⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 188 898**
A2

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **85309273.2**

㉒ Date of filing: **19.12.85**

(51) Int. Cl.⁴: **C 10 G 65/04**, C 10 G 67/04

㉚ Priority: **21.12.84 US 685089**
21.12.84 US 685000
21.12.84 US 685001
29.05.85 US 738818

(43) Date of publication of application: **30.07.86**
Bulletin 86/31

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

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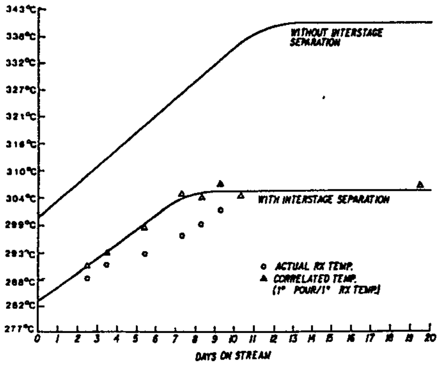
(54) **Cascade dewaxing process.**

(57) Hydrocarbon feedstocks are dewaxed in a cascade process by contacting a waxy feedstock with a large pore crystalline zeolite catalyst and then with a medium pore crystalline zeolite catalyst. Preferably both contactings are performed in the presence of added hydrogen, each zeolite being associated with a hydrogenation/dehydrogenation component: the first contacting may function as a hydroisomerisation step. In certain applications as preferred large pore zeolite is zeolite beta. In certain applications a preferred medium pore zeolite is ZSM-11. Some degree of interstage separation can be adopted.



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CASCADE DEWAXING PROCESS

This invention relates to a cascade dewaxing process using a large pore crystalline zeolite as catalyst in a first contacting with a feedstock and a medium pore crystalline zeolite catalyst in a subsequent contacting.

Refining petroleum feedstocks to obtain lubricating oils which may function effectively in diverse environments has become a highly developed and complex art. Although the broad principles involved in refining are qualitatively understood, the art is encumbered by quantitative uncertainties which require a considerable resort to empiricism in practical refining. Underlying these quantitative uncertainties is the complexity of the molecular constitution of lubricating oils. Because lubricating oils for the most part are based on petroleum fractions boiling above about 450°F (232°C), the hydrocarbon constituents are of high molecular weight and display extraordinary diversity of structure. This complexity and its consequences are referred to in well-known treatises, such as, for examples, "Petroleum Refinery Engineering", by W. L. Nelson, McGraw-Hill Book Company, Inc., New York, NY, 1958 (Fourth Edition). For purposes of this invention, lubricating oil or lube oil is that part of a hydrocarbon feedstock having a boiling point of 650°F (343°C) or higher as determined by ASTM D-97 test method.

In general, the basic premise in lubricant refining is that a suitable crude oil, as shown by experience or by assay, contains a quantity of lubricant stock having a predetermined set of properties, such as, for example, appropriate viscosity, oxidation stability, and maintenance of fluidity at low temperatures. The process of refining to isolate that lubricant stock consists of a set of subtractive unit operations which removes the unwanted components. The most important of these unit operations include distillation, solvent refining and dewaxing, which basically are physical separation processes in the sense that if all the separated fractions were recombined, one would reconstitute the crude oil.

A refined lubricant stock may be used by itself, or it may be blended with another refined lubricant stock having different properties. Prior to use it may be compounded with one or more additives which function, for example, as antioxidants, extreme pressure additives, V.I. improvers.

For the preparation of a high grade distillate lubricating oil stock, it is known to vacuum distill an atmospheric tower residuum from an appropriate crude oil as the first step. This step provides one or more raw stocks within the boiling range of about 450°F to 1050°F (232-566°C). After preparation of a raw stock of suitable boiling range, it is extracted with a solvent, e.g., furfural, phenol, sulfolane, or chlorex, which is selective for aromatic hydrocarbons, and which removes undesirable components. The raffinate from solvent refining is then dewaxed, for example, by admixing with a solvent, such as a blend of methylethyl ketone and toluene. The mixture is chilled to induce crystallization of the paraffin waxes, which are then separated from the raffinate. Sufficient quantities of wax are removed to provide the desired pour point for the raffinate.

Other processes, such as hydrofinishing or clay percolation, may be used if needed to reduce the nitrogen and sulfur content or improve the color of the lubricating oil stock.

Viscosity index (V.I.) is a quality parameter of considerable importance for distillate lubricating oils to be used in automotive engines and aircraft engines subject to wide variations in temperature. This index indicates the degree of change of viscosity with temperature. A high V.I. of 100 indicates an oil that does not tend to become viscous at low temperature or become thin at high temperatures. Measurement of the Saybolt Universal Viscosity of an oil at 100°F (38°C) and 210°F (99°C), and referral to correlations, provides a measure of the V.I. of the oil. For purposes of the present invention, whenever V.I is referred to, it is meant the V.I. as noted in the Viscosity Index tabulations of the ASTM (D567), published by ASTM, 1916 Race Street, Philadelphia, PA, or equivalent.

In recent years, catalytic techniques have become available for 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.

US-A-3,700,585 describes a process for catalytic dewaxing with a catalyst comprising zeolite ZSM-5. Such a process combined with catalytic hydrofinishing is described in US-A-3,894,936. US-A-3,956,102 discloses a particular method for dewaxing a petroleum distillate with a ZSM-5 catalyst. US-A-3,769,202 teaches catalytic conversion of hydrocarbons using as a catalyst two different crystalline silicate zeolites, one having a pore size greater than 8 Angstroms and the other having a pore size less than 7 Angstroms, and that a conventional hydrogenation/dehydrogenation component may be added, in an amount from about 0.01 to about 30 wt. %.

It remains desirable to increase lube yield, raise product viscosity index (V.I.) and to improve catalyst stability and flexibility in catalyst regeneration.

According to the invention a process for dewaxing a hydrocarbon feedstock comprises, first, contacting said feedstock at elevated temperature with a catalyst comprising a crystalline zeolite having a constraint index less than 2, possessing acidic sites and associated with a catalytically effective quantity of a component possessing hydrogenation/dehydrogenation activity, and, second, contacting at least the majority of the effluent from said first contacting, at elevated temperature, with a catalyst comprising a crystalline zeolite having a constraint index greater than 2, possessing acidic sites and associated with a catalytically effective quantity of a component possessing hydrogenation/dehydrogenation activity, and recovering a normally liquid hydrocarbon product of reduced wax content relative to said feedstock. The first and/or second contacting is preferably carried out in the presence of added hydrogen, each hydrogenation/dehydrogenation component comprising a metal of Group VI, VII and/or VIII of the Periodic Table. When that metal is a Group VIII noble metal it usually constitutes 0.1 to 5, suitably 0.3 to 3, wt. % of the catalyst with which it is associated. When it is a non-noble metal it usually constitutes 0.3 to 25 wt. % of the catalyst with which it is associated.

The process is typically conducted at an overall liquid hourly space velocity between 0.1 and 5, preferably between 0.2 and 3.0. Each contacting may be carried out at a temperature in the range 232 to 371°C (450 to 700°F), a liquid hourly space velocity of 0.1 to 10 and a pressure no greater than 70 bar (1000 psig), advantageously below 42.5 bar (600 psig), even more advantageously below 28.5 bar (400 psig). The preferred individual stage liquid hourly space velocity is 0.2 to 6.0. The usual form of reactor for the first and/or second contacting is a fixed, slurry or moving bed unit.

Large pore zeolites for use in the first contacting embrace zeolite Y, ultrastable zeolite Y, dealuminised zeolite Y, ZSM-3, ZSM-18 or ZSM-20, medium pore zeolites for use in the second contacting, zeolite ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 or TMA Offretite. In many applications the large pore zeolite of choice is zeolite beta, and in such cases the hydrogenation/dehydrogenation component associated with the zeolite will usually be platinum. The zeolite of choice for the second contacting will in many applications be ZSM-5, or on occasion ZSM-11, usually associated with nickel.

The feedstock contains waxy components which are normal and/or slightly branched paraffins, and the majority of it may be expected to have a boiling point above 250°C. The process may advantageously be controlled so that the normally liquid effluent from the first contacting has a pour point less than that of said feedstock but no less than 50°F (10°C), optionally no less than 70°F (21°C). In a particular embodiment where the feedstock is a solvent-refined raffinate the activity of the zeolite employed in the first contacting may advantageously be reduced prior to the contacting, and optionally a 650°F- (343°C-) fraction may be removed from the effluent of the first contacting before the second contacting is performed.

Of the many ways in which the invention can be put into practice some are of particular technical merit.

Thus, in one favoured embodiment, the invention concerns a dewaxing process which comprises:

(a) passing a solvent-refined raffinate feedstock over a large pore crystaline silicate zeolite having a Constraint Index less than 2, a silica-to-alumina mole ratio of at least 10, acidic sites, and having hydrogenation/dehydrogenation activity in the presence of hydrogen at a temperature between 450°F (232°C) and 700°F (371°C), a pressure of about 400 psig (28.6 bar), a hydrogen feed rate of about 2500 SCF H_2/bbl (445 m^3/m^3) and a LHSV between 0.2 and 6.0;

(b) passing the entire effluent from step (a) over a medium pore crystalline silicate zeolite having a Constraint Index no less than 2 and having hydrogenation/dehydrogenation activity, in the presence of hydrogen at a temperature between 450°F (232°C) and 700°F (371°C), the temperature of step (b) being the same or different from the temperature of step (a), a pressure of about 400 psig, a hydrogen feed rate of about 2500 SCF H_2/bbl and a LHSV between 0.2 and 6.0; and

(c) recovering from the effluent of step (b) a hydrocarbon feed with reduced wax content.

