⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 062 985
A1

# ⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 82301524.3

㉒ Date of filing: 24.03.82

(51) Int. Cl.$^3$: C 10 G 65/04

㉚ Priority: 02.04.81 US 250357

㊸ Date of publication of application:
20.10.82 Bulletin 82/42

(84) Designated Contracting States:
AT BE DE FR GB IT NL

(71) Applicant: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: Garwood, William Everett
125 Warwick Road
Haddonfield New Jersey 08033(US)

(72) Inventor: Chen, Nai Yuen
Forrest Central Drive, R.D.
Titusville New Jersey(US)

(74) Representative: Cooper, John Anthony et al,
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

## (54) Process for making naphthenic lubestocks from raw distillate by combination hydrodewaxing/hydrogenation.

(57) There is described a process for the manufacture of low pour point lube oil basestocks from raw distillate fractions obtained from marginal naphthenic base crudes which involves dewaxing over a ZSM-5 type zeolite followed by hydrogenation.

Croydon Printing Company Ltd

# PROCESS FOR MAKING NAPHTHENIC LUBESTOCKS FROM RAW DISTILLATE BY COMBINATION HYDRODEWAXING/HYDROGENATION

This invention relates to a process for making naphthenic lubestocks from raw distillate by combination hydrodewaxing/hydrogenation.

The present invention provides a process for the production of low pour point lube oil basestocks from raw distillate fractions derived from marginal naphthenic crudes, said fraction having a boiling range of from 260° to 566°C (500° to 1050°F) and characterized as containing from 25 to 50 weight percent aromatics, from 25 to 40 weight percent naphthenes, less than 50 weight percent paraffins, a pour point below 2°C (35°F) and an API gravity of from 20 to 25 which comprises contacting the fraction at a temperature of from 260° to 357°C (500° to 675°F) with a conversion catalyst comprising an aluminosilicate zeolite having a silica/alumina ratio above 12 and a constraint index between 1 and 12, hydrotreating the resultant product by contact at a temperature of from 260° to 357°C (500 to 675°F) and a pressure of from 1480 to 13890 kPa (200 to 2000 psig) with a hydrotreating catalyst comprising a hydrogenation component on a non-acidic support and recovering a lube oil having a pour point below -23°C (-10°F).

The raw distillate fractions obtained from marginal "naphthenic base crudes" are not now used to produce either high viscosity index (V.I.) automotive lubricating oils or low pour naphthenic lubricants. They are not suitable for the manufacture of high V.I. lubricating oils because they are poor in paraffinic content and yield little or no refined stock having a viscosity index above about 60. They are not suitable for the manufacture of naphthenic lubricants by the conventional solvent dewaxing equipment because it is impractical to apply solvent dewaxing technology to produce oils of very low pour point ($<$ -23°C) ($<$ -10°F).

The wax contents of crudes vary widely from less than 1% such as the Coastal Low Pour crude which is a typical crude used for the manufacture of naphthenic lubricating oils up to wax contents of 40% or more for such waxy crudes as the Chinese Taching Crude or Utah's Altamont crude.

This invention is particularly directed to the upgrading of low wax content marginal naphthenic distillate fractions to naphthenic lube basestocks by a combination process involving first hydrodewaxing to a pour point below -23°C (-10°F) over a ZSM-5 type catalyst, followed by hydrogenation with a standard hydrogenation catalyst in order to obtain the desired product and maintain the below -23°C (-10°F) pour point.

The feed materials to which this invention is directed are described as distillate fractions boiling above 260°C (500°F) derived from marginal naphthenic crudes. By marginal naphthenic, we mean that the oil contains too high a wax content to be classified as "naphthenic" and can be classified as belonging to the low end of "intermediate" according to the classification method outlined by the Bureau of Mines.

The Bureau of Mines method consists of determining the gravity of two key boiling fractions of the crude as shown in the following table:

TABLE 1

Class B Assay

Bureau of Mines Classification of Whole Crude

(Reference: Bureau of Mines Report of Investigations #3279)

Basis: Gravity of two "Key" Fractions

Key Fraction #1 263°C (505°F) mid % Boiling Point 250-275°C (482-527°F)

| Gravity, °API | Type Crude |
|---|---|
| >40.0 | Paraffinic |
| 33 to 40 | Intermediate |
| <33.0 | Naphthenic |

Key Fraction #2 406°C (762°F) mid % Boiling Point 391-420°C (736-788°F)

| Gravity, °API | Type Crude |
|---|---|
| >30.0 | Paraffinic |
| 20 to 30 | Intermediate |
| <20.0 | Naphthenic |

The gravity of "key" fraction #1 determines the first word used in the classification, while the gravity of "key" fraction #2 determines the second word of the classification. If both words are the same, only one word is used to classify the crude.

