or more of the jet, diesel and kerosene fuel fractions will be hydroisomerize to reduce its pour and freeze points, and preferably at least the jet fuel fraction. It may also be preferable to mildly hydrotreat all or a portion of the light fraction prior to hydroisomerization. The higher boiling feed hydrocarbons will include fractions useful as lubricant basestocks, cutting oils, medicinal oils, wax and the like. The end point of the heavy, or waxy fraction, will typically be at least 850°F+. Depending on the hydrocarbon synthesis process and process variables, the actual end point may be 1050°F or 1050°F+ , with an end boiling point of 1050°F+ readily achieved in a slurry process employing a catalyst having a cobalt catalytic component.

Hydroisomerization is generally achieved by a catalytic mechanism that includes both cracking and hydrogenation. Therefore, some cracking of the hydrocarbon feed being hydroisomerized to lower boiling hydrocarbons will occur. For example, during hydroisomerization of a waxy, paraffinic feed produced by a slurry Fischer-Tropsch process employing a hydrocarbon synthesis catalyst containing a catalytic cobalt component, conversion of the 500-750°F+ hydrocarbons to hydrocarbons boiling below this range (lower boiling material), will range from about 20-80 wt. %, typically 30-70 % and sometimes from about 30- 60 %, based on a once through pass of the feed through the reaction zone. It is preferred to minimize cracking of the lighter 500-750°F- fraction, when a maximum amount of fuels distillates is desired. Therefore, a milder hydroisomerization catalyst with less cracking functionality and reduced hydrogenolysis may be used to achieve this goal. The temperature and pressure in the hydroisomerization reaction zones will typically range from 300-900°F and 0-2500 psig, with preferred ranges of 550-750°F and 300-1200 psig, respectively. Hydrogen treat rates are 300-5000 SCF/B, with a preferred range of 500-2500 SCF/B. In addition to avoiding the inhibition of the light fraction hydroisomerization, the process of the invention permits the use of different hydroisomerization conditions (e.g., LHSV and temperature) in each zone.

The hydroisomerization catalyst comprises one or more Group VIII catalytic metal components, and, depending on the reaction conditions, preferably one or more non-noble metals, such as Co, Ni and Fe, which may or may not also include a Group VIB metal (e.g., Mo, W) oxide promoters, supported on an acidic metal oxide support to give the catalyst both a hydrogenation function for hydroisomerizing the hydrocarbons and an acid hydrocracking function. However, noble metals reduce hydrogenolysis, particularly at lower temperatures and will therefore be preferred for some applications. By noble metal is meant Pt and Pd. The catalyst may also have a Group IB metal, such as copper, as a hydrocracking suppressant. The cracking and hydrogenating activity of the catalyst is determined by its specific composition, as is known. The metal Groups referred to herein are those found in the Sargent-Welch Periodic Table of the Elements, © 1968. 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 non-noble metal 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 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. This patent also discloses the use of a copper component on the catalyst, to reduce hydrogenolysis.

