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(54) **WAX HYDROISOMERIZATION PROCESS**

WACHSHYDROISOMERISIERVERFAHREN

PROCEDE D'HYDRO-ISOMERISATION DE PARAFFINE

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(56) References cited:
US-A- 4 851 109
US-A- 4 983 274
US-A- 5 275 719
US-A- 5 282 958
US-A- 5 302 279
US-A- 5 362 378

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EP 0 788 533 B1

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to co-pending application Serial No. 08/017,949 (continuation of S.N. 07/548,702) entitled Production of High Viscosity Index Lubricants, which describes a two-step process for producing high Viscosity Index lubricants by hydrocracking and hydroisomerization of petroleum wax feeds using a low acidity zeolite beta hydroisomerization catalyst. Serial No. 08/017,955, also entitled Production of High Viscosity Index Lubricants, describes a wax hydroisomerization process using zeolite catalysts of controlled low acidity at high pressures. The instant application is a continuation-in-part of Serial No. 08/017,955. The instant application is also a continuation-in-part of Serial No. 08/017,949. Serial No. 08/017,955 is incorporated by reference in the instant application. Corresponding European Patent No. 464,547A1, (which specifies the use of low acidity zeolite beta for wax isomerization) is also incorporated by reference. The instant application is also related to co-pending application S.N. 08/303,091, in which two dewaxing catalysts operate synergistically to produce a lubricant of high Viscosity Index.

FIELD OF THE INVENTION

[0002] This invention relates to the production of high Viscosity Index lubricants by isomerizing petroleum waxes using large pore zeolites of small crystal size. The waxes may be hydrocracked prior to isomerization. The isomerization product may be further dewaxed by either solvent or catalytic means in order to achieve a target pour point.

BACKGROUND OF THE INVENTION

[0003] Mineral oil based lubricants are conventionally produced by a separative sequence carried out in the petroleum refinery which comprises fractionation of a paraffinic crude oil under atmospheric pressure followed by fractionation under vacuum to produce distillate fractions (neutral oils) and a residual fraction which, after deasphalting and severe solvent treatment may also be used as a lubricant basestock. This refined residual fraction is usually referred to as bright stock. Neutral oils, after solvent extraction to remove low viscosity index (V.I.) components, are conventionally subjected to dewaxing, either by solvent or catalytic dewaxing processes, to achieve the desired pour point. The dewaxed lube stock may be hydrofinished to improve stability and remove color bodies. Viscosity Index (V.I.) is a reflection of the amount of viscosity decrease a lubricant undergoes with an increase in temperature. The products of solvent dewaxing are dewaxed lube oil and slack wax. Slack wax typically contains 60% to 90% wax with the balance being entrained oil. In some instances it is desirable to purify the slack wax of entrained oil by subjecting the slack wax to a deoiling step in which the slack wax is diluted with dewaxing solvents and filtered at a temperature higher than that used in the filtering step used to produce the slack wax. The purified wax is termed deoiled wax, and contains greater than 95% wax. The byproduct of the second filtration typically contains 50% wax and is termed foots oil.

[0004] Catalytic dewaxing of lube stocks is accomplished by converting waxy molecules to light products by cracking, or by isomerizing waxy molecules to form species which remain in the dewaxed lube. Dewaxing catalysts preserve high yield primarily by having pore structures which inhibit cracking of cyclic and highly branched species, those generally associated with dewaxed lube, while permitting easier access to catalytically active sites to near-linear molecules, of which wax is generally composed. Catalysts which significantly reduce the accessibility of species on the basis of molecular size are termed shape selective. Increasing the shape selectivity of a dewaxing catalyst will frequently increase the yield of dewaxed oil.

[0005] The shape selectivity of a dewaxing catalyst is limited practically by its ability to convert waxy molecules which have a slightly branched structure. These types of species are more commonly associated with heavier lube stocks, such as bright stocks. Highly shape selective dewaxing catalysts may be unable to convert heavy, branched wax species leading to a hazy lube appearance at ambient temperature and high cloud point relative to pour point.

[0006] Conventional lube refining techniques rely upon the proper selection and use of crude stocks, usually of a paraffinic character, which produce lube fractions with desired qualities in adequate amounts. The range of permissible crude sources may, however, be extended by the lube hydrocracking process which is capable of utilizing crude stocks of marginal or poor quality, usually with a higher aromatic content than the best paraffinic crudes. The lube hydrocracking process, which is well established in the petroleum refining industry, generally comprises an initial hydrocracking step carried out under high pressure, at high temperature, and in the presence of a bifunctional catalyst which effects partial saturation and ring opening of the aromatic components which are present in the feed. The hydrocracked product is then subjected to dewaxing in order to reach the target pour point since the hydrocracked product usually contains species with relatively high pour points. Frequently the liquid product from the dewaxing step is subjected to a low temperature, high pressure hydrotreating step to reduce the aromatic content of the lube to the desired level.

[0007] Current trends in the design of automotive engines are associated with higher operating temperatures as the

efficiency of the engines increases. These higher operating temperatures require successively higher quality lubricants. One of the requirements is for higher viscosity indices (V.I.) in order to reduce the effects of the higher operating temperatures on the viscosity of the engine lubricants. High V.I. values have conventionally been attained by the use of V.I. improvers e.g. polyacrylates and polystyrenes. V.I. improvers tend to undergo degradation due to high temperatures and high shear rates encountered in the engine. The more stressing conditions encountered in high efficiency engines result in even faster degradation of oils which employ significant amounts of V.I. improvers. Thus, there is a continuing need for automotive lubricants which are based on fluids of high Viscosity Index and which are resistant to the high temperature, high shear rate conditions encountered in modern engines.

[0008] Synthetic lubricants produced by the polymerization of olefins in the presence of certain catalysts have been shown to possess excellent V.I. values, but they are relatively expensive to produce. There is therefore a need for the production of high V.I. lubricants from mineral oil stocks which may be produced by techniques comparable to those presently employed in petroleum refineries.

[0009] U.S. Patent No. 4,975,177 discloses a two-stage dewaxing process for producing lube stocks of high V.I. from waxy feedstocks. In the first stage of this process, the waxy feed is catalytically dewaxed by isomerization over zeolite beta containing a noble metal. The examples employ pressures below 6996 kPa_a (1000 psig) and a catalyst of moderate acidity, with an alpha value of about 55. The product of the isomerization step still contains waxy species and requires further dewaxing to meet target pour point. The second-stage dewaxing employs either solvent dewaxing, in which case the rejected wax may be recycled to the isomerization stage to maximize yield, or catalytic dewaxing. Catalysts which may be used in the second stage are ZSM-5, ZSM-22, ZSM-23, and ZSM-35. To preserve yield and V.I., the second stage dewaxing catalyst should have selectivity similar to solvent dewaxing. U.S. Patent 4,919,788 also teaches a two-stage dewaxing process in which a waxy feed is partially dewaxed by isomerization over a siliceous Y or beta catalyst containing a noble metal. Examples indicate pressures below 10030 kPa_a and a zeolite beta catalyst of moderate acidity with an alpha value of 55. This product is subsequently dewaxed to desired pour point using either solvent dewaxing or catalytic dewaxing. Dewaxing catalysts with high shape selectivity, such as ZSM-22 and ZSM-23, are preferred catalysts.

[0010] Serial No. 08/017,949 discloses a two stage hydrocracking and hydroisomerization process. The first stage employs a bifunctional catalyst comprising a metal hydrogenation component on an amorphous acidic support. The second stage, the hydroisomerization step, is carried out over zeolite beta. Subsequent dewaxing is optional but recommended. Either solvent dewaxing or catalytic dewaxing maybe used subsequently in order to obtain target V.I. and pour point.

[0011] In S.N. 08/017,955, petroleum wax feed is subjected to hydroisomerization over a noble metal-containing zeolite catalyst of low acidity. The paraffins present in the feed are selectively converted to iso-paraffins of high V.I. but lower pour point so that a final lube product of good viscometric properties is produced with a minimal degree of subsequent dewaxing. The process, which operates under high pressure, is well suited for upgrading waxy feeds such as slack wax with aromatic contents greater than about 15 wt% to high Viscosity Index lubricating oils with high single pass yields and limited requirement for product dewaxing.

[0012] U.S. Pat. No. 5,302,279 (and the analogous European patent application EP 464 547 Al) teaches the use of a low acidity form of zeolite beta for isomerizing and dewaxing furfural raffinates. The improved selectivity of a catalyst of low acidity over one of high acidity was demonstrated in the examples.

[0013] U.S. Pat. No. 5,282,958 has demonstrated improved isomerization selectivity for n-hexadecane using unipore zeolites of small crystal size, although the crystal sizes quoted are all.extremely small and are inconsistent with measurements made by others in the field of catalyst preparation. Additionally, constrained intermediate pore zeolites such as ZSM-22 and ZSM-23, which are used in this patent, do not permit access to the framework of the catalyst as readily as other intermediate and large pore molecular sieves. Reactions of lubricant-type molecules are likely to occur near the pore mouth of intermediate pore catalysts. The crystal size of ZSM-22 or ZSM-23 is not likely to impact isomerization selectivity as strongly as for catalysts with a less restrictive pore structure.

SUMMARY OF THE INVENTION

[0014] The concept of the instant invention involves a process for isomerizing and dewaxing waxy feedstocks using large pore molecular sieves with small crystal size for producing high quality, at least 130 VI lubricant base stocks. Large pore molecular sieves applicable to this invention are defined as having a Constraint Index less than one and include zeolites beta, mordenite and Y. Large pore molecular sieves have accessible pore structures for forming highly branched paraffins from waxy feed stocks, particularly those stocks containing high molecular weight species. Such branched paraffins have a high VI and low pour point. Because isomerization occurs within the pores of the catalyst, small crystal size enables branched paraffins to readily diffuse from the zeolite pores without cracking, thus resulting in high lube yields.

[0015] The instant invention involves processing a waxy hydrocarbon feedstock over an isomerization catalyst which

converts waxy species to branched paraffins. The formation of these branched paraffins which have high Viscosity Indices and low pour points, results in a lubricant base stock having superior quality.

