

LOW-PRESSURE HYDROCRACKING PROCESS

The present invention relates to petroleum hydrocracking and, in particular, to converting a high boiling point range petroleum stream to a predominantly distillate product
5 utilizing improved zeolite catalysts. In addition, the hydrocracking process can be coupled with a dewaxing process to produce high distillate yields and dewaxed bottoms.

Zeolites have been described structurally as "framework" aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygen atoms. Such zeolites have pores of uniform size
10 which are uniquely determined by the structure of the crystal. The zeolites are referred to as "molecular sieves" because the uniform pore size of the zeolite material allows it to selectively sorb molecules of certain dimensions and shapes.

The particular faujasitic or Y-type zeolite preferred in this invention has come to be known as ultrastable Y (USY) and is sometimes referred to as dealuminated Y (DAY). USY
15 is not a single entity but a family of materials related to zeolite Y. USY is similar to zeolite Y in that its characteristic x-ray diffraction lines are substantially those of zeolite Y. USY differs from as-synthesized zeolite Y in that by the nature of the various processing schemes and the degree to which zeolite Y is dealuminated, the effective framework silica-to-alumina ratio is increased.

20 Hydrocracking utilizing a zeolite catalyst is a process which has achieved widespread use in petroleum refining for converting various petroleum fractions to lighter and more valuable products, especially gasoline and distillates such as jet fuels, diesel oils and heating oils.

Large pore zeolites such as zeolites X and Y possessing relatively low silica to alumina
25 ratios, e.g., less than 40:1, have been conventionally used in hydrocracking reactions because the principal components of the feedstock are high molecular weight hydrocarbons which will not enter the internal pore structure of the smaller pore zeolites and will therefore not undergo conversion. Large pore zeolites also possess a high degree of intrinsic cracking activity.

U.S. Patent No. 5,171,422 claims a process for producing a lubricating oil base stock
30 by hydrocracking a feedstock utilizing a zeolite of the faujasite structure possessing a silica to alumina ratio of at least 50:1, preferably 100:1, more preferably 150:1. U.S. Patent No.

4,820,402 describes a process for increasing the selectivity of production of higher boiling distillate range product and hydrocracking reactions by utilizing a large pore zeolite with a silica to alumina ratio of at least 50:1, preferably up to 200:1.

Even with these higher silica to alumina ratio catalysts, a significant amount of
5 unwanted secondary cracking of paraffins occurs along with the desired cracking of aromatic and naphthenic components because of the acidic alumina sites within the catalyst. This secondary cracking results in distillate yield loss. Thus, there is a need for a distillate selective hydrocracking catalyst with a very high silica to alumina ratio.

Processes for dewaxing petroleum distillates are well known. High pour points are
10 caused by higher molecular weight, straight chain, normal and slightly branched paraffins which must be removed to obtain adequately low pour points.

In order to obtain the desired selectivity, the dewaxing catalyst used has usually been a zeolite having a pore size which admits the straight chain n-paraffins, but which excludes more highly branched materials such as cycloparaffins and aromatics. Since dewaxing processes of
15 this kind function by means of cracking reactions, a number of useful products become degraded to lower molecular weight materials.

Another unit process frequently encountered in petroleum dewaxing is isomerization. In this process, n-paraffins are converted to iso-paraffins in the presence of an acidic catalyst such as an acidic zeolite. These processes operate at relatively high temperatures and
20 pressures, which causes extensive cracking thereby degrading useful distillate products into less valuable lighter products. Thus, there is a need for a dewaxing process which does not result in significant distillate yield loss.

In accordance with the present invention, a catalytic hydrocracking process is provided for converting a high boiling point range petroleum stream to distillate product. A petroleum
25 feedstock having a boiling range from 600° to 1100°F is contacted with a hydrocracking catalyst containing a zeolite component with a framework silica to alumina molar ratio of at least 200:1 and a hydrogenation component. The catalyst and feedstock are contacted at superatmospheric hydrogen partial pressure for a residence time sufficient to effect at least 20% conversion, with at least 50% of the converted product remaining in the boiling range of
30 330° to 730°F.

The preferred feedstock has a 10% boiling point above 650°F and a nitrogen level of less than 200 ppm.

The zeolite component can be selected from the group consisting of faujasite, zeolite X, zeolite Y, zeolite USY, ZSM-3, ZSM-20, ENT, ECR-30, CSZ-1, preferably zeolite USY.