Figure 1 is a schematic flow diagram of a hydroisomerization process according to the practice of the invention, which comprises a feed stripper 10, a single-stage hydroisomerization reactor vessel 12 and a hydroisomerized product fractionater 14. Reactor vessel 12 comprises two zones inside, shown as A and B. Zone A comprises two fixed catalyst beds, 16 and 18, for hydroisomerizing the light hydrocarbon fraction and comprises the first zone. Zone B comprises two fixed catalyst beds, 20 and 22 for hydroisomerizing primarily the heavy hydrocarbon fraction and comprises the second zone. Spaces 24, 26 and 28 permit the use of distribution trays (not shown) for uniformly distributing the effluent from a catalyst bed or zone, onto the catalyst bed or zone below. The hydrocarbons synthesized in an upstream hydrocarbon synthesis reactor (not shown) are initially separated into rough light and heavy fractions by means of strippers, rough fractionaters, coolers and simple drum separators, and the like, explained in more detail for Figure 2 below. This is done to remove the lighter C_{4-} hydrocarbons and water produced by the synthesis reaction. The heavier fraction typically contains hydrocarbons that are solid at room temperature and pressure and will be referred to as the waxy product. The initial boiling point of the heavy, waxy hydrocarbon product that is liquid at the reaction conditions and initially recovered from the synthesis reactor, will vary, depending on the type of process (e.g., fixed bed or slurry), synthesis catalyst, reaction conditions, and first or rough separation from the gas and vapor effluent. This liquid product, which includes the heavy fraction, typically also contains significant amounts of the lighter fraction hydrocarbons boiling in the distillate fuels range, as is shown in the Tables below. This liquid is passed, via feed line 30, into stripping column 10, to remove hydrocarbons boiling in the distillate fuels range. Not shown are simple trays or packing inside the stripper. At the same time, hydrogen treat gas is passed up into the stripper via line 32, as the stripping gas. The gas strips out and separates lighter boiling, 600-750°F- hydrocarbons. The actual boiling range of the stripped hydrocarbons will vary, depending on the intended product slate downstream, the stripper design and the make-up of the hydrocarbon liquid fed to the stripper. Typically, these will be 600-750°F- hydrocarbons. Those skilled in the art will appreciate that a stripper will yield a rough cut, not having the precision of that obtained from a fractionater. However, this is permissible in the practice of the invention. If desired, a fractionater may be used instead of a simple stripper. This is more precise, but also much more costly and a simple stripper is preferred. For the sake of illustration, the cut point will be taken at about 600°F. Thus, the hydrocarbons boiling below 600°F (600°F- fraction) are separated from the hydrocarbon feed and removed from the stripper as vapor, along with the hydrogen stripping-treat gas, as overheads via line 34. The remaining 600°F+ heavy fraction is removed from the bottom of the stripper as liquid, via line 36 and passed into the hydroisomerization reactor 12, in the interzone space 26, above the first catalyst bed of the second zone, B. The C_{5+} light hydrocarbons removed upstream of the stripper and having an end boiling point in the range of from about 400-650^{O}F, contain oxygenates. These oxygenates can be valuable as lubricants in distillate fuels, but can also have adverse effects on the performance of some hydroisomerization catalysts. Therefore, unless the hydroisomerization catalyst(s) is resistant to oxygenates, such as the catalyst comprising cobalt and molybdenum oxides on an amorphous alumina-silica support referred to above, it may be necessary to hydrotreat oxygenate-containing hydrocarbons, prior to hydroisomerization. Hydrotreating catalysts and conditions are well known. Irrespective of whether or not all or a portion of the light fraction to be hydroisomerized has been hydrotreated, it is passed into the first zone, A, of the hydroisomerization reactor via lines 33, 34 and 38. The mixture of the stripped 600^{O}F- fraction vapor and the hydrogen stripping gas also passes, via lines 34 and 38 into the first zone, in which it mixes with the C_{5+} fraction. The resulting mixture, along with the hydrogen stripping gas, also passes down into the top of the first zone, A, in the upper portion of the hydroisomerizing reaction vessel 12. If additional hydrogen is required for the overall product hydroisomerization, it is passed, either via lines 40 and 38 down into vessel 12, line 41 into the interzone space 26, or both. The hydrogen and light hydrocarbons pass down through the two hydroisomerization catalyst beds, 16 and 18. The catalyst(s) in each of beds 16 and 18 may be the same or different.

The hydroisomerized light fraction hydrocarbons and unreacted hydrogen treat gas leaving the first zone A, pass down into interzone space 26, and from there pass down through the first catalyst bed 20 of the heavy fraction or waxy product hydroisomerization zone B. It is mostly the heavy fraction that is hydroisomerized in the second or heavy zone B. This is due not only to the more successful competition for the reactive catalyst sites by the heavier material, it is also because the hydroisomerized lighter fraction is at least partially vaporized. The heavy fraction fed into zone B is substantially liquid. The second zone effluent passing out through the bottom of the reactor comprises a mixture of hydrogen gas and hydroisomerized hydrocarbon products boiling in the range of from as low as about C_{5+}, up to the end point of the heavy fraction, which may be $1050^{O}F$ or more. Some cracking to lower boiling hydrocarbons occurs during the hydroisomerization. It is preferred to minimize cracking of the lighter distillate fractions in the first zone A. If the heavy hydroisomerate is to be used primarily for lubricants, it is preferred to minimize cracking it also. However, if maximization of distillate fuels is desired, all or a portion of the heavy fraction hydrocrackate may be recycled back into zone B of the hydroisomerization reactor after fractionation, to produce more hydrocarbons boiling in the lighter distillate fuels range. The hydroisomerized hydrocarbons are withdrawn from the bottom of the reactor and passed, via line 42, into fractionater 14, in which they are separated into various product fractions of different boiling ranges. However, as an alternative, the hydroisomerate product may be sold or transported as a synthetic crude, instead of being separated into the various product fractions. In the illustration in Figure 1, the fractionater produces a $300^{O}F$- naphtha fraction (~ C_5-300) in line 44, a $320\text{-}500^{O}F$ jet fuel fraction in line 46 and a $500\text{-}700^{O}F$ diesel fuel fraction in line 48. A $700^{O}F+$ lubricant and wax fraction is removed from the bottom, via line 50. Gaseous C_{3-} $-C_{4-}$ hydrocarbons, along with any unreacted H_2, are removed as overheads via line 52. The boiling ranges of these different product fractions given here are nominal and will vary. The important point and the object of the invention is that the pour and freeze points of the separate fuels fractions and the lubricant fraction or fractions are greatly reduced by the hydroisomerization, and are able to meet specifications, with minimal or no addition of pour point reducing additives. A portion of the gas overheads from the fractionater may be recycled, via line 54, back into line 32, as part of the striping gas, if necessary. The rest is removed via line 56 and sent to further processing and/or a flare, or consumed as fuel.