[0016] The feedstocks used in this invention contain at least 20% wax and preferably they contain more than 50% wax. The feedstock may be pretreated prior to isomerization to remove nitrogen and sulfur-containing species and to reduce its aromatics content. The raw or pretreated feedstock is contacted with a noble metal-containing low-acidity large pore molecular sieve over which a substantial fraction of the wax in the feed is isomerized to form species typically associated with lube base stocks. Isomerization occurs typically at a pressure between 4238 kPa_a(600 psig) and 20,786 kPa_a (3000 psig) . The effluent from isomerization may be hydrotreated to remove residual aromatics. The zeolite beta catalyst discussed in the examples of this invention has a crystal diameter of less than 0.1 microns in order to maximize the relative rates of isomerization to cracking. Small diameter crystals allow isomerized species to diffuse readily from the catalyst framework, thereby reducing the potential for their cracking. The prior art, discussed in the Background, supra, demonstrates improved selectivity of a catalyst of low acidity over one of higher acidity. Low zeolitic acidity coupled with high metals activity is necessary for high isomerization selectivity but does not guarantee such selectivity. The crystal size of the certain molecular sieves has been found to be an important factor impacting isomerization selectivity. Large crystals increase the diffusion path for isomerized species to exit the framework, thus increasing the possibility that the isomerized molecule will crack within the framework. The invention detailed here illustrates the selectivity benefit for isomerizing waxy feeds, such as slack waxes, with a small crystal, low-acidity zeolite beta catalyst.

[0017] The instant invention employs zeolite beta loaded with a noble metal such as Pt to selectively isomerize waxy species to high VI lubricants. This catalyst has high isomerization selectivity, tolerance for moderate levels of sulfur and nitrogen, and an accessible pore structure to permit conversion of bulky wax molecules. The selectivity of zeolite beta loaded with Pt is optimized if it has low zeolitic acidity, high metals dispersion and small crystal size.

DESCRIPTION OF THE DRAWING

[0018] The Figure compares the selectivity for wax isomerization for two low-acidity silica-bound zeolite beta catalysts loaded with Pt. One possesses a small crystal size and the other possesses a large crystal size.

DETAILED DESCRIPTION OF THE INVENTION

[0019] In the present process feeds with a relatively high wax content are converted to high V.I. lubricants in a hydroisomerization process using a low acidity zeolite hydroisomerization catalyst having a small crystal size. Subsequent dewaxing may be required to remove residual wax from the isomerization step. The products are characterized by good viscometric properties including high-viscosity index, typically at least 140 at -17.78°C (0°F) pour point and usually in the range 143 to 147.

Feed

[0020] The processes of the instant invention are capable of operating with a wide range of feeds of mineral oil origin to produce a range of lubricant products with good performance characteristics. Such characteristics include low pour point, low cloud point, and high Viscosity Index. The quality of the product and the yield in which it is obtained is dependent upon the quality of the feed and its amenability to processing by the catalysts of the instant invention. Products of the highest V.I. are obtained by using preferred wax feeds such as slack wax, foots oil, deoiled wax, vacuum distillates derived from waxy crudes, wax from Fischer-Tropsch process, petrolatum, vacuum gas oil or raffinate from solvent extraction of vacuum distillate. Products with lower V.I. values may also be obtained from other feeds which contain a lower initial quantity of waxy components.

[0021] The feeds which may be used should have an initial boiling point which is no lower than the initial boiling point of the desired lubricant. A typical initial boiling point of the feed exceeds 343°C (650°F). Feeds of this type which may be used include vacuum gas oils as well as other high boiling fractions such as distillates from the vacuum distillation of atmospheric resids, raffinates from the solvent extraction of such distillate fractions, hydrocracked vacuum distillates and waxes from the solvent dewaxing of raffinates and hydrocrackates.

[0022] The feed may require preparation in order to be treated satisfactorily in the hydroisomerization step. The preparation steps which are generally necessary are those which remove low V.I. components such as aromatics and polycyclic naphthenes, as well as nitrogen and sulfur containing species.

[0023] Suitable pre-treatment steps for preparing feeds for the hydroisomerization are those which remove the aromatics and others low V.I. components from the initial feed. Hydrotreatment is an effective pretreatment step, particularly at high hydrogen pressures which are effective for aromatics saturation e.g. 5,600 kPa_a (800 psig) or higher. Mild hydrocracking may also be employed as pretreatment and is preferred in the instant invention, if pretreatment is required. Example 3, infra, discusses the hydrocracking conditions employed in the instant invention in order to prepare

a feed for the dewaxing process. Pressures over 6996 kPa_a (1000 psig) are preferred for hydrocracking treatment. Hydrocracking removes nitrogen containing and sulfur-containing species and reduces aromatics content as Table 6 below illustrates. Hydrocracking, in this example, has also slightly altered the boiling range of the feed, causing it to boil in a lower range. Commercially available catalysts such as fluoride nickel-tungsten on alumina ($NiWF-/Al_2O_3$) may be employed for the hydrocracking pretreatment.

[0024] The preferred gas oil and vacuum distillate feeds are those which have a high wax content, as determined by ASTM D-3235, preferably over about 30 wt% and more preferably over 50 wt%. Feeds of this type include certain South-East Asian and mainland China oils. Minas Gas oil, from Indonesia, is such a feed. These feeds usually have a high paraffin content, as determined by a conventional analysis for paraffins, naphthenes, and aromatics. The properties of typical feeds of this type are described in S.N. 07/017,955. A preferred feed has a wax content of at least 40 wt.% and an aromatics content of less than 25 wt.%.

[0025] As stated previously, the wax content of the preferred feeds is high, generally at least 30 wt% (as determined by ASTM Test D-3235) prior to pretreatment. The wax content before pretreatment is more usually at least 60 to 80 wt% with the balance being occluded oil comprising iso-paraffins, aromatics and naphthenics. These waxy, highly paraffinic wax stocks usually have low viscosities because of their relatively low content of aromatics and naphthenes although the high content of waxy paraffins gives them melting points and pour points which render them unacceptable as lubricants without further processing. Wax feeds are discussed further in S.N. 07/017,955.

[0026] The most preferred type of wax feeds are the slack waxes, (see Table 2, infra). These are the waxy products obtained directly from a solvent dewaxing process, e.g. an MEK (methyl ethyl ketone)/toluene or MEK/MIBK (methyl isobutyl ketone) or propane dewaxing process. The slack wax, which is a solid to semi-solid product, comprising primarily highly waxy paraffins (mostly n- and mono-methyl paraffins) together with occluded oil, may be used as such or it may be subjected to an initial deoiling step of a conventional character in order to remove the occluded oil. Removal of the oil results in a harder, more highly paraffinic wax which may then be used as the feed. The byproduct of the deoiling step is termed Foots Oil and it may also be used as feed to the process. Foots Oil contains most of the aromatics present in the original slack wax and with these aromatics, most of the heteroatoms. Slack wax and foots oil typically require pretreatment prior to catalytic dewaxing. The oil content of deoiled waxes may be quite low and for this purpose, measurement of the oil content by the technique of ASTM D721 may be required for reproducibility, since the D-3235 test referred to above tends to be less reliable at oil contents below about 15 wt%.

[0027] The compositions of some typical waxes are given in Table 1 below.

Table 1

Wax Composition - Arab Light Crude				
	A	B	C	D
Paraffins, wt. pct.	94.2	81.8	70.5	51.4
Mono-naphthenes, wt. pct.	2.6	11.0	6.3	16.5
Poly-naphthenes, wt. pct.	2.2	3.2	7.9	9.9
Aromatics, wt. pct.	1.0	4.0	15.3	22.2

[0028] A typical slack wax feed has the composition shown in Table 2 below. This slack wax is obtained from the solvent (MEK) dewaxing of a 65 mm^2/s (cSt) at 40°C (300 SUS) neutral oil obtained from an Arab Light crude.

Table 2

Slack Wax Properties	
API	39
Hydrogen, wt. pct.	15.14
Sulfur, wt. pct.	0.18
Nitrogen, ppmw	11
Melting point, °C (°F)	57 (135)
KV at 100°C, cSt	5.168
PNA, wt pct:	
Paraffins	70.3

Table 2 (continued)

Slack Wax Properties		
Naphthenes		13.6
Aromatics		16.3
Simulated Distillation:		
%	°C	(°F)
5	375	(710)
10	413	(775)
30	440	(825)
50	460	(860)
70	482	(900)
90	500	(932)
95	507	(945)

[0029] Another slack wax suitable for use in the present process has the properties set out in Table 6 infra as part of Example 3. This wax is prepared by the solvent dewaxing of a heavy neutral furfural raffinate. As discussed previously, hydrocracking may be employed to prepare the slack wax for hydroisomerization.

Hydrocracking Process (Optional)

[0030] If hydrocracking is employed as a pretreatment step an amorphous bifunctional catalyst is preferably used to promote the saturation and ring opening of the low quality aromatic components in the feed to produce hydrocracked products which are relatively more paraffinic. Hydrocracking is carried out under high pressure to favor aromatics saturation but the boiling range conversion is maintained at a relatively low level in order to minimize cracking of the saturated components of the feed and of the products obtained from the saturation and ring opening of the aromatic materials. Consistent with these process objectives, the hydrogen pressure in the hydrocracking stage is at least about 5500 kPa_a. (800 psig) and usually is in the range of 6900 kPa_a (1,000 psig) to 20700 kPa_a (3,000 psig). Normally, hydrogen partial pressures of at least 10500 kPa_a (1500 psig) are best in order to obtain a high level of aromatic saturation. Hydrogen circulation rates of at least about 178 $n.l.l.^{-1}$ (1000 SCF/Bbl), preferably in the range of 900 $n.l.l.^{-1}$ (2,000 SCF/Bbl) to 1800 $n.l.l.^{-1}$ (8000 SCF/Bbl) are suitable.

[0031] In the hydrocracking process, the conversion of the feed to products boiling below the lube boiling range, typically to 345°C- (650°F-) products is limited to no more than 50 wt% of the feed and will usually be not more than 30 wt% of the feed in order to maintain the desired high single pass yields which are characteristic of the process. The actual conversion is dependent on the quality of the feed with slack wax feeds requiring a lower conversion than petrolatum where it is necessary to remove more low quality polycyclic components. For slack wax feeds derived from the dewaxing of neutral stocks, the conversion to 345°C-(650°F-) products will, for all practical purposes not be greater than 10 to 20 wt%, with 5-15 wt% being typical for most slack waxes. Higher conversions may be encountered with petrolatum feeds because they typically contain more low quality components. With petrolatum feeds, the hydrocracking conversion will typically be in the range of 15 to 25 wt% to produce high VI products. The conversion may be maintained at the desired value by control of the temperature in the hydrocracking stage which will normally be in the range 315° to 430°C (600° to 800°F) and more usually in the range of about 345° to 400°C (650° to 750°F). Space velocity variations may also be used to control severity although this will be less common in practice in view of mechanical constraints on the system. Generally, the space velocity will be in the range of 0.25 to 2 LHSV, $hr.^{-1}$ and usually in the range of 0.5 to 1.5 LHSV.

