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HYDROCONVERSION OF HYDROCARBONS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocracking catalysts which have been partially deactivated by polycyclic aromatic hydrocarbons present in the charge stock are reactivated by introducing a feed having a lower polycyclic aromatic content.

This invention relates to the conversion of hydrocarbons. More particularly it is concerned with the conversion of hydrocarbons in the presence of hydrogen to lighter hydrocarbons. In its most specific aspects it is concerned with the conversion of hydrocarbon feed stocks boiling approximately in the kerosine-gas oil range in the presence of hydrogen and a cracking catalyst into hydrocarbons boiling in the naphtha-kerosine range.

Hydrocracking, previously known as destructive hydrogenation, has come into prominence recently in the refining of petroleum hydrocarbons. In the hydrocracking process various reactions take place such as the cleaving of long straight carbon chains, the saturation of aromatic rings with subsequent rupture of cycloparaffinic structure, the isomerization of paraffinic chains into isoparaffinic chains and the dealkylation of alkyl aromatics. Ordinarily, the charge to a hydrocracking unit will comprise a hydrocarbon fraction boiling above the boiling range of the desired product. For example, if a motor fuel is desired, the charge to the hydrocracking unit will generally have an initial boiling point of about 400–450° F. whereas if the desired products are motor fuels and jet fuels, then the charge to the hydrocracking unit will generally have an initial boiling point of about 550–600° F. Advantageously, charge stocks such as straight run kerosine and gas oil stocks from catalytic cracking, vacuum gas oil and light distillates obtained from coal and shale may be charged to the hydrocracking unit. Ordinarily, product boiling above the desired end point is recycled to the hydrocracking unit.

Hydrocracking is preferably carried out in the presence of a catalyst which contains two components, a hydrogenating component and a cracking component. Numerous hydrogenating components such as Group VIII metals, for example platinum, palladium and nickel and the oxides and sulfides of molybdenum, nickel, copper, tungsten, and cobalt, and the like or mixtures thereof, have been disclosed in the prior art. The hydrogenating component is supported on a cracking base which advantageously is acidic in nature. Such bases comprise refractory oxides of two or more elements of Groups II, III, and IV of the Periodic Table. Suitable cracking supports include silica-magnesia, silica-alumina, silica-alumina-zirconia and the like. Preferably the cracking support is a crystalline aluminosilicate of the natural or synthetic zeolite type having uniform pore openings of 6–14 angstrom units.

While these catalysts are eminently suitable for the hydrocracking of various petroleum charge stocks, they are subject to a loss of activity as the reaction proceeds. As a measure of the catalyst activity it is customary to institute a hydrocracking reaction and to conduct the process at certain conditions of temperature, pressure, space velocity and hydrogen circulation rate to maintain a pre-

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determined conversion of the charge into material having a particular end boiling point. As the reaction is continued, the catalyst is subject to loss in activity and to compensate for the reduced activity the temperature in the catalytic zone is increased to maintain a constant conversion rate. This increase in temperature necessary to maintain the desired amount of conversion is called the aging rate. For convenience, the aging rate is measured in °F./100 hours, that is, the number of °F. the catalyst bed temperature must be increased per 100 hours to maintain a constant rate of conversion.

In commercial operation, it has been found uneconomical to extend the on-stream production step beyond a catalyst bed temperature of about 775° F. At this stage the aging rate of the catalyst becomes so rapid that it has been deemed advisable to terminate the production step and to regenerate the catalyst. The inactivity of the catalyst when this temperature has been reached is usually due either to poisoning by the nitrogen in the charge stock or to the deposition of coke or carbon on the catalyst or a combination of both. In any event, the catalyst is regenerated by oxidative combustion.

Oxidative regeneration is a costly procedure in that first it requires the termination of the flow of reactants to the reaction zone and purging of combustible materials from the system by sweeping with an inert gas. Oxygen diluted to a very low concentration by an inert gas such as nitrogen is then introduced into the reactor and the temperature is very carefully controlled to prevent overheating of the catalyst by the combustion of the deposited coke. When all of the coke has been removed by oxidation, the system is then again swept by an inert gas to remove all of the oxygen and when this has been effected the production step is reinstituted. This procedure is not only costly in itself, but also in the fact that it requires that the unit be shut down in some instances for as much as one week.