- 5 In the preferred embodiment, the silica to alumina molar ratio is greater than 2000:1 and the superatmospheric hydrogen partial pressure is 1000 psi or less.

The hydrogenation component can be platinum, palladium, gold, silver, iridium, rhodium, ruthenium, osmium, or a combination thereof.

- 10 The process of the invention can also include pour point and/or cloud point reduction of the unconverted bottoms fraction by contacting the feedstock with a dewaxing catalyst before, simultaneous with, or after contact with the hydrocracking catalyst. Any conventional dewaxing catalyst may be used including zeolite beta, ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, and SAPO-11. Zeolite beta is preferred.

- 15 The hydrocracking process and the dewaxing process can be performed simultaneously by having the hydrocracking zeolite and the dewaxing zeolite catalyst co-formulated in one extrudate.

- 20 The process of the invention also includes contacting the unconverted bottoms fraction produced by the hydrocracking process having a boiling point above approximately 730°F with a dewaxing catalyst so as to reduce the pour point and/or cloud point of the unconverted bottoms fraction.

- 25 The process of the invention is primarily a hydrocracking process selective for distillate product, with dewaxed bottoms as a byproduct if the dewaxing catalyst is incorporated. While known methods have been fairly effective in reducing high boiling point hydrocarbon feeds, the distillate yields begin to decrease due to paraffin selective secondary crackings at high 650°F⁺ conversions (i.e., conversion above 50%). With the use of a hydrocracking catalyst with an exceptionally high silica to alumina ratio, the process of the present invention permits conversions above 50%, e.g., 70% to 80%, with little or no loss in distillate yield. When combined with a dewaxing catalyst, reduced pour point bottoms can be produced.

Figure 1 is a graph showing the overall yield structure for a process of the invention.

Figure 2 is a graph showing a comparison between a catalyst used in the process of the invention and a conventional catalyst in converting the bottoms feed to distillate range product.

Figure 3 is a graph showing the gas yield for a process of the invention.

5 Figure 4 is a graph showing the naphtha yield for a process of the invention.

Figure 5 is a graph showing the yield structure for a process of the invention at higher hydrogen partial pressure.

Figure 6 is a graph showing the aging of a catalyst used in the process of the invention.

It has now been found that enhanced hydrocracking can be achieved by utilizing a
10 catalyst comprising a zeolite component with an exceptionally high silica to alumina ratio, i.e., greater than 200:1. Such catalysts provide superior distillate selectivity, are capable of running at high conversion levels, i.e., at or about 70%, provide low LPG yield, operate with lower hydrogen consumption, operate at a lower psi, i.e., 400 psi, and have a low aging rate.

When waxy feedstocks are hydrocracked with a large pore catalyst, such as zeolite Y,
15 in combination with a hydrogenation component, the viscosity of the oil is reduced by cracking most of the 650°F⁺ material into material that boils at 330° to 650°F. Although the viscosity is reduced, the unconverted 650°F⁺ material retains a relatively high pour point, i.e., the lowest temperature at which a liquid will flow when a test container is inverted. The unconverted fraction also retains a relatively high cloud point, i.e., the temperature at which solids start to
20 separate from solution when the oil is cooled. The pour point and/or cloud point can be reduced through catalytic dewaxing.

The hydrocarbon feed materials suitable for use in the hydrocracking step of the present invention include crude petroleum, reduced crudes, vacuum tower residua, vacuum gas oils, deasphalted residua and other heavy oils. These feedstocks contain a substantial
25 amount of components boiling above 260°C (500°F) and normally have an initial boiling point of 290°C (554°F) and more usually 343°C (650°F). Typical boiling ranges are from 316° to 593°C (from 600° to 1100°F) or from 343° to 510°C (from 650° to 950°F). Generally, the feedstock will have a 10% boiling point above 650°F, meaning that approximately 10% of the feedstock will initially boil below 650°F, with a very small portion boiling below 600°F.

The hydrocarbon feedstock can be treated prior to hydrocracking in order to reduce or substantially eliminate its heteroatom content. As necessary or desired, the feedstock can be hydrotreated under mild or moderate hydroprocessing conditions to reduce its sulfur, nitrogen, oxygen and metal content. The preferred feedstock for the process of the invention contains
5 less than 200 ppm nitrogen. Conventional hydrotreating process conditions and catalysts can be employed, e.g., those described in U.S. Patent No. 4,283,272.