This embodiment may be regarded as directed to a cascade catalytic dewaxing process wherein a solvent-refined raffinate feedstock is sequentially passed over a first reaction zone containing a zeolite from the group having the structure of TEA Mordenite, Zeolite Y, Deal Y, USY, REY, Zeolite Beta, ZSM-4, ZSM-20, H-Zeolon and amorphous alumina, and having a silica/alumina ratio greater than 10, and having associated therewith acidic sites and 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the metals of Groups VI, VII, and VIII, passing the entire effluent from the first reaction zone into a second reaction zone containing a medium pore zeolite having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, TMA Offretite and Erionite, and containing from 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the group of Group VI, VII and VIII and mixtures thereof, to produce a hydrocarbon liquid product with a reduced wax content.

It may also be regarded as directed to a dual catalyst cascade dewaxing process involving intermediate separation, comprising:

(a) passing a solvent-refined raffinate feedstock over a cataylst comprising a crystalline silicate zeolite having a Constraint Index less than 2, having acidic sites, and having hydrogenation/ dehydrogenation activity;

(b) separating the product of step (a) into a 650°F$^-$ fraction and a 650°F$^+$ fraction (650°F=343°C); and

(c) passing at least a majority of the 650°F$^+$ fraction over a zeolite having a Constraint Index between 2 and 12 and having hydrogenation/dehydrogenation activity.

The intermediate-separation feature of this embodiment may also be expressed as a process comprising:

(a) passing a hydrocarbon feedstock containing long chain normal paraffins and long chain slightly branched parffins, wherein at least a majority of said feedstock has a boiling point in excess of 482°F (250°C), over Zeolite Beta, said Zeolite Beta having catalytically effective amounts of hydrogenation/dehydrogenation component, in the presence of hydrogen at a temperature between 450° and 750°F (232-399°C), a pressure of about 400 psig, a hydrogen feed rate of about 2500 SCF H_2/BBL and a LHSV between 0.2 and 6.0;

(b) separating the product of step (a) into a 650°F$^-$ fraction and a 650°F$^+$ fraction; and

(c) passing the 650°F$^+$ fraction from step (a) over a zeolite selected from the group having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and TMA Offetite, said zeolite having catalytically effective amounts of hydrogenation/ dehydrogenation component in the presence of hydrogen at a temperature between 500° and 700°F (260-371°C), a pressure of about 400 psig, a hydrogen feed rate of about 2500 SCF H_2/BBL and a LHSV between 0.2 and 6.0.

Brief Description of the Drawings

Fig. 1 compares viscosity index to pour point for a single zone and a cascade reactor system dewaxing a solvent-refined raffinate; and

Fig. 2 illustrates the effect of days onstream to reactor temperature for both a single zone and a cascade reactor system.

Fig. 3 illustrates the effect of the presence of interstage separation on the temperature of the second stage reactor with regard to days onstream.

If Zeolite Beta is place in the first stage reactor, it is optional, and in fact preferred in the embodiment, to discard the reaction product of the first stage for the first 1 or 2 days after fresh catalyst has been added to the first reactor. It is believed that the product of the chargestock as it passes through the highly active fresh catalyst of the first reactor, will contain poisons which will damage the shape-selective catalyst in the second reactor. After a period of 1 or 2 days onstream, the fresh catalyst will have had a chance to age and stabilize in order to produce a chargestock product which will be suitable for feeding to the second stage catalyst. Other methods of aging the catalyst of the first reactor are known to the art, such as, for example, steaming the catalyst.

The interstage separation step offers a variety of advantages over and above those disclosed by a cascade reaction system without interstage separation. It is speculated that the interstage separaion process rids a variety of poisons from the chargestock. The 650°-F stock is not considered a lube stock, and contains such components as alkyl aromatics, nitrogen components, and other "poisons". Some of these products are useful for the production of naphthas, gasoline and distillates. However, they may damage the effectiveness of the second and subsequent stages of a cascade reactor process.

Another advantage of the interstage separation step is that it lowers the start of cycle (SOC) and line out (LO) temperatures. The SOC temperature is the temperature at which catalysis is initiated. The LO temperature is that temperature where the activity of the catalyst begins to level out. It is well known in the field of catalytic conversion that a fresh catalyst exhibits high activity and aging during the first part of the catalytic conversion process. After a certain amount of time, generally about 2 to 12 days, the activity and the aging process of the catalyst begin to settle or line out. By ridding the chargestock of the 650°-F component, the SOC and LO temperatures are much lower. This will be considered more directly with respect to the examples.

A further advantageous embodiment of the invention concerns a dual catalyst cascade dewaxing process comprising:

(a) passing a hydrocarbon feedstock containing waxy components comprising normal paraffins and/or slightly branched chain paraffins over a catalyst comprising a crystalline silicate zeolite having a Constraint Index less than 2, having acidic sites, and having associated therewith a catalytically effective amount of hydrogenation/dehydrogenation component;

(b) passing at least a majority of the normally liquid hydrocabon recovered from step (a) over a zeolite having the structure of ZSM-11 and a catalytically effective amount of a hydrogenation/dehydrogenation component; and

(c) recovering a normally liquid hydrocarbon product having a reduced wax content relative to the feedstock, from the product of step (b).

The embodiment may be defined in greater detail as comprising:

(a) passing a hydrocarbon feedstock containing long chain normal paraffins and long chain slightly branched paraffins, wherein at least a majority of the feedstock has a boiling point in excess of 482°F (250°C), over a large pore crystalline silicate zeolite having a Constraint Index less than 2, a silica to alumina mole ratio of at least 10, acidic sites, and having catalytically effective amounts of a hydrogenation/dehydrogenation component in the presence of hydrogen at a temperature between 450°F (232°C) and 700°F (371°C), a pressure of about 400 psig (28.6 bar), a hydrogen feed rate of about 2500 SCF H_2/bbl (445 m^3/m^3) and a LHSV between 0.2 and 6.0;

(b) passing the entire effluent from step (a) over zeolite ZSM-11, having catalytically effective amounts of a hydrogenation/dehydrogenation component, in the presence of hydrogen at a temperature between 500°F (260°C) and 700°F (371°C), the temperature of step (b) being the same or different from the temperature of step (a), a pressure of about 400 psig, a hydrogen feed rate of about 2500 SCF H_2/bbl and a LHSV between 0.2 and 2.0; and

(c) recovering from the effluent of step (b) a hydrocarbon feed with reduced wax content.

In practice this embodiment will frequently take the form of a cascade catalytic dewaxing process wherein a hydrocarbon feedstock with a boiling point in excess of 482°F (250°C) and containing normal paraffins and slightly branched chain paraffins is sequentially passed over a first reaction zone containing a zeolite from the group having the structure of Mordenite, Zeolite Y, Zeolite Beta, ZSM-4 and ZSM-20, and having a silica/alumina ratio greater than 10, and having associated therewith acidic sites and 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the metals of Groups VI, VII and VIII, passing the entire effluent from the first reaction zone into a second reaction zone containing a medium pore zeolite having the structure of ZSM-11, and containing from 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the group of Group VI, VII and VIII and mixtures thereof, to produce a hydrocarbon liquid product with a reduced wax content. In the first stage, the feedstock is hydroisomerized over the high silica, large pore zeolite catalyst, followed by shape selective dewaxing in the second stage over ZSM-11. It is believed that a cascade relationship of the large pore zeolite and ZSM-11, in the right proportion, offers superior dewaxing activities and lube yield, higher V.I., improved catalyst stability in the second stage and flexibility in catalyst regeneration in comparison with the prior art.

ZSM-11 has a Constraint Index between 6 and 8.7 and an effective pore size of generally not greater than about 7 Angstroms, so as freely to sorb normal hexane. In many process applications it has shown little or no difference from ZSM-5. However, as reported in Faraday Disc. Chem. Soc., 72, p. 353 (1982), ZSM-11 has shown high hydroisomerization activity where ZSM-5 exhibits only shape-selective cracking. Additionally, the structure of ZSM-11 has intersecting linear channels, rather than the intersecting linear and tortuous channels of ZSM-5. Although conventional dewaxing catalysts generally utilize a zeolite having the structure of ZSM-5, it will be seen in the Exmaples which follow that the ZSM-11 can be more active and selective for dewaxing than ZSM-5.

Although it is not necessary, the acidity of the ZSM-11 zeolite will usually be very similar to the acidity of the large pore zeolite. If it is desired, for reasons of economy or otherwise, to use a noble metal promoter in association with a large pore zeolite, and a base metal promoter in association with ZSM-11, it may be beneficial to operate with different acidities or silica/alumina ratios in the large pore zeolite and ZSM-11. Best results will be obtained when the acidity of the ZSM-11 zeolite is matched to the strength and amount of the hydrogenation/dehydrogenation component incorporated in the ZSM-11 zeolite.

It will usually be beneficial to incorporate the ZSM-11 zeolite into a conventional matrix. It is possible, and preferable, to operate with the same matrix for both the ZSM-11 zeolite and the large pore zeolite.

In its simplest form, a cascade operation in this embodiment may be achieved by using a large down flow reactor, wherein the lower portion contains the catlyst comprising the ZSM-11 zeolite and the upper portion contains the catalyst comprising the large pore zeolite.

Two or more reactors in series may also be used, e.g., a three-reactor system may be used. The first one or two reactors in series would contain the relatively large pore zeolite, while the last, and optionally all or a portion of the second reactor would contain the ZSM-11 zeolite. Both stages, i.e., the large pore zeolite reactor and the ZSM-11 zeolite reactor are operated in the presence of hydrogen and under the same pressure.

According to yet a further embodiment the invention is directed to a cascade catalytic dewaxing process comprising:

(a) passing a hydrocarbon feedstock containing waxy components selected from a group of normal paraffins and slightly branched chain paraffins over a catalyst comprising a crystalline silicate zeolite having a Constraint Index less than 2, having acidic sites, and having associated therewith a catalytically effective amount of a hydrogenation/dehydrogenation component under conditions such that the hydrocarbon product of step (a) has a pour point no less than about +50°F;

(b) passing at least a majority of the normally liquid hydrocarbon recovered from step (a) over a medium pore crystalline silicate zolite, having acidic sites and a catalytically effective amount of a hydrogenation/dehydrogenation component; and

(c) recovering a normally liquid hydrocarbon product having a reduced wax contant relative to the feedstock, from the product of step (b).