By the process of the present invention, the aging rate of a partially deactivated catalyst can be reduced and its conversion can be improved by charging to the catalyst a hydrocarbon feed stock of reduced polycyclic aromatic content. It has now been found that an increase in the polycyclic aromatic content of the charge results in a corresponding increase in the aging rate of the catalyst and that a decrease in the polycyclic aromatic content of the charge not only results in a decrease in the aging rate but also restores the catalyst to its initial conversion activity prior to the introduction of the charge stock of higher polycyclic aromatic content. This latter is evidenced by the fact that the same conversion rate can be obtained at a considerably reduced temperature.

The catalysts used in the hydrocracking process of the present invention comprise a hydrogenating component such as a Group VIII metal or metal compound such as platinum, palladium, nickel and the oxides of nickel and cobalt alone or in conjunction with compounds of molybdenum or tungsten. The hydrogenating component is supported on a cracking component comprising a refractory oxide such as alumina, magnesia, silica and the like and mixtures thereof. Particularly suitable cracking components comprise natural or synthetic zeolitic aluminosilicates having uniform pore openings in the 6–14 angstrom unit range, preferably in the 10–14 angstrom unit range and in which the alkali metal ions have been replaced by hydrogen ions or divalent metal ions such as magnesium.

The hydrogen used in the present process may be suitably obtained as a by-product from catalytic reforming, by the electrolysis of water or by the partial combustion of carbonaceous or hydrocarbonaceous material to produce synthesis gas which is then subjected to shift con-

version to produce relatively pure hydrogen. It is not necessary in the present process that the hydrogen be pure. Ordinarily, a hydrogenating gas having only 40 volume percent hydrogen may be satisfactorily used although a gas containing 89-90 volume percent hydrogen is preferred. In this specification and in the appended claims the term "hydrogen" is intended to include dilute or impure hydrogen.

The reaction conditions within the hydrocracking unit generally include a temperature range from about 450-775° F. although a temperature from 500 to about 725-750° F. is preferred. Pressure will range from about 500-10,000 p.s.i.g. or higher although a pressure of from about 1,000 to 3,000 p.s.i.g. is preferred. The hydrogen rate may range from 1,000 to about 20,000 s.c.f.b. (standard cubic feet per barrel) of normally liquid charge. Preferred hydrogen rates are from about 3,000-8,000 s.c.f.b. Preferably the space velocity, that is the volumes of liquid charge per volume of catalyst per hour, will be between 0.5 and 3 although rates ranging from 0.1-10 may be used.

If the charge stock to the hydrocracking unit contains not more than about 2-20 p.p.m. nitrogen it may be charged directly to the hydrocracking unit. Preferably as in the case of higher nitrogen containing stocks, the hydrocarbon feed is first charged to a catalytic denitrogenation zone where it is contacted with a catalyst such as a mixture of oxides of cobalt and molybdenum generally referred to as cobalt molybdate on a support such as magnesia or alumina. Suitable other catalysts comprise the oxides or sulfides or mixtures thereof of metals such as nickel, molybdenum, cobalt, tungsten and the like, for example sulfided nickel tungsten on alumina or a mixture of nickel and molybdenum in either the oxide or the sulfide form on alumina. Satisfactory denitrogenation conditions include a temperature range of 700-900° F., a pressure of 100-5,000 p.s.i.g., a space velocity of 0.1-10, and a hydrogen rate of from 500-10,000 s.c.f.b.

In the two-stage denitrogenation and hydrocracking operation each stage may have its own hydrogen circulation system or the hydrogen may circulate serially through both reaction zones. However, if the hydrogen from the denitrogenation zone is to be used in the hydrocracking zone and the hydrocracking catalyst is sensitive to ammonia, the hydrogen may be subjected to a basic nitrogen removal treatment as for example by washing with dilute acid and the charge to the hydrocracking unit after removal from the denitrogenation zone is advantageously stripped with an inert gas for the removal of nitrogen compounds such as ammonia therefrom. Apparently, the use of molecular nitrogen as a stripping gas, even though it is retained to the extent of 100 p.p.m. in the stripped hydrocracking unit charge stock, exerts no deleterious effect on the nitrogen-sensitive hydrocracking catalyst. The denitrogenation treatment also effectively removes oxygen containing compounds from the charge. If the hydrocracking catalyst is not sensitive to ammonia, the entire effluent from the denitrogenation zone may be sent directly without intermediate treatment to the hydrocracking zone.

