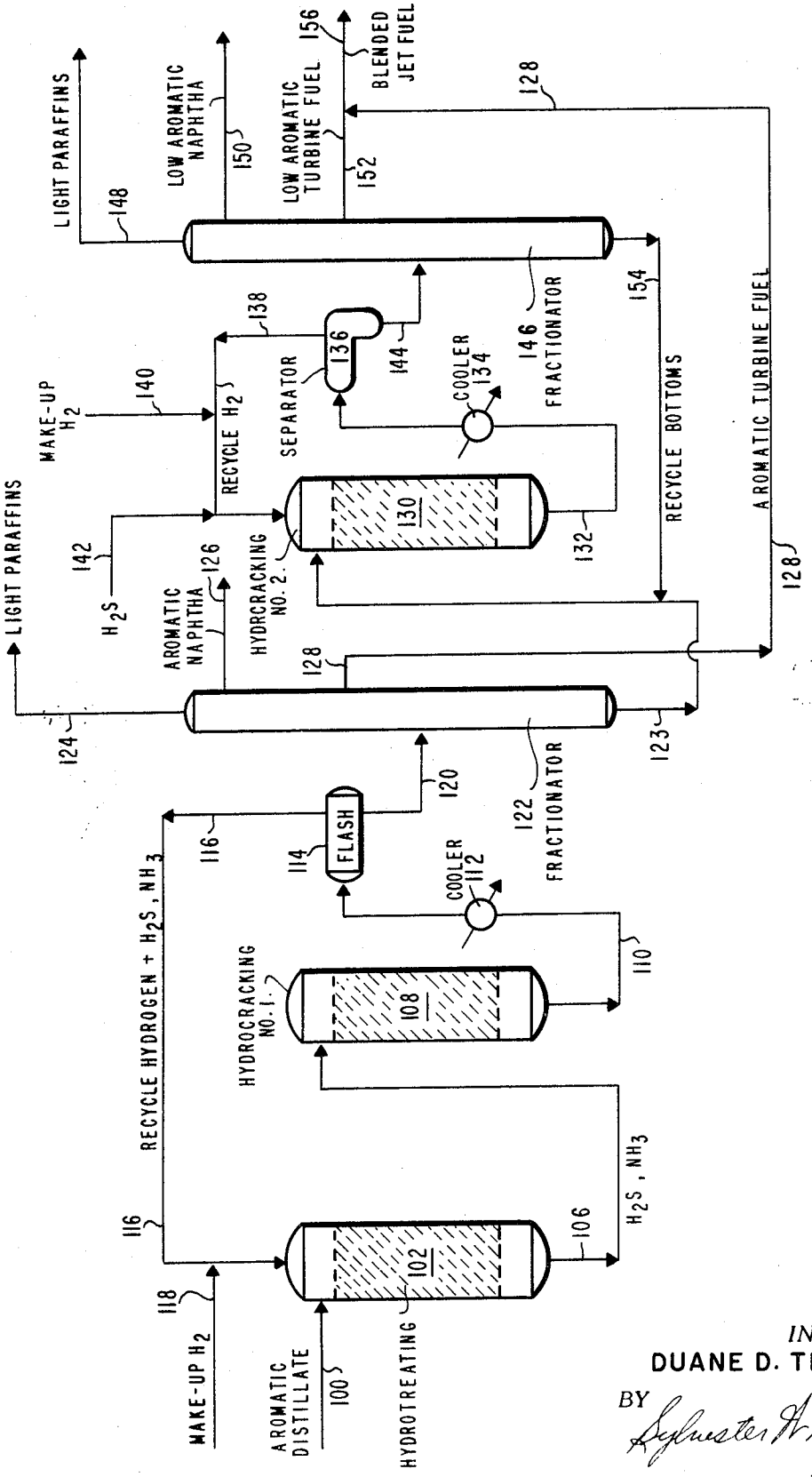
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TWO-STAGE HYDROCRACKING WITH INTERMEDIATE FRACTIONATION

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TWO-STAGE HYDROCRACKING WITH INTERMEDIATE FRACTIONATION

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ABSTRACT OF THE DISCLOSURE

A two-stage hydrocracking process, utilizing palladium on synthetic zeolite catalyst, is carried out with intermediate fractionation between the stages and with hydrogen sulfide and ammonia present in the first stage and hydrogen sulfide present in the second stage so as to obtain a high-aromatic naphtha product and a low-aromatic jet fuel product. Alternatively, the process can be used to obtain segregated streams of a high octane naphtha and a lower octane naphtha.