Turning now to Figure 2, there is shown a schematic flow diagram of a slurry hydrocarbon synthesis process, in which the waxy hydrocarbon liquid is synthesized from synthesis gas in a slurry hydrocarbon synthesis reactor and then hydroisomerized according to an embodiment of the invention. In this embodiment, the hydroisomerization unit is the same as for Figure 1 and comprises stripper 10, hydroisomerization reactor 12 and hydroisomerate product fractionater 14. An optional hydrotreating reactor 70, is shown in phantom, if it is desired to remove oxygenates from the lighter hydrocarbons prior to hydroisomerization. The associated lines, catalyst beds and zones, are identical to those shown and described for Figure 1 and serve the same function, to obtain the same results. A slurry hydrocarbon synthesis reactor is shown upstream of the hydroisomerization unit, as comprising a cylindrical reaction vessel 60, sequentially connected hot and cold heat exchangers 62 and 64, and associated hot and cold knock-out drums 66 and 68. The slurry reactor contains a slurry 72 within. Slurry 72 comprises a hydrocarbon liquid, with gas bubbles and a particulate catalyst dispersed in the liquid, with the small circles representing uprising gas bubbles and the solid circles or dots representing the solid catalyst particles. The hydrocarbon liquid comprises synthesized hydrocarbons that are liquid at the reaction conditions in the reactor. A synthesis gas comprising a mixture of H_2 and CO is passed up into the bottom of the reactor via line 74 and is injected up into the slurry by gas injection means (not shown). In the slurry, the H_2 and CO in the synthesis gas contact the catalyst particles and react to form hydrocarbons. Unreacted H_2 and CO, along with vaporous light hydrocarbon products of the synthesis reaction, pass up through the slurry and are removed overhead as gas and vapor, via line 76. The slurry liquid is separated from the catalyst particles, by means of a filter in the slurry, briefly illustrated as box 78. The slurry hydrocarbon liquid is continuously withdrawn and passed into the stripper 10, via line 80.

Shown in Table 1 below is the fractional make-up (± 10 wt. % for each fraction) of the hydrocarbons synthesized in a slurry hydrocarbon synthesis reactor using a catalyst comprising cobalt and rhenium on a titania support.

Table 1

Boiling Temperature Ranges, °F	Wt. % of Fraction
IBP-320	13
320-350	23
500-700	19
700-1050	34
1050+	11
Total	100

The boiling point distribution for the slurry liquid or waxy product removed from the reactor by filtration is shown on Table 2 below.

Table 2

Wt. % Boiling Point Distribution of Fischer-Tropsch Reactor Waxy Product	
IBP-500°F	1.0
500-700°F	28.1
700°F+	70.9
(1050°F+)	(6.8)

Thus, it is readily seen that there are significant amounts of the 500-700°F-hydrocarbons boiling in the higher distillate fuels range. These are the hydrocarbons stripped out by the stripping gas and passed into first zone, A, of the hydroisomerization reactor as hydrocarbon vapor, where they, along with additional fuels hydrocarbons, are hydroisomerized separate from the heavier hydrocarbons. The heavy, 700°F+ hydrocarbons are removed from the bottom of the stripper as liquid and passed into the top of the second zone, B, in reactor 12, as is the case for the embodiment shown in Figure 1.

