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Description

This invention is concerned with manufacture of high grade viscous oil products from crude petroleum fractions or other hydrocarbon materials. It is particularly directed to the manufacture of high quality lube basestock oils from crude stocks of high boiling point as opposed to using so-called light stocks. The latter crudes have lower boiling points and for reasons which are not fully understood, do not show any advantage in the novel process of this invention over commercially practiced technology. More specifically, the invention is concerned with dewaxing a lube basestock oils having an initial boiling point higher than 371°C (700°F) and a 50 volume percent boiling point of at least 482°C (900°F).

High quality lube basestock oils are conventionally prepared by refining distillate fractions or the residuum prepared by vacuum distilling a suitable crude oil from which the lighter portion has been removed by distillation in an atmospheric tower. Thus, the charge to the vacuum tower is commonly referred to as a "long rediuum" and residuum from the vacuum tower is distinguished from the starting material by referring to it as the "short residuum".

The vacuum distillate fractions are upgraded by a sequence of unit operations, the first of which is solvent extraction with a solvent selective for aromatic hydrocarbons. This step serves to remove aromatic hydrocarbons of low viscosity index and provides a raffinate of improved viscosity index and quality. Various processes have been used in this extraction stage, and these employ solvents such as furfural, phenol, sulfur dioxide, and others. The short residuum because it contains most of the asphaltenes of the crude oil, is conventionally treated to remove these asphalt-like constituents prior to solvent extraction to increase the viscosity index.

The raffinate from the solvent extraction step contains parraffins which adversely affect the pour point. Thus, the waxy raffinate, regardless of whether prepared from a distillate fraction or from the short residuum, must be dewaxed. Various dewaxing procedures have been used, and the art has gone in the direction of treatment with a solvent such as methyl ethyl ketone/toluene mixtures to remove the wax and prepare a dewaxed raffinate. The dewaxed raffinate may then be finished by any number of sorption or catalytic processes to improve colour and oxidation stability.

In recent years techniques have become available for catalytic dewaxing the 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, United States Patent No. 3,668,113.

In United States No. Reissue 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 United States Patent No. 3,894,938 for reducing the pour point of a sulfur and nitrogen-containing gas oil boiling within the range of 204 to 482°C (400 to 900°F).

United States Patent No. 3,755,145 discloses a process for preparing lube oil having low pour points involving using a catalyst mixture comprising hydrogenation components, a conventional cracking catalyst and a crystlline aluminosilicate zeolite of the ZSM—5 type. At Column 8 there is specifically disclosed the use of an extrudate having a 1/16th of an inch diameter.

United States Patent No. 3,894,938 discloses the catalytic dewaxing and desulfurization of gas oils with a ZSM—5 zeolite containing a hydrogenation component. At Column 3 it is specifically pointed out that the ZSM—5 can be incorporated into a matrix and that the catalyst particles can be sized between 0.8 and 3.2 mm (1/32nd and 1/8th of an inch).

EP—A—0104855 discloses a process for preparing a high quality lube base stock oil of low pour point and excellent stability from a waxy cude oil fraction in a single-stage hydrodewaxing process. The process uses ZSM—5 catalyst containing Ni—Mo or Co-Mo. The feed is a propane-deasphalted fraction having an initial boiling point of at least 232°C and a final boiling point of less than 593°C. 1.59 mm (1/16th inch) diameter extrudate was used in those examples where catalyst diameter was reported.

United States 3,846,337 discloses silica-bound silicate particles of improved strength within the range of 0.8 to 3.2 mm (1/32 to about 1/8 inch) average extrudate diameter and their use in various catalysts reactions.

These processes dis not provide any guidance as to how to achieve an more stable operation when processing heavy lubricating oil stocks, such as bright stock.

We discovered that more efficient dewaxing of these heavy stocks could be achieved using a special dewaxing catalyst with certain physical properties.

Accordingly, the present invention provides a process for dewaxing a petroleum feedstock having an initial boiling point of at least 371°C (700°F) and a 50 volume percent boiling point of at least 482°C (900°F) wherein said hydrocarbon is contacted in the presence of added hydrogen at a temperature of 232 to 427°C (450 to 800°F) with a dewaxing catalyst comprising aluminosilicate zeolite having a silica-to-alumina ratio of greater than 12 and a Constraint Index of 1 to about 12 and wherein said aluminosilicate zeolite is composited with an inorganic oxide binder and characterised by using a catalyst composite having a maximum diffusion distance of less than 0.6 mm (0.025 inch).

As used herein the term "diffusion distance" is defined as the ratio of the volume of the shape of catalyst composite to the surface through which the reactants diffuse into this volume.

Figure 1 is a graph of actual experimental data illustrating the temperature requirements to catalytically dewax a lube stock whose boiling range lies outside the scope of the present invention, over a prior art catalyst.

Figure 2 is a graph of actual experimental data illustrating the temperature requirements to catalytically dewax with the invention catalyst a lube stock whose boiling range lies outside the scope of the invention.

Figure 3 is a graph of actual experimental data showing the effect of treating a heavy neutral feedstock with an extruded catalyst having a particle diameter of 8.0 mm (0.03125 inch) compared to a prior art catalyst.