High specific gravity (low API gravity) is indicative of condensed molecules such as naphthenes and aromatics whereas low specific gravity indicates long chain paraffins. The gravity values of these two key fractions determine the wording of the classification, e.g. paraffinic-intermediate or intermediate-naphthenic. Of more importance to the present invention is the gravity of the second key fraction. It should be greater than 20 API but less than 25 API. Truly naphthenic oils having API gravity of the second key fraction less than 20 are suitable as feed materials for the conventional technology. Those higher than 25 API are not preferable feed materials for the manufacture of naphthenic basestocks because of poor lube oil yield or poor quality.

Naphthenic lube oil basestocks are key ingredients of lubricating greases and other specialty oils such as transformer oils and refrigerator oils. They represent a significant (more than 25%) percentage of the total lubricating oil products. Because the supply of truly naphthenic crudes is being exhausted, there is a great need to find alternate sources of raw materials. One of the specific objectives of the present invention is to fulfill this need.

Another specific objective of the present invention is to devise an all-catalytic route for lubricating oil production to replace solvent refining such as aromatic extraction or acid treating.

In recent years, techniques have become available for catalytic dewaxing of petroleum stocks. A process of that nature developed by British Petroleum is described in The Oil and Gas Journal, dated January 6, 1975, at pages 69-73. See also U.S. Patent No. 3,668,113.

In U.S. Reissue Patent No. 28,398 is described a process for catalytic dewaxing with a catalyst comprising zeolite ZSM-5. Such process combined with catalytic hydrofinishing is described in U.S. Patent No. 3,894,938.

However, in the vast majority of these prior art catalytic dewaxing processes, the feed material has been one which has been substantially high in paraffins since these paraffin-based crudes or fractions are those which the art has long recognized contain the undesirable components which must be removed by dewaxing operations. Dewaxing is not normally applied to naphthenic base crudes since these materials are relatively lean in straight-chain paraffins and yield viscous fractions by distillation which inherently possess low pour points, i.e. see U.S. Patent No. 4,137,148. Additionally, as pointed out in U.S. Patent No. 4,176,050, naphthene based crudes are not ordinarily subjected to dewaxing operations since the benefits obtained therefrom would be minimal due to the fact that these materials by definition do not contain a large percentage of paraffinic material.

As has heretofore been stated, the novel process of this invention is concerned with a raw distillate fraction of a marginal naphthenic crude that has a boiling range of from 260° to 566°C (500° to 1050°F). The marginal naphthenic crudes are defined by a method similar to the method described by the Bureau of Mines in classifying whole crudes. The method consists of distilling a fraction boiling between 391° and 420°C (736° and 788°F) from the crude and measuring the gravity of the distillate. The distillates from marginal naphthenic crudes should have API gravity between 20 and 25. The raw distillate fraction from various marginal naphthenic crudes vary in chemical composition but generally contain from 25 to 50% aromatics, from 25 to 40% naphthenes and less than 50% paraffins. They are low in wax and generally have a pour point below 2°C (35°F). The novel process of this invention is carried out by subjecting the naphthenic charge stock without the necessity of any solvent extraction step whatsoever to a catalytic conversion step which is conducted at temperatures ranging from 260° to 357°C (500° to 675°F), at liquid hourly space velocities ranging from 0.1 to 10, and hydrogen pressures ranging from 1480 to 13890 kPa (200 to 2000 psig).

The conversion catalyst is a composite of hydrogenation metal, preferably a metal of Group VIII of the Periodic Table, associated with the acid form of an aluminosilicate zeolite having a silica/alumina ratio above 12 and a constraint index of 1 to 12.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from the intracrystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred type zeolites useful in this invention possess, in combination: a silica to alumina mole ratio of at least about 12; and a structure providing constrained access to the crystalline free space.