THE DRAWING

The sole figure is a schematic flow diagram representing the process of the present invention in a preferred mode.

THE SPECIFICATION

The present invention is based upon the discovery that a two-stage hydrocracking process, with two fractionating steps, can be employed in the hydro-cracking of an aromatic hydrocarbon stream to obtain both a high-aromatic naphtha product and a low-aromatic turbine fuel product. The high-aromatic naphtha product is desired in order to obtain motor gasolines of high octane numbers whereas the turbine fuel is desired with a low aromatics content so as to obtained a satisfactory luminosity number and freeze point. By a modification of the present invention, a high-aromatic naphtha is recovered in the first stage while a lower aromatic naphtha, which requires reforming into a motor gasoline blend stock, is obtained as a separate stream from the second stage.

By the present invention, the first stage hydrocracking reaction is carried out in the presence of from 0.2 to 1.0 weight percent H_2S and from 0.02 to 0.2 weight percent of ammonia (based on the liquid feedstock), and at a temperature of 600° F. to 850° F. so as to suppress the hydrogenating function of the hydrocracking catalyst, thereby allowing the aromatics in the naphtha fraction to remain unreacted. By carrying out the second stage reaction in the presence of a treat gas containing from about 10 to about 500 weight p.p.m. hydrogen sulfide, and at a temperature of 500° F. to 750° F., the hydrogenation of the turbine fuel constituents is accomplished while the hydrogenation of aromatics is partly suppressed so as to conserve hydrogen. When the process is employed primarily to produce two naphtha products, the second stage reaction is carried out in the presence of a treat gas containing from 100 weight p.p.m. to 2 weight percent of H_2S.

The hydrocracking reaction in the first stage reactor occurs in the presence of hydrogen sulfide and ammonia which are preferably obtained by the preliminary hydrotreating of the aromatic hydrocarbon stream employed as a feedstock. Hyrodrogen sulfide and ammonia may also be present in the hydrogen-gas stream, since it is desirable to employ a recycle of the unconverted hydrogen after it has been passed through the hydrocracking zone. In the presence of the hydrocracking catalyst, hydrogen sulfide strongly suppresses the saturation of aromatic rings. The ammonia acts as a temporary depressant on

the activity of the hydrocracking catalyst so that a higher reactor temperature is required for a given amount of conversion that if the ammonia were not present. An exothermic reaction, such as the hydrogenation of aromatics, is supressed by a rise in temperature so that the presence of ammonia and the higher temperature employed cause the hydrogenation of aromatics to be suppressed in the first hydrocracking zone. Due to the combined effect of the hydrogen sulfide and ammonia, the product from the first stage hydrocracking zone contains a large concentration of aromatic hydrocarbons. Consequently, the naphtha product which is withdrawn from the first stage fractionator is high in aromatics content. The high aromatics content provides an exceptionally desirable high octane number.

The first stage hydrocracking reactor effluent is flashed and cooled, to obtain the hydrogen recycle stream, a mixed stream of light parafins, various hydrocarbon streams with high aromatics content (including the high aromatics naphtha and, if desired, a high aromatics turbine fuel product) and a bottoms product which is a high boiling, high aromatic hydrocarbon stream. The bottoms stream is mixed with hydrogen containing little or no ammonia and a controlled concentration of hydrogen sulfide. This mixed stream is then introduced into the second stage hydrocracking reactor which is run at a low conversion to lighter products. The low level conversion, in conjunction with the low concentration of ammonia, allows the second stage hydrocracking reactor to operate approximately 100° F. lower in temperature temperatures would favor the hydrogenation of aromatic hydrocarbons. Therefore a controlled amount of hydrogen sulfide is introduced in order to conserve hydrogen by suppressing the hydrogenation of aromatics to that minimum which will allow the jet fuel product to meet the desired aromatics specifications. The hydrogenation of aromatic hydrocarbons in the turbine fuel boiling range is not unduly suppressed, so that a low aromatics product in the turbine fuel boiling range is obtained.

In order to understand the present invention, the various aspects thereof will be separately discussed in the specification following.