Figure 4 is a graph of actual experimental data showing the dewaxing of a heavy neutral feedstock on the subsequent cycle to Figure 3 comparing the same reference and invention catalysts.

Figure 5 shows experimental data on the dewaxing of a bright stock using the same reference and invention catalysts shown in Figures 3 and 4.

Figure 6 shows experimental data on the dewaxing of bright stock comparing extruded catalyst and finely crushed catalyst.

The wax base crudes (sometimes called "paraffin base") from which the chargestock is derived by distillation constitute a well-recognized class of crude petroleums. Many scales have been devised for classification of crude, some of which are described in Chapter VII, "Evaluation of Oil Stocks of *Petroleum Refinery Engineering*, by W. L. Nelson, McGraw Hill, 1941. A convenient scale identified by Nelson at page 69 involves determination of the cloud point of the Bureau of Mines (key fraction #2) which boils between 275°C (527°F) and 300°C (572°F) at 40 mm pressure. If the cloud point of this fraction is above −15°C (5°F), the crude is considered wax base.

In practice of the present invention, a suitable chargestock such as a propane deasphalted short residium fraction or a fraction having an initial boiling point of at least 468°C (875°F), and preferably at least 482°C (900°F.) and a final boiling point greater than 649°C (1200°F) is prepared by distillation of such wax base crude. Such fraction can then be solvent refined by counter current extraction with at least an equal volume (100 volume percent) of a selective solvent such a furfural. It is preferred to use about 1.5—3.0 volumes of solvent per volume of oil. The furfural raffinate has an initial boiling point of greater than 371°C (700°F) and a 50 volume percent boiling point of at least 482°C (900°F). It is then subjected to catalytic dewaxing by mixing in hydrogen and contacting at 232 to 427°C (450 to 800°F), preferably at 260 to 371°C (500 to 700°F), with a catalyst containing a hydrogenation metal, an inorganic oxide binder and zeolite ZSM—5 or other related silicate zeolites having a silica-to-alumina ratio of at least 12 and a Constraint Index of 1—12 and a liquid hourly space velocity (LHSV) of 0.1—2.0 volumes of charge oil per volume of catalyst per hour. The preferred space velocity is 0.5—1.0 LHSV.

The catalyst is extruded or otherwise shaped so as to have a maximum diffusion distance of less than 0.6 mm (0.025 inch).

The catalytic dewaxing reaction is preferably carried out at hydrogen partial pressures of 1,100 to 21,000 kPa (150 to 300 psig), at the reactor inlet, and preferably at 1,800 to 10,400 kPa (250 to 1500 psig). Dewaxing operates at a hydrogen circulation of 90 to 900 volumes of liquid at standard conditions per volume of H_2 at standard conditions, v/v, (500 to 5000 standard cubic feet per barrel of feed (SCFB)), preferably 270 to 530 v/v (1500 to 3000 SCFB).

The solvent extraction technique is well understood in the art and needs no detailed review here. The severity of extraction is adjusted to composition of the chargestock to meet specifications for the particular lube basestock and the contemplated end-use; this severity will be determined in practice of this invention in accordance with well-established practices.

The catalytic dewaxing step is conducted at 232 to 427°C (450 to 800°F). However, at temperatures above 357°C (675°F), bromine number of the product generally increases and the oxidation stability decreases.

The dewaxing catalyst is a composite of hydrogenation metal, such as nickel, cobalt, molybdenum, chromium, tungsten, palladium, platinum or compositions thereof associated with the acid form of a novel class of aluminosilicate zeolite having a silica-to-alumina ratio of at least about 12, and a constrained access to the intracrystalline free space, as more fully described herinbelow.

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 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 characteristic is advantageous in the present invention.

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-methylphentane over a small sample, approximately 1 gram or less, of catalyst at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudates, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolites 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 temeprature adjusted to give an overall conversion between 10% and 60 percent. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (LHSV) (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 to 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:

$$\text{Constraint Index} \; \frac{\text{Log}_{10}\text{ (fraction of n-hexane remaining)}}{\text{Log}_{10}\text{ (fraction of 3-methylpentane remaining)}}$$

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	CI
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-23	9.1
ZSM-35	4.5
ZSM-38	2
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 test temperature, 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 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.

The class of zeolites defined herein is exemplifed by ZSM—5, ZSM—11, ZSM—12, ZSM—23, 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—23 is described in U.S. Patent No. 4,076,842.

ZSM—35 is described in U.S. Patent No. 4,016,245.

ZSM—38 is described in U.S. Patent No. 4,046,859.

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 in inert atmosphere, followed by base exchange with ammonium salts followed by calcination.

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—23, ZSM—38 and ZSM—35, with ZSM—5 particularly preferred.

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, by way of example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired conversion process, it is 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 families, which families include the sub-bentonites and the kaolins commonly known as Dixie, NcNamee-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 relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from between 1 to 99 percent by weight and more usually in the range of 55 to about 80 percent by weight of the composite.