The silica to alumina ratio referred to may be determined by conventional analysis. This ratio is meant to represent as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type zeolites useful in this invention freely sorb normal hexane and benzene and have a pore dimension greater than about 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering or pore blockage may render these zeolites ineffective. Twelve-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions, although puckered structures exist such as TMA offretite which is a known effective zeolite. Also, structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of catalyst at atmospheric pressure according to the following precedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 538°C (1000°F) for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 288° and 510°C (550° and 950°F) to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e. 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10}\text{ (fraction of n-hexane remaining)}}{\log_{10}\text{ (fraction of 3-methylpentane remaining}}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a constraint index in the approximate range of 1 to 12. Constraint Index (CI) values for some typical zeolites are:

| CAS | C.I. |
|---|---|
| ZSM-5 | 8.3 |
| ZSM-11 | 8.7 |
| ZSM-12 | 2 |
| ZSM-38 | 2 |
| ZSM-35 | 4.5 |
| TMA Offretite | 3.7 |
| Beta | 0.6 |
| ZSM-4 | 0.5 |
| H-Zeolon | 0.4 |
| REY | 0.4 |
| Amorphous Silica-Alumina | 0.6 |
| Erionite | 38 |

It is to be realized that the above constraint index values typically characterize the specified zeolites but that such are the cumulative result of several variables used in determination and calculation thereof. Thus, for a given zeolite depending on the temperature employed within the aforenoted range of 288° to 510°C (550° to 950°F), with accompanying conversion between 10% and 60%, the constraint index may vary within the indicated approximate range of 1 to 12. Likewise, other variables such as the crystal size of the zeolite, the presence of possible occluded contaminants and binders intimately combined with the zeolite may affect the constraint index. It will accordingly be understood by those skilled in the art that the constraint index, as utilized herein, while affording a highly useful means for characterizing the zeolites of interest is approximate, taking into consideration the manner of its determination, with probability, in some instances, of compounding variable extremes. However, in all instances, at a temperature within the above-specified range of 288° to 510°C (550° to 950°F), the constraint index will have a value for any given zeolite of interest herein within the approximate range of 1 to 12.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38 and other similar materials. U.S. Patent No. 3,702,886 describes ZSM-5, ZSM-11 is described in U.S. Patent No. 3,709,979, ZSM-12 is described in U.S. Patent No. 3,832,449, ZSM-38 is described U.S. Patent No. 4,046,859. This zeolite can be identified, in terms of mole ratios of oxides and in the anhydrous state, as follows:

$$(0.3\text{-}2.5)R_2O : (0\text{-}0.8)M_2O : Al_2O_3 : > xSiO_2$$

wherein R is an organic nitrogen-containing cation derived from a 2-(hydroxyalkyl) trialkylammonium compound and M is an alkali metal cation, and is characterized by a specified X-ray powder diffraction pattern.

In a preferred synthesized form, these zeolites have a formula, in terms of mole ratios of oxides and in the anhydrous state, as follows:

$$(0.4\text{-}2.5)R_2O : (0\text{-}0.6)M_2O : Al_2O_3 : xSiO_2$$

wherein R is an organic nitrogen-containing cation derived from a 2-(hydroxyalkyl) trialkylammonium compound, wherein alkyl is methyl, ethyl or a combination thereof, M is an alkali metal, especially sodium, and x is from greater than 8 to about 50.

The synthetic ZSM-38 zeolite possesses a definite distinguishing crystalline structure whose X-ray diffraction pattern shows substantially the significant lines set forth in Table 2. It is observed that this X-ray diffraction pattern (significant lines) is similar to that of natural ferrierite with a notable exception being that natural ferrierite patterns exhibit a significant line at 11.33 Angstroms.

## TABLE 2

| d(Angstroms) | I/Io |
|---|---|
| 9.8 ± 0.20 | Strong |
| 9.1 ± 0.19 | Medium |
| 8.0 ± 0.16 | Weak |
| 7.1 ± 0.14 | Medium |
| 6.7 ± 0.14 | Medium |
| 6.0 ± 0.12 | Weak |
| 4.37 ± 0.09 | Weak |
| 4.23 ± 0.09 | Weak |
| 4.01 ± 0.08 | Very Strong |
| 3.81 ± 0.08 | Very Strong |
| 3.69 ± 0.07 | Medium |
| 3.57 ± 0.07 | Very Strong |
| 3.51 ± 0.07 | Very Strong |
| 3.34 ± 0.07 | Medium |
| 3.17 ± 0.06 | Strong |
| 3.08 ± 0.06 | Medium |
| 3.00 ± 0.06 | Weak |
| 2.92 ± 0.06 | Medium |
| 2.73 ± 0.06 | Weak |
| 2.66 ± 0.05 | Weak |
| 2.60 ± 0.05 | Weak |
| 2.49 ± 0.05 | Weak |

A further characteristic of ZSM-38 is its sorptive capacity providing the zeolite with increased capacity for 2-methylpentane (with respect to n-hexane sorption by the ratio n-hexane/2-methylpentane) when compared with a hydrogen form of natural ferrierite resulting from calcination of an ammonium exchanged form. The characteristic sorption ratio n-hexane/2-methylpentane for ZSM-38 (after calcination at 600°C) is less than 10, whereas the ratio for the natural ferrierite is substantially greater than 10, for example, as high as 34 or higher.