In practice this embodiment usually takes the form of:

(a) passing a hydrocarbon feedstock containing long chain normal paraffins and long chain slightly branched paraffins, wherein at least a majority of the feedstock has a boiling point in excess of 482°F (250°C), over a large pore crystalline silicate zeolite having a Constrain Index less than 2, a silica to alumina mole ratio of at least 10, acidic sites, and having catalytically effective amounts of a hydrogenation/dehydrogenation component in the presence of hydrogen at a temperature between 500°F (260°C) and 700°F (371°C), a pressure no greater than 600 psig (42.5 bar) and a LHSV between 0.2 and 2.0 such that the hydrocarbon liquid product of step (a) has a pour point no less than +70°F (21°C);

(b) passing the entire effluent from step (a) over a medium pore zeolite having a silica to alumina ratio in excess of 10, acidic sites associated therewith, and having catalytically effective amounts of a hydrogenation/dehydrogenation component in the presence of hydrogen at a temperature between 500°F (260°C) and 700°F (371°C), the temperature of step (b) being the same or different from the temperature of step (a), a pressure of no greater than 600 psig and a LHSV between 0.2 and 2.0; and

(c) recovering from the effluent of step (b) a hydrocarbon feed with reduced wax content.

This embodiment may also be regarded as directed to a cascade catalytic dewaxing process wherein a hydrocarbon feedstock with a boiling point in excess of 482°F (250°C) and containing normal paraffins and slightly branched chain paraffins is sequentially passed over a first reaction zone containing a zeolite from the group having the structure of Mordenite, Zeolite Y, Zeolite Beta, ZSM-4 and ZSM-20, and having a silica/alumina ratio greater than 10, and having associated therewith acidic sites and 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the metals of Groups VI, VII and VIII, passing the entire effluent from the first reaction zone into a second reaction zone containing a medium pore zeolite selected from the group having the structure of ZSM-5 and ZSM-11, having a silica to alumina ratio greater than 10 and containing from 0.1 to 25 wt. % of a hydrogenation/dehydrogenation component selected from the group of Groups VI, VII and VIII and mixtures thereof, to produce a hydrocarbon liquid product with a reduced wax content.

Reverting to its generality, the present invention is preferably arranged in a two-stage cascading relationship whereby, in the first stage, the feedstock is hydroisomerized over a high silica large pore zeolite catalyst, followed by shape selective dewaxing in the second stage over a medium pore zeolite catalyst. It is believed that a cascade relationship of the large pore zeolite and the medium pore zeolite, in the right proportion, will offer superior dewaxing activities and lube yield, higher V.I., improved catalyst stability in the second stage and flexibility in catalyst regeneration than the lube dewaxing catalysts of the prior art.

The present process may be used to dewax a variety of feedstocks ranging from relatively light distillate fractions up to high boiling stocks, such as whole crude petroleum, reduced crudes, vacuum tower residua, propane deasphalted residua, e.g., brightstock, cycle oils, FCC tower bottoms, gas oils, vacuum gas oils, deasphalted residua and other heavy oils. The feedstock will normally be a C_{10}+ feedstock since lighter oils will usually be free of significant quantities of waxy components. However, the process is also particularly useful with waxy distillate stocks, such as gas oils, kerosenes, jet fuels, lubricating oil stocks, heating oils, hydrotreated oil stock, solvent-refined raffinate, furfural-extracted lubricating oil stock, and other distillate fractions whose pour point and viscosity need to be maintained within certain specification limits. Lubricating oil stocks, for example, will generally boil above 450°F (230°C), and more easily above 600°F (313°C). The process is also useful for solvent refined neutral oil and hydrocracked oil produced by the catlytic hydrocracking or hydrotreating of hydrocarbon feedstocks boiling about 650°F (343°C).

The catalysts used according to the invention are zeolites, a term employed herein to designate not only aluminosilicates having a crystal lattice made up of SiO_4 and AlO_4 tetrahedra cross-linked by the sharing of oxygen atoms but also such structures from which aluminum is absent, and which may thus be termed crystalline silicates, or is replaced by a different lattice component. Such other components may be present in minor amounts, usually less than 14 mole %, and preferably less than 4 mole %, and include gallium, iron, boron and the like.

The silica-to-alumina mole ratio of an aluminosilicate zeolite may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the zeolite crystal lattice and to exclude aluminum in the binder or in cationic or other forms within the channels. Although zeolites with a silica-to-alumina mole ratio of at least 10 are useful, it is preferred to use zeolites having much higher silica-to-alumina mole ratios, i.e., ratios of at least 50:1. In addition zeolites which are substantially free of aluminum, i.e., having silica-to-alumina mole ratios of the order of 500, and up to and including infinity, are found to be useful and even preferable in some instances. Such zeolites, after activation, acquire an intracrystalline sorption affinity for normal hexane which is greater than that for water, i.e., they exhibit "hydrophobic" properties.

A convenient measure of the extent to which a zeolite impedes access by molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. Zeolites which provide a highly restricted access to and egress from their internal structure have a high Constraint Index, and zeolites of this kind usually have pores of small size. On the other hand, zeolites which provide relatively free access to the internal zeolite structure have a low Constraint Index. The method by which Constraint Index is determined is described fully in US-A-4,016,218, to which reference is made for details of the method.

Constraint Index CI) values for some typical materials are:

	CI
ZSM-4	0.5
ZSM-5	6-8.3
ZSM-11	6-8.7
ZSM-12	2
ZSM-20	0.5
ZSM-23	9.1
ZSM-34	30-50
ZSM-35	4.5
ZSM-38	2
ZSM-48	3.5
TMA Offretite	3.7
TEA Mordenite	0.4
Clinoptilolite	3.4
Mordenite	0.5
REY	0.4
Amorphous Silica-Alumina	0.6
Dealuminzed Y (Deal Y)	0.5
Chlorinated Alumina	<1
Erionite	38
Zeolite Beta	0.6-1+

Constraint Index is a critical factor in the definiton of those zeolites which are useful in the invention. The very nature of this parameter and the technique by which it is determined, however, admit of the possibility that a given zeolite can be tested under somewhat different conditions and thereby exhibit different Constraint Indices. Constraint Index seems to vary somewhat with severity of operation (conversion) and the presence or absence of binders. Likewise, other variables, such as crystal size of the zeolite, the presence of occluded contaminants, etc., may affect the Constraint Index. Therefore, it will be appreciated that it may be possible to so select test conditions as to establish more than one value for the Constraint Index of a particular zeolite. This explains the range of Constraint Indices provided for some zeolites, such as ZSM-5, ZSM-11, ZSM-34 and Zeolite Beta.

Zeolites ZSM-3, -4, -5, -11, -12, -18, -20, -23, -34, -35, -38, -48 and beta are defined by the x-ray data set forth in US-A-3,415,736; 3,923,639; 3,702,886; 3,709,979; 3,832,449; 3,950,496; 3,972,983; 4,076,342; 4,086,186; 4,016,245; 4,046,859; 4,397,827; and 3,308,069, respectively.

Low sodium Ultrastable Y molecular sieve (USY) is described in US-A-3,293,192 and 3,449,070.

Large pore zeolites, i.e., those zeolites having a Constraint Index less than 2 and used in the first contacting hereof, are well known to the art and have a pore size sufficiently large to admit the vast majority of components normally found in a feed charge stock. They are generally considered to have a pore size in excess of 7 Angstroms and are represented by, e.g., Zeolite Beta, Zeolite Y, Mordenite, ZSM-3, ZSM-4 ZSM-18 and ZSM-20. An exceptionally suitable large pore material is zeolite beta, although all of these zeolites provide hydroisomerization activity.

The preferrred hydrogenation components to be associated with the large pore zeolite are the noble metals of Group VIIIA, especially platinum, but other noble metals, such as palladium, rhenium or rhodium, may also be used. Combinations of noble metals, such as platinum-rhenium, platinum-palladium, platinum-iridium or platinum-iridium-rhenium, with combinations with non-noble metals, particularly of Groups VIA and VIIIA are of interest, particularly with metals such as cobalt, nickel, vanadium, tungsten, titanium and molybdenum, for example, platimum-tunsgten, platinum-nickel or platinum-nickel-tungsten. Base metal hydrogenation components may also be used, expecially nickel, cobalt, molybdenum, tungsten, copper or zinc. Combinations of base metals, such as cobalt-nickel, cobalt-molybdenum, nickel-tungsten, cobalt-nickel-tungsten or cobalt-nickel-titanium, may also be used. The metal may be incorporated into the catalyst by any suitable method, such as impregnation or exchange. The metal may be incorporated in the form of a cationic, anionic or neutral complex.

The large-pore-catalysed (isomerization) reaction is one which requires a relatively small degree of acidic functionality in the catalyst. Because of this, the zeolite may have a very high silica:alumina ratio, since this ratio is inversely related to the acid site density of the catalyst. Thus, as mentioned previously, structural silica:alumina ratios of 50:1 or higher are preferred and, in fact, the ratio may be much higher, e.g., 100:1, 200:1, 500:1, 1000:1, or even higher. Since zeolites are known to retain their acidic functionality even at very high silica:alumina ratios of the order of 25,000:1, ratios of this magnitude or even higher are contemplated.

The original cations associated with the zeolites utilized herein may be replaced by a wide variety of other cations, according to techniques well known in the art. Replacing cations include hydrogen and metal cations, including mixtures of the same. Of the replacing metallic cations, particular reference is made to cations of metals such as rare earth metals, manganese, as well as metals of Group II A and B of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g. nickel, platinum and palladium.

The intermediate or medium pore size zeolites used in the second contacting hereof have a Constraint Index between 2 and 12 and an effective pore size of generally not greater than about 7 Angstroms, and freely sorb normal hexane. In addition, the structure provides 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 silicon and aluminum 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 of the rings or pore blockage may render these zeolites ineffective. The preferred medium pore zeolites in this invention include those having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and TMA Offretite.