Returning to Figure 2, the gas and vapor slurry reactor overheads comprise valuable C_{4+}-C_{5+} hydrocarbons, as well as methane and other C_{4-} hydrocarbon vapors, oxygenates, unreacted synthesis gas, water vapor and CO_2. This mixture is passed through the sequential two-zone cooling and separation operation shown. The overheads are cooled in the first heat exchanger 62 to condense out some of the water vapor produced by the synthesis reaction and the heavier hydrocarbon vapors (e.g., ~500-700°F boiling range) to liquid, with the cooled gas and liquid mixture then passed via line 82 into the hot separation vessel 66, which may be a simple knock-out drum. In the separation vessel the remaining gas and vapors separate from the condensed liquids. The water forms a layer in the bottom of the vessel and is withdrawn via line 84. The condensed hydrocarbon liquid forms a layer above the water and is removed via line 86. The remaining gas and vapors are removed via line 88 and passed through the second heat exchanger, 64, which cools it down further (e.g., 50-150^{O}F), to condense out more water and lighter (e.g., C_{5+} up to about 500^{O}F boiling range) hydrocarbon vapors as liquid, with the gas and liquid mixture passed into cold separator 68, via line 90. The water is withdrawn via line 92 and the hydrocarbon liquid via line 94. The remaining gas and vapor is removed via line 96. The separated lighter hydrocarbon liquid is passed via line 94 into line 86, in which it mixes with the heavier liquid from drum 66. The combined stream is then passed directly into the hydroisomerization reactor via lines 86 and 94 if it is desired to save the oxygenates. Optionally and at the discretion of the practitioner, the oxygenates-containing light fraction may be passed via line 94 into a mild hydrotreater 70, for removal of the oxygenates. In this case, hydrogen treat gas is also passed into the hydrotreater, via lines 98 and 94 and reacts with the oxygenates in the presence of a catalyst in bed 100, which converts them to hydrocarbons and water. Not shown is a cooler and separator for separating the gas effluent which contains the water vapor from the hydrotreating, from the hydrotreated hydrocarbons. The treated hydrocarbons are then passed into reactor 12 via lines 102, 86 and 38. In this case, the hydroisomerization catalyst need not be resistant to deactivation by oxygenates or water. The rest of the process and process streams are identical to those in the embodiment shown in Figure 1, along with the option of recycling all or a portion of the heavy bottoms from fractionater 14, back into reactor 12, to convert all or a portion of these relatively heavy hydrocarbons to lower boiling hydrocarbons boiling in the distillate fuels range, if desired. In another embodiment, the hydrotreating catalyst may be located in the hydroisomerization reactor vessel 12, instead of a separate reaction vessel. In this case, the combination of hydrogen treat gas entering the top of vessel 12 and the hydrotreating reaction water much be such that, there is sufficient dilution of the hydrotreating reaction water in the hydroisomerization catalyst beds in reactor vessel 12, such that the water vapor doesn't deactivate the hydroisomerization catalysts. Alternately, all of the hydroisomerization catalyst must be resistant to deactivation by water vapor. Thus, in this case, the combination hydrotreating zone and two-zone hydroisomerization, all form part of a single reaction stage, because all of the hydrotreating effluent passes into the first hydroisomerization zone and all of the first hydroisomerization zone effluent passes into the second hydroisomerization zone. Still further, the hydrotreating may occur in a separate vessel and the entire effluent fed into the first hydroisomerizing zone. This still constitutes a single stage process, because no pumps or compressors will be used to pass the total hydrotreater effluent from the hydrotreater into the first hydroisomerization zone. Thus, except for catalyst bed pressure drops, the pressure for all three zones is about the same and there is no interzone effluent separation.

The process of the invention is useful for upgrading paraffinic hydrocarbons produced by fixed bed, fluid bed and slurry hydrocarbon synthesis processes, all of which form hydrocarbons from a synthesis gas comprising a mixture of H_2 and CO and are well known and documented in the literature. In all of these processes the synthesis gas is reacted in the presence of a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective to form hydrocarbons. With the fixed bed and slurry processes, some of these hydrocarbons will be liquid, some solid (e.g., wax) and some gas at standard room temperature conditions of temperature and pressure of $25^{O}C$ and one atmosphere, particularly if a catalyst having a catalytic cobalt component is used. Slurry hydrocarbon synthesis processes are often preferred because of their superior heat (and mass) transfer characteristics for the strongly exothermic synthesis reaction and because they are able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In a slurry hydrocarbon synthesis process 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. Slurry hydrocarbon synthesis process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+}-C_{200}) and preferably C_{10+} paraffins, 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 hydrocarbon products of a Fischer-Tropsch hydrocarbon synthesis reactor may be relatively pure, having substantially nil amounts of sulfur and nitrogen compounds, compared to hydrocarbons derived from petroleum oil, tar sands, coal and the like, with the catalyst and process conditions adjusted to substantially eliminate aromatics production. Therefore, they typically do not require the hydrotreating or hydrorefining to remove sulfur and nitrogen compounds prior to hydroisomerization, that hydrocarbons derived from petroleum, tar sands and coal do.