FEEDSTOCK

The liquid hydrocarbon feedstock to the present process will generally boil within the range from about 430° F. to about 1000° F., a preferred boiling range being from 550° F. to 850° F. The feedstock will contain from 20 to 70 volume percent aromatic hydrocarbons, as determined by silica gel analysis. The feedstock to the present process may suitably comprise one or more streams obtained from the catalytic cracking of aromatic gas oils, for example, an admixture of 74% catalytic heating oil with 26% excess gas oil. The excess gas oil has a boiling range of approximately 520° F. to 760° F. and is obtained by the vacuum fractionation of a catalytic cracking unit bottoms stream.

A suitable feedstock for the present process is the aforesaid admixture of catalytic heating oil and excess gas oil. The inspection data on this admixture is shown below in Table I.

TABLE I

Hydrotreater feedstock inspections

Feed type	74% catalytic heating oil, 26% excess gas oil
Gravity, ° API	25.8
Aniline point, ° F.	119.3
Sulfur, wt. percent	0.36
N, w.p.p.m.	314
Distillation (stem corr)	D–1160
Initial, ° F.	--

TABLE I—Continued

5%	468
10	493
20	510
30	530
40	547
50	572
60	592
70	617
80	650
90	678
95	708
FBP, ° F.	733
Refractive index @ 67° C.	1.4935
Carbon, wt. percent	87.85
Hydrogen, wt. percent	11.70
Oxygen wt. percent	0.145
Conradson Carbon, wt. percent	0.004
Bromine No.	6.26
Viscosity, VSK:	
@ 100° F.	3.716
@ 210° F.	1.347
Pour point, ° F.	25
Karl Fisher water, p.p.m.	167
Dissolved water, p.p.m.	127
PM flash, ° F.	170
PONA, vol. percent:	
Paraffins	18.8
Olefins	2.0
Naphthenes	13.2
Aromatics	66.0

The feedstock may contain combined sulfur and nitrogen, as is shown in Table I wherein the nitrogen content was 314 p.p.m. by weight and the surfur content was 0.36 weight percent. Under these circumstances, it is desirable to pretreat the feedstock by contact with hydrogen and a hydrotreating catalyst in a hydrotreating zone, to convert the combined nitrogen and sulfur into ammonia and hydrogen sulfide, respectively. The total effluent from the hydrotreating zone, including ammonia, hydrogen sulfide and unconverted hydrogen, can then be passed through the first stage hydrocracking zone. Additional hydrogen sulfide and ammonia, if needed, can be introduced into the effluent from the hydrotreating zone before introduction of the effluent into the first stage hydrocracking zone. The use of recycle hydrogen will, of course, also result in the recycle of hydrogen sulfide and ammonia.

Other suitable aromatic distillate feedstocks are heavy coker naphthas, coker gas oils, and aromatic virgin gas oils.

HYDROTREATING ZONE

The aromatic feed may be hydrotreated in the presence of a hydrotreating catalyst and hydrogen, under hydrotreating conditions as are well known in the art.

The hydrotreating catalysts to be employed are of a conventional variety, and can be obtained on the open market. Without being limited to any particular catalyst, the hydrotreating catalyst can typically comprise an alumina or silica-alumina support carrying one or more iron group metals and one or more metals of Group VI–B of the Perodic Table in the form of the oxides or sulfides. In particular, a combination of one or more Group VI–B metal oxides or sulfides with one or more Group VIII metal oxides or sulfides are preferred. For example, suitable catalyst metal combinations which can be employed are the oxides and/or sulfides of cobalt-molybdenum, nickel-tungsten, nickel-molybdenum-tungsten, cobalt-nickel-molybdenum, nickel-molybdenum, etc. As a typical example, one catalyst which is suitable will comprise a high metal content sulfided cobalt-molybdenum-alumina catalyst containing about 1 to 10 weight percent cobalt oxide and about 5 to 40 weight percent molybdenum oxide, especially about 2 to 5 weight percent cobalt oxide and about 10 to 30 weight percent molybdenum oxide. It

will be understood that other oxides and sulfides will be useful, such as those of iron, nickel, chromium, tungsten, etc. The preparation of these catalysts is now well known in the art. The active metals can be added to the relatively inert carrier by impregnation from aqueous solutions followed by drying and calcining to activate the composition. Carriers include, for example, activated alumina, activated alumina-silica, zirconia, titania, etc., and mixtures thereof. A suitable silica alumina support will comprise about 1.5 to 5 weight percent silica as a stabilizer for the alumina. Activated clays, such as bauxite, bentonite and montmorillonite may also be employed.