[0032] A characteristic feature of the hydrocracking operation is the use of a bifunctional catalyst comprising an acidic support. In general terms, these catalysts include a metal component for promoting the desired aromatics saturation reactions and usually a combination of base metals is used, with one metal from the iron group (Group VIII) in combination with a metal of Group VIB. Thus, the base metal such as nickel or cobalt is used in combination with molybdenum or tungsten. The preferred combination is nickel/tungsten since it has been found to be highly effective for promoting the desired aromatics hydrocracking reaction. Noble metals such as platinum or palladium may be used since they have good hydrogenation activity in the absence of sulfur but they will normally not be preferred. The amounts of the metals present on the catalyst are conventional for lube hydrocracking catalysts of this type and generally will range from 1 to 10 wt% of the Group VIII metal and 10 to 30 wt% of the Group VI metal, based on the total weight of the catalyst. If a noble metal component such as platinum or palladium is used instead of a base metal such as nickel

or cobalt, relatively lower amounts are in order in view of the higher hydrogenation activities of these noble metals, typically from about 0.5 to 5 wt% being sufficient. The metals may be incorporated by any suitable method including impregnation onto the porous support after it is formed into particles of the desired size or by addition to a gel of the support materials prior to calcination. Addition to the gel is a preferred technique when relatively high amounts of the metal components are to be added e.g. above 10 wt% of the Group VIII metal and above 20 wt% of the Group VI metal. These techniques are conventional in character and are employed for the production of lube hydrocracking catalysts.

[0033] The metal component of the catalyst is generally supported on a porous, amorphous metal oxide support and alumina is preferred for this purpose although silica-alumina may also be employed. Other metal oxide components may also be present in the support although their presence is less desirable. Consistent with the requirements of a lube hydrocracking catalyst, the support should have a pore size and distribution which is adequate to permit the relatively bulky components of the high boiling feeds to enter the interior pore structure of the catalyst where the desired hydrocracking reactions occur. To this extent, the catalyst will normally have a minimum pore size of about 50 Å i.e with no less than about 5 percent of the pores having a pore size less than 5 nm (50 Å) pore size, with the majority of the pores having a pore size in the range of 5-40 nm (50-400 Å) (no more than 5 percent having a pore size above 40 nm (400 Å)), preferably with no more than about 30 percent having pore sizes in the range of 20-40 nm (200-400 Å). Preferred catalysts for hydrocracking have at least 60 percent of the pores in the 5-20 nm (50-200 Å) range. The pore size distribution and other properties of some typical lube hydrocracking (LHDC) catalysts suitable for use in the hydrocracking are shown in Table 3 below:

Table 3

LHDC Catalyst Properties			
Form	1.5mm cyl.	1.5 mm. tri.	1.5 mm.cyl.
Pore Volume, cc/gm	0.331	0.453	0.426
Surface Area, m2/gm	131	170	116
Nickel, wt. pct.	4.8	4.6	5.6
Tungsten, wt. pct.	22.3	23.8	17.25
Fluorine, wt. pct.	-	-	3.35
SiO_2/Al_2O_3 binder	-	-	62.3
Real Density, gm/cc	4.229	4.238	4.023
Particle Density, gm/cc	1.744	1.451	1.483
Packing Density, gm/cc	1.2	0.85	0.94

[0034] If necessary in order to obtain the desired conversion, the catalyst may be promoted with fluorine, either by incorporating fluorine into the catalyst during its preparation or by operating the hydrocracking in the presence of a fluorine compound which is added to the feed. Fluorine containing compounds may be incorporated into the catalyst by impregnation during its preparation with a suitable fluorine compound such as ammonium fluoride (NH_4F) or ammonium bifluoride ($NH_4F•HF$) of which the latter is preferred. The amount of fluorine used in catalysts which contain this element is preferably from about 1 to 10 wt%, based on the total weight of the catalyst, usually from about 2 to 6 wt%. The fluorine may be incorporated by adding the fluorine compound to a gel of the metal oxide support during the preparation of the catalyst or by impregnation after the particles of the catalyst have been formed by drying or calcining the gel. If the catalyst contains a relatively high amount of fluorine as well as high amounts of the metals, as noted above, it is preferred to incorporate the metals and the fluorine compound into the metal oxide gel prior to drying and calcining the gel to form the finished catalyst particles.

[0035] The catalyst activity may also be maintained at the desired level by in situ fluoriding in which a fluorine compound is added to the stream which passes over the catalyst in this stage of the operation. The fluorine compound may be added continuously or intermittently to the feed or, alternatively, an initial activation step may be carried out in which the fluorine compound is passed over the catalyst in the absence of the feed e.g. in a stream of hydrogen in order to increase the fluorine content of the catalyst prior to initiation of the actual hydrocracking. In situ fluoriding of the catalyst in this way is preferably carried out to induce a fluorine content of about 1 to 10 percent fluorine prior to operation, after which the fluorine can be reduced to maintenance levels sufficient to maintain the desired activity. Suitable compounds for in situ fluoriding are orthofluorotoluene and difluoroethane.

[0036] The metals present on the catalyst are preferably used in their sulfide form and to this purpose pre-sulfiding of the catalyst should be carried out prior to initiation of the hydrocracking. Sulfiding is an established technique and it is typically carried out by contacting the catalyst with a sulfur-containing gas, usually in the presence of hydrogen. The mixture of hydrogen and hydrogen sulfide, carbon disulfide or a mercaptan such as butol mercaptan is conventional

for this purpose. Presulfiding may also be carried out by contacting the catalyst with hydrogen and a sulfur-containing hydrocarbon oil such as a sour kerosene or gas oil.

Hydroisomerization

[0037] The paraffinic components present in the original wax feed possess high viscosity indices but have relatively high pour points. The objective of the process of the invention is, therefore, to effect a selective conversion of waxy species while minimizing conversion of more branched species characteristic of lube components. The conversion of wax occurs preferentially by isomerization to form more branched species which have lower pour points and. cloud points. Some degree of cracking accompanies isomerization, the extent of cracking varying with the degree of wax conversion.

Hydroisomerization Catalyst

[0038] The catalyst used in hydroisomerization in this invention is one which has a high selectivity for the isomerization of waxy, linear or near linear paraffins to less waxy, isoparaffinic products. Catalysts of this type are bifunctional in character, comprising a metal component on a large pore size, porous support of relatively low acidity. The acidity is maintained at a low level in order to reduce conversion to products boiling outside the lube boiling range during this stage of the operation. In general terms, the catalyst should have an alpha value not more than 30 prior to metals addition, with preferred values not more than 20. (See Example 1)

The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec^{-1}). The alpha test is described in U.S. Patent 3,354,078 and in J. Catalysis, 1, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538 °C and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980).

[0039] The hydroisomerization catalyst comprises a large pore molecular sieve, generally a zeolite or silica: aluminophosphate. The large pore sieve is supported by a porous binder. Large pore zeolites usually have at least one pore channel consisting of twelve-membered oxygen rings . Zeolites beta, Y and mordenites are large pore zeolites. The catalysts of this invention possess a crystal diameter of less than 0.1 micrometers in order to maximize the relative rates of isomerization to cracking. Small diameter crystals allow isomerized species to diffuse readily from the crystal framework reducing the potential for their cracking.

[0040] The preferred hydroisomerization catalyst employs zeolite beta since this zeolite has been shown to possess outstanding activity for paraffin isomerization in the presence of aromatics, as disclosed in U.S. 4, 419 , 220. The low acidity forms of zeolite beta may be obtained by synthesis of a highly siliceous form of the zeolite e.g with a silica-alumina ratio above about 500:1 or, more readily, by steaming zeolites of lower silica-alumina ratio to the requisite acidity level. They may also be obtained by extraction with acids such as dicarboxylic acid, as disclosed in U.S. Patent No. 5,200,168. U.S. Patent No. 5,238,677 discloses the synthesis of dealuminated mordenite by oxalic acid extraction. U.S. Patent No. 5,164,169 discloses the preparation of highly siliceous zeolite beta employing a chelating agent such as tertiary alkenolamines in the synthesis mixture. U.S. Patent No. 3,308,069 describes the synthesis of zeolite beta with a crystal size ranging from 0.01 to 0.05 microns. Catalysts with crystal sizes of this range are used in the instant invention. The crystal size in the instant invention is not to exceed 0.1 micron, although crystal size between 0.01 and 0.05 microns are preferred.

[0041] The most preferred zeolites are severely steamed and possess a framework silica-alumina ratio if at least 200:1 and more preferably above 400:1.

[0042] The steaming conditions should be adjusted in order to attain the desired alpha value in the final catalyst and typically utilize atmospheres of 100 percent steam, at temperatures of from about 427° to 595°C (800° to about 1100°F). Normally, the steaming will be carried out at temperatures above 538°C (1000°F), for about 12 to 120 hours, typically about 96 hours, in order to obtain the desired reduction in acidity.

[0043] Another method of producing a low acidity zeolite beta catalyst is by replacement of a portion of the framework aluminum of the zeolite with another trivalent element such as boron which results in a lower intrinsic level of acid activity in the zeolite. The preferred zeolites of this type are those which contain framework boron. Boron is usually added to the zeolite framework prior to the addition of other metals. In zeolites of this type, the framework consists principally of silicon tetrahedral coordinated and interconnected with oxygen bridges. The minor amount of an element (alumina in the case of alumina-silicate zeolite beta) is also coordinated and forms part of the framework. The zeolite also contains material in the pores of the structure although these do not form part of the framework constituting the characteristic structure of the zeolite. The term "framework" boron is used here to distinguish between material in the

framework of the zeolite which is evidenced by contributing ion exchange capacity to the zeolite, from material which is present in the pores and which has no effect on the total ion exchange capacity of the zeolite. Zeolite beta possesses a constraint index between 0.60 and 2.0 at temperatures between 316°C and 399°C although Constraint Indexes less than 1 are preferred.

