

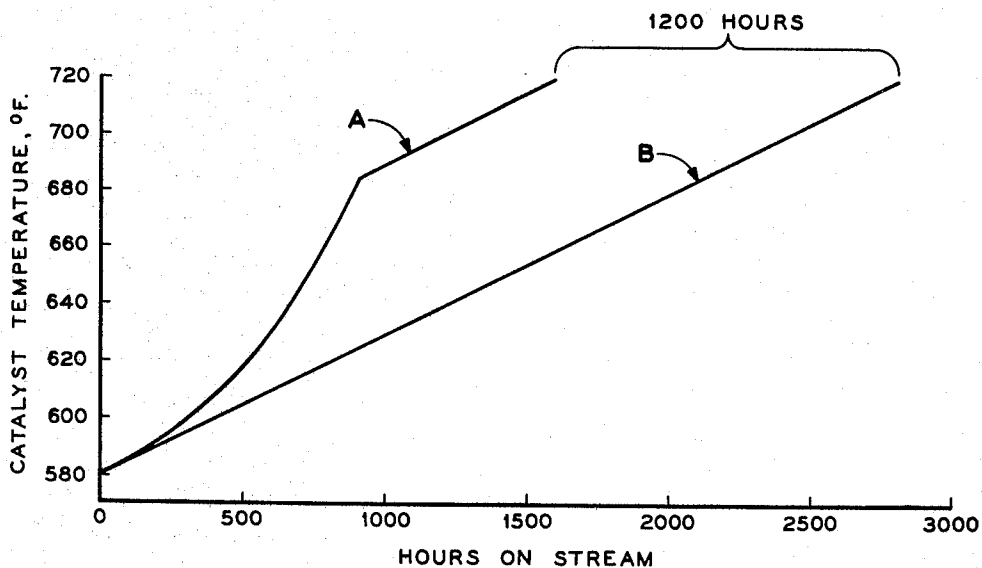
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MULTI-STAGE HYDROFINING-HYDROCRACKING PROCESS EMPLOYING  
AN INTERMEDIATE TREATING OPERATION

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**MULTI-STAGE HYDROFINING-HYDROCRACKING  
PROCESS EMPLOYING AN INTERMEDIATE  
TREATING OPERATION**

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This invention relates to a process for the catalytic conversion of hydrocarbon distillates and, more particularly, to a process involving the sequential hydrofining, intermediate treating and hydrocracking of such distillates to lower boiling products.

As is well known to those skilled in the petroleum refining art, hydrocracking is a reaction wherein mixtures of hydrocarbons are converted to lower boiling products in the presence of added hydrogen and a catalyst at elevated temperatures and pressures. One of the major lines of development that has occurred in the hydrocracking art has been the employment of catalysts comprising acidic supports having a hydrogenating component disposed thereon. In the earlier stages of the development, temperatures on the order of 800° to 1100° F. and pressures in excess of 3,000 p.s.i.g. were characteristic of the process. More recently it was found that naturally occurring petroleum constituents, such as sulfur and nitrogen containing compounds, adversely affected both the hydrogenating component and the acid support of the catalyst and that if such undesirable compounds were removed, as by hydrofining, lower temperatures and pressures and longer catalyst life were realized. This result was desirable since it allowed a considerable reduction in high temperature and pressure equipment, and the desired liquid products were at a maximum due to the inherent reduction in coke and light gas production at the lower temperatures and pressures.

It has now been found that further improvements, particularly in the extension of effective catalyst life in relatively low temperature hydrocracking reactions, can be realized by incorporating a specific treating operation between the initial hydrofining and the final hydrocracking operations.

According to the present invention, a normally liquid distillate feed fraction, along with added hydrogen is contacted in a first conversion (hydrofining) zone with a sulfur-resistant hydrogenation catalyst under hydrogenation conditions. The effluent from the zone is then stripped of any ammonia present, and at least a portion of the normally liquid remainder of the effluent is then passed into an intermediate treating zone for contact therein with a siliceous cracking catalyst at temperatures below that at which appreciable cracking occurs, i.e., below about 650° F. At least the major portion of the effluent of the intermediate zone, along with added hydrogen, is passed into a second conversion (hydrocracking) zone for contact therein with a catalyst comprising a hydrogenating-dehydrogenating component dispersed on an active acid cracking catalyst support at pressures of at least 400 p.s.i.g. and temperature of from about 300° to 800° F. In the latter zone there are consumed at least 750 s.c.f. of hydrogen per barrel of intermediate zone

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effluent converted in the hydrocracking zone to products boiling below the initial boiling point of the intermediate zone effluent.