The catalyst used in the hydrocracking step of the present process contains a large pore zeolite of the faujasite family as the acidic component. The zeolite has a silica to alumina ratio of at least 200:1, preferably at least 2000:1, and a hydrocarbon sorption capacity for n-
10 hexane of at least 6%.

The catalyst also contains at least one hydrogenation component which may be at least one noble metal and/or at least one non-noble metal or a combination thereof. Suitable noble metals include platinum, palladium, gold, silver, iridium, rhodium, ruthenium, osmium, or a combination thereof. Platinum, palladium or a combination thereof are preferred.

15 The metal can be incorporated into the zeolite by any suitable method such as impregnation or exchange. The metal can be incorporated in the form of a cationic, anionic or neutral complex; $\text{Pt}(\text{NH}_3)_4^{2+}$ and other cationic complexes of this type are convenient for exchanging metals onto the zeolite.

The amount of hydrogenation component can range from 0.01 to 30% by weight and
20 is normally from 0.1 to 15% by weight. The precise amount will, of course, vary with the nature of the component; less of the highly active noble metals, particularly platinum, being required than of the less active metals.

The hydrocarbon sorption capacity of a zeolite is determined by measuring its sorption at 25°C and at 40 mm Hg (5333 Pa) hydrocarbon pressure in an inert carrier such as helium.
25 The sorption test is conveniently carried out in a thermogravimetric analysis (TGA) with helium as a carrier gas flowing over the zeolite at 25°C. The hydrocarbon of interest, e.g., n-hexane, is introduced into the gas stream adjusted to 40 mm Hg hydrocarbon pressure and the hydrocarbon uptake, measured as an increase in zeolite weight, is recorded. Sorption capacity is then calculated as a percentage in accordance with the relationship:

$$\text{Hydrocarbon Sorption Capacity (\%)} = \frac{\text{Wt. of Hydrocarbon Sorbed}}{\text{Wt. of Zeolite}}$$

It should be understood that the silica:alumina ratio referred to in this specification is the structural or framework ratio, that is, the ratio of the SiO_4 to the AlO_4 tetrahedra which, together, constitute the structure of the zeolite. This ratio can vary according to the analytical procedure used for its determination. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by TGA of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealuminization methods described below, which result in the presence of ionic aluminum free of the zeolite structure, are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined. The preferred method of determining silica:alumina ratio is NMR (nuclear magnetic resonance) analysis.

Included among the zeolites which can be used in the hydrocracking operation of this invention are faujasite, zeolite X, zeolite Y, ultrastable zeolite Y (USY), ZSM-3, ZSM-20, ENT (hexagonal faujasite), ECR-30, and CSZ-1. USY is preferred.

A number of different methods are known for increasing the structural silica:alumina ratio of various zeolites. Many of these methods rely upon the removal of aluminum from the structural framework of the zeolite employing suitable chemical agents. Specific methods for preparing dealuminized zeolites are described in the following to which reference may be made for specific details: "Catalysis by Zeolites" (International Symposium on Zeolites, Lyon, Sep. 9-11, 1980), Elsevier Scientific Publishing Co., Amsterdam, 1980 (dealuminization of zeolite Y with silicon tetrachloride); U.S. Patent No. 3,442,795 and U.K. Patent No. 1,058,188 (hydrolysis and removal of aluminum by chelation); U.K. Patent No. 1,061,847 (acid extraction of aluminum); U.S. Patent No. 3,493,519 (aluminum removal by steaming and chelation); U.S. Patent No. 3,591,488 (aluminum removal by steaming); U.S. Patent No. 4,273,753 (dealuminization by silicon halide and oxyhalides); U.S. Patent No. 3,691,099 (aluminum extraction with acid); U.S. Patent No. 4,093,560 (dealuminization by treatment with salts); U.S. Patent No. 3,937,791 (aluminum removal with Cr(III) solutions); U.S. Patent

No. 3,506,400 (steaming followed by chelation); U.S. Patent No. 3,640,681 (extraction of aluminum with acetylacetonate followed by dehydroxylation); U.S. Patent No. 3,836,561 (removal of aluminum with acid); German Offenleg. No. 2,510,740 (treatment of zeolite with chlorine or chlorine-containing gases at high temperatures), Dutch Patent No. 7,604,264 (acid extraction), Japanese Patent No. 53/101,003 (treatment with EDTA -ethylene diamine tetra-acetic acid- or other materials to remove aluminum) and J. Catalysis, 54, 295 (1978) (hydrothermal treatment followed by acid extraction).