[0044] Methods for preparing high silica content zeolites containing framework boron are known and are described, for example, in U.S. Patents Nos. 4,269,813. A method for preparing zeolite beta containing framework boron is disclosed in U.S. Patent No. 4,672,049. As noted there, the amount of boron contained in the zeolite may be varied by incorporating different amounts of borate ion in the zeolite forming solution e.g. by the use of varying amounts of boric acid relative to the forces of silica and alumina. Reference is made to these disclosures for a description of the methods by which these zeolites may be made.

[0045] The low acidity zeolite beta catalyst should contain at least 0.1 wt% framework boron, preferably at least 0.5 wt% boron. Boron may be added to the framework prior to the addition of other metals. Normally, the maximum amount of boron will be about 5 wt% of the zeolite and in most cases not more than 2 wt% of the zeolite. The framework will normally include some alumina. The silica:alumina ratio will usually be at least 30:1, in the conditions of the zeolite as synthesized. A preferred boron-substituted zeolite beta catalyst is made by steaming an initial boron-containing zeolite containing at least 1 wt% boron (as B_2O_3) to result in an ultimate alpha value no greater than about 20 and preferably no greater than 10.

Properties

[0046] Acidity may be reduced by the introduction of nitrogen compounds, e.g. NH_3 or organic nitrogen compounds, with the feed to the hydroisomerization catalyst. However, the total nitrogen content of the feed should not exceed 100 ppm and should be preferably less than 20 ppm. The catalyst may also contain metals which reduce the number of strong acid sites of the catalyst and improve the selectivity of isomerization reactions to cracking reactions. Metals which are preferred for this purpose are those belong to the class of Group IIA metals such as calcium and magnesium.

[0047] The zeolite will be composites with a matrix material to form the finished catalyst and for this purpose conventional very low-acidity matrix materials such as alumina, silica-alumina and silica are suitable although aluminas such as alpha boehmite (alpha alumina monohydrate) may also be used, provided that they do not confer any substantial degree of acidic activity on the matrixed catalyst. The zeolite is usually composited with the matrix in amounts from 80:20 to 20:80 by weight, typically from 80:20 to 50:50 zeolite:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion into the desired finished catalyst particles. A preferred method for extruding the zeolite with silica as a binder is disclosed in U.S. 4,582,815. If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional. The preferred binder for the steamed catalyst is alumina.

[0048] The hydroisomerization catalyst also includes a metal component in order to promote the desired hydroisomerization reactions which, proceeding through unsaturated transitional species, require mediation by a hydrogenation-dehydrogenation component. In order to maximize the isomerization activity of the catalyst, metals having a strong hydrogenation function are preferred and for this reason, platinum and the other noble metals such as rhenium, gold, and palladium are given a preference. The amount of the noble metal hydrogenation component is typically in the range 0.1 to 5 wt% of the total catalyst, usually from 0.1 to 2 wt%: a preferred catalyst comprises 0.3 to 2 %wt. Pt on a support comprising zeolite beta. The platinum may be incorporated into the catalyst by conventional techniques including ion exchange with complex platinum cations such as platinum tetraamine or by impregnation with solutions of soluble platinum compounds, for example, with platinum tetraammine salts such as platinum tetraamminechloride. The catalyst may be subjected to a final calcination under conventional conditions in order to convert the noble metal to its reduced form and to confer the required mechanical strength on the catalyst. Prior to use the catalyst may be subjected to presulfiding as described above for the . hydrocracking pretreatment catalyst.

Hydroisomerization Conditions

[0049] The conditions for hydroisomerization (also called isomerization) are adjusted to achieve the objective of isomerizing the waxy, linear and near-linear paraffinic components in the waxy feed to less waxy but high V.I. isoparaffinic materials of relatively lower pour point. The process is preferably carried out in the presence of hydrogen to convert from 40 to 90 wt.% of the wax contained in the feed. This end is achieved while minimizing conversion to non-lube boiling range products 345°C- (650°F-) materials. Since the catalyst used for hydroisomerization has a low acidity, conversion to lower boiling products is usually at a relatively low level and by appropriate selection of severity, the operation of the process may be optimized for isomerization over cracking. At conventional space velocities of about 1, using a Pt/zeolite beta catalyst with an alpha value below 20, temperatures for the hydroisomerization will typically be in the range of about 288 to 427°C (550-800°F), preferably 300° to 415°C (about 570° to about 780°F) with con-

version to 345°C- (650°F-) typically being from about 5 to 30 wt%, more usually 10 to 25 wt%, of the waxy feed.

[0050] Hydroisomerization is accomplished at hydrogen partial pressures (reactor inlet) of at least 5516 kPa_a (800 psig), usually 5516 to 20785 kPa_a (800 to 3000 psig) and in most cases 5516 to 17340 kPa_a (800-2500 psig). Hydrogen circulation rates are usually in the range of about 90 to 900 $n.l.l.^{-1}$ (500 to 5000 SCF/Bbl). Since some saturation of aromatic components present in the original feed takes place in the presence of the noble metal hydrogenation component on the catalyst, hydrogen is consumed in the hydroisomerization even though the desired isomerization reactions are in hydrogen balance; for this reason, hydrogen circulation rates may need to be adjusted in accordance with the aromatic content of the feed and also with the temperature used in the hydroisomerization since higher temperatures will be associated with a higher level of cracking and, consequently, with a higher level of olefin production, some of which will be in the lube boiling range so that product stability will need to be assured by saturation. Hydrogen circulation rates of at least 180 $n.l.l.^{-1}$ (1000 SCF/Bbl) will normally provide sufficient hydrogen to compensate for the expected hydrogen consumption as well as to ensure a low rate of catalyst aging.

[0051] An interbed quench is desirable to maintain temperature in the process. Cold hydrogen is generally used as the quench, but a liquid quench, usually recycled product, may also be used.

Dewaxing

[0052] Although a final dewaxing step may be necessary in order to achieve the desired product pour point, depending on the wax content of the feed. It is a notable feature of the present process that the extent of dewaxing required is relatively small. Typically, the loss during the final dewaxing step will be no more than 15-20 wt% of the dewaxer feed and may be lower. Either catalytic dewaxing or solvent dewaxing may be used at this point and if a solvent dewaxer is used, the removed wax may be recycled to the hydroisomerization for a second pass through the isomerization step. The demands on the dewaxer unit for the product are relatively low and in this respect the present process provides a significant improvement over the process employing solely amorphous catalysts where a significant degree of dewaxing is required. The high isomerization selectivity of the large-pore zeolite catalysts enables high single pass wax conversions to be achieved, typically about 80% as compared to 50% for the amorphous catalyst process so that unit throughput is significantly enhanced.

[0053] A shape-selective dewaxing catalyst maybe alternately employed rather than a solvent dewaxing approach. This catalyst removes the n-paraffins together with the waxy, slightly branched chain paraffins, while leaving the more branched chain iso-paraffins in the process stream. Shape-selective catalytic dewaxing processes employ catalysts which are more highly selective for removal of n-paraffins and slightly branched chain paraffins than is the large-pore isomerization catalyst, such as zeolite beta. Selective catalytic dewaxing is carried out as described in U.S. Patent No. 4,919,788, to which reference is made for a description of: this phase. The catalytic dewaxing step in the present process is preferably carried out with a constrained, shape-selective dewaxing catalyst based on a constrained intermediate pore crystalline material, such as an aluminosilicate. A constrained intermediate crystalline material has at least one channel of 10-membered oxygen rings with any intersecting channel having 8-membered rings. ZSM-23 is the preferred zeolite for this purpose although other highly shape-selective zeolites such as ZSM-22 or the synthetic ferrierite ZSM-35 may also be used, especially with lighter stocks. Silicoaluminophosphates such as SAPO-11 and SAPO-41 maybe used as selective dewaxing catalysts.

[0054] The preferred catalysts for use as the dewaxing catalysts are the relatively constrained intermediate pore size zeolites. Such preferred zeolites have a Constraint Index in the range of 1-12, as determined by the method described in U.S. Patent No. 4,016,218. These preferred zeolites are also characterized by specific sorption properties related to their relatively constrained diffusion characteristics. These sorption characteristics are those which are set out in U.S. Patent No. 4,810,357 for the zeolites such as zeolite ZSM-22, ZSM-23, ZSM-35 and ferrierite. These zeolites have pore openings which result in a specific combination of sorption properties, namely, (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than about 3, wherein sorption is determined at a P/P_o of 0.1 and at a temperature of 50°C for n-hexane and 80°C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 1000°F and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/2,3-dimethylbutane, with the ratio of rate constants k_{3MD}/k_{DMB} determined at a temperature of 538°C (1000°F) being in excess of about 2.

[0055] The expression, "P/P_o", is accorded its usual significance as described in the literature, for example, in "The Dynamical Character of Adsorption" by J.H. deBoer, 2nd Edition, Oxford University Press (1968) and is the relative pressure defined as the ratio of the partial pressure of sorbate to the vapor pressure of sorbate at the temperature of sorption. The ratio of the rate constants, k_{3MP}/k_{DMB}, is determined from 1st order kinetics, in the usual manner, by the following equation:

$$k = (1/T_c)\ 1n\ (1/1-\varepsilon)$$

where k is the rate constant for each component, T_c is the contact time and ε is the fractional conversion of each component.

[0056] Zeolites conforming to these sorption requirements include the naturally occurring zeolite ferrierite as well as the synthetic zeolites ZSM-22, ZSM-23 and ZSM-35. These zeolites are at least partly in the acid or hydrogen form when they are used in the present process.

[0057] The preparation and properties of zeolite ZSM-22 are described in U.S. Patent No. 4,810,357 (Chester) to which reference is made for such a description.

[0058] The synthetic zeolite ZSM-23 is described in U.S. Patent Nos. 4,076,842 and 4,104,151 to which reference is made for a description of this zeolite, its preparation and properties.

[0059] The intermediate pore-size synthetic crystalline material designated ZSM-35 ("zeolite ZSM-35" or simply "ZSM-35"), is described in U.S. patent No. 4,016,245, to which reference is made for a description of this zeolite and its preparation. The synthesis of SAPO-11 is described in U.S. Patent Nos. 4,943,424 and 4,440,871. The synthesis of SAPO-41 is described in U.S. Patent No. 4,440,871.

[0060] Ferrierite is a naturally-occurring mineral, described in the literature, see, e.g., D.W. Breck, ZEOLITE MOLECULAR SIEVES, John Wiley and Sons (1974), pages 125-127, 146, 219 and 625, to which reference is made for a description of this zeolite.