The medium pore zeolite is associated with a hydrogenation/dehydrogenation component, just as disclosed in relation to the large pore zeolites. It is not essential, but may be beneficial, to use different hydrogenation/dehydrogenation components for the medium pore and large pore zeolites.

The acidity of the medium pore zeolite will usually be very similar to the acidity of the large pore zeolite. If it is desired, for reasons of economy or otherwise, to use a noble metal promoter in association with a large pore zeolite, and a base metal promoter in association with a medium pore zeolite, it may be beneficial to operate with different acidities, or silica/alumina ratios, in the large pore and medium pore zeolites. Best results will be obtained when the acidity of the medium pore zeolite is matched to the strength and amount of the hydrogenation/dehydrogenation component incorporated in the medium pore zeolite.

It will usually be beneficial to incorporate the medium pore zeolite into a conventional matrix, as discussed previously with regard to the use of matrix encapsulating agents for the large pore zeolites. It is possible, and preferable, to operate with the same matrix material for both the medium pore zeolite and the large pore zeolite.

In general, hydrodewaxing conditions include a temperature of between about 450°F (230°C) and about 750°F (400°C), and a pressure between 0 (1 bar) and 1000 psig (70 bar), preferably below 600 psig (42.5 bar). The liquid hourly space velocity (LHSV), i.e., volume of feedstock per volume of catalyst per hour, is generally in the range of 0.1 to 5.0, and preferably in the range of 0.2 to 2.0. Both stages of the cascade process are operated in the presence of hydrogen at a hydrogen-to-feedstock ratio of generally between about 400 and about 8000 (71 to 1424 m^3/m^3) and preferably between about 800 and 4000 standard cubic feet (SCF) (142.5 to 712 m^3/m^3) of hydrogen per barrel of feed.

In cascade operation at least 90%, and

preferably all, of the material passed over the large pore zeolite is also passed over the medium pore zeolite. In some embodiments there is no intermediate separation or cooling of fluid passing from one reaction zone to the next.

In its simplest form, a cascade operation may be realised by using a large down flow reactor wherein the lower portion contains the catalyst comprising the medium pore zeolite and the upper portion contains the catalyst comprising the large pore zeolite.

Two or more reactors in series may also be used, e.g., a three-reactor system, the first one or two reactors in series containing the relatively large pore zeolite, the last, and optionally all or a portion of the second reactor, containing the medium pore zeolite. According to one embodiment, however, it is critical in a two-stage cascade process to operate the first stage under mild conditions, such that the pour point of the charge stock is only reduced to no less than +50°F (+10°C), preferably no less than +70°F (+21°C). Another criticality in this process is that the pressure must be no greater than 1000 psig, preferably below 600 psig. Although both reactors are confined to the same temperature range of 450° to 750°F (230°-400°C), and preferably 500 to 700°F (276-371°C), they can be operated under the same or different temperatures as desired.

It is frequently advantageous to conduct hydrotreating either immedidately before or after catalytic dewaxing. Hydrotreating will usually be practised when necessary to remove sulfur or nitrogen or to meet some other product specification. Hydrotreating the feed before subjecting it to catalytic dewaxing advantageously converts many of the catalyst poisons in the hydrotreater or deposits them on the hydrotreating catalyst. Any conventional hydrotreating catalyst and processing conditions may be used.

Example 1

The charge stock was a severely hydrotreated waxy heavy neutral base stock having the following properties:

Specific Gravity	
API°	32.8
Pour Point, °F (°C)	+130 (+54)
Viscosity KV at 100°C, cs	10.39
Nitrogen, ppm	19
CCR	<0.1

A fixed-bed, down-flow operation was employed for both the cascade two-stage scheme and the single-stage processing. In the cascade two-stage operation, 10cc of 0.6% Pt/Zeolite Beta/Al_2O_3 extrudate catalyst was mixed with an equal volume of sand and placed in the first reactor. The platinum catalyst was steamed at 1000°F (538°C) for 72 hours prior to platinum exchange. 10cc of a steamed 1.1% Ni/ZSM-5 extrudate catalyst was mixed with an equal volume of sand and placed in the second reactor. Both catalysts were presulfided prior to catalytic lube processing after the cascade operation. For single-stage processing, the first catalyst was by-passed and the feedstock was directly charged into the second reactor. The results and process conditions are given in Table 1.

Table 1

Operating Mode	Cascade Two-Stage	Single-Stage
Pressure, psig	400	400
H_2 Circulation, SCF/B (m^3/m^3)	4000 (712)	4000 (712)
Temp., °F (°C)		
1st Reactor (Pt/Zeolite Beta)	575 (302)	----
2nd Reactor (Ni/ZSM-5)	530 (277)	605 (472)
LHSV		
1st Reactor	1.1	----
2nd Reactor	1.1	1.1
Product Yield, wt.%		
C_1+C_2	0.1	0.5
C_3+C_4	5.6	15.6
C_5 - 330°F Naphtha	15.7	19.3
330°-650°F Distillate	10.8	2.6
650°F$^+$ Lube	67.8	62.0
Properties of Lube		
Pour Point (1st Reactor)	+75°F (24°C)	----
Pour Point (2nd Reactor)	+20°F (-6.7°C)	+20°F
VI (2nd Reactor)	97	88
Catalyst Aging Rate, °F/Day		
1st Reactor	*	----
2nd Reactor	*	2.7 (1.5°C)

* No aging was observed during 21 days on stream under constant conditions.

(330°F=166°C; 650°F=343°C)

Example 2

For this example, a severely hydrotreated waxy bright stock was used having the following properties:

Specific Gravity	
API°	28.8
Pour Point, °F (°C)	+160 (+71)
Viscosity KV at 100°C, cs	26.99
Nitrogen, ppm	2
CCR, %	0.4

The same experimental procedures as in Example 1 were employed except that a Ni/ZSM-5 catalyst was used for the single-stage processing. The results and the processing conditions are presented in Table 2:

Table 2

Operating Mode	Cascade Two-Stage	Single-Stage
Pressure, psig	400	400
H_2 Circulation,		
SCF/B (m^3/m^3)	4000 (712)	4000 (712)
Temp., °F (°C)		
1st Reactor		
(Pt/Zeolite Beta)	575 (302)	----
2nd Reactor		
(Ni/ZSM-5)	548 (287)	616 (324)
LHSV		
1st Reactor	1.1	----
2nd Reactor	1.1	1.0
Product Yield, wt.%		
C_4-	9.5	19.0
C_5 - 330°F Naphtha	17.6	18.0
330°-650°F Distillate	8.6	4.0
650°F$^+$ Lube	64.3	59.0
Properties of Lube		
Pour Point (1st Reactor)	+75°F (24°C)	----
Pour Point (2nd Reactor)	+10°F (-12.2°C)	+10°F
Catalyst Aging Rate, °F/Day		
1st Reactor	0.3 (0.17°C)	----
2nd Reactor	0.5 (0.28°C)	9.7*(5.4°C)

* 1.4°F/Day (0.78°C) after the transition temperature of 616°F (324.5°C).

Example 3

Example 3 was designed to show the effective differences of pressure on the lube yield obtained from the first stage (hydroisomerization) reactor using hydrotreated waxy bright stock as a charge stock. The same catalyst and experimental procedures as in Example 1 for the first reactor were employed. The results and the processing conditions are given in Table 3:

Table 3

Effect of Pressure on Lube Yield
From First Stage Hydroisomerization

Pressure, psig	400	2800	400	2800
Pour Point of Lube °F (°C)	+75(24)	+75	+30(-1.1)	+30
Temp., °F (°C)	575(302)	573(300)	602(316)	616(324)
Product Yield, wt %				
C_4	0.9	0.0	5.1	0.9
C_5-330°F Naphtha	3.4	3.9	23.7	32.1
330-650°F Distillate	7.2	9.9	20.9	21.9
650°F+ Lube	88.5	86.2	50.3	44.9

From Table 1, it is noted that in the cascade two-stage operation, the lube fraction in the first reactor effluent had a pour point of +75°F and was further reduced to +20°F (-6.6°C) as a result of the second stage dewaxing. The cascade two-stage operation gave an increased lube yield (67.8% vs. 62.0% at the same +20°F pour point), a higher VI (97 vs. 88) and improved ZSM-5 catalyst stability.

Referring now to Table 2, the pour point of the lube fraction was reduced from +75° to +10°F as a result of the second stage dewaxing process. Again, the cascade operation exhibited enhanced lube yield at the same pour point for the waxy bright stock.

Table 3 shows the effect of pressure on the lube yield obtained from the first stage (hydroisomerization) process using the hydrotreated waxy bright stock as a charge stock. At a given pour point of lube product, it can be seen that the lower pressure gave a higher lube yield. Table 3 also shows that the lube yield from the first stage reactor at 400 psig was decreased from 88.5 wt. % to 50.3 wt. % when the pour point of the lube fraction was reduced from +75° to +30°F. This indicates that severe conditions in the first stage reactor would significantly reduce the overall yield in the cascade two-stage operation. It should be noted that the 50.3 wt. % lube yield is already below the 59 wt. % lube yield which can be achieved from single-stage shape selective dewaxing alone, as illustrated in Table 2. Therefore, it is not desirable in this context to operate the first stage in such a way that the pour point of the lube fraction is reduced to below approximately +50°F, and preferably +70°F.

Thus, it can be seen that the use of a large pore zeolite catalyst and a medium pore zeolite catalyst in a cascade catalytic lube process results in a better lube yield, a more valuable by-product in terms of distillate yield, a higher viscosity index, and improved catalyst stability for the second stage process than with a standard lube dewaxing process in which lube base stocks are dewaxed only over medium pore zeolite catalysts.