The method of forming the particle or extrudate of the desired diameter size is accomplished according to conventional techniques in the prior art, and no particular novelty is claimed in the method of making the material. In general for forming cylindrical extrudates, a mixture of a suitable zeolite such as ZSM—5 containing a hydrogenation component and an inorganic oxide matrix such as alumina in a suitable weight ratio, i.e., 65 weight percent zeolite; 35 weight percent alumina; are mixed with water and extruded through a .0625 inch to a conventional commercial extruder such as a Califormia pellet mill having the appropriate diameter hole, i.e., from 0.3 to 1.3 mm (.0125 to .05 inch). The extrudate is then dried and calcined at elevated temperatures, i.e. 538°C (1000°F) for about 3 hours. Neither the drying nor the calcination time is particularly critical, and it is the conventional time used in making extrudates.

Polylobes including trilobes and quadrulobes are known in the art and conventional processes for their preparation are disclosed in U.S. Patent 4,447,314.

Extrusion is also useful for forming other shapes of particles that are desirable for this catalyst. These are formed by using suitable shaped orifices in the die plate of the extruder. U.S. Patent No. 3,674,680 to *Hoekstra et al.* represents a suitable extrudate shape; U.S. 3,674,680 uses small catalyst shapes wherein all points in the particles are less than 0.4 mm (0.015 inch) from a surface of the particle. Shapes having a configuration of cross, clover leaf, quadrulobe or trilobe such as in U.S. 3,857,780 are operable here, so long as the maximum dimension of the cross section of the lobes or shapes in such that the maximum diffusion distance is less than 0.6 mm (0.025 inches) from the particle surface.

Spherical or near-spherical particles within the specified dimension range of the surface are also operable herein. These generally are formed from freshly extruded material, for example, by a process where the extrudate is reshaped in spinning vessel or drum. Such equipment is available commercially as marumerizers from the Eli Lily Company and others.

Examples 1—3

Three different lube basestocks were prepared from an Arabian Light crude. Typical properties of the three materials are given in Table 1.

Charge stock A, a 345 bright stock, was prepared by propane deasphalting the vacuum resid. The deasphalted oil was then furfural extracted to reduce the aromatics content.

Charge stock B, a 339 heavy neutral, was prepared by vacuum distillation. This heavy vacuum distillate was then furfural extracted to reduce the aromatics content.

Charge stock C, a 318 light neutral, was also prepared by vacuum distillation. This light vacuum distillate was also furfural extracted to lower the aromatics content.

TABLE 1

Charge Stock Properties

	A	B	C
FEED	Arab Lt. BS	Arab Lt HN	Arab Lt. LN
Density, g/cl			
°API	26.2	27.5	30.8
H, wt percent	13.1	13.5	13.58
S, wt percent	1.18	1.05	.82
N, ppm	130	97	60
Total Acid No.	0.25	0.12	—
CCR, wt percent (Conradson Carbon Residue)	.77	0.05	--
Pour Point, °C/F°	49/120	49/120	38/100
KV 54°C/130°F, cs		48.15	17.68
KV 100°C/212°F, cs	27.77	11.3	5.32
KV 149°C/300°F, cs	8.749		
Distillation			
IBP, °C/°F	433/812	396/744	365/689
5 Vol Percent	484/903	452/846	399/751
10	501/933	466/870	407/765
20	519/966	477/890	
30	534/993	483/902	424/796
40	543/1009	488/910	
50	555/1031	492/918	435/815
60	568/1054	496/925	
70	579/1074	502/935	
80		508/947	
90		519/967	463/866
95		528/982	469/877
EP (End Point)		540/1004	---

Example 4

A nickel ZSM—5 catalyst combined with an alumina matrix and extruded to a diameter of 1.6 mm (0.0625 inch) was prepared as follows:

Dried sodium form ZSM—5 crystals and Kaiser SA alumina powder (alpha alumina monohydrate) were blended in a ratio of 65 parts by wt ZSM—5 and 35 parts by wt Al_2O_3 (both on a dry basis), extruded to 1.6 mm (.0625 inch) diameter cylinders and calcined for three hours at 538°C (1000°F). The calcined product was exchanged with NH_4NO_3 solution to low sodium and then with $ni(NO_3)_2$ solution. It was dried and then calcined at 538°C (1000°F). The nickel content was 1.3 weight percent and the sodium was 0.02 weight percent.

The calcined extrudate was then steamed at 482°C (900°F) for six hours. The measured alpha activity was 68.

Example 5

A nickel ZSM—5 catalyst combined with an alumina matrix and extruded to a diameter of 0.8 mm (0.03125 inch) was prepared as follows:

This catalyst was prepared by the same procedure as Example 4, except that the extrudates produced were 0.8 mm (1/32 inch) diameter.

The nickel content was 1.0 weight percent and the sodium was 0.03 weight percent. The measured alpha activity was 75.

The physical properties of the catalyst prepared in accordance with Examples 4 and Examples 5 are shown in Table 2.

