

1. Field of the Invention

This invention relates to a process for the production of middle distillate fuels from waxy hydrocarbons. In particular, it relates to a process for the production of distillate fuels, notably kerosene, diesel fuels, jet fuels, lube base stocks and high quality blending components useful for the production of such fuels, via the hydroisomerization of waxy hydrocarbon feeds.

2. Background

It is known to produce distillate fuels from waxy hydrocarbon feeds via catalytic hydrocracking or hydroisomerization, or by both catalytic hydrocracking and hydroisomerization reactions. Conventionally, e.g., a waxy product made by the reaction of a synthesis gas over a Group VI or VIII metal catalyst, is mildly hydroisomerized and/or mildly hydrocracked over a suitable catalyst to produce some distillate fuel, or refinery feedstock useful for conversion to a distillate fuel. Typically however, the operation of these reactors, and catalysts, at high productivity e.g., high 700°F+ conversion and space velocities >1.5 LHSV, has resulted in undesirable shifts in product selectivity wherein the distillates are re-cracked to gas and naphtha before exiting the catalyst particle and flashing into the vapor phase. This phenomenon, which arises from pore diffusion limitations, limits the use of these catalysts, and leads to large investments for staged, fixed bed reactors, operating at relatively low space velocities.

Moreover, middle distillate fuels made from waxy products generally possess notoriously poor cold flow properties. This makes it difficult or even impossible to use such products in many environments since low freeze points are required to maintain fluidity, or flowability of the fuel at low temperatures.



In recently issued U.S. Patent 5,378,348, good yields of distillate fuels with excellent cold flow properties are produced from waxy Fischer-Tropsch products via an improved fixed bed process wherein the waxy Fischer-Tropsch product is separated into 500°F- and 500°F+ feed fractions and separately hydroisomerized to make middle distillates. The 500°F- fraction, e.g., a 320-500°F fraction, is hydrotreated in a first step at mild conditions over a Group VI or non-noble Group VIII metal catalyst to remove hetero-atoms, and hydroisomerized in a second step over a fixed bed of a Group VIII noble metal catalyst, suitably a platinum or palladium catalyst, to yield jet fuel and a light naphtha byproduct. The heavier 500°F+ fraction, on the other hand, is directly hydrocracked over a fixed bed of catalyst to produce a 320-700°F fraction which is useful as a diesel or jet fuel, or as a blending component of a diesel or jet fuel. Whereas this process demonstrates the feasibility of producing distillates with improved cold flow properties from waxy hydrocarbons there remains a desire, inter alia, to provide further improvements in hydroisomerization processes; both as relates to process improvements, and to improvements in product quality.

3. The Invention

The present invention, accordingly, relates to a hydroisomerization process, or further improved hydroisomerization process, for producing distillates with good cold flow properties in good yield from C₅+ paraffinic, or waxy hydrocarbon feeds, contacted and reacted, with added hydrogen, over a small particle size hydroisomerization catalyst dispersed, or slurried, in a paraffinic or waxy liquid hydrocarbon medium. The hydroisomerization reaction is conducted at conditions which produce C₅- 700°F distillate products including jet fuel, diesel fuel, lubes and high quality blending components for the production of these materials. In general, the hydroisomerization reaction is conducted at controlled temperatures ranging from about 400°F to about 850°F, preferably from about 500°F to about 700°F, at pressures ranging generally from about 100 pounds per square inch gauge (psig) to about 1500 psig, preferably from about 300 psig to about 1000 psig. The reaction is generally conducted at hydrogen treat gas rates ranging from about 1000 SCFB to about 10,000 SCFB, preferably from about 2000 SCFB to about 5000 SCFB. Space velocities range

generally from about 0.5 LHSV to about 20 LHSV, preferably from about 2 LHSV to about 10 LHSV.