Highly siliceous forms of zeolite Y can be prepared either by steaming or by acid extraction of structural aluminum or by both. Due to its convenience, steaming is the preferred method. Since zeolite Y in its normal, as-synthesized condition is unstable to acid, the zeolite must ordinarily be converted to an acid-stable form prior to dealumination by acid treatment. Methods for doing this are known and one of the most common forms of acid-resistant zeolite Y is known as "Ultrastable Y" (USY). Zeolite USY is described in U.S. Patent Nos. 3,293,192 and 3,402,996. In general, "ultrastable" refers to a Y-type zeolite which is highly resistant to degradation of crystallinity by high temperature and steam treatment and is characterized by a R_2O content (wherein R is Na, K or any other alkali metal ion) of less than 4 wt.% and preferably less than 1 wt.%, a unit cell size of less than 24.5 Å and a silica:alumina mole ratio in the range of 3.5:1 to 7:1 or higher. The ultrastable form of Y-type zeolite is obtained primarily by a substantial reduction of the alkali metal ions and the unit cell size.

The ultrastable form of the Y-type zeolite can be prepared by successively base exchanging a Y-type zeolite with an aqueous solution of an ammonium salt such as ammonium nitrate until the alkali metal content of the zeolite is reduced to less than 4 wt.%. The base exchanged zeolite is then calcined at a temperature of from 540° to 800°C for up to several hours, cooled and successively base exchanged with an aqueous solution of an ammonium salt until the alkali metal content is reduced to less than 1 wt.%, followed by washing and calcination again at a temperature of from 540° to 800°C to produce an ultrastable zeolite Y. The sequence of ion exchange and heat treatment results in the substantial reduction of the alkali metal content of the original zeolite and results in a unit cell shrinkage which is believed to lead to the ultra high stability of the resulting Y-type zeolite.

The ultrastable zeolite Y can then be extracted with acid to produce a highly siliceous form of the zeolite which is then suitable for use in the hydrocracking operation of the present process. Other methods for increasing the silica:alumina ratio of zeolite Y by acid extraction are described in U.S. Patent Nos. 4,218,307; 3,591,488 and 3,691,099.

5 It may be desirable to incorporate the zeolite in another material which is resistant to the temperature and other conditions employed in the process. Such matrix, or binder materials include synthetic or natural substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter can be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally
10 occurring clays which can be composited with the catalyst include those of the montmorillonite and kaolin families. These clays can be used in the raw state as originally mined or they can be initially subjected to calcination, acid treatment or chemical modification.

The zeolite can be composited with a porous matrix material, e.g., an inorganic oxide binder such as alumina, silica, titania, zirconia, silica-alumina, silica-magnesia, silica-zirconia,
15 silica-thoria, silica-beryllia, silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia zirconia, and the like. The matrix can be in the form of a cogel with the zeolite. The relative proportions of zeolite component and inorganic oxide binder material can vary widely with the zeolite content ranging from 1 to 99, and more usually from 5 to 80, percent by weight of the composite.

20 In the hydrocracking step of the present process, the feedstock is contacted with the hydrocracking catalyst in the presence of hydrogen under hydrocracking conditions of elevated temperature and pressure. Conditions of temperature, pressure, space velocity, hydrogen:feedstock ratio and hydrogen partial pressure which are similar to those used in conventional hydrocracking operations can conveniently be employed herein. Process
25 temperatures of from 230° to 500°C (from 446° to 932°F) can conveniently be used although temperatures above 425°C (797°F) will normally not be employed because of standard reactor metallurgy limits. Generally, temperatures of from 260° to 425°C (from 500° to 800°F) will be employed. The process is operated in the presence of hydrogen with superatmospheric hydrogen partial pressures normally being from 496 to 19,300 kPa (from 72 to 2,800 psi),
30 preferably from 2,069 to 13,790 kPa (from 300 to 2000 psi). Relatively low superatmospheric hydrogen partial pressures are required to increase distillate yield and prevent desired paraffins

from being further hydrocracked to gaseous by-products. The hydrogen:feedstock ratio (hydrogen circulation rate) is normally from 10 to 3,500 n.l.l.⁻¹ (from 56 to 19,660 SCF/bbl.), preferably from 18 to 713 n.l.l.⁻¹ (from 100 to 4000 SCF/bbl). The space velocity of the feedstock will normally be from 0.1 to 20 LHSV and preferably from 0.3 to 5.0 LHSV. In all
5 circumstances, the process of the invention requires a feedstock residence time sufficient to effect at least 20% conversion, with at least 50% of the converted product remaining in the distillate product boiling range of 330° to 730°F.