TABLE 2

Example	4	5
Extrudate Diam., in./mm	.0625/1.6	.03125/0.8
Packed Density, g/cc	0.57	0.616
Particle Density, g/cc	0.919	1.037
Real Density, g/cc	2.736	2.760
Pore Volume, cc/g	0.722	0.602
Surface Area, m^2/g	352	338
Ni, wt percent	1.3	1.0
Na, ppm	200	300
Alpha Activity	68	75
Pore Volume Distribution PV Percent of Pores in		
0 - 30 Angstrom Diam.	19	24
30 - 50	9	7
50 - 80	19	13
80 - 100	10	9
100 - 150	13	22
150 - 200	4	13
200 - 300	6	9
300+	20	3

It is to be understood that the catalyst can be employed in the fresh state or can be subjected to a mild steaming treatment at elevated temperatures from 427 to 816°C (800 to 1500°F) and preferably 427 to 649°C (800 to 1200°F). The treatment may be accomplished in atmospheres of 100 percent steam or at atmospheres consisting of steam and a gas which is substantially inert to the zeolites. A similar treatment can be accomplished at lower temperatures and elevated pressures, e.g., 177 to 371°C (350 to 700°F) at 10 to about 200 atmospheres.

In the experiments which follow a catalyst of Examples 4 and 5 were treated with steam at 482°C (900°F) for 6 hours.

Example 6

In order to demonstrate that the novel process of this invention does not result in increased benefit with all feedstocks, experiments were carried out using the raffinate identified as Feed C in Table 1. As can be seen, this feedstock is outside the scope of this invention since its 50 volume percent boiling point is below 482°C (900°F). Catalysts of Examples 4 and 5 were used to process this feed material to a pour point of −7°C (+20°F). The dewaxing conditions are as follows:

Pressure	400 PSIG/2,900 kPa
LHVS	1.0
Hydrogen Circulation	2500 SCFB/450 v/v
Temperature	282—360°C/540—680°F

Figure 1 shows the results obtained utilizing the catalyst of Example 4 having a 1.6 mm (0.0625 inch) diameter extrudate. Figure 2 shows the results obtained using the catalyst of the invention, 0.8 mm (0.03125 inch) diameter extrudate (Example 5). Both catalysts had undergone previous dewaxing cycles with subsequent high temperature hydrogen reactivations.

Following relatively rapid initial aging 2.8 to 3.9°C (5 to 7°F) per day, both catalysts lined out and aged at about 0.56°C (1°F) per day. Thus, no advantage is evident for dewaxing light stocks with catalysts having maximum diffusion distances less than 0.8 mm (.03125 inch) i.e., 1.6 mm (.0625 inch) diameter extrudate.

Example 7

The catalysts of Examples 4 and 5 are used to dewax the heavy neutral raffinate identified as Feed B to a pour point of −7°C (+20°F). The dewaxing conditions were identical to those used in Example 6.

The results of this experiment are shown in Figure 3. and can be seen in Figure 3 the dotted line represents the results obtained with the 1.6 mm (0.0625 inch) diameter catalyst, i.e., Example 4, whereas the solid line represents a plot of the catalyst of Example 5, i.e., 0.8 mm (.03125 inch) diameter. As can be seen, a lower part of cycle temperature was obtained using the 0.8 mm (.03125 inch) catalyst, i.e., 282°C (540°F) as opposed to the 1.6 mm (.0625 inch) catalyst, i.e., 291°C (555°F). The 1.6 mm (.0625 inch) catalyst aged at 2.22°C (4°F) per day, whereas the 0.8 mm (.03125 inch) catalyst aged at 2.44°C (4.4°F) per day, essentially equivalent. As can be seen from the above data, although the 0.8 mm (.03125 inch) catalyst resulted in a lower start-of-cycle temperature, its aging rate was equal to the 1.6 mm (.0625 inch) catalyst.

Example 8

After reaching end of cycle conditions, both the catalysts used in Example 6 were reactivated by treatment with hydrogen at about 482°C (900°F) for 24 hours. They were then recontacted with the same feedstock used in Example 6 under the exact same operating conditions, and the results are shown in Figure 4. As can be seen, during the second cycle, the 0.8 mm (.03125 inch) diameter catalyst represented by the solid line had a start-of-cycle temperature of 289°C (552°F) as compared to 293°C (560°F) for the 1.6 mm (.0625 inch) diameter catalyst. However, the 0.8 mm (.03125 inch) diameter catalyst aged at 3.11°C (5.6°F) per day whereas the 1.6 mm (.0625 inch) diameter catalyst aged at 5.56°C (10°F) per day.

Quite obviously, the above experimental results demonstrate the lower aging characteristics of utilizing the smaller extrudate. This advantage was not observed with 318LN (Example 6). Moreover, the advantages of the invention become more pronouned with reactivated catalysts.

Example 9

Following the runs of Example 8 both catalysts were again reactivated by heating the same in the presence of hydrogen at 482°C (900°F) for 24 hours. The two catalysts were then used to dewax a bright stock having the properties set forth under Feed A in Table 1. The results of the experimentation are shown in Figure 5. The base case catalyst 1.6 mm (0.0625 inch) diameter extrudate, as shown by the dashed line, had a 299°C (570°F) start-of-cycle activity and aged at 5°C (9°F) per day. The invention catalyst 0.8 mm (0.03125 inch) diameter extrudate, as shown by the solid line, had a 284°C (544°F) start-of-cycle activity and aged at only 2.33°C (4.2°F) per day. This result demonstrates that lowering the catalyst's maximum diffusion distance improved performance for dewaxing bright stock lube material.