The feed stocks employed in the subject process are those petroleum distillates boiling in the range of from about 200° to 850° F. and preferably, in the range of from about 325° to 650° F. In general, suitable feeds are those normally defined as naphthas, kerosene distillates and, especially preferred, those fractions known as heavy cracked and straight-run naphthas and cycle oils. The latter include straight-run and cracked gas oils and recycle oils boiling below about 650° F. The feeds may be of straight-run origin as obtained from petroleum, or they may be derived from various process operations and, in particular, from thermal or catalytic cracking of stocks obtained from petroleum, gilsonite, shale, coal tar, or other similar sources.

As noted above, the feed stock is first subjected to a hydrofining operation. This entails contacting the feed at temperatures of from about 600° to 900° F., pressures of at least 300 p.s.i.g., liquid hourly space velocities (LHSV) of from about 0.3 to 5, along with at least 500 s.c.f. of hydrogen per barrel of feed, with a sulfur-resistant hydrogenation catalyst. Any of the known sulfactive hydrogenation catalysts may be used in the present process. The preferred catalysts have as their main active ingredient one or more oxides or sulfides of the transition metals, such as cobalt, molybdenum, nickel, and tungsten. These various materials may be used in a variety of combinations with or without such stabilizers and promoters as the oxides and carbonates of K, Ag, Be, Mg, Ca, Sr, Ba, Ce, Bi, Cr, Th, Si, Al and Zr. These various catalysts may be employed per se or in combination with various conventional supporting materials. Examples of the latter are charcoal, fuller's earth, kieselguhr, silica gel, alumina, bauxite, and magnesia. While any of the noted classes of conventional sulfactive hydrogenation catalysts may be employed, it has been found that a molybdenum oxide catalyst promoted by a minor amount of cobalt oxide and supported upon an activated alumina or a tungsten sulfide on activated alumina are particularly preferred catalysts for this hydrofining operation. The catalyst may be in the form of fragments or formed pieces such as pellets and cast pieces of any suitable form or shape.

Following hydrofining, the effluent from this zone is treated so as to remove any ammonia, and preferably any hydrogen sulfide present, therefrom. A preferred removal method involves injecting water into the total effluent from the catalytic reactor and passing the resulting mixture into a high pressure separator operating under such conditions of temperature and pressure (for example, 100° F. and 950 p.s.i.g.) that a gaseous overhead is removed that is predominantly hydrogen but which also normally contains some hydrogen sulfide and light hydrocarbons. This overhead can be recycled to the first conversion zone. Within the separator are formed two phases, an upper hydrocarbon phase and a lower aqueous phase. The latter, containing essentially all of the ammonia present (and some of the H<sub>2</sub>S if present) in the effluent (in the form of ammonium sulfide), is removed from the system. The hydrocarbon layer is then passed into a stripper or into a distillation column wherein any

traces of hydrogen sulfide, ammonia and water are removed overhead.

At least a portion, and preferably all of the remaining hydrofiner effluent, is passed into an intermediate zone for contact therein with a siliceous cracking catalyst. In the present process, this catalyst is not employed as a cracking catalyst inasmuch as the contact between the normally liquid components of the hydrofiner effluent and the siliceous material are conducted at temperatures below those at which any appreciable cracking of these normally liquid components occurs. Substantial cracking should in fact be avoided in order that the siliceous material not be fouled and rendered inactive. Treating the liquid hydrofiner effluent with the cracking catalyst modifies the properties of this stream in a manner not completely understood with the result that much longer on-stream periods are realized when the treated liquid is passed into the subsequently described second conversion zone. Among the treating materials, herein generically defined as siliceous cracking catalysts, that have been found effective are those conventional catalytic cracking catalysts such as silica-magnesia, silica-boria, or silica-alumina-zirconia composites as well as acid-treated or activated natural aluminosilicates. If desired, the siliceous material may contain various halides, preferably fluorides. The preferred siliceous material is a silica-alumina composite and, especially preferred, a synthetically prepared composite of silica and alumina containing from about 60 to 99 weight percent of the silica component and having a surface area in excess of 200 m.<sup>2</sup>/gm. The siliceous cracking catalysts can be employed in the intermediate zone in the form of powder, microspheres, spheres and other preformed shapes, with the latter two forms preferred. Prior to use in the intermediate zone, it has been found advantageous to dry the siliceous material by heating to a temperature in the range of from about 300° to 650° F.