The improved process of our invention is particularly applicable to partially deactivated catalyst and serves to delay the time when oxidative regeneration becomes necessary. It also permits the same conversion to be obtained at a lower temperature. The improvement is particularly noticeable when the charge stock has a polycyclic aromatic content of more than about 11 weight percent and when polycyclic aromatic content of the charge is reduced to below about 11 weight percent.

In an example of the invention, a sulfided nickel tungsten on silica alumina catalyst containing 5.9% nickel, 18.6% tungsten, 50.9% silica and 17.3% alumina was used at conditions of 1500 p.s.i.g., 6000 s.c.f. hydrogen per barrel of liquid feed, 1.0 space velocity (volume of

liquid charge per volume of catalyst per hour) and temperature to obtain a 50% conversion of material boiling about 400° F. to material boiling below 400° F. The following fluid catalytic cracking cycle gas oils were used.

	A	B	C
Gravity, ° API	31.6	32.0	34.5
ASTM distillation, ° F. (percent):			
IPB, 5	396-442	388-390	160-258
10-20	480-526	447-497	346-454
30-40	554-580	536-568	516-554
50	606	589	535
60-70	626-646	612-633	614-640
80-90	658-698	656-682	666-695
95, E.P.	720-740	704-727	720-750
Polycyclic aromatics, weight percent	8.0	11.3	14.2
Total aromatics	32.4	32.8	39.6
Total nitrogen, p.p.m.	1.5	0.9	1.1

Charge A was fed at the above conditions for a 280 hour induction period to stabilize the catalyst. Charge B was then fed for 171 hours at which time feed was switched to Charge C. After 53 additional hours Charge A was reinstituted as the feed. The temperatures for 50% conversion to 400° F. material are shown below.

	Charge	Deg., F.	Hours on stream
25	A	618	65
	A	622	79
	A	641	177
	A	645	217
	A	661	280
30	B	657	303
	B	659	327
	B	660	350
	B	661	374
	B	663	400
	B	661	451
35	C	676	480
	C	684	504
40	A	666	539
	A	667	566
	A	666	615
	A	664	641
	A	662	666
	A	665	688
	A	667	716
	A	667	738

These data show that the aging rates after the initial induction period are Charge B, 4.9° F./100 hours; Charge C, 38° F./100 hours; and Charge A, 3.5° F./100 hours. More significant is the fact, that after Charge C had been run for 50 hours, a temperature of 684° F. was required for a 50% conversion yet when Charge A was restored as the feed, a 50% conversion was obtained at 666° F. which, at a 3.5° F. aging rate, is equivalent to extending the life of the catalyst 500 hours.

Obviously, many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method for improving the activity and reducing the aging rate of a hydrocracking catalyst comprising a hydrogenating component and a cracking component which has become partially deactivated in a process for the hydrocracking of a hydrocarbon charge stock containing polycyclic aromatic hydrocarbons which comprises bringing the catalyst into contact under hydrocracking conditions with a hydrocarbon charge stock having a polycyclic aromatic content lower than that of the original hydrocarbon charge stock.

2. The process of claim 1 in which the original charge stock contains less than 5 p.p.m. nitrogen.

3. The process of claim 1 in which the original charge stock is a cycle gas oil obtained from catalytic cracking.

4. The process of claim 1 in which the catalyst comprises nickel.

5. The process of claim 4 in which the catalyst comprises sulfided nickel and tungsten.

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6. The process of claim 1 in which the original charge stock contains more than about 11 weight percent polycyclic aromatic hydrocarbons.

7. The process of claim 1 in which the charge stock of lower polycyclic aromatic content contains less than about 11 weight percent polycyclic aromatic hydrocarbons.

8. The process of claim 1 in which the original charge stock is subjected to a preliminary denitrogenation step.

9. The process of claim 8 in which the entire effluent from the preliminary denitrogenation step is passed to the hydrocracking zone.

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