The hydroisomerization catalyst is contained in the slurry in concentration greater than about 10 percent, preferably greater than about 25 percent, based on the total weight of the slurry, and the particles are of small average particle diameter, ranging generally from about 30 microns to about 150 microns, preferably from about 40 microns to about 60 microns average diameter. The catalyst is bifunctional, containing an active metal hydrogenation component or components, and a support component. The active metal component is preferably a Group IB, Group VIB, and/or Group VIII metal, or metals, of the Periodic Table Of The Elements (Sargent-Welch Scientific Company Copyright 1968) in amount sufficient to be catalytically active for hydroisomerization in the slurry within which the catalyst is dispersed. Generally, metal concentrations range from about 0.05 percent to about 20 percent, based on the total weight of the catalyst (wt.%), preferably from about 0.1 wt. percent to about 10 wt. percent. Exemplary of such metals are such non-noble Group VIII metals as nickel and cobalt, or mixtures of these metals with each other or with other metals, such as copper, a Group IB metal, or molybdenum, a Group VIB metal. Palladium is exemplary of a suitable Group VIII noble metal. The metal, or metals, is incorporated with the support component of the catalyst by known methods, e.g., by impregnation of the support with a solution of a suitable salt or acid of the metal, or metals, drying and calcination.

The catalyst support is constituted of metal oxide, or metal oxides, components at least one component of which is an acidic oxide active in producing olefin cracking and hydroisomerization reactions. Exemplary oxides include silica, silica-alumina, clays, e.g., pillared clays, magnesia, titania, zirconia, halides, e.g., chlorided alumina, and the like. The catalyst support is preferably constituted of silica and alumina, a particularly preferred support being constituted of up to about 35 wt.% silica, preferably from about 2 wt.% to about 35 wt.% silica, and having the following pore-structural characteristics:

<u>Pore Radius, Å</u>	<u>Pore Volume</u>
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 Å radius
100-300	<40% of the volume of the pores with 0-300 Å radius

The base silica and alumina materials can be, e.g., soluble silica containing compounds such as alkali metal silicates (preferably where $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$ to $1:4$), tetraalkoxy silane, orthosilic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates; or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within a range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material. The support may also contain small amounts, e.g., 1-30 wt.%, of materials such as magnesia, titania, zirconia, hafnia, or the like.

Support materials and their preparation are described more fully in U.S. Patent No. 3,843,509 incorporated herein by reference. The support materials generally have a surface area ranging from about 180-400 m^2/g , preferably 230-375 m^2/g , a pore volume generally of about 0.3 to 1.0 ml/g, preferably about 0.5 to 0.95 ml/g, bulk density of generally about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The feed materials that are isomerized with the catalyst of this invention are waxy feeds, i.e., C_5+ , preferably boiling above about 350°F (117°C) preferably above about 550°F (288°C) and may be obtained either from a Fischer-Tropsch process which produces substantially normal paraffins, or it may be obtained from slack waxes. Slack waxes are the byproducts of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal

growth, the wax being removed from the lubricating oil base stock by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (316°C), preferably in the range of 600°F (316°C) to about 1050°F (566°C), and may contain from about 1 to about 35 wt% oil. Waxes with low oil contents, e.g., 5-20 wt.% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and hetero-atom compounds by techniques known in the art; e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds.

In operation, total conversion of the 700°F+ feed to produce a 700°F- product, based on the weight of the feed, is maintained at a level ranging from about 30 percent to about 90 percent, preferably from about 50 percent to about 80 percent on a once-through, or fresh feed basis.