Employing the foregoing hydrocracking conditions, conversion of feedstock to distillate range product having a boiling point range of between 330° to 730°F can be made to
10 come within the range of from 20 to 80 wt.%. The hydrocracking conditions are advantageously selected so as to provide a conversion of from 30 to 80 wt.%, and preferably from 40 to 50 wt.%.

The conversion can be conducted by contacting the feedstock with a fixed stationary bed of catalyst, a fixed fluidized bed or with a transport bed. A simple configuration is a
15 trickle-bed operation in which the feed is allowed to trickle through a stationary fixed bed. With such a configuration, it is desirable to initiate the hydrocracking reaction with fresh catalyst at a moderate temperature which is raised as the catalyst ages in order to maintain catalytic activity.

As defined herein, dewaxing refers to a removal of at least some of the normal paraffin
20 content of the feed so as to reduce its pour point and/or cloud point. Any conventional petroleum dewaxing catalysts now used or hereinafter developed may be used for the dewaxing process. Although isomerization dewaxing catalysts are preferred to maximize distillate yields, a significant amount of hydrocracking is acceptable, and may be preferred when maximum conversion of feed to lighter materials is desired. Preferred catalysts include
25 zeolite beta, ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, SAPO-11. Zeolite beta is most preferred.

Zeolite beta is disclosed in U.S. Patent No. 4,419,220. This patent discloses that hydrocarbons such as distillate fuel oils and gas oils may be dewaxed primarily by
isomerization of the waxy components over a zeolite beta catalyst. The process may be
30 carried out in the presence or absence of added hydrogen, although operation with hydrogen is

preferred. The patent demonstrates that the process may also be carried out on a wide range of feedstocks.

The feedstock for the dewaxing process is the feedstock previously discussed for the hydrocracking process. The dewaxing process can occur before, simultaneously with, or after
5 the hydrocracking process described above. The feedstock can be contacted with the dewaxing catalyst in a separate reactor or the same reactor. Within the same reactor, the hydrocracking catalyst and dewaxing catalyst can be located in separate layers or comprise a mixed layer. The dewaxing catalyst and hydrocracking catalyst can also be co-formulated into one extrudate.

10 The optimal catalyst configuration and ratio of the hydrocracking catalyst to the dewaxing catalyst will vary for a given feedstock and desired product yield end properties. The preferred range of hydrocracking catalyst to dewaxing catalyst is between 9:1 and 1:9, respectively; more preferably between 2:1 and 1:2, respectively.

Instead of contacting the initial feedstock to the dewaxing catalyst, it is also possible,
15 and preferred in some circumstances, to recycle the heavy fraction of the product from the hydrocracking process for use as the feed for the dewaxing process.

In general, the process conditions for the dewaxing process are within the same ranges as those specified for the hydrocracking process, as must be the case when both types of catalysts are in the same reactor. However, it is known in the art that certain adjustments in
20 the preferred process conditions, within the ranges specified above, may be desired when incorporating the dewaxing process into the process of the invention. For example, when the dewaxing process is introduced, a lower superatmospheric partial hydrogen pressure is preferred, usually in the range of from 1,379 to 6,895 kPa (200 to 1000 psi), more preferably from 2,758 to 5,516 kPa (400 to 800 psi). If the dewaxing process is conducted in a separate
25 reactor, high end hydrocracking pressures can be utilized, e.g. 2800 psi. Adjustments may also be made based upon the ratio of hydrocracking to dewaxing catalyst. For example, if the hydrocracking to dewaxing catalyst ratio within the reactor is high, a lower range LHSV may be preferred, within the range specified above, so as to achieve the desired level of pour point and/or cloud point reduction. The temperature and hydrogen circulation ranges can be the
30 same as those specified for the hydrocracking process alone.