Example 4

This Example employs a solvent-refined raffinate oil chargestock having the following properties:

Specific Gravity	0.877
API°	29.8
Pour Point, °F (°C)	120 (50)
Cloud Point, °F (°C)	>120 (>50)
Viscosity KV at 100°C	11.45
Sulfur, wt. %	0.98
Basic Nitrogen, ppm	61
Nitrogen, ppm	61
Hydrogen, wt. %	13.79
CCR, wt. %	0.08
Bromine Number	1.0
ASTM Color	4.5

It is a comparative example, illustrating the effect of steamed 1% Ni-ZSM-5 (alpha = 70) catalyst on the chargestock as it was passed over the catalyst in a single reactor application. The catalyst was loaded into a fixed-bed reactor. The catalyst was reduced *in situ* at 900°F (482°C) and 400 psig (28.6 bar) H_2. Thereafter, the reactor temperature was lowered to the desired setting and the chargestock was passed over the catalyst along with hydrogen under the controlled process conditions which are recited in Table 4.

Table 4

Temperature, ^{o}F (^{o}C)	614 (323)
Gas	H_2
Circulation, SCF/bbl	340 (60.5 m^3/m^3)
LHSV, v/v/hr	.99
Yields, wt. %	
$C_1 + C_3$	3.5
C_4	5.3
C_5	3.2
C_6 - 330^{o}F	3.5
330-650^{o}F	1.7
650$^{o}F^{+}$ Lube	83
API^{o} Gravity	25.5
Pour Point, ^{o}F (^{o}C)	25 (-3.9)
Cloud Point, ^{o}F (^{o}C)	28 (-2.2)
Flash Point (COC), ^{o}F (^{o}C)	558 (292)
KV at 40^{o}C	145.0
KV at 100^{o}C	13.66
SUS at 100 ^{o}F (38^{o}C) (calc)	764
Viscosity Index	88
Bromine Number	0.8
Sulfur, wt. %	1.22

(330-650^{o}F = 166-343^{o}C)

Examples 5-23

Examples 5-23 illustrate a dual catalyst cascade operation employing steamed 0.6% Pt/Zeolite Beta in the first zone and steamed 1.0% Ni/ZSM-5 in the second zone of a two-zone reactor. A fixed-bed, down-flow operation was employed for the cascade two-zone scheme. Both catalysts were reduced *in situ* of 400 psig of hydrogen and 900°F (480°C) for 1 hour. The results and process conditions are given in Table 5.

Table 5

Example No.	5	6	7	8	9
Temperature, °F (°C)					
First Reactor	650 (343)	650	650	650	650
Second Reactor	630 (332)	550 (288)	684 (362)	689 (365)	608 (320)
Time on Stream, Days	2.5	4.5	5.6	6.5	7.5
Run Time, Hrs	64.5	20.5	20.5	19.5	19.5
LHSV	1.14	0.83	0.92	1.01	0.93
650°F Lube Yield, Wt %	90.6	87.4	90.1	88.9	85.5
Specific Gravity	0.8911	0.8887	0.8891	0.8901	0.8924
API°	27.3	27.7	27.7	27.5	27.1
Pour Point, °F (°C)	90 (32)	85 (29.5)	70 (21)	55 (13	35 (1.66)
Cloud Point, °F (°C)	104 (40)	120 (49)	120	62 (16.5)	50 (10)
KV at 100°F, cs (38°C)	128.6	120.9	121.7	129.6	138.5
KV at 210°F, cs (99°C)	11.90	12.02	12.29	12.67	12.97
KV at 40°C, cs	113.5	107.2	108.0	114.8	122.4
KV at 100°C, cs	11.56	11.68	11.95	12.31	12.60
SUS at 100°F	598	560	564	600	642
SUS at 210°F	66.1	66.5	87.5	68.9	70.1
Viscosity Index	87.1	96.2	99.3	97.3	93.9
Sulfur, Wt %	0.93	0.64	0.75	0.69	0.73
Basic Nitrogen, ppm	55	56	62	61	60
Nitrogen, ppm	73	72	75	62	70
Hydrogen, Wt %	13.73	13.70	13.69	13.71	13.65
CCR, Wt %	0.06	0.04	0.06	0.08	0.09
Bromine Number	2.6	0.8	0.5	1.3	2.2
ASTM Color	L3.5	L3.5	L3.0	L2.5	L2.5

L = Lighter Than

Table 5 (Cont.)

Example No.	10	11	12	13	14
Temperature, °F (°C)					
First Reactor	650 (343)	650	650	650	650
Second Reactor	628 (331)	639 (337)	642 (339)	649 (343)	648 (342)
Time on Stream, Days	9.5	11.5	12.5	13.6	14.5
Run Time, Hrs	85	21	21	20.5	20
LHSV	0.91	0.87	1.02	1.00	1.06
650°F Lube Yield, Wt %	82.2	82.0	81.5	81.7	82.5
Specific Gravity	0.8938	0.8938	0.8936	0.8939	0.8933
API°	26.8	26.8	26.9	26.8	26.9
Pour Point, °F (°C)	20 (-6.6)	15 (-9.5)	20	20	25 (-3.9)
Cloud Point, °F (°C)	26 (-3.3)	22 (-5.6)	30 (-1.1)	26	42 (5.6)
KV at 100°F, cs	143.4	144.2	144.2	144.6	142.40
KV at 210°F, cs	13.09	13.09	13.10	13.09	13.07
KV at 40°C, cs	126.5	127.7	127.2	127.5	125.7
KV at 100°C, cs	12.71	12.71	12.72	12.71	12.69
SUS at 100°F	664	668	668	670	660
SUS at 210°F	70.5	70.5	70.5	70.5	70.4
Viscosity Index	91.5	90.8	91.0	90.6	92.0
Sulfur, Wt %	0.75	0.72	0.75	0.75	0.84
Basic Nitrogen, ppm	64	70	60	65	61
Nitrogen, ppm	72	70	69	81	75
Hydrogen, Wt %	13.65	13.59	13.53	13.60	13.58
CCR, Wt %	0.07	0.08	0.09	0.08	0.04
Bromine Number	2.6	2.0	2.3	2.4	2.1
ASTM Color	L2.0	L2.0	L2.0	L2.0	L2.5

L = Lighter Than

Table 5 (Cont.)

Example No.	15	16	17	18	19
Temperature, °F					
First Reactor	650	650	650	650	650
Second Reactor	648	648	648	650	649
Time on Stream, Days	15.5	16.5	17.5	19.5	21.5
Run Time, Hrs	19.5	19	19	65	19
LHSV	0.96	0.96	0.98	0.96	0.93
650°F Lube Yield, Wt %	80.8	81.1	82.4	82.3	82.9
Specific Gravity	0.8933	0.8935	0.8934	0.8933	0.8939
API°	26.9	26.9	26.9	26.9	26.8
Pour Point, °F	20	15	20	15	25
Cloud Point, °F (°C)	30	28 (-2.2)	36 (2.2)	40 (4.5)	40
KV at 100°F, cs	143.1	143.8	143.2	143.1	142.5
KV at 210°F, cs	13.05	13.08	13.17	13.09	13.07
KV at 40°C, cs	126.3	126.9	126.4	126.3	125.8
KV at 100°C, cs	12.67	12.70	12.79	12.71	12.69
SUS at 100°F	663	666	663	663	660
SUS at 210°F	70.3	70.5	70.8	70.5	70.4
Viscosity Index	91.1	91.0	92.7	91.7	91.9
Sulfur, Wt %	0.76	0.78	0.78	0.78	0.78
Basic Nitrogen, ppm	67	68	67	68	66
Nitrogen, ppm	71	64	63	75	74
Hydrogen, Wt %	13.50	13.48	13.49	13.47	13.43
CCR, Wt %	0.08	0.06	0.08	0.07	0.08
Bromine Number	1.8	2.4	2.0	1.0	0.8
ASTM Color	2.0	2.0	2.0	L2.5	2.0

L = Lighter Than

Table 5 (Cont.)

Example No.	20	21	22	23
Temperature, °F				
First Reactor	650	650	650	650
Second Reactor	648	649	649.2	649
Time on Stream, Days	22.5	23.5	24.5	26.5
Run Time, Hrs	23	22	30	65
LHSV	0.95	0.90	0.93	0.95
650°F Lube Yield, Wt %	83.9	83.7	83.8	84.4
Specific Gravity	0.8935	0.8935	0.8933	0.8929
API°	26.9	26.9	26.9	27.0
Pour Point, °F	25	30	25	30
Cloud Point, °F (°C)	46 (7.8)	44 (6.7)	46	52 (11.1)
KV at 100°F, cs	140.4	141.1	140.0	137.7
KV at 210°F, cs	13.02	13.05	13.00	12.95
KV at 40°C, cs	124.0	124.6	123.7	121.7
KV at 100°C, cs	12.65	12.68	12.63	12.58
SUS at 100°F	650	654	649	638
SUS at 210°F	70.3	70.4	70.2	70
Viscosity Index	93.0	92.9	93.0	94.3
Sulfur, Wt %	0.79	0.76	0.77	0.80
Basic Nitrogen, ppm	66	66	66	64
Nitrogen, ppm	76	77	74	67
Hydrogen, Wt %	13.64	13.53	13.76	13.58
CCR, Wt %	0.09	0.08	0.06	0.08
Bromine Number	1.0	0.1	1.5	2.1
ASTM Color	L2.5	L2.0	L2.0	2.0

L = Lighter Than

Compared to the Ni-ZSM-5 catalyst in the single stage reactor, the cascade reactor system of Examples 5-23 improved viscosity index by up to 4 numbers. As illustrated in Fig. 1, which shows the effect of pour point on viscosity index for both a cascade and a single zone reactor, the viscosity index of solvent-refined raffinate is higher in the cascade reactor system than in the single zone reactor system at the designated pour point.

Fig. 2 illustrates the effect of the number of days a catalyst is on-stream for both a single zone and cascade reactor with regard to the temperature of the catalyst. It can be seen that after approximately 20 days on-stream, the temperature of the single zone reactor must operate in excess of 675°F (357°C) for efficient reaction to occur. In contrast, the cascade reactor system may operate in excess of 27 days below a reactor temperature of 675°F (357°C). Thus, the cascade reactor system operates more efficiently, for a larger period of time and produces a superior product for a solvent-refined raffinate chargestock, when compared to the single zone reactor.