Example 10

The previous examples have cited 0.8 mm (1/32nd inch) diameter extrudate catalyst. This example demonstrates that a similar catalyst stability benefit can also be achieved by crushing large extrudates to smaller particles having a diffusion length encompassed in this invention. The catalyst of Example 4 was crushed and sieved to two sizes: 0.60—0.84 mm (20/30 mesh) and 0.18—0.25 mm (60/80 mesh). The average particle sizes were 0.6 mm (0.025 inch) and 0.1 mm (.005 inch), respectively. Maximum diffusion distances were 0.3 mm (0.0125 inch) and 0.6 mm (0.0025 inch), respectively. These three catalysts were used to dewax an Arabian Light bright stock (see Table 3 for properties) at 0.75 LHSV. The results are shown in Figure 6. The catalyst of Example 4 extrudate catalyst had a start-of-cycle activity of 278°C (533°F) and aged at 1.67°C (3°F) per day. The 0.60—0.84 mm (20/30 mesh) catalyst had a start-of-cycle activity of 278°C (532°F) and aged at only 0.83°C (1.5°F) per day. Going to even smaller particles gave a slight start-of-cycle activity benefit.

TABLE 3
Arabian Light Bright Stock Properties

Stock	D
Specific Gravity, g/cl	0.90
Viscosity KV@ 100°C	29.71
KV@ 149°C (300°F)	9.31
Aniline Point	251
Elemental Analysis Weight Percent	
Carbon	85.53
Hydrogen	13.16
Sulfur	1.31
Nitrogen (ppm)	130
Basic Nit. (ppm)	100
Metals (ppm)	
Ni	0.4
V	ND
Fe	ND
Cu	ND
Na	5.2
Furfural (ppm)	8.0
Oil Content weight percent	80.62
Refractive Index (70°C)	1.4872
CCR (weight percent)	0.71
Paraffins	18.8
Naphthenes	42.0
Aromatics	39.2
Distillation Weight Percent	°C/°F
1BP	427/800
5	489/912
10	507/944
20	527/980
30	537/998
40	546/1014
50	554/1030
56	563/1045

Claims

1. A process for dewaxing a petroleum feedstock having an initial boiling point of at least 371°C (700°F) and a 50 volume percent boiling point of at least 482°C (900°F) wherein said hydrocarbon is contacted in the presence of added hydrogen at a temperature of 232 to 427°C (450 to 800°F) with a dewaxing catalyst comprising aluminosilicate zeolite having a silica-to-alumina ratio of greater than 12 and a Constraint Index of 1 to about 12 and wherein said aluminosilicate zeolite is composited with an inorganic oxide binder and characterized by using a catalyst composite having a maximum diffusion distance of less than 0.6 mm (0.025 inch).

2. The process of claim 1 wherein the catalyst composite is in extrudate form having a diameter of less than about 1.3 mm (0.05 inch).

3. The process of claim 1 wherein the catalyst composite is in extrudate form with a diameter of about 0.8 mm (0.03125 inch).

4. The process of claim 1 wherein the catalyst composite is in bead or spherical form with a maximum diffusion distance of less than 0.6 mm (0.025 inch).

5. The process of claim 1 wherein the catalyst composite is in the form of a hollow centered shaped extrudate or monolithic form having a maximum diffusion distance of less than 0.6 mm (0.025 inch).

6. The process of claim 1 wherein the catalyst composite is a trilobe or quadrulobe extrudate having a maximum diffusion distance of less than 0.6 mm (0.025 inch).

7. The process of claim 1 wherein the catalyst composite is in pelleted form having a maximum diffusion distance of less than about 0.6 mm (0.025 inch).

8. The process of claim 1 wherein the inorganic oxide is alumina, silica, magnesia, titania, or a combination thereof.

9. The process of any of claims 1 to 8 wherein the zeolite is ZSM—5.

10. The process of any of claims 1 to 9 wherein the catalyst composite includes a hydrogenation component.

Patentansprüche

1. Verfahren zur Entparaffinierung eines Erdöleinsatzmaterials mit einem Anfangssiedepunkt von mindestens 371°C (700°F) und einem 50-Volumen-prozent-Siedepunkt von mindestens 482°C (900°F) wobei der Kohlenwasserstoff in Gegenwart von zugesetztem Wasserstoff bei einer Temperatur von 232°C bis 427°C (450°F bis 800°F) mit einem Entparaffinierungskatalysator in Kontakt gebracht wird, der einen Aluminosilicatzeolith mit einem Siliciumdioxid/Aluminiumoxid-Verhältnis von größer als 12 und einem Zwangsindex von 1 bis etwa 12 umfaßt, wobei dieser Aluminosilicatzeolith mit einem Bindemittel eines anorganischen Oxids zusammengesetzt ist, gekennzeichnet durch die Verwendung eines Katalysatorschichtkörpers bzw. einer Katalysatorszusammensetzung mit einem maximalen Diffusionsabstand von weniger als 0,6 mm (0.025 Inch).

2. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung in Extrudatform mit einem Durchmesser von weniger als etwas 1,3 mm (0.05 Inchy) vorliegt.

3. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung in Extrudatform mit einem Durchmesser von etwa 0,8 mm (0,03125 Inch) vorliegt.

4. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung in Kügelchenform oder spherischer Form mit einem maximalen Dissusionsabstand von weniger als 0,6 mm (0,025 Inch) vorliegt.

5. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung in Form eines hohlen zentrisch geformten Extrudats oder in Monolithform mit einem maximalen Diffusionsabstand von weniger als 0,6 mm (0,025 Inch) vorliegt.

6. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung ein dreiblättriges oder vierblättriges Extrudat mit einem maximalen Diffusionsabstand von weniger als 0,6 mm (0,025 Inch) ist.

7. Verfahren nach Anspruch 1, worin die Katalysatorzusammensetzung in Tabletten- bwz. Pelletform mit einem maximalen Diffusionsabstand von weniger als 0,6 mm (0,025 Inch) vorliegt.

8. Verfahren nach Anspruch 1, worin das anorganische Oxid Aluminiumoxid, Siliciumdioxid, Magnesiumoxid, Titandioxid oder eine Kombination davon ist.

9. Verfahren nach einem der Ansprüche 1 bis 8, worin der Zeolith ZSM—5 ist.

10. Verfahren nach einem der Ansprüche 1 bis 9, worin die Katalysatorzusammensetzung eine Hydrierungskomponente einschließt.

Revendications

1. Un procédé de déparaffinage d'une charge pétrolière dont le point d'ébullition est au moins égal à 371°C (700°F) et le point d'ébullition pour 50% du volume est au moins égal à 482°C (900°F), dans lequel on met cet hydrocarbure, en présence d'hydrogène alimenté à une température de 232 à 427°C (450 à 800°F) au contact d'un catalyseur de déparaffinage comprenant une zéolite à base d'aluminosilicate dont le rapport silice/alumine est supérieur à 12 et l'indice de contrainte est compris entre 1 et environ 12 et dans lequel cette zéolite d'aluminosilicate est associée à un liant formé d'un oxyde minéral, et est caractérisé en ce que l'on utilise un catalyseur composite présentant une distance maximum de diffusion inférieure à 0,6 mm (0,025 pouce).

2. Le procédé selon la revendication 1, caractérisé en ce que le catalyseur composite se trouve sous forme d'extrudat dont le diamètre est inférieur à environ 1,3 mm (0,05 pouce).

3. Le procédé selon la revendication 1, dans lequel le catalyseur composite se trouve sous forme d'un extrudat d'un diamètre d'environ 0,8 mm (0,03125 pouce).

4. Le procédé selon la revendication 1, dans lequel le materiau composite se trouve sous forme de perle ou sous une forme sphérique présentant une distance de diffusion maximum inférieure à 0,6 mm (0,025 pouce).

5. Le procédé selon la revendication 1, dans lequel le catalyseur composite se trouve sous la forme d'un extrudat façonné creusé en son centre ou sous une forme monolithique présentant une distance de diffusion maximum inférieure à 0,6 mm (0,025 pouce).

6. Le procédé selon la revendication 1, dans lequel le catalyseur composite est un extrudat trilobé ou quadrilobé dont la distance de diffusion maximum est inférieure à 0,6 mm (0,025 pouce).

7. Le procédé selon la revendication 1, dans lequel le catalyseur composite se trouve sous forme de pastille présentant une distance maximum de diffusion inférieure à environ 0,6 mm (0,025 pouce).

8. Le procédé selon la revendication 1, dans lequel l'oxyde minéral est l'un des suivants: alumine, silice, magnésie, titane ou leur association.

9. Le procédé selon l'une quelconque des revendications 1 à 8, dans lequel la zéolite est une ZSM—5.

10. Le procédé selon l'une quelconque des revendications 1 à 9, dans lequel le catalyseur composite inclut un composant d'hydrogénation.

Fig.1

Dewaxing of Arabian Light
318 LN (Stock C)