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 single stage process for hydroisomerizing the light and heavy hydrocarbon fractions produced by a hydrocarbon synthesis reactor, comprises passing hydrogen or a hydrogen treat gas and at least a portion of said light fraction into a first hydroisomerization zone, in which said light fraction reacts with said hydrogen in the presence of a hydroisomerization catalyst to form a first zone effluent comprising unreacted hydrogen and a light hydroisomerate, followed by passing said first zone effluent and said heavy fraction into a second hydroisomerization zone, in which said heavy fraction reacts with hydrogen to form a second zone effluent comprising a hydroisomerized hydrocarbon product.

2. A process according to claim 1 wherein each zone comprises at least one bed of hydroisomerization catalyst.

3. A process according to claim 2 wherein said both said light fraction and hydroisomerized hydrocarbon product comprise hydrocarbons boiling in the distillate fuels range.

4. A process according to claim 3 wherein said distillate fuels includes at least one of (i) a naphtha fraction, (ii) a jet fuel fraction, (iii) a diesel fraction, and (iv) a kerosene fraction.

5. A process according to claim 4 wherein said hydroisomerized hydrocarbon product is fractionated into at least two fractions, one of which comprises hydrocarbons boiling in the distillate fuels range.

6. A process according to claim 5 wherein the cut point separating said light and heavy fractions is between 500-750^{O}F.

7. A process according to claim 6 wherein at least a portion of said light fraction is removed from said heavy fraction prior to said hydroisomerization, by stripping with said hydrogen or hydrogen treat gas.

8. A process according to claim 7 wherein both said synthesis reactor light fraction and said hydroisomerized hydrocarbon product include a jet fuel fraction.

9. A process according to claim 8 wherein said zones are present in the same reaction vessel.

10. A process according to claim 9 wherein most of said hydrogen for both zones is introduced into said first zone and wherein said first zone effluent contains sufficient unreacted hydrogen to achieve said second zone hydroisomerization.

11. A process according to claim 1 wherein most of said hydrogen for both zones is introduced into said first zone and wherein said first zone effluent contains sufficient unreacted hydrogen to achieve said second zone hydroisomerization.

12. A Fischer-Tropsch hydrocarbon synthesis process, in which the H_2 and CO in a synthesis gas comprising a mixture of H_2 and CO react in the presence of a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, to form a hydrocarbon product comprising 500-750^{O}F- lower boiling hydrocarbons and waxy, 500-750^{O}F+ higher boiling hydrocarbons, wherein hydrogen or a hydrogen treat gas and at least a portion of said lower boiling hydrocarbons are passed into a first hydroisomerization zone in which they react with said

hydrogen in the presence of a hydroisomerization catalyst to form a first zone effluent comprising unreacted hydrogen and hydroisomerized hydrocarbons, wherein said effluent and said higher boiling hydrocarbons are passed into a second hydroisomerization zone, in which said heavy hydrocarbons react with hydrogen to form a second zone effluent comprising a hydroisomerized hydrocarbon product, and wherein both said zones are part of a single reaction stage.

13. A process according to claim 12 wherein each zone comprises at least one bed of hydroisomerization catalyst.

14. A process according to claim 13 wherein said both light fraction and hydroisomerized hydrocarbon product comprise hydrocarbons boiling in the distillate fuels range.

15. A process according to claim 14 wherein said distillate fuels includes at least one of (i) a naphtha fraction, (ii) a jet fuel fraction, (iii) a diesel fraction, and (iv) a kerosene fraction.

16. A process according to claim 15 wherein said hydroisomerized hydrocarbon product is fractionated into at least two fractions, one of which comprises hydrocarbons boiling in the distillate fuels range.

17. A process according to claim 16 wherein the cut point separating said light and heavy fractions is between 500-750^{O}F.