Along with reducing the pour point and/or cloud point, the dewaxing process also creates a high hydrogen content in the bottoms fraction. The low pour point, together with the high hydrogen content of the bottoms fraction, makes it suitable as a high performance turbine fuel.

- 5 The following examples serve to provide further appreciation of the invention but are not meant in any way to restrict the effective scope of the invention.

EXAMPLE 1

- This example illustrates the properties of two distillate selective catalysts. Pt/USY/ Al_2O_3 possess the properties required by the method of the invention. Pt/zeolite
10 beta/ Al_2O_3 is a distillate selective hydroprocessing catalyst presently used in the art. The properties of Pt/USY and Pt/zeolite beta are set forth in Table 1 below.

Table 1
Distillate Selective Catalyst Properties

Identification	Pt/USY	Pt/zeolite beta
Catalyst Alpha	6	2
$\text{SiO}_2/\text{Al}_2\text{O}_3$ Molar Ratio (Determined by NMR)	3,300	800
Unit Cell Size, Å	24.22	N/A
X-Ray Crystallinity, %	—	20
Particle Density, g/cc	0.833	0.977
Real Density, g/cc	2.581	2.255
Surface Area, m^2/g	557	344
Pore Volume, cc/g	0.813	0.580
Platinum, wt. %	0.56	0.57
Zeolite, wt. %	65	65
Alumina Binder, wt. %	35	35

- 15 The catalyst utilized in the method of the invention, Pt/USY/ Al_2O_3 was prepared by steaming a commercially available low acidic USY catalyst for 16 hours at 1025°F. The

finished extrudate consisted of 65 wt.% zeolite supported on gamma alumina. The extrudate was exchanged with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ in 0.2N ammonium nitrate solution; and calcined in air at 660°F for 3 hours. The resulting Pt/USY has an extremely high silica to alumina ratio of 3300.

5

EXAMPLE 2

This example illustrates the method for increasing the selectivity for distillate range product from hydrocracked bottoms feedstock, the properties of which are set forth in Table 2 below. Two different, but very similar, bottoms feedstocks were contacted with Pt/USY and Pt/zeolite beta, respectively.

10

Table 2**Hydrocracked Bottoms Feedstock Properties (650°F+ fraction)**

Catalyst Contacted	Pt/USY	Pt/zeolite beta
Hydrogen, wt. %	14.04	13.91
Nitrogen, ppm	27	10
Basic Nitrogen, ppm	5	5
Sulfur, wt. %	<0.002	0.016
API Gravity	31.8	31.9
Pour Point, °F	110	100
Paraffin, wt. %	43.9	48.5
Naphthenes, wt. %	36.0	30.2
Aromatics, wt. %	20.1	21.3

The reduction of the hydrocracked bottoms feedstock was carried out in a packed-bed, trickle-flow reactor to compare the performance of Pt/USY and Pt/zeolite beta described in Example 1. The operations were conducted in a cascade mode with a hydrotreating catalyst loaded upstream in a 1:1 volume ratio. In each case, the distillate selective catalyst was pre-sulfided with 2% H_2S in hydrogen at 500 psi for 12 hours. The sulfiding temperature starting from 550°F was raised step-wise to 700°F, at an increment of 50°F each period. The reaction was carried out under various reactor temperatures and hydrogen pressure, with an LHSV of 1.0.

20

The overall yield structure for Pt/USY, a catalyst utilized in the process of the invention, is shown in Figure 1 where the 330° to 730°F fraction is designated as distillate, the C₃ to 330°F fraction as naphtha, and total C₁-C₄ as LPG. Even after 150 days on stream, catalyst Pt/USY demonstrated excellent distillate selectivity. Unlike conventional catalysts, the distillate yield does not show a maximum with temperature range tested, up to 58% at 75% of 650°F+ conversion, and with only 4% LPG. This indicates the ability of running the catalyst at very high conversion levels, resulting in high distillate yields and low unconverted bottom fractions, while still keeping hydrogen consumptions very low. Most importantly, the distillate yield increased with conversions, even for conversion levels approaching 80%, and remained very close to the 100% distillate selective limit. This demonstrates that secondary cracking reactions were reduced by the ultra high silica Pt/USY catalyst.