[0061] The dewaxing catalysts used in the shape-selective catalytic dewaxing preferably include a metal hydrogenation-dehydrogenation component. Although it may not be strictly necessary to promote the selective cracking reactions, the presence of this component has been found to be desirable to promote certain isomerization reactions which contribute to the synergy of the two catalyst dewaxing system. The presence of the metal component leads to product improvement, especially VI, and stability as well as helping to retard catalyst aging. The shape-selective, catalytic dewaxing is normally carried out in the presence of hydrogen under pressure. The metal will be preferably platinum or palladium. The amount of the metal component will typically be 0.1 to 10 percent by weight. Matrix materials and binders may be employed as necessary.

[0062] Shape selective dewaxing using the highly constrained, highly shape-selective catalysts may be carried out in the same general manner as other catalytic dewaxing processes, such as those described above for. the initial isomerization phase. Reference is made to U.S. Patent 4,919,788 for a more extended discussion of the shape-selective catalytic dewaxing step.

[0063] The degree of conversion to lower boiling species in the dewaxing stage will vary according to the extent of dewaxing desired at this point, i.e. on the difference between the target pour point and the pour point of the effluent from the isomerization stage. It will also depend upon the selectivity of the shape-selective catalyst which is used. At lower product pour points, and with relatively less selective dewaxing catalysts, higher conversions and correspondingly higher hydrogen consumptions will be encountered.

[0064] After the pour point of the oil has been reduced to the desired value by selective dewaxing, the dewaxed oil may be subjected to treatments such as hydrotreating, in order to remove color bodies and produce a lube product of the desired characteristics. Fractionation may be employed to remove light ends and to meet volatility specifications. Suitable hydrotreating procedures are set forth in claims 15, 16, 27 and 28.

Products

[0065] The products from the process are high VI, low pour point materials which are obtained in excellent yield. Besides having excellent viscometric properties they are also highly stable, both oxidatively and thermally and to ultraviolet light. VI values in the range of 130 to 150 are typically obtained with the preferred wax feeds to the process and values of at least 140, are readily achievable with product yields of at least 50 wt%, usually at least 60 wt%, based on the original wax feed.

EXAMPLES

Example 1

[0066] A low-acidity zeolite beta-containing catalyst was prepared by first extruding a mixture of 65 parts by weight of zeolite beta with 35 parts by weight silica (SiO_2). The zeolite beta used in this preparation has a SiO_2:Al_2O_3 ratio of 600, an average crystal size of 1-3 micrometres as measured using scanning electron microscopy (SEM). Details of the synthesis are given in U.S. patents 5,232,579, 5,164,169, and 5,164,170. The mixture of zeolite beta and silica was mixed with an aqueous caustic solution to form a paste and extruded following standard procedures known to those skilled in the art of catalyst preparation. The extrudate was dried for 8 hours at 121°C (250°F), contacted with 5 v/v of a 1N NH_4NO_3 solution to reduce its sodium level. The sodium-reduced extrudate was then heated in N_2 to 482°C (900°F) and held there for 3 hours before exposure to air at 538°C (1000°F) for 6 hours to decompose the

organic compounds used in the preparation of the zeolite beta. This catalyst was then exposed to 100% steam at 101 kPa_a (0 psig) for a sufficient time (24 hours) to reduce its alpha activity to below 15.

[0067] This steam-deactivated zeolite beta containing material was then exchanged with an aqueous solution of platinum tetrammine chloride dihydrate maintained at a pH of between 7-8. The platinum exchanged catalyst was rinsed with water. to remove chlorides and then heated to 349°C (660°F) in air and held there for 3 hours. The final catalyst contained 0.6 wt% platinum and has properties given in Table 4.

Table 4

Silica-Bound Pt/β Catalyst Properties		
Catalyst	Example 1	Example 2
Platinum, wt%	0.5	0.5
Sodium, ppm	130	245
Surface Area, m^2/g	318	316
Pore Volume, cc/g	-	0.97
Alpha (prior to Pt Addition)	13	8
Crystal Size, μ	1-3	0.05

Example 2

[0068] A zeolite beta-containing catalyst was prepared by first extruding a mixture of 65 parts by weight of zeolite beta with 35 parts by weight silica (SiO_2). The zeolite beta used in this preparation had a SiO_2:Al_2O_3 ratio of 50, an average crystal size of less than 0.05 microns as measured using SEM, and was synthesized following standard. procedures for MIDW-grade zeolite beta. The mixture of zeolite beta and silica was mixed with an aqueous caustic solution to form a paste and extruded following standard procedures known to those in the catalyst art. The extrudate was dried for 8 hours at 121°C (250°F). The sodium-containing extrudates were then heated in N_2 to 482°C (900°F) and held there for 3 hours before exposure to air at 538°C (1000°F) for 6 hours to decompose the organic compounds used in the preparation of the zeolite beta. This catalyst was then exposed to an 2M aqueous solution of: oxalic acid for a total of 6 hours at 71°C (160°F). The oxalic-acid treated zeolite beta catalyst was then heated to 538°C (1000°F) for 2 hours. This material had an alpha value less then 10 and a sodium content of 525 ppmw.

[0069] This oxalic acid-treated zeolite beta catalyst was then exchanged with an aqueous solution of platinum tetrammine chloride dihydrate maintained at a pH of between 5-6. The platinum exchanged catalyst was rinsed with water to remove chlorides and then heated to 349°C (660°F) in air and held there for 3 hours. The final catalyst contained 0.5 wt% platinum and has properties given in Table 4, supra.

Example 3

[0070] A slack wax derived from solvent dewaxing a 97 mm^2/s (cSt) (450 SUS) heavy neutral furfural raffinate was hydrocracked at mild severity to reduce its sulfur and nitrogen contents. Conditions for the mild hydrocracking step were: 2 LHSV, 404°C (760°F), 13891 kPa_a (2000 psig H_2) partial pressure. Properties of the slack wax and the stripped hydrocracked product are given by Table 5.

[0071] The mild hydrocracking step converted 16% of the slack wax feed to products boiling below 343°C (650°F) and also converted 17% of the wax in the feed. Wax conversion and lube yield are calculated by the following equations. Dewaxed oil yield was corrected to a 0°F pour point for consistency.

$$\text{Wax Conversion} = 100x \frac{\text{Wax Content of Feed - Wax Content of Reaction Product}}{\text{Wax Content of Feed}}$$

$$\text{Wax Yield} = (\text{Yield of Distillation Bottom on Waxy Feed})$$

$$x\ (\text{Yield of Oil Free Wax From Solvent Dewaxing ou Solvent Dewaxer Feed Basis})$$

$$\text{Lube Yield} = 100 - \text{Wax Yield} - 650°\text{F+ Conversion Measured By Simulated Distillation}$$

Table 5

Feed Stock Properties		
Description	450 Heavy Neutral Slack Wax	Mildly Hydrocracker 450 Heavy Neutral Slack Wax
Oil Content on 343°C+ (650°F+) Basis, %	38	48
Nitrogen, ppm	68	<7
Sulfur, ppm	1920	<20
Simulated Distillation. °C		
IBP	366	128
5% Off	420	245
10%	441	312
20%	459	397
50%	495	463
90%	550	527
FBP	586	572
343°F+ Solvent Dewaxed Oil		
Kinematic Viscosity at 100°C, cst	11.3	6.1
VI at -17.78°C (0°F) Pour	92	138
Yield, wt% Heavy Neutral Slack Wax	37	33
343°C (650°F+) Conversion, %	-	16
Wax Conversion, %	-	17

Example 4

[0072] The mildly hydrocracked slack wax of Example 3 was reacted over the Pt/β catalysts of Example 1 and 2 in separate experiments. Reaction conditions were 13891 kPa_a (2000 psig) and 1 LHSV for the catalyst of Example 1 and 1.25 LHSV for the catalyst of Example 2. Catalyst temperature was varied to effect changes in reaction severity. Prior to the introduction of liquid feed, both catalysts were presulfided with a mixture of 2 vol% H_2S/98 vol% H_2 to a maximum temperature of 371°C (700°F).

[0073] The reactor effluent from these experiments was analyzed by simulated distillation to determine the conversion to 343°C (650°F-) products and then distilled to a nominal 343°C (650°F) cutpoint. Wax and lube yields and wax conversions were calculated based on the equations of Example 3 and are given by Table 6. The Figure illustrates the relative dependence of lube yield on wax conversion for the two catalysts.

[0074] The wax isomerization selectivity of the small crystal catalyst (Example 2) was significantly higher than that of the large crystal catalyst (Example 1). Lube yield peaked at 64% for the small crystal Pt/β catalyst while reaching only 52% for the large crystal catalyst. Consistent with the sequential reaction network of isomerization followed by shape-selective cracking, both catalysts gave similar yields at low wax conversions (less than 40%). However, as the reaction severity was increased, the rate of cracking in the large crystal catalyst relative to the isomerization rate increased substantially so that at 50% wax conversion, the rate of creation of lube by isomerization matched the rate of lube loss by cracking. Increasing the wax conversion beyond that point resulted in a decrease in lube yield. In contrast, the ratio of isomerization to cracking remained high for the small crystal catalyst up to high wax. conversions. The rates of the two reactions did not become equivalent until 80% wax conversion was reached.

[0075] The practical application of the invention, beyond the obvious higher yields for the small crystal catalyst, is the catalyst's ability to selectively function at high wax: conversion. This reduces the amount of wax recycle and reduces the size of the reactors required to produce a given quantity of high VI base stock.

[0076] Zeolitic acidity can also play an important role in determining isomerization selectivity. While the large crystal Pt/β catalyst had a higher alpha value compared to the small crystal version (13 vs. 8), it is likely that the selectivity difference observed between the catalysts was not primarily a function of acidity. The difference in alpha values is not

significantly large.