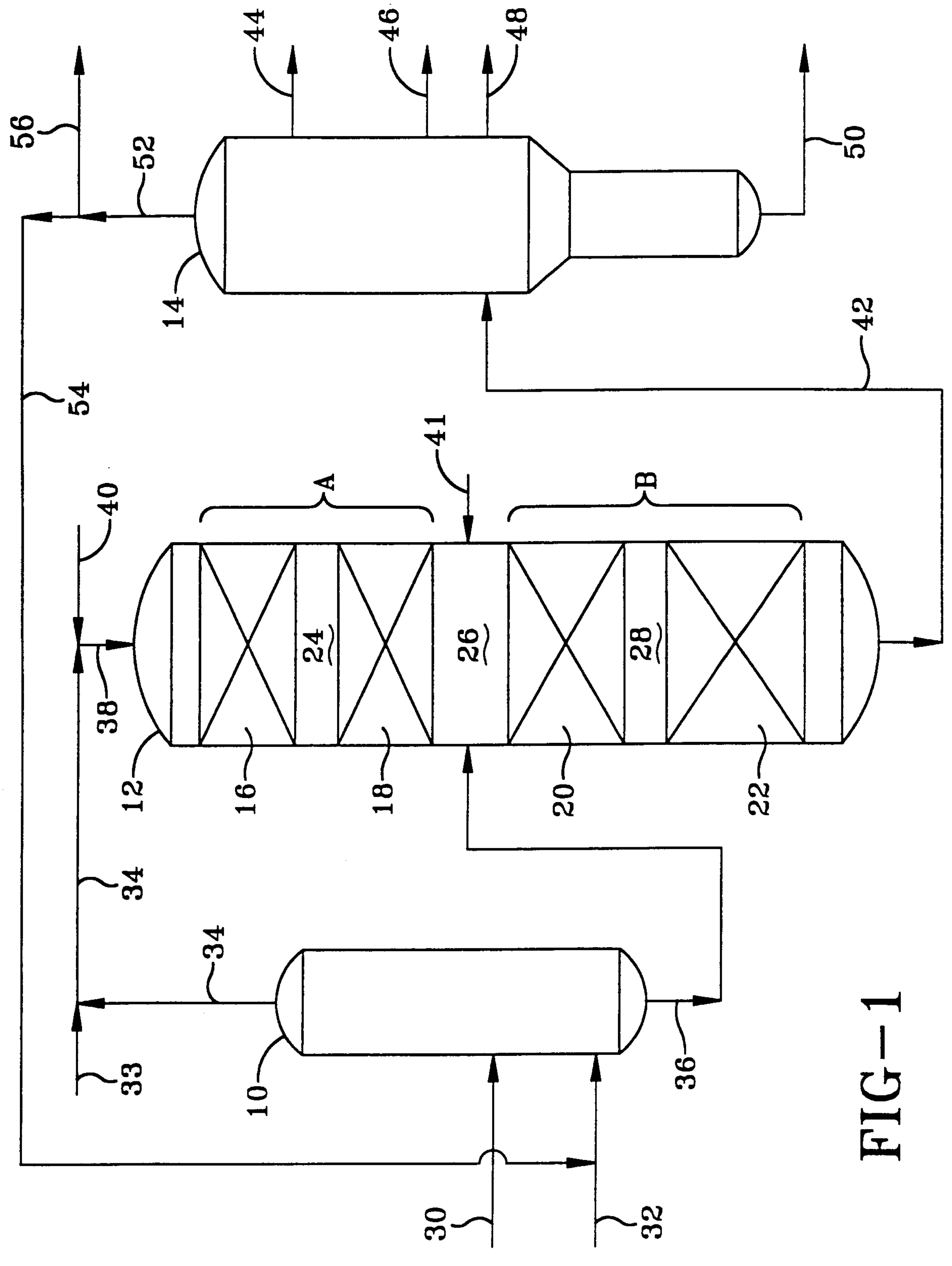
18. A process according to claim 17 wherein at least a portion of said light fraction is removed from said heavy fraction prior to said hydroisomerization, by stripping with said hydrogen or hydrogen treat gas.

19. A process according to claim 18 wherein both said synthesis reactor light fraction and said hydroisomerized hydrocarbon product include a jet fuel fraction.