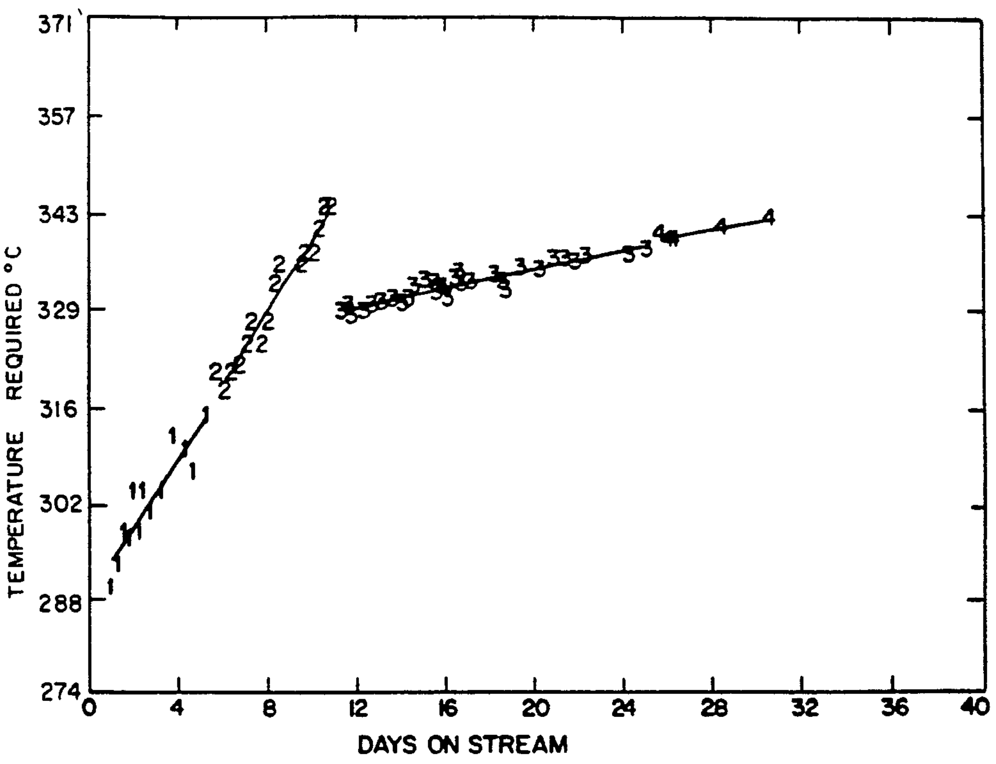


Fig.2

Dewaxing of Arabian Light
318LN (Stock C)

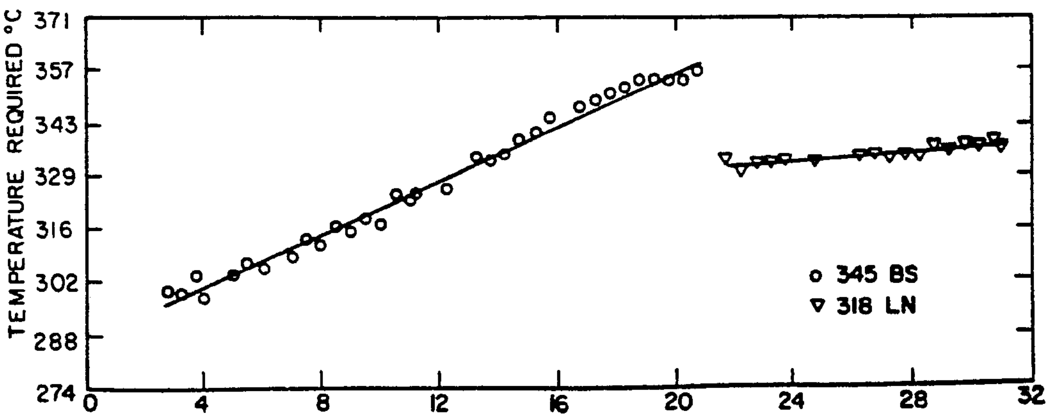


Fig.3

Dewaxing of Arabian Light
339 HN (Stock B)
Catalysts Example 4 and Example 5
Cycle 1

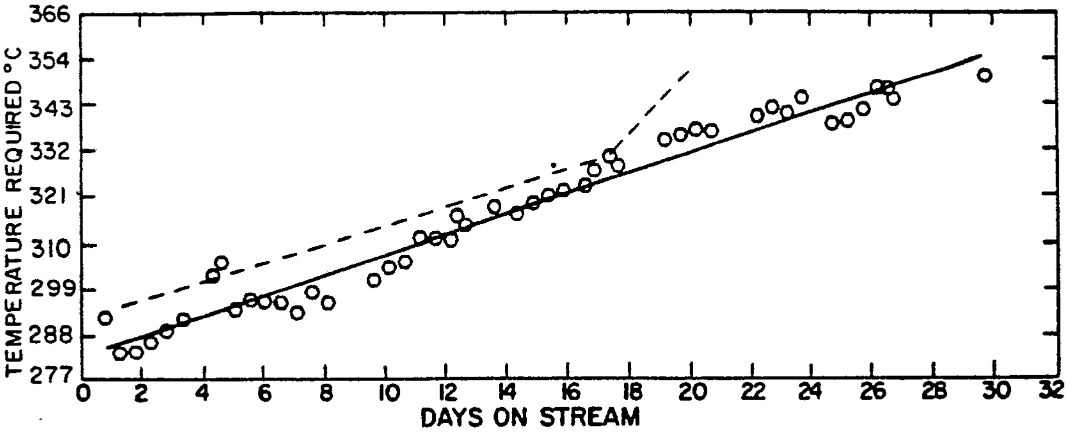
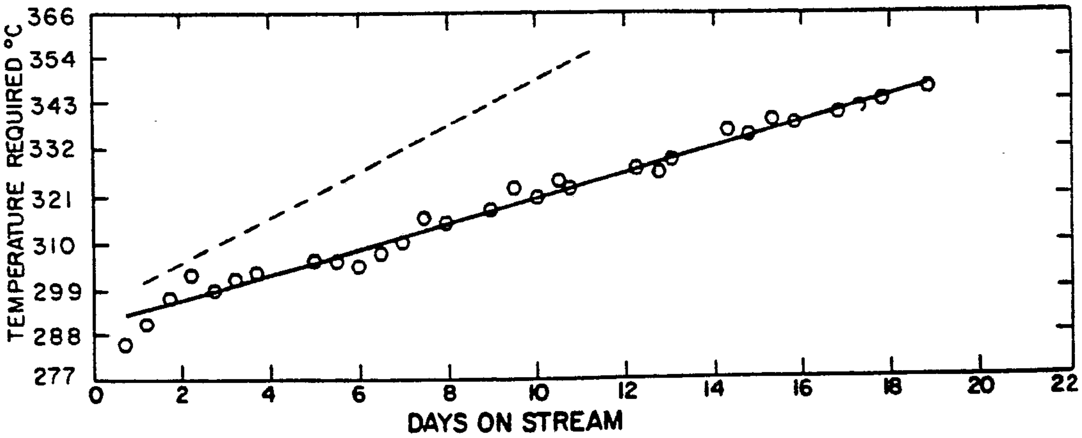