Examples 24-37

These examples illustrate the effect of interstage separation employing a 0.6% Pt/Zeolite Beta catalyst in the first reactor and steamed 1% Ni-ZSM-5 zeolite in the second reactor. A fixed-bed, down-flow operation was employed for the cascade 2-zone scheme. The chargestock was first processed over the 0.6% Pt/Zeolite Beta under the following conditions:

Temperature °F (°C)	633-640 (334-338)
LHSV	1
SCF H_2/bbl	2500
H_2, psig	400

The 650°F$^+$ portion was then fractioned out by conventional means and processed over steamed 1% Ni/ZSM-5. The results and process conditions of the second stage are given below in Table 6.

Table 6

Example No.	24	25	26	27
Average Temperature, °F (°C)	551 (289)	556 (291)	560 (293)	567 (297)
Time on Stream, Days	2.5	3.5	5.4	7.3
650°F Lube Yield, Wt %	84.6	84.5	84.5	86.3
API° Gravity	26.9	26.8	27.1	26.9
Pour Point, °F	25	25	30	35
Cloud Point, °F	46	42	48	46
KV at 40°C, cs	124.3	125.1	119.7	123.8
KV at 100°C, cs	12.69	12.72	12.46	12.67
Viscosity Index	93.3	93.0	94.5	93.5

Table 6 (Cont.)

Example No.	28	29	30	31
Average Temperature, °F (°C)	571 (299)	576 (302)	581 (305)	587 (308)
Time on Stream, Days	8.3	9.3	10.3	12.3
650°F Lube Yield, Wt %	85.5	85.6	84.9	84.7
API° Gravity	26.8	26.7	26.6	26.5
Pour Point, °F	30	30	20	15
Cloud Point, °F (°C)	40	40	28	24 (-4.5)
KV at 40°C, cs	125.2	126.3	127.8	130.6
KV at 100°C, cs	12.70	12.75	12.77	12.87
Viscosity Index	92.6	92.3	91.1	90.0

Table 6 (Cont.)

Example No.	32	33	34	35
Average Temperature, °F (°C)	587 (308)	590 (310)	593 (311)	593 (311)
Time on Stream, Days	14.4	15.5	16.5	17.4
650°F Lube Yield, Wt %	86.0	85.7	85.8	85.9
API° Gravity	26.6	26.6	26.6	26.6
Pour Point, °F	15	15	15	15
Cloud Point, °F	28	26	22	24
KV at 40°C, cs	129.0	129.3	129.2	129.5
KV at 100°C, cs	12.81	12.80	12.80	12.81
Viscosity Index	90.6	90.1	90.2	90.1

Table 6 (Cont.)

Example No.	36	37
Average Temperature, °F (°C)	592 (311)	591 (310)
Time on Stream, Days	19.5	21.5
650°F Lube Yield, Wt %	86.1	87.0
API° Gravity	26.7	26.8
Pour Point, °F	20	30
Cloud Point, °F	22	40
KV at 40°C, cs	127.9	126.6
KV at 100°C, cs	12.75	12.70
Viscosity Index	90.7	92.0

Figure 3 illustrates the effect of the presence of interstage separation on the second stage reactor temperature with regard to days onstream. It can be seen that in the first few days onstream, the dewaxing catalyst aged at approximately 5°F (2.8°C) per day with an SOC temperature of 542°F (283°C). After 20 days onstream, the dewaxing catalyst lined out at about 585°F (307°C). In contrast, the cascade dewaxing process without interstage separation had an SOC temperature of 575°F (302°C) and lined out at 650°F. The aging rate after line-out was 0.5°F (0.28°C) per day. With the conventional dewaxing process, the SOC temperature was 550°F (288°C) and aged at a rate of approximately 5°F/day until the end of cycle temperature (set at 675°F (357°C)). The results indicate that the pretreatment of the chargestock over a large pore zeolite, preferably Zeolite Beta, and the removal of light ends, e.g., the 650°F$^-$ stock, can significantly reduce the severity level for the second reactor.

In the following Examples the chargestock was a light neutral lubricating oil chargestock having the following properties:

Specific Gravity	.8774
API°	29.8
Pour Point, °F (°C)	85 (35)
Viscosity KV at 100°C)	5.341
Sulfur, wt. %	0.76
ASTM Color	*L1.0

*L = Lighter than

Examples 38 to 42 are comparative examples, showing the effects of three different catalysts on the chargestock as it was passed over the catalyst in a single reactor operation.

Example 38

Steamed 1% Ni-ZSM-5 was loaded into a fixed-bed reactor. The catalyst was reduced *in situ* at 900°F (482°C) and 400 psig H_2 for 1 hour. Thereafter, the reactor temperature was lowered to the desired setting, the chargestock being passed over the catalyst together with hydrogen under the process conditions set forth in Table 7. The product stream leaving the reactor was passed through a heated trap, a cold-water trap, and a gas-sampling bomb. The gas samples were analyzed by mass spectrometry for C_1-C_6 components. Liquid products were topped, under less than 0.1 mm Hg pressure and miximum pot temperature of 400°F (204.5°C), to isolate the 650°F$^+$ fraction. Some of the topped samples were processed through a simulated distillator. The light liquid products, i.e., the condensate from the cold trap and the overhead from the topped samples, were analyzed by gas chromatography. Overall material balances were made based on total liquid feed charge plus hydrogen. The results are set forth in Table 7.

Table 7

Temperature, ^{o}F (^{o}C)	580 (304)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
LHSV, v/v/hr	1.00
Yields, wt. %	
C_1 +C_2	0.1
C_3	1.5
C_4	4.0
C_5	4.3
C_6 - 650^{o}F	10.8
650^{o}F^{+} Lube	79.5 (610^{o}F)
API^{o} Gravity	28.6
Pour Point, ^{o}F	15
KV at 40^{o}C	42.99
KV at 100^{o}C	6.325
Viscosity Index	92.8

Example 39

This Example illustrates the effect of a 0.5% Pt-ZSM-5 catalyst on the chargestock. The platinum catalyst was reduced *in situ* at 900^{o}F (482^{o}C) and 400 psig of hydrogen for one hour before introducing the feed into the reactor. The procedure of Example 38 was followed under conditions specified in Table 8, which also recites the results.

Table 8

Temperature, °F (°C)	565 (296)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
LHSV, v/v/hr	1.28
Yields, wt. %	
$C_1 + C_2$	0.2
C_3	4.4
C_4	5.4
C_5	1.5
C_6 - 650°F	8.8
650°F^+ Lube	80.6 (610°F)
API° Gravity	28.3
Pour Point, °F	5
KV at 40°C	45.35
KV at 100°C	6.505
Viscosity Index	91.5

Example 40

This example illustrates the effect of a .44% pt-Zeolite Beta on the chargestock. The procedure of Example 39 was followed under conditions specified in Table 9, which also recites the results:

Table 9

Temperature, °F (°C)	800 (427)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
Time on Stream, Days	6
LHSV, v/v/hr	1.0
Yields, wt. %	
C_1 +C_2	1.0
C_3	2.1
C_4	6.1
C_5	3.3
C_6 - 650°F	35.0
650°F+ Lube	52.5
API° Gravity	29.0
Pour Point, °F	5
KV at 40°C	13.05
KV at 100°C	3.035
Viscosity Index	80.5

Example 41

This Example illustrates the effect of .44% Pt-Zeolite Beta on the chargestock under reaction conditions different from those of Example 40 (reaction temperature 550°F vs. 800°F). The procedure of Example 39 was followed under conditions specified in Table 10, which also recites the results:

Table 10

Temperature, °F (°C)	550 (288)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
Time on Stream, Days	0.5
LHSV, v/v/hr	1.0
Yields, wt. %	
C_1 +C_2	0.2
C_3	0.1
C_4	0.1
C_5	0.1
C_6 - 650°F	3.6
650°F^+ Lube	95.9
API° Gravity	29.0
Pour Point, °F (°C)	95 (35)
KV at 40°C	27.98
KV at 100°C	5.143

Example 42

This Example illustrates the effect of .5% Pt/ZSM-11 on the chargestock. The procedure of Example 39 was followed under conditions specified in Table 11, which also recites the results.

Table 11

Temperature, °F (°C)	540 (282)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
Time on Stream, Days	4
LHSV, v/v/hr	1.0
Yields, wt. %	
$C_1 + C_2$	0.3
C_3	2.3
C_4	2.8
C_5	2.4
C_6 - 650°F	10.3
650°F+ Lube	81.9
API° Gravity	29.0
Pour Point, °F	15
KV at 40°C	42.32
KV at 100°C	6.311
Viscosity Index	95.2

Example 43

This Example illustrates the effect of 0.5% Pt/ZSM-11/Zeolite Beta in admixture on the chargestock. ZSM-11 was first calcined in a nitrogen atmosphere at 1000°F (538°C) for 3 hours to decompose tetrabutyl ammonium and other organics in its structure. The ZSM-11 was subsequently NH_4NO_3 exchanged to reduce its Na content to less than 0.02%. Zeolite Beta was pretreated similarly. 32.5 parts of NH_4ZSM-11, 32.5 parts of NH_4-Zeolite Beta and 35 parts of alpha alumina monohydrate were mulled together to form a uniform mixture which was then impregnated with H_2PtCl_6 in a stream of CO_2. The sample was finally sized to 30/60 mesh and activated with an air calcination for 3 hours at 1000°F (538°C). The sample was analyzed and found to contain 0.49 wt. % and 0.01 wt. % Na.

The runs were made in a 15/32" (1.19 cm) ID fixed-bed reactor with a spiral preheater and a three-zone furnace for good temperature control. The platinum composite catalyst was reduced *in situ* at 900°F (482°C) and 400 psig of hydrogen for one hour before the reactor temeprature was lowered to 500°F (260°C) and the feed was started pumping into the reactor. The product stream leaving the reactor was passed through a heated trap, a cold water trap, and a gas-sampling bomb. The gas samples were analyzed by mass spectrometry for C_1-C_6 components. Liquid products were topped under less than 0.1 mm·Hg pressure, maximum pot temperature 400°F (204°C), to isolate the 650°F$^+$ part. Light liquid products (the condensate in the cold trap and the overhead from topping) were sent for gas chromatography analysis. Overall material balances were made based on total liquid feed charge plus hydrogen.