EXAMPLE 3

The 330° to 730°F distillate yield was compared between Pt/USY and Pt/zeolite beta. Figure 2 shows the superiority of Pt/USY over Pt/zeolite beta in converting the bottoms feed to a high quality distillate range product. At 650°F plus conversions above 50%, the distillate yields from Pt/zeolite beta begin to decrease due to paraffin selective secondary cracking. On the other hand, the larger pores in Pt/USY together with its low acidity allow the catalyst to continue processing heavier molecules in the feed non-preferentially with minimum excess cracking. This is further demonstrated by the lower gas yields of Pt/USY as shown in Figure 3. The lower level of naphtha yield by Pt/USY as compared Pt/zeolite beta is demonstrated in Figure 4.

EXAMPLE 4

The performance of high silica to alumina ratio Pt/USY was also examined at a higher hydrogen partial pressure (i.e., 800 psi H₂). The results are shown in Figure 5. In general, the lower hydrogen partial pressure achieved a higher distillate yield. For example, at 35% conversion, the change from 400 to 800 psi H₂ caused the distillate yield to decrease from 42% to 37%, respectively.

EXAMPLE 5

The normalized temperatures at 50% conversion and 1.0 LHSV under 400 psi H₂ are plotted in Figure 6. Figure 6 demonstrates that Pt/USY undergoes very little aging as the catalyst remains on stream. This is consistent with its low acidity and strong metal

5 hydrogenation function, both of which reduce the coking tendency.

EXAMPLE 6

Table 3 lists selected product properties from the process of the invention at 38% and 74% conversion.

Table 3

650°F Conv.	Product Properties	IBP-330°F Cut	330° to 650°F Cut	650°F+ Cut
38%	H ₂ Content, wt%	14.9	13.7	14.0
	Cetane Index		51	
	Freeze Pt., °F		-32	
	Pour Pt., °F		-65	85
	Cloud Pt., °F		-40	92
	Viscosity Index			100
74%	H ₂ Content, wt%	14.8	13.4	12.9
	Cetane Index		52	
	Freeze Pt., °F		-23	
	Pour Pt., °F		-65	25
	Cloud Pt., °F		-26	
	Viscosity Index			89

10

The results demonstrate that the distillate range cut (330° to 650°F) has good cetane levels and flow properties even at a high level of conversion, i.e. 74%.

The bottoms fraction contains a relatively high pour point (25°F). The pour point of the bottoms fraction can be reduced by combining the method for increasing the selectivity for

15 distillate range product with a dewaxing process. After separation of the distillate yield product, the bottom fraction can either be recycled or fed to a catalytic dewaxing unit to further reduce the pour point to produce fuel oil and lubricating oil products.

Alternatively, the dewaxing catalyst can be installed in the hydrocracking reactor to improve the bottom quality, without first separating the bottom fraction.

EXAMPLE 7

This example illustrates one use of the invention for distillate selective conversion as well as dewaxing of the high pour point unconverted bottoms.

The first of two reactors was loaded with Pt/USY catalyst. The Pt was exchanged
5 onto the extrudate at a 0.6 wt.% level. The Pt/USY catalyst was followed by a second reactor loaded with Pt/zeolite beta containing 0.6 wt.% platinum. Table 4 contains the catalyst properties.

Table 4
Catalyst Properties

Catalyst	Pt/USY	Pt/zeolite beta
Zeolite, wt. %	65	65
Alumina, wt. %	35	35
Platinum, wt. %	0.58	0.66
Particle Density, g/cc	0.836	0.821
Real Density, g/cc	2.629	2.582
Surface Area, m ² /g	532	392
Pore Volume, cc/g	0.816	0.831
Silica: Alumina ratio	200:1	35:1

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Both of the catalysts were loaded with 80 to 120 mesh sand.

The catalysts were reduced for 1 hour in flowing hydrogen at 300°F before sulfiding. The catalysts were sulfided using 400 ppmv hydrogen sulfide in hydrogen gas at 100 psi while holding catalyst temperature at 300°F. The properties of the feedstock are shown in Table 5.

15

The bottoms feedstock was started at a temperature of 300°F. After sulfiding was completed, process conditions were 400 psi H₂, 1.0 LHSV, 2,000 SCF/B hydrogen circulation, and an initial reaction temperature of 550°F.