The slurry hydroisomerization reaction is conducted in one or a plurality of reactors connected in series, generally from about 1 to about 5 reactors; but preferably the reaction is conducted in a single reactor. The waxy hydrocarbon feed; e.g., a C₅+ Fischer-Tropsch wax, preferably one boiling above about 350°F (177°C), more preferably above about 550°F (288°C), is fed, with hydrogen, into the reactor, a first reactor of the series, into a slurry of the catalyst at hydroisomerization reaction conditions to hydroisomerize and convert a portion of the waxy feed to 700°F- products which include jet fuel, diesel fuel, lubes and high quality blending components. Use of the small diameter catalyst particles at high productivity levels eliminates pore diffusion limitations, and the degradation of distillate product selectivities and product quality as occurs in packed bed hydroisomerization processes; e.g., as occurs in packed bed reactors at space velocities >2 LHSV and 700°F+ conversion levels above 40%. In fact, a single slurry reactor can be used to obtain approximately as much conversion as three packed bed reactors in series in hydroisomerizing a similar wax at similar reaction conditions. Moreover, a simple water-steam cooling coil can be used in the slurry reactor to more efficiently remove and control the exothermic heats of reaction as contrasted with the requirements of a packed bed reactor

which requires a more complex system of trays and quenching techniques to control heat release. The hydroisomerized and partially hydrocracked wax, after passage through filters located at the top of the reactor is removed as a product, or preferably, is split in a pipe still into, e.g., 700°F- and 700°F+ fractions, the 700°F- fraction is removed as product, and all or a part of the 700°F+ fraction is recycled or pumped back into the reactor for further conversion to 700°F- products. Gas and light liquids from the top of the reactor are passed to a high pressure separator and split into byproduct fractions. Flashing and recovery of the primary products are readily accomplished in the slurry reactor, or series of reactors, which is characterized by short liquid and vapor residence times.

The 700°F+ recycle or pump around feature, supra, reduces the amount of 700°F+ and unreacted heavy liquids as occurs in once-through operations. Alternatively however, a small secondary fixed bed reactor, or slurry upgrader, can be staged with the larger single slurry reactor, or staged as a last reactor of a series of larger slurry hydroisomerization reactors, to convert the heavy liquids to lighter boiling products. The slurry upgrader reactor is preferably operated at temperatures ranging from about 450°F to about 750°F, preferably at pressures ranging from about 250 psig to about 1200 psig, and preferably at residence times ranging from about 0.05 hour to about 2 hours. Preferred catalysts contain cobalt-molybdenum, palladium, or nickel-copper dispersed on acidic supports. Suitable supports include both amorphous and crystalline inorganic oxides. Examples of supports comprise silica, alumina, clays, e.g., pillared clays, magnesia, titania, zirconia, halides, e.g., chlorided alumina, and mixtures thereof.

The following examples are illustrative of the more salient features of the invention. All parts, and percentages, are given in terms of weight unless otherwise specified.

The example immediately following demonstrates the greater effectiveness of a slurry of small particle diameter catalyst at high conversion levels, an effect which is quite the opposite to the results obtained in fixed bed hydroisomerization reactions which produces undesirable cracking.

EXAMPLE 1

A bifunctional hydroisomerization catalyst comprised of 0.50 wt.% palladium on an acidic silica-alumina support containing 25 wt.% Al_2O_3 was tested for activity as a hydroconversion catalyst using, as a representative test, the preparation of *iso*- $\text{C}_{16}\text{H}_{34}$ from *n*- $\text{C}_{16}\text{H}_{34}$ (i.e., hexadecane). The test procedure was as follows:

Experiments were carried out in batch micro-reactors consisting of a 1" stainless steel SwageLok cap and plug. All experiments were conducted at 650°F at H_2 pressures ranging from 250-750 psia pressure (cold) and a residence time of 2 hours. In a typical experiment 1.00 gram of hexadecane, a catalyst having an average particle diameter of about 70-90 microns, and hydrogen were loaded into the micro-reactor. The mini-bomb was sealed and loaded onto a stainless steel rack and placed in the sandbath. The reactors were agitated at a rate of 250 rpm for two hours and then removed from the sandbath and allowed to cool to room temperature. The bombs were then opened in an evacuated pressure cell attached to a gas collection bomb. The gas was collected and analyzed by mass spectroscopy. The resulting liquid was extracted with 10.0 mL of carbon disulfide and analyzed by gas chromatography.