Table 6

Wax Isomerization Selectivity of Silica-Bound Pt/β Catalysts				
Example 1 Catalyst (1-3μ, 13∝)				
Pt/β Temp., °C	343°C+ Conv. Over Pt/β %	Wax Conv. Over Pt/β %	343°C+ Lube Yield % HNSW	343°C+Lube VI at-17.78°C Pour
313	1	26	46	141
316	3	34	49	142
322	5	45	52	144
325	10	51	51	142
333	21	63	48	143
Example 2 Catalyst (0.05 μ, 8∝)				
Pt/β Temp.,°C	343°C+ Conv. Over Pt/β %	Wax Conv. Over Pt/β %	343°C+ Lube Yield % HNSW	343°C+ Lube VI at -17.78°C (0°F) Pour
307	3	30	46	144
312	4	49	54	145
321	11	75	61	142
324	12	84	64	144
324	15	82	61	142
327	18	86	61	142
329	24	93	59	141

Claims

1. A process for producing an at least 130 Viscosity Index (VI) lubricant from a waxy hydrocarbon feed having a wax content of at least 20 %wt, which comprises catalytically dewaxing waxy paraffins present in the feed primarily by isomerization, in the presence of hydrogen and in the presence of a low acidity large pore molecular sieve selected from the group consisting of zeolite beta, Y and mordenite having at least one pore channel with a major dimension greater than 0.7 nm and having a crystal size of less than 0.1 micron, an alpha value of not more than 30 and containing a noble metal hydrogenation component.

2. The process of claim 1 wherein the large pore molecular sieve possesses at least one pore channel of 12-membered oxygen rings.

3. The process of claim 1, wherein the zeolite beta has an alpha value of not greater than 20.

4. The process claim 1, wherein the large pore molecular sieve has a crystal size less than 0.05 micron.

5. The process of claim 1, wherein the large pore molecular sieve is a low acidity zeolite beta which has been steamed, having a framework silica: alumina ratio of at least 200:1.

6. The process of claim 1, in which the large pore molecular sieve comprises a boron-containing zeolite beta isomerization catalyst in which the boron is present as a framework component of the zeolite beta.

7. The process of claim 1, in which the large pore molecular sieve comprises from 0.3 to 2 wt% Pt on a support comprising zeolite beta.

8. The process of claim 1 in which the feed comprises a waxy hydrocarbon feed having a wax content of at least 40 wt% and an aromatic content of less than 25 wt%.

9. The process of claim 1 wherein the feedstock is selected from the group consisting of a slack wax, deoiled wax,

wax from Fischer-Tropsch process, foots oils, petrolatum, vacuum gas oil, or a raffinate from solvent extraction of a vacuum distillate.

10. The process of claim 1, in which the process is carried out in the presence of hydrogen to convert from 40 to 90 wt% of the wax contained in the feed.

11. The process of claim 1, wherein conditions include a hydrogen partial pressure ranging from 4238 to 20786 kPa_a (600 to 3000 psig) and a temperature from 288°C to 427°C (550 to 800 °F).

12. The process of claim 1 in which the catalytically dewaxed feed is subjected to further selective dewaxing to achieve target pour point.

13. The process of claim 12 , in which said further dewaxing is accomplished by either solvent or catalytic means.

14. The process of claim 1, in which the catalytically dewaxed feed is hydrotreated by contacting it with a catalyst comprising a metal hydrogenation component on a porous support material at a pressure in the range from about 3549 to about 20786 kPa_a (500 to about 3000 psig), a reaction temperature in the range from about 260°C to about 427°C (500°F to about 800°F), a space velocity which is in a range from about 0.1 to about 10 LHSV, and a once-through hydrogen circulation rate which extends from about 178 to about 1780 n.l.l."[1] (1000 SCF/B to about 10 , OOOSCF/B) , in order to improve the thermal and oxidative stability of the lubricant.

15. The process of claim 12, in which the feed is hydrotreated following selective dewaxing by contacting it with a catalyst comprising a metal hydrogenation component on a porous support material at a pressure in the range from about 3549 to about 20786 kPa_a (500 to about 3000 psig) , a reaction temperature in the range from about 260 °C to about 427°C (500°F to about 800°F), a space velocity which is in a range from about 0 . 1 to about 10 LHSV, and a once-through hydrogen circulation rate which extends from about 178 to about 1780 $n.l.l.^{-1}$ (1000 SCF/B) to about 10, 000SCF/B, in order to improve the thermal and oxidative stability of the lubricant.

16. A process for producing an at least 130 Viscosity Index (VI) lubricant from a waxy hydrocarbon feed having a wax content 20 of at least 20 wt%, the process comprising the following steps:

(a) hydrocracking of the feed in order to reduce its nitrogen content as well as to remove naphthenic and aromatic components, thereby improving VI, the hydrocracking process comprising contacting the feed with a catalyst composed of a metal hydrogenation component on air acidic support;

(b) catalytically dewaxing waxy paraffins present in the feed primarily by isomerization, in the presence of hydrogen and in the presence of a low acidity large pore molecular sieve selected from the group consisting of zeolite beta, Y and mordenite having at least one pore channel with a major dimension greater than 0.7nm and a crystal size of less than 0.1 micron, an alpha value of not more than 30 and containing a noble metal hydrogen component.

17. The process of claim 16, wherein the large pore molecular sieve possesses at least one pore channel of 12-membered oxygen rings.

18. The process of claim 16, wherein the zeolite beta has an alpha value of not greater than 20.

19. The process of claim 16, wherein the large pore molecular sieve is a low acidity zeolite beta which has been steamed, having a framework silica: alumina ratio of at least 200:1.

20. The process of claim 16, in which the large pore molecular sieve comprises from 0.3 to 2 wt% Pt on a support comprising zeolite beta.

21. The process of claim J7, wherein the feedstock is selected from the group consisting of a slack wax, deoiled wax, foots oil, wax from Fischer-Tropsch process, petrolatum, vacuum gas oil, or a raffinate from solvent extraction of a vacuum distillate.

22. The process of claim 16, wherein conditions of step (b) include a hydrogen partial pressure ranging from 4238 to 20786 kPa_a (600 to 3000 psig) and a temperature from 288°C to 427°C (550 to 800°F).

23. The process of claim 16, in which the effluent of step (b) is subjected to further selective dewaxing to achieve target pour point.

24. The process of claim 23, in which said further dewaxing is accomplished by either solvent or catalytic means.

25. The process of claim 16, in which at least a portion of the effluent of step (b) is hydrotreated by contacting it with a catalyst comprising a metal hydrogenation component on a porous support material at a pressure in the range from about 3549 to about 20786 kPa_a (500 to about 3000 psig), a reaction temperature in the range from about 260°C to 427°C (500°F to about 800°F), a space velocity which is in a rage from about 0.1 to about 10 LHSV, and a once-through hydrogen circulation rate which extends from about 178 to 1780 n.l.l.$^{-1}$ (1000 SCF/B to about 10,000 SCF/B), in order to improve the thermal and oxidative stability of the lubricant.

26. The process of claim 23 in which the effluent of step (b) of claim 16 is subjected, following further selective dewaxing to hydrotreating by contacting it with a catalyst comprising a metal hydrogenation component on a porous support material at a pressure in the range from about 3549 to about 20 786 kPa_a (500 to 3000 psig), a reaction temperature in the range from about 260°C to 427°C (500°F to about 800°F), a space velocity which is in a range from about 0.1 to about 10 LSHV, and a once-through hydrogen circulation rate which extends from about 178 to 1780 n.l.l.$^{-1}$ (1000 SCT/B to about 10,000SCF/B), in order to improve the thermal and oxidative stability of the lubricant.

Patentansprüche

1. Verfahrens zur Herstellung eines Schmiermittels mit einem Viskositätsindex (VI) von mindestens 130 aus einer wachsartigen Kohlenwasserstoffbeschickung mit einem Wachsgehalt von mindestens 20 Gew.-%, das das katalytische Entparaffinieren von in der Beschickung vorhandenen wachsartigen Paraffinen, primär durch Isomerisieren, in Gegenwart von Wasserstoff und in Gegenwart eines Molekularsiebs mit großen Poren und geringer Acidität umfaßt, das aus der Gruppe ausgewählt ist, die aus Zeolith Beta, Y und Mordenit mit mindestens einem Porenkanal mit einer Hauptabmessung von mehr als 0,7 nm und mit einer Kristallgröße von weniger als 0,1 µm und mit einem α-Wert von nicht mehr als 30 besteht und eine Hydrierungskomponente aus einem Edelmetall enthält.

2. Verfahren nach Anspruch 1, wobei das Molekularsieb mit großen Poren mindestens einen Porenkanal aus 12-gliedrigen Sauerstoffringen besitzt.

3. Verfahren nach Anspruch 1, wobei der Zeolith Beta einen α-Wert von nicht mehr als 20 aufweist.

4. Verfahren nach Anspruch 1, wobei das Molekularsieb mit großen Poren eine Kristallgröße von weniger als 0,05 µm aufweist.

5. Verfahren nach Anspruch 1, wobei das Molekularsieb mit großen Poren ein Zeolith Beta mit geringer Acidität ist, der der Dampfbehandlung unterzogen wurde, der ein Verhältnis von Siliciumdioxid:Aluminiumoxid des Gitters von mindestens 200:1 aufweist.

6. Verfahren nach Anspruch 1, wobei das Molekularsieb mit großen Poren einen Isomerisierungskatalysator aus einem borhaltigen Zeolith Beta umfaßt, bei dem das Bor als Gitterkomponente des Zeoliths Beta vorliegt.

7. Verfahren nach Anspruch 1, wobei das Molekularsieb mit großen Poren 0,3 bis 2 Gew.-% Pt auf einem Träger umfaßt, der Zeolith Beta umfaßt.

8. Verfahren nach Anspruch 1, wobei die Beschickung eine wachsartige Kohlenwasserstoffbeschickung mit einem Wachsgehalt von mindestens 40 Gew.-% und einem Aromatengehalt von weniger als 25 Gew.-% umfaßt.

9. Verfahren nach Anspruch 1, wobei das Beschickungsmaterial aus der Gruppe ausgewählt ist, die aus Rohparaffin, entöltem Wachs, Wachs von einem Fischer-Tropsch-Verfahren, Bodenölen, Petrolatum, Vakuumgasöl oder einem Raffinat von der Lösungsmittelextraktion eines Vakuumdestillats besteht.

10. Verfahren nach Anspruch 1, wobei das Verfahren in Gegenwart von Wasserstoff durchgeführt wird, wodurch 40 bis 90 Gew.-% des in der Beschickung enthaltenen Wachses umgewandelt werden.

11. Verfahren nach Anspruch 1, wobei die Bedingungen einen Partialdruck von Wasserstoff im Bereich von 4238 bis 20786 kPa_a (600 bis 3000 psig) und eine Temperatur von 288 bis 427°C (550 bis 800°F) einschließen.