Table 5

Hydrogen in Petroleum Product, wt.%	14.22
Nitrogen in Petroleum Product, ppm	14
Sulfur in Petroleum Product, ppm	<20
API Gravity of Petroleum Product	32.5
Pour Point of Petroleum °F	95
IBP °F	628
30 Vol. Percent Distilled	772
50 Vol. Percent Distilled	806
70 Vol. Percent Distilled	845
90 Vol. Percent Distilled	907
End Point	960

When the temperature of the Pt/zeolite beta catalyst was increased to reaction temperature, it contributed to the conversion, and more importantly, to the dewaxing of the feed. Table 6 lists the product properties from Pt/USY alone at 60 wt.% conversion.

Table 6

Product Properties from Pt/USY at 60 wt.% Conversion

330°F to 730°F	43 wt.%
730°F+ properties:	
Hydrogen, wt.%	14.59
Nitrogen, ppmw	8
Sulfur, wt.%	<0.002
Pour Point, °F	95
n-paraffin, wt.%	6.98

Table 7 demonstrates the product properties from Pt/USY/Al₂O₃ and Pt/zeolite beta/Al₂O₃ at a 67:33 ratio at 61 wt.% conversion.

Table 7

330°F to 730°F	36 wt.%
730°F+ properties:	
Hydrogen, wt.%	14.16
Nitrogen, ppmw	4
Sulfur, wt.%	<0.002
Pour Point, °F (D97)	-35
n-paraffin, wt.%	0.44

The results demonstrate that the pour point of the 730°F⁺ cut was dramatically reduced when the dewaxing catalyst, Pt/zeolite beta, is coupled with the Pt/USY catalyst. This
5 corresponds to the much lower n-paraffins content of the cut. Further, the dramatic reduction in pour point, 95°F down to -35°F, is achieved by the tandem use of the two catalysts with an only moderate decrease in the distillate selectivity of the system, i.e., a decrease from 43 wt.% to 36 wt.% distillate yield.

The example demonstrates that the Pt/USY catalyst has high 330° to 730°F distillate
10 selectivity at high conversion, and converts only a small portion of the n-paraffins in the feed as evidenced by the high pour point of the 730°F⁺ cut. The pour point of the 730°F + cut can be reduced by coupling the high silica to alumina ratio hydrocracking Pt/USY catalyst with a dewaxing catalyst such as Pt/zeolite beta.

Thus, while there have been described what are presently believed to be the preferred
15 embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the scope of the invention.

**CLAIMS:**

1. A catalytic hydrocracking process for converting a high boiling range petroleum stream to a distillate range product, which maximizes yield, comprising contacting a petroleum feedstock having a boiling range of from 600° to 1100°F with a hydrocracking catalyst comprising a zeolite component which is selected from the group consisting of faujasite, zeolite X, zeolite Y, zeolite USY, ZSM-3, ZSM-20, ENT, ECR-30, CSZ-1, with a framework silica to alumina molar ratio of greater than 2000:1 and the superatmospheric hydrogen partial pressure is 1000 psi or less, and a hydrogenation component under a superatmospheric hydrogen partial pressure of 1000 psi or less for a residence time sufficient to effect at least 20% conversion, with at least 50% of the converted product remaining in the boiling range of 330° to 730°F.
2. A process according to claim 1, wherein the feedstock has a 10% boiling point above 650°F and a nitrogen level of 200 ppm or less.
3. A process according to claim 1, wherein the hydrogenation component is selected from the group consisting of platinum, palladium, gold, silver, iridium, rhodium, ruthenium, osmium, or a combination thereof.
4. A process according to claim 1, which further comprises contacting the feedstock with a dewaxing catalyst selected from the group consisting of zeolite beta, ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48 and SAPO-11 before, simultaneous with, or after the contact with the hydrocracking catalyst, wherein the pour point and/or cloud point of the unconverted bottoms fraction is reduced.
5. A process according to claim 4 wherein the hydrocracking catalyst contains zeolite USY and the dewaxing catalyst contains zeolite beta.



6. A process according to claim 4 wherein the hydrocracking process and the dewaxing process are performed simultaneously having the hydrocracking catalyst and the dewaxing catalyst co-formulated in one extrudate.

- 5 7. A process according to claim 4 which further comprises contacting the unconverted bottoms fraction produced by the hydrocracking process having a boiling point above approximately 730°F with a dewaxing catalyst, wherein the pour point and/or cloud point of the unconverted bottoms fraction is reduced.