Table 1A shows the conversion at three different pressures.

Table 1A. Product Distributions for Hexadecane Hydroisomerization

Pressure, psia (cold)	C_{16} /Catalyst w/w	C_{16} Conversion, wt.%
250	10:1	30.5
500	10:1	19.3
750	10:1	12.7

$$n\text{-C}_{16} \text{ conversion} = [1 - (\text{unreacted } n\text{-C}_{16} / \text{total hydrocarbon})] * 100$$

It is significant that the hexadecane:catalyst ratio of 10:1 (5.0 WHSV) produces moderate conversion levels. This illustrates the effectiveness

of the slurry reactor which may allow even higher LHSV. As expected, there is an inverse correlation between conversion and pressure.

At these low conversion levels the selectivity to *iso*-C₁₆ is essentially 100% with the majority of the isomers being single methyl branches. However, as shown in Table 1B, at higher conversion levels a significant amount of multi-methyl branches begin to appear. This is contrary to typical fixed bed reactors which produce undesirable cracking reactions at higher conversion levels.

Table 1B. Selectivity to Mono-Methyl C₁₆ Isomers

Selectivity to Mono-Methyl	
Pentadecane, wt.%	Conversion, wt.%
84.9	11.0
84.8	12.0
85.1	13.0
84.0	13.7
82.5	17.0
83.5	18.5
79.9	19.0
79.5	19.5
74.5	26.5
74.0	28.5
72.0	30.0
68.0	34.0

$$\text{iso-C}_{16} \text{ selectivity} = [\text{iso-C}_{16} / (\text{total hydrocarbon} - \text{unreacted n-C}_{16})] * 100$$

EXAMPLE 2

The catalyst described in Example 1 was further evaluated, this time at various temperatures and residence times using the same procedure as described in Example 1.

Table 2A shows the conversion and selectivity for the catalyst at a loading of 10 wt.% based on hexadecane feed at a pressure of 250 psig hydrogen and temperatures ranging from 650-700°F. Table 2B shows similar data under identical conditions with the exception of the temperature and the time. In this case, the temperature was held constant 700°F and the time varied over a range from 5-120 minutes. The weight percent conversion to C₁₆, it will be observed, increases with increasing temperature, while the weight percent selectivity to C₁₆ isoparaffins decreases with increasing temperature. As the residence time is increased the amount of C₁₆ conversion is increased, and the C₁₆ isoparaffins selectivity is decreased. The conversion/selectivity relationship is not changed. It is also noteworthy that the selectivity remains very high (i.e., >80%) over the range of conversion levels and does not drop significantly until the conversion exceeds 80%.

Table 2A. Conversion and Selectivity as a Function of Temperature

Temperature, °F	C ₁₆ Conversion wt.%	C ₁₆ Selectivity wt.%
650	27.2	97.5
660	36.3	97.3
670	48.6	95.5
680	71.6	90.7
690	82.4	84.6
700	95.2	62.2
0.50 wt.% Pd/SiO ₂ -Al ₂ O ₃		
10:1 C ₁₆ /Cat		
250 psig Hydrogen Pressure		
2 hours		

Table 2B. Conversion and Selectivity as a Function of Time

Time, min.	C ₁₆ Conversion wt.%	C ₁₆ Selectivity wt.%
5	7.8	98.3
15	22.6	96.7
30	48.4	94.2
60	76.7	86.2
90	88.9	75.3
120	95.2	62.2