The run conditions and results are specified in

Table 12.

Table 12

Temperature, °F (°C)	580 (304)
Pressure, psig	400
Gas	H_2
Circulation, SCF/bbl	2500
Time on Stream, Days	6
LHSV, v/v/hr	1.0
Yields, wt. %	
$C_1 + C_2$	0.1
C_3	2.6
C_4	2.9
C_5	2.8
C_6 - 650°F	7.3
650°F$^+$ Lube	84.3
API° Gravity	29.1
Pour Point, °F	20
KV at 40°C	41.06
KV at 100°C	6.236
Viscosity Index	97.5

Examples 44 and 45

These Examples ilustrate a dual catalyst cascade operation employing 0.44% Pt/Zeolite Beta in the first zone and 0.5% Pt/ZSM-11 in the second zone of a two-zone reactor. A fixed-bed, down-flow operation was employed for the cascade two-zone scheme. Both catalysts were reduced *in situ* under 400 psig of hydrogen at 900°F 480°C) for 1 hour. The results and process conditions are given in Table 13.

Table 13

Example No.	44	45
Temperature, °F (°C)		
First Reactor	554 (290)	555 (290)
Second Reactor	546 (286)	545 (285)
Pressure, psig	400	400
H_2 Circulation, SCF/bbl	2500	2500
Time on Stream, Days	2	3
LHSV, v/v/hr (Overall)	.5	.5
LHSV (First Reactor)	1.0	1.0
LHSV (Second Reactor)	1.0	1.0
Yields, wt. %		
C_1 +C_2	.3	.1
C_3	1.4	1.8
C_4	3.1	3.3
C_5	2.6	2.6
C_6 - 650°F	9.4	7.2
650°F$^+$ Lube	83.2	85.0
API° Gravity	28.8	29.0
Pour Point, °F	15	20
KV at 40°C, cs	42.63	41.46
KV at 100°C, cs	6.322	6.250
Viscosity Index	93.4	96.3

Compared to the Ni-ZSM-5 (Example 38) and Pt-ZSM-5 (Example 39) in the single reactor operation, Pt/ZSM-11 (Example 42) improved product yields by approximately 5% and 4%, respectively, and VI by about 2 and 4 numbers, respectively.

Compared to Ni-ZSM-5 in the single reactor operation, the cascade operation (Examples 44 and 45) enhanced catalyst activity by 25°-35°F (13.9-19.5°C) and improved product yields by 5% and VI by 3 numbers, respectively. Compared to Pt/Zeolite Beta, the cascade operation enhanced catalyst activity by at least 150°F (83.5°C), lube yield by 32% and VI by 16 numbers. As illustrated in Example 41, Pt-Zeolite Beta exhibits very little dewaxing activity at a temperature of 550°F; however, the dewaxing activity is greatly enhanced by the use of Zeolite Beta and ZSM-11 in a cascade relationship.

The cascade operation had a slightly lower catalyst activity, i.e., 5°-15°F (2.8-8.5°C), than Pt/ZSM-11 in the single reactor operation, but the cascade operation produced 3% more lube yield. Equivalent lube yield and product VI were observed between the cascade operation and the single reactor operation utilizing the composite Pt-ZSM-5/Zeolite Beta catalyst. Further, the cascade operation offered a catalyst activity advantage of 25°-35°F. Thus, it can be seen that a dual catalyst cascade operation utilizing a large pore zeolite catalyst and ZSM-11 results in enhanced catalyst activity, better lube yield and a higher viscosity index over the single reactor operation.

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims.

CLAIMS

1. A process for dewaxing a hydrocarbon feedstock which comprises, first, contacting said feedstock at elevated temperature with a catalyst comprising a crystalline zeolite having a constraint index less than 2, possessing acidic sites and associated with a catalytically effective quantity of a component possessing hydrogenation/dehydrogenation activity, and, second, contacting at least the majority of the effluent from said first contacting, at elevated temperature, with a catalyst comprising a crystalline zeolite having a constraint index greater than 2, possessing acidic sites and associated with a catalytically effective quantity of a component possessing hydrogenation/dehydrogenation activity, and recovering a normally liquid hydrocarbon product of reduced wax content relative to said feedstock.

2. A process according to claim 1 wherein the first and/or second contacting is carried out in the presence of added hydrogen.

3. A process according to claim 1 or claim 2 wherein each hydrogenation/dehydrogenation component comprises a metal of Group VI, VII and/or VIII of the Periodic Table.

4. A process according to claim 3 wherein said metal is a Group VIII noble metal and constitutes 0.1 to 5 wt. % of the catalyst with which it is associated.

5. A process according to claim 5 wherein the metal constitutes from 0.3 to 3 wt. % of the catalyst.

6. A process according to claim 3 wherein said metal is a non-noble metal and constitutes 0.3 to 25 wt. % of the catalyst with which it is associated.

7. A process according to any preceding claim of which the overall liquid hourly space velocity is between 0.1 and 5.

8. A process according to claim 7 wherein the overall liquid hourly space velocity is between 0.2 and 3.0.

9. A process according to any preceding claim wherein each contacting is carried out at a temperature in the range 232 to 371°C (450 to 700°F), a liquid hourly space velocity of 0.1 to 10 and a pressure no greater than 70 bar (1000 psig).

10. A process according to any preceding claim wherein each contacting is carried out at a pressure below 42.5 bar (600 psig).

12. A process according to claim 11 wherein the pressure is below 28.5 bar (400 psig).

13. A process according to any preceding claim wherein each contacting is carried out at a liquid hourly space velocity of 0.2 to 6.0.

14. A process according to any preceding claim wherein the first and/or second contacting is carried out in a fixed, slurry or moving bed unit.

15. A process according to any preceding claim wherein the zeolite employed in said first contacting is zeolite Y, ultrastable zeolite Y, dealuminised zeolite Y, ZSM-3, ZSM-18 or ZSM-20.

16. A process according to any preceding claim wherein the zeolite employed in said second contacting is zeolite ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 or TMA Offretite.

17. A process according to any of claims 1 to 14 wherein the zeolite employed in said first contacting is zeolite beta.

18. A process according to any preceding claim where the hydrogenation/dehydrogenation component associated with the zeolite is platinum.

19. A process according to any preceding claim wherein said feedstock contains waxy components which are normal and/or slightly branched paraffins.

20. A process according to any preceding claim wherein the normally liquid effluent from said first contacting has a pour point less than that of said feedstock but no less than 50°F (10°C).

21. A process according to claim 20 wherein said pour point is no less than 70°F (21°C).

22. A process according to any preceding claim wherein the zeolite employed in said second contacting is zeolite ZSM-5.

23. A process according to claim 22 wherein the hydrogenation/dehydrogenation component associated with the zeolite is nickel.

24. A process according to any preceding claim wherein said feedstock is a solvent-refined raffinate.

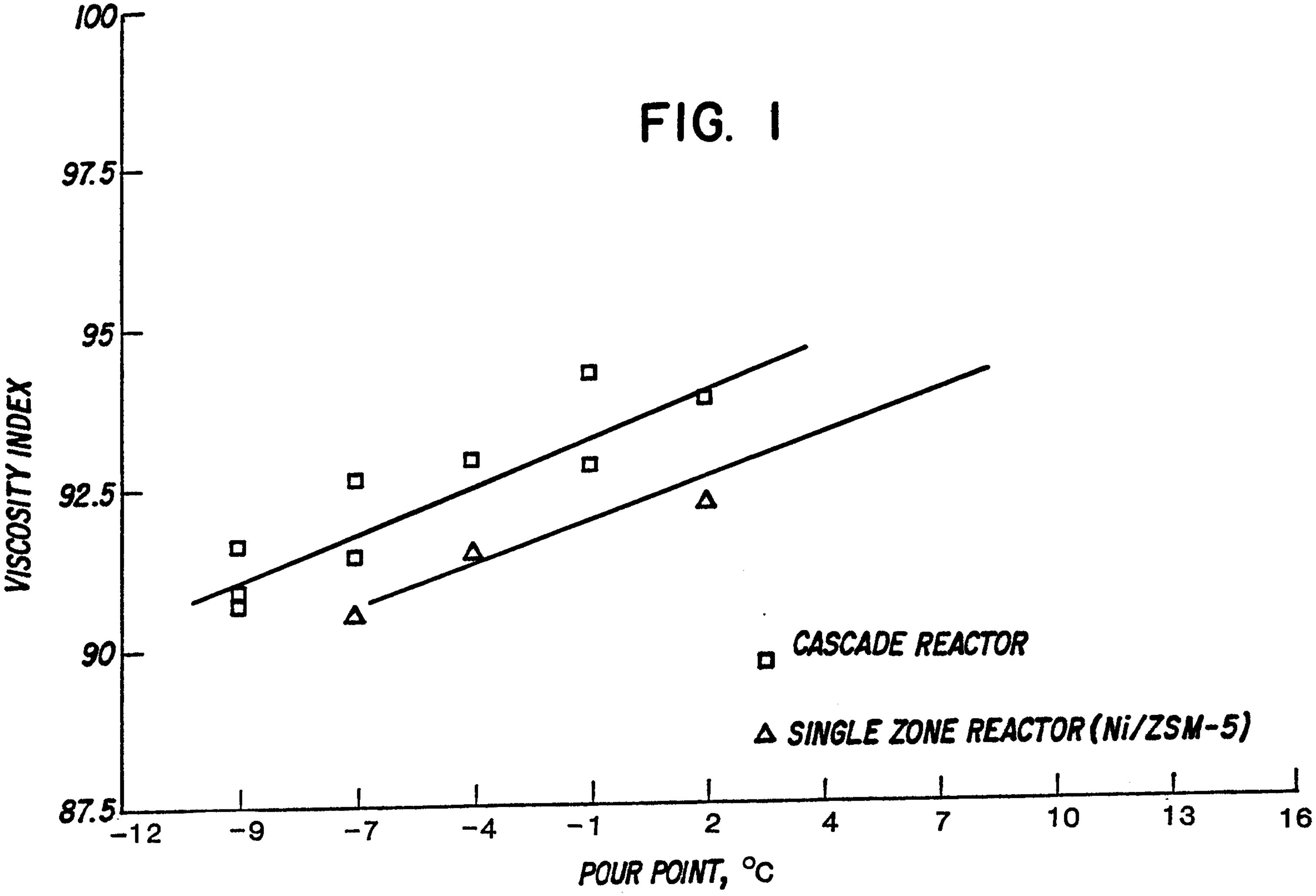
25. A process according to claim 24 wherein the activity of the zeolite employed in said first contacting is reduced prior to the contacting.