Fig.4

Dewaxing of Arabian Light
339 HN (Stock B)
Catalysts Example 4 and Example 5
Cycle 2



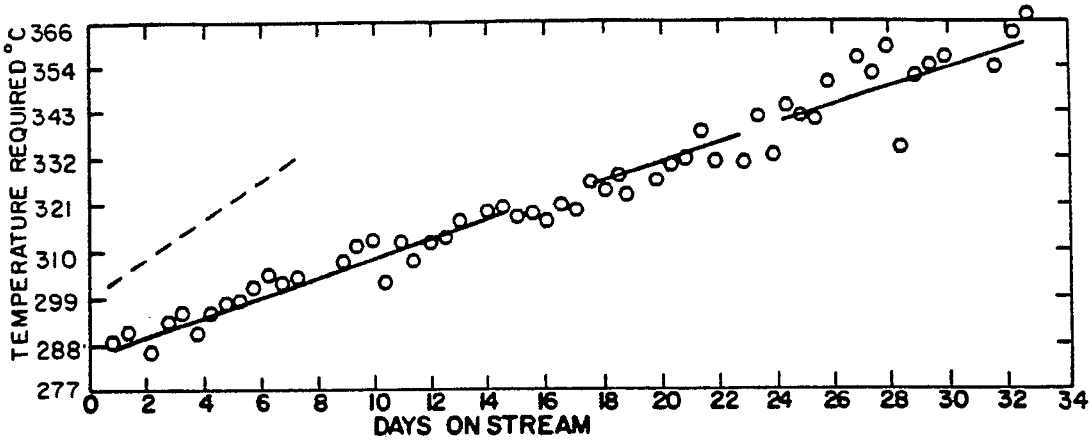


Fig.5

Dewaxing of Arabian Light
345 BS (Stock A)
Catalysts Example 4 and Example 5
Cycle 3

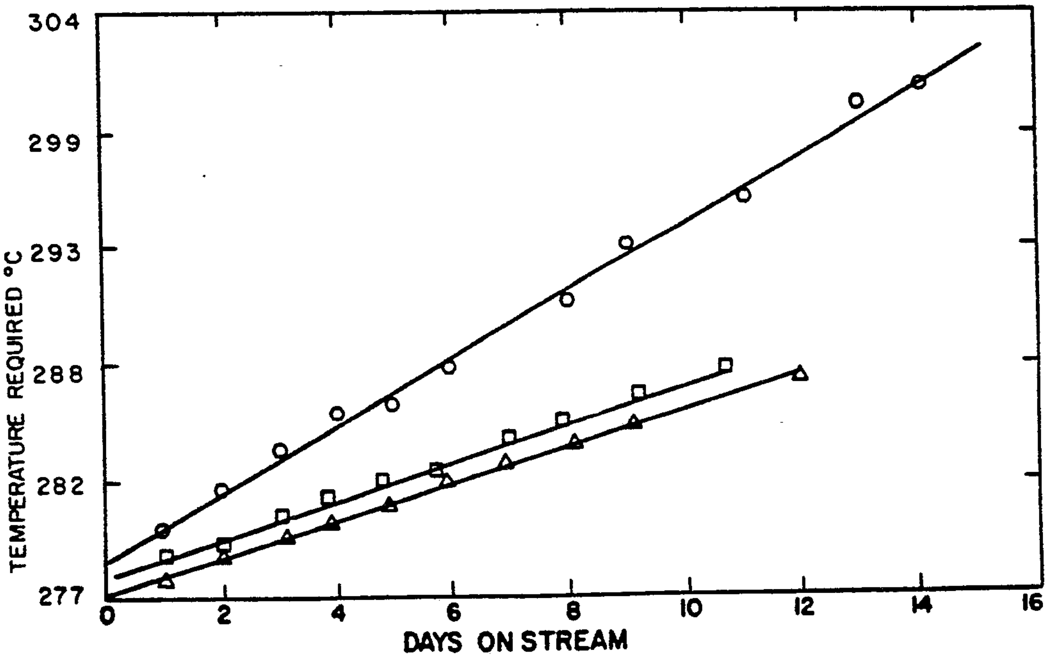


Fig.6

Dewaxing of Arabian Light
Bright Stock (Stock D)
Effect of Catalyst Particle Size