0.50 wt.% Pd/SiO₂-Al₂O₃
10:1 C₁₆/Cat
250 psig Hydrogen Pressure
700°F

EXAMPLE 3

A bifunctional catalyst was prepared using a pillared interlayer clay (PILC) as the acidic support with palladium (0.50 wt.%) as the dehydrogenation source. Pillared clays are microporous materials formed by intercalating inorganic polyoxocations between clay layers. In this case, a zirconium pillared bentonite clay (Zr-PILC) was prepared from Na bentonite (Volclay HPM-20, American Colloid Co.) and zirconium acetate solution (ZAA Solution, Magnesium Elektron). The zirconium acetate and Na bentonite were added to an aqueous solution and stirred for three hours at room temperature, centrifuged, and washed with excess water. The catalyst was then dried at 120°C for two days and calcined at 400°C for two hours. The resulting Zr-PILC had a layer repeat distance 21Å and a BET surface area of 350 m²/gram. Palladium (0.50 wt.%) was added by incipient wetness using an aqueous solution of palladium amine nitrate (Aldrich).

As in Example 1, the catalyst was tested for activity as a hydroconversion catalyst using, as a representative test, the preparation of *iso*-C₁₆ from *n*-C₁₆ (i.e., hexadecane). The test procedure was identical to Example 1.

Table 3 shows the conversions and selectivity for the Pd/Zr-PILC catalyst at a loading of 10 wt.% based on hexadecane feed at a pressure of 250 psig hydrogen and temperatures ranging from 500-575°F. In making activity comparisons between the Pd/SiO₂-Al₂O₃ and Pd/Zr-PILC it will be observed that, though the Pd/Zr-PILC catalyst is more active, the selectivities of the two catalysts is essentially the same. This illustrates the effectiveness of the slurry hydroisomerization operation over significantly different catalyst.

Table 3. Conversion and Selectivity for Pd/Zr-PILC

Temperature, °F	C ₁₆ Conversion wt.%	C ₁₆ Selectivity wt.%
500	9.3	98.4
540	56.4	95.2
550	61.4	90.4
560	82.6	84.9
575	97.8	38.0

0.50 wt.% Pd/Zr-bentonite
 10:1 C₁₆/Cat
 250 psig Hydrogen Pressure
 2 hours

EXAMPLE 4

For demonstrative purposes, and for purposes of comparison, a catalyst prepared in accordance U.S. Patent No. 5,187,138 containing 4% SiO₂, 3% Co, 0.5% Ni, and 12% Mo supported on a silica alumina support initially containing 10% bulk silica was tested for activity and selectivity in conversion of a 500°F+ Fischer Tropsch wax at several processing conditions. In these tests, the catalyst was evaluated in a fixed bed reactor as 1/20" quadrilobe extrudates using a 200 cc catalyst charge. Table 4A summarizes results of these studies.

As in Example 1, conversion activity was improved with equivalent selectivity and product quality when the pressure was reduced from 1000 psig to 500 psig and the space velocity was increased from 0.5 to 1.0 LHSV. However, when the wax feed rate was increased to 3.0 LHSV and the temperature was increased to maintain conversion, the selectivity changed dramatically reflecting pore diffusion limitations, e.g., yields of jet fuel and diesel were lowered in favor of gas and naphtha production, and the quality of the jet fuel was also impaired as reflected by an increased freeze point. The critical space velocity where pore diffusion limitations begin to detrimentally affect the fixed bed catalytic behavior are not fully understood, but become apparent at reaction severities that provide 40-50% conversion of non-hydrotreated Fischer Tropsch waxes in reaction times of less than about 30 minutes; e.g., LHSV >2.

Table 4A.

Conditions	Relative Rate Constant for 700°F+ Wax Conversion	Selectivity
700°F/1000 psig/0.5 LHSV	1.0-Base	Base
700°F/500 psig/1.0 LHSV	2.0	Base
725°F/1000 psig/3.0 LHSV	4-5 -8% jet/diesel; +7% gas/naphtha	

For purpose of comparison, the kinetics for Fischer Tropsch wax conversion over the Pd/silica alumina catalyst of Examples 1 and 2 was investigated in a small upflow pilot plant using catalyst particles (ground extrudates) that were sized to 14/35 mesh. By varying the reaction temperature at constant pressure and space velocity (750 psig, 0.5 LHSV, 2500 SCF/B H₂ treat rate), it was established that the conversion of 700°F+ waxy hydrocarbons followed zero order kinetics with an apparent activation energy of 30-35 kcal/mole for the range of conversion near 30-70%.