12. Verfahren nach Anspruch 1, wobei die katalytisch entparaffinierte Beschickung einem weiteren selektiven Entparaffinieren unterzogen wird, um den zu erzielenden Pourpoint zu erreichen.

13. Verfahren nach Anspruch 12, wobei das weitere Entparaffinieren entweder durch Lösungsmittel oder katalytische Maßnahmen erreicht wird.

14. Verfahren nach Anspruch 1, wobei die katalytisch entparaffinierte Beschickung der Wasserstoffbehandlung unterzogen wird, indem sie bei einem Druck im Bereich von etwa 3549 bis etwa 20786 kPa_a (500 bis etwa 3000 psig), einer Reaktionstemperatur im Bereich von etwa 260 bis etwa 427°C (500 bis etwa 800°F), einer Raumgeschwindigkeit, die im Bereich von etwa 0,1 bis etwa 10 LHSV liegt, und bei einer Zirkulationsrate von Wasserstoff bei einem Durchgang, die von etwa 178 bis etwa 1780 nl/l (1000 bis etwa 10000 scf/b) reicht, mit einem Katalysator in Kontakt gebracht wird, der eine Hydrierungskomponente aus einem Metall auf einem porösem Trägermaterial umfaßt, um die Wärme- und Oxidationsbeständigkeit des Schmiermittels zu verbessern.

15. Verfahren nach Anspruch 12, wobei die Beschickung nach dem selektiven Entparaffinieren der Wasserstoffbehandlung unterzogen wird, indem sie bei einem Druck im Bereich von etwa 3549 bis etwa 20786 kPa_a (500 bis etwa 3000 psig), einer Reaktionstemperatur im Bereich von etwa 260 bis etwa 427°C (500 bis etwa 800°F), einer Raumgeschwindigkeit, die im Bereich von etwa 0,1 bis etwa 10 LHSV liegt, und bei einer Zirkulationsrate von Wasserstoff bei einem Durchgang, die von etwa 178 bis etwa 1780 nl/l (10000 scf/b) reicht, mit einem Katalysator in Kontakt gebracht wird, der eine Hydrierungskomponente aus einem Metall auf einem porösem Trägermaterial umfaßt, um die Wärme- und Oxidationsbeständigkeit des Schmiermittels zu verbessern.

16. Verfahren zur Herstellung eines Schmiermittels mit einem Viskositätsindex (VI) von mindestens 130 aus einer wachsartigen Kohlenwasserstoffbeschickung mit einem Wachsgehalt von 20 von mindestens 20 Gew.-%, wobei das Verfahren die folgenden Schritte umfaßt:

a) Hydrocracken der Beschickung, um sowohl deren Stickstoffgehalt zu verringern als auch naphthenische und aromatische Komponenten zu entfernen, wodurch der VI verbessert wird, wobei das Hydrocrackverfahren den Kontakt der Beschickung mit einem Katalysator umfaßt, der aus einer Hydrierungskomponente aus einem Metall auf Luft saurem Träger besteht.

b) Katalytisches Entparaffinieren der in der Beschickung vorhandenen wachsartigen Paraffine, primär durch Isomerisierung, in Gegenwart von Wasserstoff und in Gegenwart eines Molekularsiebs mit großen Poren und geringer Acidität, das aus der Gruppe ausgewählt ist, die aus Zeolith Beta, Y und Mordenit mit mindestens einem Porenkanal mit einer Hauptabmessung von mehr als 0,7 nm und einer Kristallgröße von weniger als 0,1 μm, einem α-Wert von nicht mehr als 30 besteht und eine Wasserstoffkomponente aus einem Edelmetall enthält.

17. Verfahren nach Anspruch 16, wobei das Molekularsieb mit großen Poren mindestens einen Porenkanal aus 12-gliedrigen Sauerstoffringen besitzt.

18. Verfahren nach Anspruch 16, wobei der Zeolith Beta einen α-Wert von nicht mehr als 20 aufweist.

19. Verfahren nach Anspruch 16, wobei das Molekularsieb mit großen Poren ein Zeolith Beta mit geringer Acidität ist, der der Dampfbehandlung unterzogen wurde, der ein Verhältnis von Siliciumdioxid:Aluminiumoxid des Gitters von mindestens 200:1 aufweist.

20. Verfahren nach Anspruch 16, wobei das Molekularsieb mit großen Poren 0,3 bis 2 Gew.-% Pt auf einem Träger umfaßt, der Zeolith Beta umfaßt.

21. Verfahren nach Anspruch J7, wobei das Beschickungsmaterial aus der Gruppe ausgewählt ist, die aus Rohparaffin, entöltem Wachs, Bodenöl, Wachs vom Fischer-Tropsch-Verfahren, Petrolatum, Vakuumgasöl oder einem Raffinat von der Lösungsmittelextraktion eines Vakuumdestillats besteht.

22. Verfahren nach Anspruch 16, wobei die Bedingungen des Schrittes (b) einen Partialdruck von Wasserstoff im

Bereich von 4238 bis 20786 kPa_a (600 bis 300 psig) und eine Temperatur von 288 bis 427°C (550 bis 800°F) einschließen.

23. Verfahren nach Anspruch 16, wobei der Abfluß vom Schritt (b) einem weiteren selektiven Entparaffinieren unterzogen wird, um den zu erzielenden Pourpoint zu erreichen.

24. Verfahren nach Anspruch 23, wobei das weitere Entparaffinieren entweder durch ein Lösungsmittel oder durch katalytische Maßnahmen erreicht wird.

25. Verfahren nach Anspruch 16, wobei zumindest ein Teil des Abflusses vom Schritt (b) der Wasserstoffbehandlung unterzogen wird, indem er bei einem Druck im Bereich von etwa 3549 bis etwa 20786 kPa_a (500 bis etwa 3000 psig), einer Reaktionstemperatur im Bereich von etwa 260 bis etwa 427°C (500 bis etwa 800°F), einer Raumgeschwindigkeit, die im Bereich von etwa 0,1 bis etwa 10 LHSV liegt, und bei einer Zirkulationsrate von Wasserstoff bei einem Durchgang, die von etwa 178 bis etwa 1780 nl/l (1000 bis etwa 10000 scf/b) reicht, mit einem Katalysator in Kontakt gebracht wird, der eine Hydrierungskomponente aus einem Metall auf einem porösem Trägermaterial umfaßt, um die Wärme- und Oxidationsbeständigkeit des Schmiermittels zu verbessern.

26. Verfahren nach Anspruch 23, wobei der Abfluß vom Schritt (b) von Anspruch 16 nach dem weiteren selektiven Entparaffinieren der Wasserstoffbehandlung unterzogen wird, indem er bei einem Druck im Bereich von etwa 3549 bis etwa 20786 kPa_a (500 bis etwa 3000 psig), einer Reaktionstemperatur im Bereich von etwa 260 bis etwa 427°C (500 bis etwa 800°F), einer Raumgeschwindigkeit, die im Bereich von etwa 0,1 bis etwa 10 LHSV liegt, und bei einer Zirkulationsrate von Wasserstoff bei einem Durchgang, die von etwa 178 bis etwa 1780 nl/l (1000 sct/b bis etwa 10000 scf/b) reicht, mit einem Katalysator in Kontakt gebracht wird, der eine Hydrierungskomponente aus einem Metall auf einem porösem Trägermaterial umfaßt, um die Wärme- und Oxidationsbeständigkeit des Schmiermittels zu verbessern.

Revendications

1. Procédé de production d'un lubrifiant ayant un indice de viscosité (VI) d'au moins 130 à partir d'une charge d'hydrocarbures cireux ayant une teneur en cire d'au moins 20 % en poids, qui consiste à déparaffiner de manière catalytique les paraffines cireuses présentes dans la charge essentiellement par isomérisation, en présence d'hydrogène et en présence d'un tamis moléculaire à larges pores de faible acidité choisi dans le groupe constitué de la zéolite béta, Y et mordénite ayant au moins un canal de pore avec une dimension majeure supérieure à 0,7 nm et ayant une taille de cristal inférieure à 0,1 micron, une valeur alpha ne dépassant pas 30 et contenant un composant d'hydrogénation de type métal noble.

2. Procédé selon la revendication 1 dans lequel le tamis moléculaire à larges pores possède au moins un canal de pore composé de noyaux à oxygène à 12 chaînons.

3. Procédé selon la revendication 1 dans lequel la zéolite béta a une valeur alpha ne dépassant pas 20.

4. Procédé selon la revendication 1 dans lequel le tamis moléculaire à larges pores possède une taille de cristal inférieure à 0,05 micron.

5. Procédé selon la revendication 1 dans lequel le tamis moléculaire à larges pores est une zéolite béta de faible acidité qui a été balayée par de la vapeur, ayant un rapport silice:alumine dans le squelette d'au moins 200:1.

6. Procédé selon la revendication 1 dans lequel le tamis moléculaire à larges pores comprend un catalyseur d'isomérisation à base de zéolite béta contenant du bore, dans lequel le bore est présent en tant que composant de squelette de la zéolite béta.

7. Procédé selon la revendication 1 dans lequel le tamis moléculaire à larges pores comprend 0,3 à 2 % en poids de Pt sur un support comprenant de la zéolite béta.

8. Procédé selon la revendication 1 dans lequel la charge comprend une charge d'hydrocarbures cireux ayant une teneur en cire d'au moins 40 % en poids et une teneur en composés aromatiques de moins de 25 % en poids.

9. Procédé selon la revendication 1 dans lequel la charge d'alimentation est choisie dans le groupe comprenant une paraffine huileuse, une cire déshuilée, une cire issue d'un procédé de Fischer-Tropsch, des huiles de queues, du pétrolatum, du gas-oil sous vide, ou un raffinat issu d'une extraction au solvant d'un distillat sous vide.

10. Procédé selon la revendication 1 dans lequel le procédé est effectué en présence d'hydrogène pour convertir 40 à 90 % en poids de la cire contenue dans la charge.

11. Procédé selon la revendication 1 dans lequel les conditions incluent une pression partielle d'hydrogène allant de 4238 à 20 786 kPa_a (600 à 3000 psi au manomètre) et une température de 288°C à 427°C (550 à 800°F).

12. Procédé selon la revendication 1 dans lequel la charge déparaffinée de manière catalytique est soumise à un déparaffinage sélectif supplémentaire pour parvenir à un point d'écoulement cible.