As noted, the maximum contact temperature within the intermediate zone is below the temperature wherein appreciable catalytic cracking occurs, i.e., below about 650° F. Contact at ambient temperatures has been found to be eminently satisfactory. The effective capacity of active siliceous cracking catalysts employed in the intermediate zone can vary over relatively wide limits but, will, in general, fall within the range of from about 100 to 5,000 volumes of feed per volume of catalyst. When its capacity to remove the undesirable components in the hydrofiner effluent is exhausted, as evidenced by a comparatively rapid increase in fouling rate of the catalyst employed in the second conversion zone (described below), the catalyst material can be regenerated for reuse in the same manner as used in conventional catalytic cracking processes, or can be entirely replaced with fresh siliceous material.

At least a major portion, and preferably all, of the effluent from the intermediate zone is passed, along with added hydrogen, into the second conversion zone wherein it is contacted with a catalyst comprising a hydrogenating-dehydrogenating component dispersed on an active acid cracking support under elevated temperatures and pressures.

The catalyst used in the second conversion zone employs a catalyst support of the same type as the contact material in the aforescribed intermediate zone. Thus, it can be described as a siliceous cracking catalyst and includes materials such as silica-alumina, silica-magnesia, etc., previously noted. Likewise, the preferred catalyst support is comprised of synthetically prepared composites of silica and alumina having a silica content of from about 60 to 99 weight percent.

The hydrogenating-dehydrogenating component of the catalyst can be selected from any one or more of the various group VI and group VIII metals, as well as the oxides and sulfides thereof, representative materials being the oxides and sulfides of molybdenum, tungsten, chro-

mium, and the like, and/or such metals as nickel or cobalt and the various oxides and sulfides thereof. Also suitable are certain group I (B) or group II (B) metals, such as copper or cadmium and their oxides and sulfides. If desired, more than one hydrogenating component may be present, e.g., composites of two or more of the oxides and/or sulfides of molybdenum, cobalt, nickel, copper, chromium and zinc.

Depending on the activity thereof, the amount of the hydrogenating-dehydrogenating components may be varied within relatively wide limits of from about 0.1 to 35%, based on the weight of the entire catalyst composition. Within these limits, the amount of said component present should be sufficient to provide a reasonable catalyst on-stream period at any desired conversion levels. Particularly good results from the standpoint of selectivity and the ability to withstand repeated regeneration with relatively minor decrease in activity are obtained with catalysts composed of from 1 to 35% nickel sulfide or cobalt sulfide deposited on the aforementioned synthetically prepared silica-alumina and composites.

The effluent, or portion thereof, from the intermediate zone along with at least 1,500 standard cubic feet (s.c.f.) of hydrogen per barrel of said effluent, contacts the above-described catalyst in the second conversion zone at an LHSV of from about 0.2 to 5.0 and at a temperature of from about 300° to about 800° F. In preferred practice, the temperature at which the conversion is initiated in a given on-stream period should be as low as possible (within the noted range and commensurate with the maintenance of the desired per-pass conversion levels) since the lower the starting temperature, the longer will be the duration of the on-stream period. The pressure employed in the second conversion zone is in excess of 400 p.s.i.g. and can range upwardly to as high as 5,000 p.s.i.g., with a preferred pressure range being from about 600 to 2,500 p.s.i.g.

The reactions in both the first and second conversion zones can be conducted by employing fixed or moving catalyst beds, fluid catalysts or slurry catalyst systems with fixed bed operations preferred. The present invention, with its sequence of processing steps, will in many cases reduce the fouling rate of the second conversion zone catalyst to the point where it is possible to extend on-stream times over such long periods that it becomes uneconomical to provide catalyst regeneration facilities. However, catalyst regeneration can be done, either in situ or in separate regeneration zones by conventional regeneration techniques.

The effluent from the second conversion zone can, of course, be separated in many ways. Preferably, the effluent is passed into a high pressure separator wherein a hydrogen-rich recycle stream is flashed off and returned to the conversion zone. The hydrogen-free effluent is then preferably reduced to about atmospheric pressure and subjected to fractional distillation in one or more columns for recovering of the desired fractions. Thus, separation can be made of the products boiling below the initial point of the feed to the second conversion zone into a variety of products, such as gasoline blending stocks and other valuable products, and all or a portion of the remainder recycled to said zone.

As an example of the efficacy of the present process, extensive experimental data have been correlated to show what can be expected in the way of increased catalyst life when the process of the present invention is compared with a process not incorporating the intermediate contacting siliceous cracking catalyst treatment but essentially identical in all other processing steps and conditions. For comparative purposes only, the following Example 1 shows the results without the intermediate zone treating operation and Example 2 is illustrative of the present process. In both examples, results were predicated on employing a catalytic cycle oil feedstock having the following inspections.