20. A process according to claim 18 wherein said zones are present in the same reaction vessel.

21. A process according to claim 20 wherein most of said hydrogen for both zones is introduced into said first zone and wherein said first zone effluent contains sufficient unreacted hydrogen to achieve said second zone hydroisomerization.

22. A process according to claim 12 wherein most of said hydrogen for both zones is introduced into said first zone and wherein said first zone effluent contains sufficient unreacted hydrogen to achieve said second zone hydroisomerization.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FIG—1

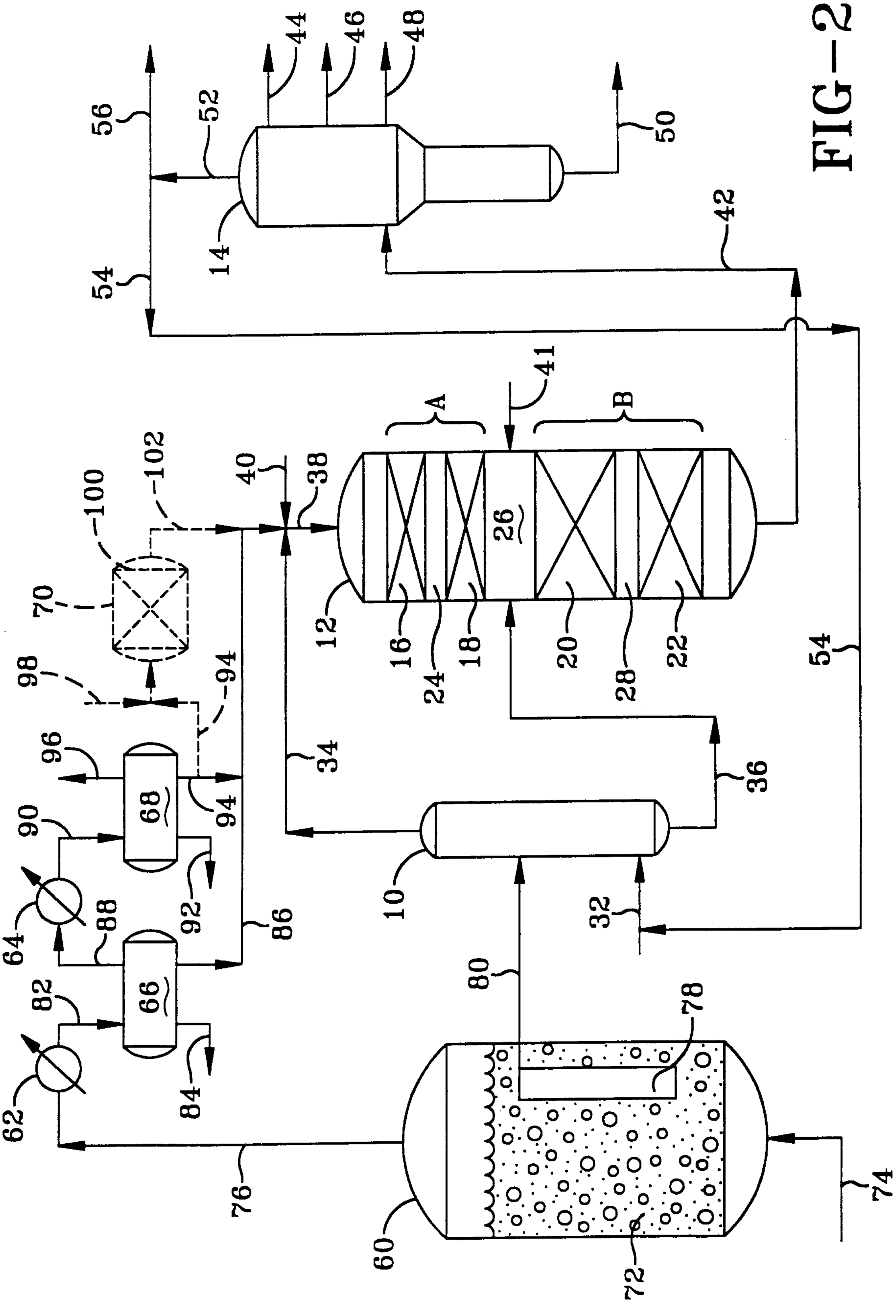
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FIG-2

INTERNATIONAL SEARCH REPORT

Inte .ional Application No
PCT/US 01/01765

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G65/00

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 25 April 2001	Date of mailing of the international search report 04/05/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Michiels, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte[illegible]ional Application No

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