13. Procédé selon la revendication 12 dans lequel ledit déparaffinage supplémentaire est accompli par des moyens de type solvant ou catalytiques.

14. Procédé selon la revendication 1 dans lequel la charge déparaffinée de manière catalytique est hydrotraitée par mise en contact de celle-ci avec un catalyseur comprenant un composant d'hydrogénation métallique sur un matériau support poreux à une pression dans la gamme d'environ 3549 à environ 20 786 kPa_a (500 à environ 3000 psi au manomètre), une température réactionnelle dans la gamme d'environ 260°C à environ 427°C (500°F à environ 800°F), une vitesse spatiale qui se situe dans une gamme d'environ 0,1 à environ 10 LHSV, et une vitesse de circulation d'hydrogène en circuit ouvert qui s'étend d'environ 178 à environ 1780 $n.l.l.^{-1}$ (1000 SCF/B à environ 10 000 SCF/B), afin d'améliorer la stabilité thermique et oxydative du lubrifiant.

15. Procédé selon la revendication 12 dans lequel la charge est hydrotraitée à la suite du déparaffinage sélectif par mise en contact de celle-ci avec un catalyseur comprenant un composant d'hydrogénation métallique sur un matériau support poreux à une pression dans la gamme d'environ 3549 à environ 20 786 kPa_a (500 à environ 3000 psi au manomètre), une température réactionnelle dans la gamme d'environ 260°C à environ 427°C (500°F à environ 800°F), une vitesse spatiale qui se situe dans une gamme d'environ 0,1 à environ 10 LHSV, et une vitesse de circulation d'hydrogène en circuit ouvert qui s'étend d'environ 178 à environ 1780 $n.l.l.^{-1}$ (1000 SCF/B à environ 10 000 SCF/B), afin d'améliorer la stabilité thermique et oxydative du lubrifiant.

16. Procédé de production d'un lubrifiant ayant un indice de viscosité (VI) d'au moins 130 à partir d'une charge d'hydrocarbures cireux ayant une teneur en cire d'au moins 20 % en poids, le procédé comprenant les étapes suivantes :

(a) l'hydrocraquage de la charge afin de réduire sa teneur en azote et d'enlever des composants naphténiques et aromatiques, améliorant ainsi le VI, le procédé d'hydrocraquage consistant à mettre en contact la charge avec un catalyseur composé d'un composant d'hydrogénation métallique sur un support acide aérien ;
(b) le déparaffinage catalytique des paraffines cireuses présentes dans la charge essentiellement par isomérisation, en présence d'hydrogène et en présence d'un tamis moléculaire à larges pores de faible acidité choisi dans le groupe constitué de la zéolite béta, Y et mordénite ayant au moins un canal de pore avec une dimension majeure supérieure à 0,7 nm et une taille de cristal inférieure à 0,1 micron, une valeur alpha ne dépassant pas 30 et contenant un composant d'hydrogénation de type métal noble.

17. Procédé selon la revendication 16, dans lequel le tamis moléculaire à larges pores possède au moins un canal de pore composé de noyaux à oxygène à 12 chaînons.

18. Procédé selon la revendication 16 dans lequel la zéolite béta a une valeur alpha ne dépassant pas 20.

19. Procédé selon la revendication 16 dans lequel le tamis moléculaire à larges pores est une zéolite béta de faible acidité qui a été balayée par de la vapeur, ayant un rapport silice:alumine dans le squelette d'au moins 200:1.

20. Procédé selon la revendication 16 dans lequel le tamis moléculaire à larges pores comprend 0,3 à 2 % en poids de Pt sur un support comprenant de la zéolite béta.

21. Procédé selon la revendication 17 dans lequel la charge d'alimentation est choisie dans le groupe comprenant une paraffine huileuse, une cire déshuilée, une huile de queues, une cire issue d'un procédé de Fischer-Tropsch,

du pétrolatum, du gas-oil sous vide, ou un raffinat issu d'une extraction au solvant d'un distillat sous vide.

22. Procédé selon la revendication 16 dans lequel les conditions de l'étape (b) incluent une pression partielle d'hydrogène allant de 4238 à 20 786 kPa_a (600 à 3000 psi au manomètre) et une température de 288°C à 427°C (550 à 800°F).

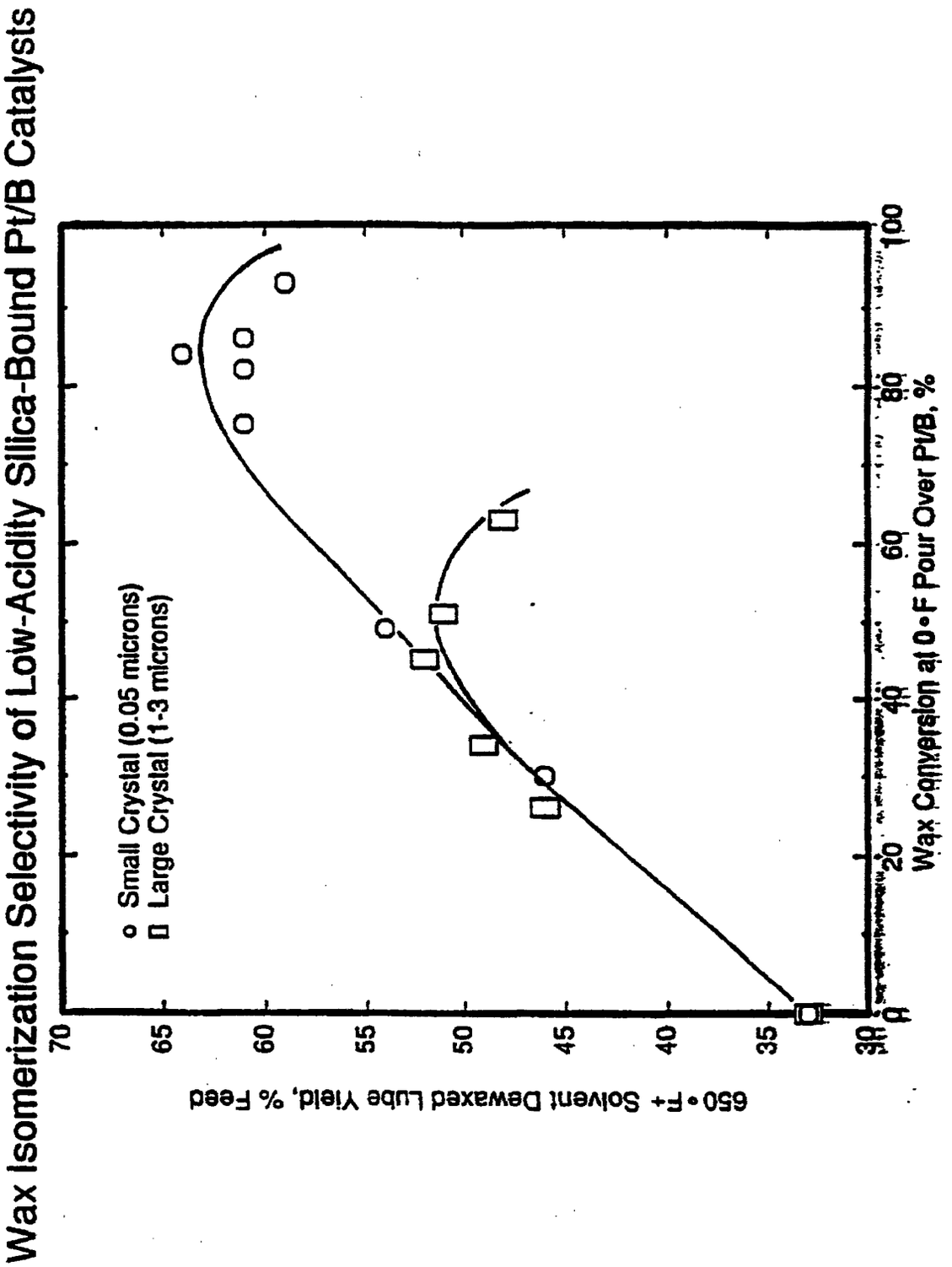
23. Procédé selon la revendication 16 dans lequel l'effluent de l'étape (b) est soumis à un déparaffinage sélectif supplémentaire pour parvenir à un point d'écoulement cible.

24. Procédé selon la revendication 23 dans lequel ledit déparaffinage supplémentaire est accompli par des moyens de type solvant ou catalytiques.

25. Procédé selon la revendication 16 dans lequel au moins une portion de l'effluent de l'étape (b) est hydrotraité par mise en contact de celui-ci avec un catalyseur comprenant un composant d'hydrogénation métallique sur un matériau support poreux à une pression dans la gamme d'environ 3549 à environ 20 786 kPa_a (500 à environ 3000 psi au manomètre), une température réactionnelle dans la gamme d'environ 260°C à environ 427°C (500°F à environ 800°F), une vitesse spatiale qui se situe dans une gamme d'environ 0,1 à environ 10 LHSV, et une vitesse de circulation d'hydrogène en circuit ouvert qui s'étend d'environ 178 à environ 1780 $n.l.l.^{-1}$ (1000 SCF/B à environ 10 000 SCF/B), afin d'améliorer la stabilité thermique et oxydative du lubrifiant.

26. Procédé selon la revendication 23 dans lequel l'effluent de l'étape (b) selon la revendication 16 est soumis, à la suite du déparaffinage sélectif supplémentaire, à un hydrotraitement par mise en contact de celui-ci avec un catalyseur comprenant un composant d'hydrogénation métallique sur un matériau support poreux à une pression dans la gamme d'environ 3549 à environ 20 786 kPa_a (500 à 3000 psi au manomètre), une température réactionnelle dans la gamme d'environ 260°C à environ 427°C (500°F à environ 800°F), une vitesse spatiale qui se situe dans une gamme d'environ 0,1 à environ 10 LHSV, et une vitesse de circulation d'hydrogène en circuit ouvert qui s'étend d'environ 178 à environ 1780 $n.l.l.^{-1}$ (1000 SCF/B à environ 10 000 SCF/B), afin d'améliorer la stabilité thermique et oxydative du lubrifiant.

Figure


Wax Isomerization Selectivity of Low-Acidity Silica-Bound Pt/B Catalysts
Small Crystal (0.05 microns)
Large Crystal (1-3 microns)
650°F+ Solvent Dewaxed Lube Yield, % Feed
Wax Conversion at 0°F Pour Over Pt/B, %
70
65
60
55
50
45
40
35
30
0
20
40
60
80
100