26. A process according to claim 24 or claim 25 wherein a 650°F- (343°C-) fraction is removed from the effluent of said first contacting before said second contacting is performed.

27. A process according to any of claims 1 to 19 wherein at least the majority of said feedstock has a boiling point greater than 250°C.

28. A process according to claim 27 wherein the zeolite employed in said second contacting is ZSM-11.

FIG. I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97.5
95
92.5
90
87.5
VISCOSITY INDEX
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−9
−7
−4
−1
2
4
7
10
13
16
POUR POINT, °C
□ CASCADE REACTOR
△ SINGLE ZONE REACTOR (Ni/ZSM-5)

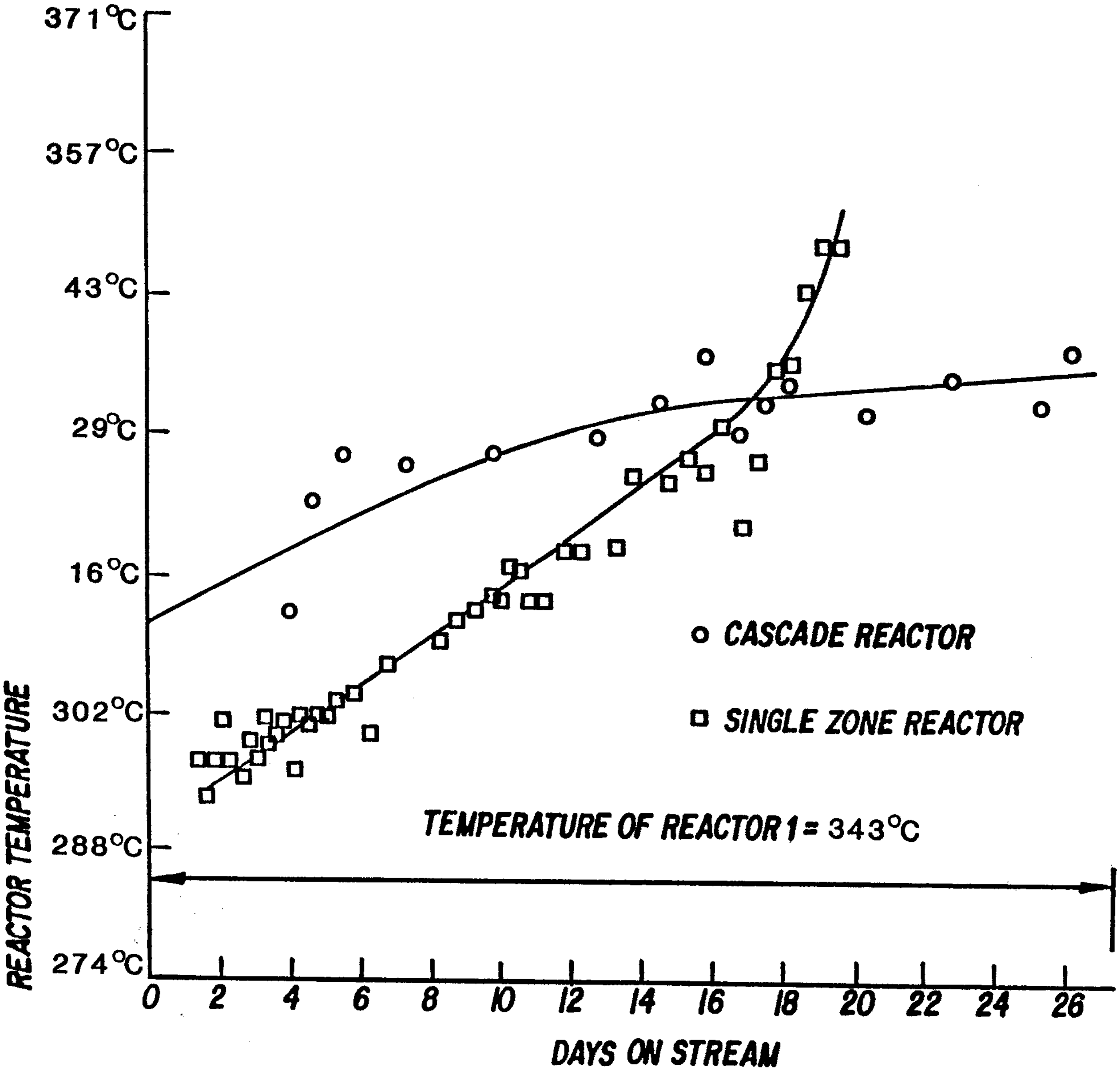
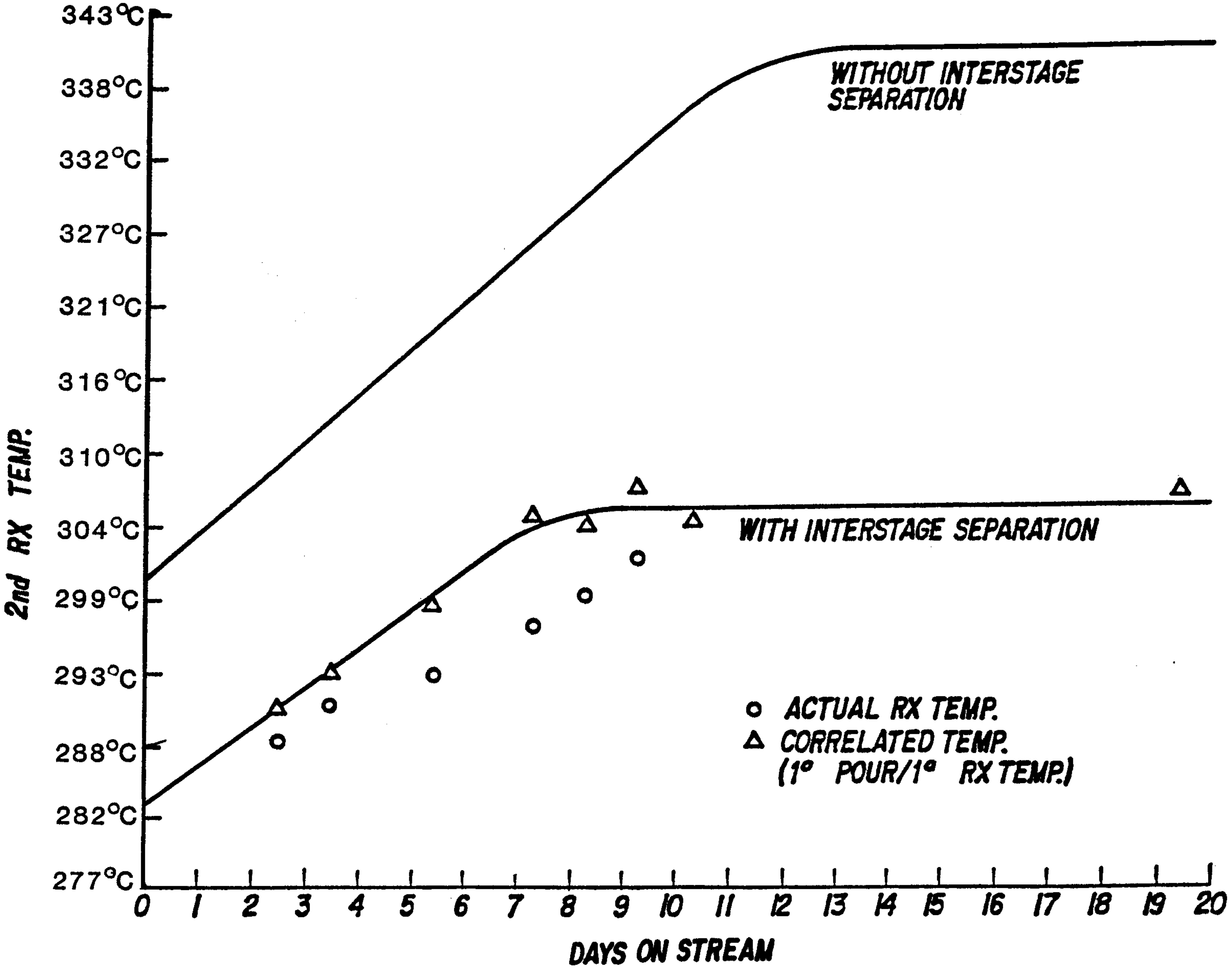

371°C
357°C
43°C
29°C
16°C
302°C
288°C
274°C
REACTOR TEMPERATURE
0
2
4
6
8
10
12
14
16
18
20
22
24
26
DAYS ON STREAM
○ CASCADE REACTOR
□ SINGLE ZONE REACTOR
TEMPERATURE OF REACTOR 1 = 343°C

FIG. 2

FIG. 3


343°C
338°C
332°C
327°C
321°C
316°C
310°C
304°C
299°C
293°C
288°C
282°C
277°C
2nd RX TEMP.
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
DAYS ON STREAM
WITHOUT INTERSTAGE SEPARATION
WITH INTERSTAGE SEPARATION
○ ACTUAL RX TEMP.
△ CORRELATED TEMP. (1° POUR/1° RX TEMP.)