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(54) **Process for the conversion of olefinic compounds into high viscosity lubes.**

(57) A two-stage process is provided whereby in the first stage light olefins are converted over a ZSM-5 type catalyst to gasoline and distillate liquids which are then converted in a second catalytic stage under milder conditions of temperature and/or pressure over substantially the same or a different ZSM-5 type catalyst to yield lube range products having superior viscosity index properties.

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# PROCESS FOR THE CONVERSION OF OLEFINIC COMPOUNDS INTO HIGH VISCOSITY LUBES

This invention relates to a two-stage process for the conversion of light olefins into high VI lubes or lubricating oils. In the first stage, light olefins are oligomerized to gasoline and distillate range products which are then further converted into lubes in a second stage.

It has long been known to contact various hydrocarbon, e.g., olefinic fractions with crystalline aluminosilicate zeolites for a wide variety of reactions. U.S. Patent No. 3,760,024 is concerned with the conversion of hydrocarbons consisting essentially of $C_2$-$C_4$ paraffins, olefins and mixtures thereof wherein the crystalline aluminosilicate utilized therein is of the ZSM-5 type. U.S. Patent No. 4,150,062 relates to the processing of light olefins of from 2 to 4 carbon atoms to products comprising high octane gasoline components which comprises contacting said olefin feedstock with a ZSM-5 type catalyst. U.S. Patent No. 4,227,992 relates to the conversion of $C_3$ and higher olefins into products comprising both gasoline and fuel oils from a mixture of ethylene and said olefins. Thus, the broad concept of contacting an olefinic charge stock with zeolites is known in the art.

Additionally, U.S. Patent No. 4,021,502 discloses conversion of olefins over ZSM-12 and U.S. Patent No. 3,827,968 discloses a two step aromatization process wherein in the first step an olefin is contacted over a ZSM-5 type zeolite. U.S. Patent No. 4,361,477 discloses a 2-step process wherein a catalytic dewaxer effluent containing lower olefins is stabilized by contacting such effluent with a ZSM-5 type catalyst. However, none of this prior art is directed toward the concept of the use of a dual or two-stage process wherein light olefins are converted over ZSM-5 type catalyst to gasoline and/or distillate liquids which are then converted under milder conditions and to lube range products.

The invention is directed to a process for converting light olfins into high viscosity index lubricating oils. In particular the invention is directed to a two-stage process involving a feedstock containing at least one $C_2$-$C_6$ olefin or a mixture of such olefins. In a first stage, such a feedstock is contacted under conversion conditions with a catalyst comprising a ZSM-5 type zeolite, i.e., a zeolite having a Constraint Index of from about 1 to 12 and a silica to alumina molar ratio of at least about 12. In this first stage the $C_2$-$C_6$ olefins in the feedstock are converted to form a first stage effluent containing gasoline and distillate range hydrocarbons. First stage effluent is thereafter contacted in a second process stage with a catalyst also comprising a ZSM-5 type zeolite, which may be the same or different as the zeolite of the first stage catalyst. Conversion conditions in the second stage include a lower conversion temperature and/or lower conversion pressure than employed in the first stage, thereby producing lubricant range hydrocarbons of improved viscosity index characteristics.

As noted, the catalyst used in both stages of the present process will comprise a zeolite of the ZSM-5 type. ZSM-5 type zeolites, i.e., zeolites of silica/alumina molar ratio greater than 12 and Constraint Index of 1 to 12 are well known. Their use as olefin conversion catalysts has, for example, been described in U.S. Patent 4,227,992. Crystalline zeolites of the type useful in the catalysts of the present invention include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, and ZSM-48, preferably ZSM-5, ZSM-12 and ZSM-23, with ZSM-5 being particularly preferred.

ZSM-5 is described in greater detail in U.S. Patent Nos. 3,702,886 and RE 29,948, which patents provide the X-ray diffraction pattern of the therein disclosed ZSM-5.

ZSM-11 is described in U.S. Patent No. 3,709,979, which discloses in particular the X-ray diffraction pattern of ZSM-11.

ZSM-12 is described in U.S. Patent No. 3,832,449, which discloses in particular the X-ray diffraction pattern of ZSM-12.

ZSM-23 is described in U.S. Patent No. 4,076,842, which discloses in particular the X-ray diffraction pattern of ZSM-23.

ZSM-35 is described in U.S. Patent No. 4,016,245, which discloses in particular the X-ray diffraction pattern of ZSM-35.