Zeolite ZSM-38 can be suitably prepared by preparing a solution containing sources of an alkali metal oxide, preferably sodium oxide, an organic nitrogen-containing oxide, an oxide of aluminum, an oxide of silicon and water and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

| | Broad | Preferred |
|---|---|---|
| $R+/R+ + M+$ | 0.2-1.0 | 0.3-0.9 |
| $OH^-/SiO_2$ | 0.05-0.05 | 0.07-0.49 |
| $H_2O/OH^-$ | 41-500 | 100-250 |
| $SiO_2/Al_2O_3$ | 8.8-200 | 12-60 |

wherein R is an organic nitrogen-containing cation derived from a 2-(hydroxyalkyl) trialkylammonium compound and M is an alkali metal ion, and maintaining the mixture until crystals of the zeolite are formed. (The quantity of $OH^-$ is calculated only from the inorganic sources of alkali without any organic base contribution). Thereafter, the crystals are separated from the liquid and recovered. Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from 90°C to 400°C for a period of time of from 6 hours to 100 days. A more preferred temperature range is from 150°C to 400°C with the amount of time at a temperature in such range being from 6 hours to 80 days.

The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering and water washing. The crystalline product is thereafter dried, e.g. at 110°C (230°F) for from 8 to 24 hours.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 538°C (1000°F) for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 538°C (1000°F) in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type of catalyst by base exchange with ammonium salts followed by calcination in air at about 538°C (1000°F) for from 15 minutes to 24 hours.

Natural zeolites may sometimes be converted to this type zeolite catalyst by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38, with ZSM-5 particularly preferred.

In a preferred aspect of this invention, the zeolites hereof are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred zeolites of this invention are those having a constraint index as defined above of about 1 to about 12, a silica to alumina ration of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meier included in "Proceedings of the Conference on Molecular Sieves, London, April 1967," published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pyknometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density, of course, must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites are:

| Zeolite | Void Volume | Framework Density |
|---|---|---|
| Ferrierite | 0.28 cc/cc | 1.76 g/cc |
| Mordenite | 0.28 | 1.7 |
| ZSM-5, -11 | 0.29 | 1.79 |
| Dachiardite | 0.32 | 1.72 |
| L | 0.32 | 1.61 |
| Clinoptilolite | 0.34 | 1.71 |
| Laumontite | 0.34 | 1.77 |
| ZSM-4 (Omega) | 0.38 | 1.65 |
| Heulandite | 0.39 | 1.69 |
| P | 0.41 | 1.57 |
| Offretite | 0.40 | 1.55 |
| Levynite | 0.40 | 1.54 |
| Erionite | 0.35 | 1.51 |
| Gmelinite | 0.44 | 1.46 |
| Chabazite | 0.47 | 1.45 |
| A | 0.5 | 1.3 |
| Y | 0.48 | 1.27 |

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table including for example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired conversion process, it may be desirable to incorporate the above-described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin familes, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from 1 to 99 percent by weight and more usually in the range of from 5 to 80 percent by weight of the composite.

Preferably, the effluent of the first step including the hydrogen is cascaded into a hydrotreating reactor of the type now generally employed for finishing of lubricating oil stocks. The distillation necessary to remove light products for conformance to fire and flash point specifications may be conducted between the dewaxing and hydrotreating steps. However, since there are indications that inter-stage distillation and/or storage results in less stable product, and also to avoid need for separation and recharging of hdyrogen with intermediate distillation, cascade type operation is preferred.

Any of the known hydrotreating catalysts consisting of a hydrogenation component on a non-acidic support may be employed, for example, cobalt-molybdate, or nickel-molybdate, or molybdenum oxide, on an alumina support. Here again, temperature control is required for production of high quality product, the hydrotreater being preferably held at 260° to 357°C (500° to 675°F) at a pressure of 1480 to 13890 kPa (200 to 2000 psig).

When the preferred cascade configuration is used, the effluent of the hydrotreater is topped by distillation, i.e. the most volatile components are removed, to meet flash and fire point specifications.

## EXAMPLE

A raw distillate was obtained from a Venezuelan Melones crude by vacuum distillation to yield a 288° to 416°C (550° to 780°F) fraction. It has a pour point of -23°C (-10°F). High molecular weight mass spectrometric analysis shows that it contains 30% aromatics, 30% naphthenes and 40% paraffins.