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|                                   |         |
|-----------------------------------|---------|
| Gravity, ° API                    | 25.5    |
| Aniline point, ° F.               | 75      |
| Composition, percent:             |         |
| Aromatics                         | 58      |
| Olefins                           | 10      |
| Paraffins and naphthenes          | 32      |
| ASTM distillation No. D158, ° F.: |         |
| Start/5%                          | 410/451 |
| 10%/30%                           | 459/472 |
| 50%                               | 480     |
| 70%/90%                           | 492/511 |
| 95%/end point                     | 523/549 |
| Sulfur, wt. percent               | 0.98    |
| Nitrogen, p.p.m.                  | 900     |

In both examples, the noted feedstock, along with 6,000 s.c.f. of hydrogen per barrel of feed, is contacted at an LHSV of 0.5, a maximum catalyst temperature of 720° F. and a pressure of 800 p.s.i.g. with a sulfactive hydrogenation catalyst comprising cobalt (3.7 wt. percent as CoO) and Mo (10.5 wt. percent as MoO<sub>3</sub>) on alumina. The effluent from the hydrofining zone is water washed and stripped of ammonia and hydrogen sulfide (as described hereinbefore) and recovered. Inspection of the effluent is as follows.

|                                   |         |
|-----------------------------------|---------|
| Gravity, ° API                    | 29.5    |
| Aniline point, ° F.               | 85.4    |
| Composition, percent:             |         |
| Aromatics                         | 55      |
| Olefins                           | 0       |
| Paraffins and naphthenes          | 45      |
| ASTM distillation No. D158, ° F.: |         |
| Start/5%                          | 379/426 |
| 10%/30%                           | 436/456 |
| 50%                               | 470     |
| 70%/90%                           | 483/506 |
| 95%/end point                     | 518/549 |
| Sulfur, wt. percent               | 0.016   |
| Nitrogen, p.p.m.                  | 0.5     |

#### EXAMPLE 1

A portion of the noted hydrofiner effluent is then passed, along with 12,000 s.c.f. of hydrogen per barrel of effluent, into a second conversion zone and contacted with a fixed bed of catalyst at an initial temperature of 580° F. and a pressure of 1,200 p.s.i.g. The catalyst employed is one wherein 2.5 weight percent (of the entire catalyst) nickel, in the form of nickel sulfide, is disposed on an active synthetic silica-alumina composite cracking catalyst containing about 90 weight percent silica and about 10 weight percent alumina. The reaction is initiated at 580° F. at a per-pass conversion level of about 60 volume percent to products boiling below 360° F. This conversion is maintained at a constant level by progressively increasing the reaction temperature to allow for reduced catalyst activity attributable to fouling of the catalyst. In this example, the hydrocracking reaction is halted at 720° F.

During the reaction, an exemplary sample (at a 600° F. catalyst temperature) is taken and its inspection and yields are shown in Table I below.

The catalyst on-stream period, from the initial temperature of 580° F. to the final temperature of 720° F., is 1,600 hours. Hydrogen consumption is about 1,000 s.c.f. of hydrogen per barrel of feed converted to products boiling below 360° F.

#### EXAMPLE 2

A portion of the noted hydrofiner effluent is passed at an LHSV of 0.8, a temperature of 140° F. and at atmospheric pressure into contact with a siliceous cracking catalyst. The latter is a synthetic silica-alumina composite (about 90% silica and 10% alumina) having a surface area in excess of 200 m.<sup>2</sup>/gm. (480 m.<sup>2</sup>/gm.) The en-

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tire, treated effluent is then subjected to an essentially identical reaction as that disclosed in Example 1. However, in this example, because of the treatment of the hydrofiner effluent with the siliceous cracking catalyst, the on-stream catalyst period in the temperature range 580° to 720° F. is 2,800 hours. Hydrogen consumption is about 1,000 s.c.f./barrel of feed converted to products boiling below 360° F.

As in Example 1, a sample is taken at 600° F. and its inspection and yields are shown in Table I.