ZSM-38 is described in U.S. Patent No. 4,046,859, which discloses in particular the X-ray diffraction pattern of ZSM-38.

ZSM-48 is described in U.S. Patent No. 4,375,573 and European Patent Publication EP-A-0015132, which disclose in particular the X-ray diffraction pattern of ZSM-48.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solutions. They may be activated by heating in an inert atmosphere at 1000°F (538°C) for 1 hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F (538°C) in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about 1000°F (538°C) for from about 15 minutes to about 24 hours.

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

In practicing the olefin conversion process of the present invention, it may be desirable to incorporate the above-described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides.

The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modifications.

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

Depending upon crystallization conditions, the zeolites used in the catalysts of the present process may be synthesized in varying crystallite size. In the first stage of the present process the zeolite is preferably of the large crystal type. Thus in the first stage, the crystallite diameter of the zeolite is desirably greater than about 0.5 micron and more preferably greater than about 1.0 micron. In the second stage of the present process, it is desirable to employ catalysts containing zeolites of somewhat smaller crystallite size. Zeolites used in the second stage catalysts preferably are of crystallite diameter of 0.5 micron or smaller, preferably 0.1 micron or smaller.

It may be preferred to use a catalyst of controlled acid activity in some process embodiments embraced by the present invention. This controlled acid activity of the catalyst is attainable in any of several ways or a combination of these. A preferred method to reduce catalyst activity is to use a zeolite of high silica to alumina mole ratio, i.e., above 200, preferably above 500. Very high dilution with an inert matrix is also effective. For example, compositions of a more active form of zeolite ZSM-5 with alumina at a ratio of 5 parts of zeolite with 95 parts of the inert matrix provide a suitable catalyst as described in U.S. Patent No. 4,152,363.

Activity of the zeolite catalysts used herein may also be reduced by thermal treatment with steam at high temperature as described in U.S. Patents Nos. 3,965,209 and 4,106,218. Another method of reducing activity is to provide basic cations such as sodium at a significant proportion of the cationic sites of the zeolite. That technique is described in U.S. Patent No. 3,899,544.

As noted, conversion conditions employed in the process of the present invention are important. Such conditions as conversion temperature and pressure and to some extent space velocity, etc. can determine the nature and yield of the products of the process. Conversion conditions in the first stage of the present process will generally include a conversion temperature of 500°F (260°C) or higher. Preferably conversion temperature in the first stage ranges between 500°F and 800°F (260°C and 427°C), more preferably between 550°F and 750°F (288°C and 399°C). Conversion pressure in the first stage can range from about atmospheric (101 kPa) up to about 2000 psig (13891 kPa) and is more preferably greater than atmospheric (101 kPa), i.e. from greater than atmospheric (101 kPa) to about 650 psig (4583 kPa). The liquid hourly space velocity in the first stage can range from about 1.0 $hr^{-1}$ to about 20.0 $hr^{-1}$, preferably from about 2 $hr^{-1}$ to about 20 $hr^{-1}$.

The conversion conditons under which the second stage of the present process is carried out are generally milder in terms of temperature and pressure than conditions in the first process stage. Temperature in the second stage can, for example, range from about 200°F to 500°F (93°C to 260°C), more preferably from about 300°F to 450°F (149°C to 232°C). Conversion pressure in the second stage is preferably less than that of the first stage and can advantageously range from about atmospheric (101 kPa) to about 650 psig (4583 kPa). The liquid hourly space velocity in the second stage is advantageously less than 1.

The conversion of the light olefin feedstock will generally be carried out in the vapor-phase by contact in the reaction zones, using, for example, a fixed bed of catalyst composition under effective conversion conditions. The process stages may be conducted in either a batch or continuous flow reaction or batch in one stage and continuous flow in the other. Since contact time of reactants with catalyst will generally be much longer in the second process stage than in the first, it is frequently suitable to run the first process stage as a continuous flow reaction and the second process stage as a batch reaction.

The feedstock for the present two-stage process essentially comprises olefins of from 2 to 6 carbon atoms, such as, for example, mixtures of the $C_2$ and $C_3$ olefins, propylene and butylene. The feedstock may be comprised of a single olefin or a mixture of different olefins, preferably with a minimum of non $C_2$ - $C_6$ olefinic material. The feedstock can and frequently will contain non-olefinic diluents such as $C_1$-$C_4$ paraffins and hydrogen sulfide.