The distillate is processed over a ZnHZSM-5, the preparation of which is described in accordance with U.S. Reissue Patent No. 28,398 under the following reaction conditions:

| | |
|---|---|
| Pressure | 3549 kPa (500 psig) |
| LHSV | 1 |
| Temperature (SOC) | 304°C (580°F) |
| $H_2$ circulation | 445 Nl/l (2500 SCF/B) |

The conversion product was found to yield 3 weight percent gaseous products including 0.3 weight percent dry gas (ethane and lighter), 1.2 weight percent propane and 1.5 weight percent butanes, and 97 weight percent $C_5$+ liquid product. The liquid product is fractionated to yield (based on distillate charged) 6.9 weight percent $C_5$ to 166°C (330°F) naphtha, 3.1 weight percent 166° to 288°C (330 to 550°F) diesel fuel and 87 weight percent 288°C+ (550°F+) liquid. The 288°C+ (550°F+) liquid has a pour point of -51°C (-60°F) and has the following chemical composition: 32.3 weight percent aromatics, 31.5 weight percent naphthenes, and 36.2 weight percent paraffins.

Eighteen grams of the 288°C+ (550°F+) liquid is dissolved in 100 ml cyclohexane, charged together with 11 grams of reduced Harshaw Ni kieselguhr to a 300 ml stirring autoclave, pressured to 3549 kPa (500 psig) with hydrogen heated at 316°C (600°F) with stirring for two hours, cooled, filtered to remove the catalyst and the hydrogenated liquid topped to remove chclohexane solvent. Properties of the product are shown in the following table:

| | |
|---|---|
| Specific gravity at 16°C (60°F) | 0.88 |
| Pour Point, °C(°F) | -51(-60) |
| KV at 38°C (100°F), cs | 11.0 |
| KV at 99°C (210°F), cs | 2.5 |
| Viscosity Index | 40 |

Mass spectrometric analysis of the hydrogenated product shows that it contains 23 weight percent aromatics, 41 weight percent naphthenes, and 35 weight percent paraffins.

1. Process for the production of low pour point lube oil basestocks from raw distillate fractions derived from marginal naphthenic crudes, said fraction having a boiling range of from 260° to 566°C (500° to 1050°F) and characterized as containing from 25 to 50 weight percent aromatics, from 25 to 40 weight percent naphthenes, less than 50 weight percent paraffins, a pour point below 2°C (35°F) and an API gravity of from 20 to 25 which comprises contacting the fraction at a temperature of from 260° to 357°C (500 to 675°F) with a conversion catalyst comprising an aluminosilicate zeolite having a silica/alumina ratio above 12 and a constraint index between 1 and 12, hydrotreating the resultant product by contact at a temperature of from 260° to 357°C (500° to 675°F) and a pressure of from 1480 to 13890 kPa (200 to 2000 psig) with a hydrotreating catalyst comprising a hydrogenation component on a non-acidic support and recovering a lube oil having a pour point below -23°C (-10°F).

2. The process of claim 1 wherein the conversion catalyst comprises ZSM-5 and a hydrogenation metal.

3. The process of claim 1 or 2 wherein the reaction is carried out in the presence of added hydrogen.

4. The process of claim 2 or 3 wherein the ZSM-5 zeolite is partially in the hydrogen form.

5. The process of any of claims 2 to 4 wherein the ZSM-5 zeolite has zinc associated therewith.

European Patent Office

# EUROPEAN SEARCH REPORT

0062985

Application number

EP 82 30 1524

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. ³) |
|---|---|---|---|
| Y | GB-A-2 010 321 (MOBIL OIL)<br>* claims 1-11 *<br>--- | 1-5 | C 10 G 65/04 |
| Y | GB-A-2 001 668 (MOBIL OIL)<br>* claims 1-10 * & US - A - 4 137 148<br>--- | 1-5 | |
| Y | US-A-3 730 876 (SEQUEIRA)<br>* claims 1-5,9 *<br>--- | 1 | |
| A | US-A-3 438 887 (MORRIS et al.)<br>* claims 1,4,5 *<br>--- | | |
| A | US-A-3 974 060 (ALEXIS VOORHIES)<br>* claim 1 *<br>--- | | **TECHNICAL FIELDS SEARCHED (Int. Cl. ³)** |
| D,Y | US-A-4 176 050 (CHEN et al.)<br>* claims 1-11 *<br>----- | 2-5 | C 10 G |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 02-07-1982 | MICHIELS P. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document