These kinetics were used to estimate the major design parameters for a slurry hydroisomerization process operating at 750 psig, 20 minutes nominal liquids residence time, 40-70% 700°F+ conversion, and 20-35 vol% catalyst solids on slurry operated at 650-700°F. Two different processing options were considered based on a fresh feed rate of 60,000 barrels per day of wax, a once through process providing about 50% 700°F+ conversion, and a bottoms recycle configuration operating at 100% 700°F+ conversion and 50% conversion of fresh feed per pass. Table 4B summarizes selected results from the design calculations where it was found that slurry hydroconversion can be accomplished in a large single train reactor.

Table 4B.

Slurry Process Bases:

- 60 kB/D fresh feed
- 50% (once through) or 100% (recycle, 50% C/P) 700°F+ conversion
- 10% gas hold-up
- 25 vol% catalyst solids on slurry
- 15 vol% reactor internals (filtration, heat removal)
- 10' reactor freeboard zone

<u>Case</u>	<u>Reactor Volume (cu. ft.)</u>	<u>Nominal inside cylindrical reactor dimensions (ft)</u>
Once Through	7840	16' x 50'
Recycle	15500	20' x 60'

The hydroisomerization process of this invention can be practiced over a wide variety of hydrodynamic regimes, particularly those characterized as bubbling flow, turbulent flow and churn turbulent flow slurry operations. The process is particularly adapted to achieve effective use of reactor volume over a variety of processing conditions.

It is apparent that various modifications and changes can be made without departing the spirit and scope of the invention.



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CLAIMS:

1. A hydroisomerization process for the conversion of a C₅+ paraffinic feedstock to middle distillates which comprises contacting, and reacting at hydroisomerization reaction conditions said C₅+ paraffinic feedstock, and hydrogen, with a catalyst comprising a Group IB metal, a Group VIB metal, a Group VIII metal, or mixture of two or more of said metals, supported on an acidic particulate solid, of average particle diameter ranging from about 30 microns to about 150 microns, dispersed in a paraffinic liquid hydrocarbon.
2. The process of Claim 1 wherein the catalyst contains at least one Group VIII metal.
3. The process of Claim 1 wherein the catalyst contains at least one Group VIII metal, and at least one Group IB or Group VIB metal.
4. The process of any of Claims 1, 2 and 3 wherein the metal concentration contained in the catalyst ranges from about 0.05 percent to about 20 percent, based on the total weight of the catalyst.
5. The process of any of Claims 1, 2, 3 or 4 wherein the acidic support component of the catalyst is silica-alumina.
6. The process of Claim 1 wherein the hydroisomerization reaction conditions are characterized as having temperatures ranging from about 400°F to about 850°F, pressures ranging from about 100 psig to about 1500 psig, hydrogen treat gas rates ranging from about 1000 SCFB to about 10,000 SCFB, and space velocities ranging from about 0.5 LHSV to about 20 LHSV.
7. The process of any of Claims 1 through 6 wherein the average particle diameter of the catalyst ranges from about 40 microns to about 60 microns.
8. The process of Claim 1 wherein the C₅+ paraffinic feedstock is a Fischer-Tropsch reaction product.

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9. The process of Claim 1 wherein the hydroisomerization reaction is conducted in one or a plurality of serially connected reactors.

10. The process of Claim 9 wherein the feed to the single hydroisomerization reactor, or feed to the lead hydroisomerization reactor of the series, is a C₅-700°F+ feedstock and the product removed from the single reactor, or product from the last reactor of the series is split into C₅-700°F- and C₅-700°F+ fractions, the C₅-700°F- product is recovered and the C₅-700°F+ fraction is recycled to the single reactor, or lead reactor of the series.

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