The following specific examples will serve to illustrate the process of the present invention without unduly limiting same.

The catalysts used in the specific examples were prepared by techniques known in the art and can be prepared by any convenient technique.

## EXAMPLE 1

A distillate of boiling point 280-580°F (138°C-304°C), was formed in 98 percent yield from a $C_3$-$C_4$ charge stock containing 62 percent olefins at 500°F (260°C), 1500 psig (10443 kPa), 1 liquid hourly space velocity with gasoline recycle, and 65 percent conversion. In addition, a 2 percent yield of 98.6 viscosity index lube was produced. The catalyst used in this first stage was a large crystal size HZSM-5 zeolite having a particle size greater than about 0.5 micron.

In the second stage 100 grams of said olefinic distillate were then heated in an autoclave at 210°C for 48 hours with 10 g of a small crystal HZSM-5 catalyst having a particle size of less than about 0.5 micron.

The yield of $600°F^+$ ($316°C^+$) lube product was 40 percent, and the viscosity index was 100.

### EXAMPLE 2

100 grams of unhydrotreated distillate, prepared in similar manner to that of stage 1 in Example 1, containing 8 percent $600°F^+$ ($316°C^+$) material was reacted with 10 g of the small crystal HZSM-5 at 210°C for 72 hours. The yield of $600°F^+$ ($316°C^+$) lube was 57 percent and the viscosity index was 81-83. Furthermore, the yield of $750°F^+$ ($400°C^+$) lube was 30 percent, substantially higher than normally observed.

### EXAMPLE 3

100 g of distillate prepared in similar manner to stage 1 in Example 1, was reacted with 3.8 g of HZSM-12 for 7 hours at 240°C, a $600°F^+$ ($316°C^+$) lube yield of 34 percent was obtained. It had a viscosity index of 87-92.

### EXAMPLE 4

Reaction of 100 g of distillate described in Example 2 with 4.8 g of HZSM-23 ($Si/Al_2$ -320) at 240°C for 24 hours, resulted in a 18 percent yield of $600°F^+$ ($316°C^+$) lube with a viscosity index of 113.

From the above examples it is clear that light olefins can be efficiently converted to high viscosity index lubestock having superior properties in improved yields using the two stage process of the present invention.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

CLAIMS

1. A two-stage catalytic process for the conversion of olefinic components in a feedstock containing at least one $C_2$-$C_6$ olefin or mixtures thereof into high viscosity index lubricating oils, said process comprising:

A) contacting said feedstock in a first stage under conversion conditions with a catalyst comprising a crystalline zeolite characterized by a Constraint Index of 1 to 12 and a silica to alumina molar ratio of at least 12, to thereby convert said $C_2$-$C_6$ olefins and form an effluent comprising gasoline and distillate range hydrocarbons; and thereafter

B) contacting said first stage effluent in a second stage with a catalyst comprising a crystalline zeolite characterized by a Constraint Index of 1 to 12 and a silica to alumina molar ratio of at least 12 under conversion conditions of lower temperature and/or pressure than employed in said first stage, to thereby form a product comprising lubricant range hydrocarbons of improved viscosity index characteristics.

2. A process according to Claim 1 wherein

A) the conversion temperature in said first stage is 260°C or higher;

B) the conversion temperature in said second stage is less than 260°C; and

C) the conversion pressure in said second stage is less than the conversion pressure in said first stage.

3. A process according to Claim 1 or Claim 2 wherein the conversion pressure in said first stage is greater than 101 kPa.

4. A process according to any of Claims 1 to 3 wherein the zeolite used in the first stage has a crystallite size of greater than 0.5 micron and wherein the zeolite used in the second stage has a crystallite size of 0.5 micron or smaller.

5. A process according to any of Claims 1 to 4 wherein the zeolites used in the first and second stages are of the same crystal structure.

6. A process according to any of Claims 1 to 4 wherein the zeolites used in the first and second stages are of different crystal structures.

7. A process according to any of Claims 1 to 6 wherein the zeolite employed is selected from ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, or ZSM-48.

8. A process according to any of Claims 1 to 7 wherein said feedstock comprises a mixture of $C_3$ and $C_4$ olefins.

9. A process according to any of Claims 1 to 8 wherein said feedstock also comprises $C_1$ to $C_4$ paraffins in addition to olefins.

10. A process according to any of Claims 1 to 9 wherein said first stage is operated as a continuous flow reaction and said second stage is operated as a batch reaction.