Table I

| Designation                          | Sample from Example 1     |          | Sample from Example 2     |          |
|--------------------------------------|---------------------------|----------|---------------------------|----------|
|                                      | C <sub>5</sub> to 360° F. | 360° F.+ | C <sub>5</sub> to 360° F. | 360° F.+ |
| Gravity, ° API                       | 55.7                      | 38.6     | 55.4                      | 38.0     |
| Aniline Point                        | 98.4                      | 125.0    | 91.8                      | 116.0    |
| Composition, percent:                |                           |          |                           |          |
| Aromatics                            | 22                        | 29       | 25                        | 35       |
| Olefins                              | 0                         | 0        | 0                         | 0        |
| Paraffins and naphthenes             | 78                        | 71       | 75                        | 65       |
| ASTM Distillation No., ° F.          | D86                       | D158     | D86                       | D158     |
| Start/5%                             | 117/150                   | 378/397  | 123/150                   | 373/397  |
| 10%/30%                              | 164/204                   | 400/409  | 162/223                   | 400/409  |
| 50%                                  | 245                       | 423      | 246                       | 421      |
| 70%/90%                              | 279/310                   | 443/479  | 276/309                   | 440/477  |
| 95%/End Point                        | 321/342                   | 494/523  | 319/337                   | 492/529  |
| Yields, based on feed volume:        |                           |          |                           |          |
| Vol. percent C <sub>5</sub> +        | 104.2                     |          | 104.9                     |          |
| C <sub>5</sub> to 360° F.            | 61.9                      |          | 64.1                      |          |
| 360° F.+                             | 42.3                      |          | 40.8                      |          |
| Wt. percent C <sub>4</sub> -         | 8.35                      |          | 8.45                      |          |
| Vol. percent Converted below 360° F. | 60                        |          | 60                        |          |

The accompanying FIGURE shows typical results of the constant per-pass conversion of the hydrocracking reactions of Examples 1 and 2. Curve A shows that when the feed stock is hydrofined only, prior to conversion (Example 1), the total on-stream period (or catalyst life prior to regeneration or replacement) from the initial temperature of 580° F. to the final catalyst temperature of 720° F. is 1,600 hours. Curve B shows that when a feed stock is both hydrofined and treated with a siliceous cracking catalyst prior to conversion according to the present invention (Example 2), all other conditions being essentially identical, that the catalyst on-stream period within the same initial and final reaction temperature can be extended to 2,800 hours, an increase of 1,200 hours or 75 percent. The tremendous advantages of this extension are readily apparent.

With respect to the designations of boiling ranges and feed and product distillation points, it must be understood that a 10 percent by volume tolerance is to be permitted in order to more closely approximate the practical limitations of refinery distillation equipment and practices. Thus, the designation of the preferred feedstock boiling range as being from about 325° to 650° F. resolves itself to those feeds wherein at least the 10 percent and 90 percent distillation points fall within the stated range.

We claim:

1. In a hydrocracking process wherein a normally liquid, nitrogen-containing feed is substantially denitrified by contact in a hydrofining zone in the presence of hydrogen with a sulfur-resistant hydrogenation catalyst having at least one hydrogenation component selected from the group consisting of cobalt oxide, cobalt sulfide, nickel oxide, nickel sulfide, molybdenum oxide, molybdenum sulfide, tungsten oxide and tungsten sulfide, said hydrogenation component when supported being supported on a material selected from the group consisting of charcoal, fuller's earth, kieselguhr, silica gel, alumina, activated alumina, bauxite and magnesia, at temperatures from 600° to 900° F., a space velocity of 0.3 to 5.0 and pressures of at least 300 p.s.i.g., essentially all of the resulting ammonia is removed from the effluent from said zone, and at least a substantial portion of the de-ammoniated effluent is hy-

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drocracked in a hydrocracking zone in the presence of at least 1500 s.c.f. of hydrogen per barrel of feed to said hydrocracking zone over a hydrocracking catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of metals of group VI and group VIII, compounds of metals of group VI and group VIII, copper, copper oxide, copper sulfide, cadmium, cadmium oxide and cadmium sulfide, dispersed on an active acid cracking support selected from the group consisting of silica-magnesia, silica-boria, silica-alumina, silica-alumina-zirconia and activated natural aluminosilicates, at temperatures from 300° to 800° F. and pressures of at least 400 p.s.i.g. to produce synthetic hydrocracked products boiling below the initial boiling point of the feed to said hydrocracking zone, with a net hydrogen consumption in said hydrocracking zone of at least 750 s.c.f. of hydrogen per barrel of feed to said hydrocracking zone converted to said synthetic products, the improvement which comprises extending the life of said hydrocracking catalyst by passing said substantial portion of said deammoniated effluent from said hydrofining zone through a fixed bed of siliceous cracking catalyst prior to hydro-

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cracking, the catalyst in said fixed bed being selected from the group consisting of silica-magnesia, silica-boria, silica-alumina, silica-alumina-zirconia and activated natural aluminosilicates, said fixed bed of catalyst being maintained at temperatures below those at which substantial cracking occurs, and using at least the major portion of the effluent from said fixed bed as the feed to said hydrocracking zone.

2. A process as in claim 1, wherein the process is operated with 100 to 5000 volumes of feed per volume of catalyst.

3. A process as in claim 1, wherein said catalyst in said fixed bed is silica-alumina.

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