The hydrotreating conditions are also well known in the art and are chosen to accomplish the removal of nitrogen and sulfur without the substantial hydrogenation or cracking of the aromatic distillate feedstock, so that the boiling range of the aromatic distillate feedstock is not substantially changed by reason of the hydrotreating step. Suitable hydrotreating conditions will include a temperature from about 550° F. to about 850° F. (preferably about 700° F.), a pressure from about 1400 p.s.i.g. to about 2000 p.s.i.g. (preferably about 1700 p.s.i.g.), a liquid hourly space velocity (LHSV) from about 0.3 to about 1.5 v./hr./v. (preferably about 0.8 v./hr./v.), a hydrogen treat rate from about 2000 to about 8000 s.c.f./b. (preferably about 5000 s.c.f./b.) and a hydrogen uptake from about 200 to about 1000 s.c.f./b. (preferably about 600 s.c.f./b.). The conditions in the hydrotreater are so correlated as to obtain a conversion of from about 95 to about 99.5 (preferably 99) weight percent of the combined sulfur into hydrogen sulfide, and a conversion from 94 to 99.5 (preferably 99) weight percent of the combined nitrogen into ammonia.

After addition of extrinsic H_2S and NH_3, if required, the effluent gas stream from the hydrotreater will typically contain from 1 to 5 weight percent H_2S and from 0.1 to 0.5 weight percent NH_3. Expressed on the basis of the liquid content of the hydrotreater effluent, the H_2S content is from 0.2 to 1.0 weight percent, and the NH_3 content is from 0.02 to 0.2 weight percent.

As stated before, it is preferable to pass the entire effluent from the hydrotreater into the first stage hydrocracker. If this preferred mode is employed, the gas phase from the first stage hydrocracker is separated from the liquid product and recycled through the first stage hydrotreating zone, thereby retaining the hydrogen sulfide and ammonia in a recycle stream. The excess hydrogen sulfide and ammonia can be removed in a bleed stream taken from the recycle hydrogen, and replaced by makeup hydrogen which is very low in ammonia and hydrogen sulfide content, or the recycle gas may be water-scrubbed, if desired, resulting in substantial ammonia removal.

FIRST STAGE HYDROCRACKING ZONE

The total effluent from the hydrotreating zone can be charged into the first stage hydrocracking zone. If a low-sulfur and low-nitrogen fresh aromatic distillate stream is charged into the first stage hydrocracking zone instead, then it will be necessary to add sufficient hydrogen sulfide and ammonia to reach the desired level.

In the first stage hydrocracking zone, a suitable hydrocracking catalyst (as hereinafter specified) will be employed under hydrocracking conditions including a temperature from about 600 to about 850° F. (preferably 700° F.), a pressure from about 1400 to 2000 p.s.i.g. (preferably 1700 p.s.i.g.), an LHSV from about 1 to about 3 v./hr./v. (preferably about 1.5 v./hr./v.), a hydrogen treat rate from 2000 to about 8000 s.c.f./b. (preferably about 5000 s.c.f./b.), the conditions being correlated so as to obtain a conversion (single pass) from about 20 to about 70 volume percent, and a hydrogen uptake from about 500 to about 1500 s.c.f./b. (preferably 800 s.c.f./b.) The conversion is stated as the volume percent of materials boiling above 520° F. which are converted into materials boiling lower than 520° F.

In order to suppress the hydrogenation of aromatics, the first stage hydrocracking reaction is carried out in the presence of hydrogen sulfide and ammonia. The hydrogen sulfide and ammonia concentration is expressed on the basis of the liquid feedstock charged into the first stage hydrocracking zone. The hydrogen sulfide concentration can vary from 0.2 to 1.0 weight percent (preferably 0.5 weight percent) while the ammonia concentration can range from 0.02 to 0.2 weight percent (preferably 0.05 weight percent). When the total product from the hydrotreater is charged into the first stage hydrocracking zone, and where the initial aromatic distillate feedstock contains at least 0.05 weight percent sulfur, no extraneous hydrogen sulfide need be added, since the hydrotreating products will contain sufficient H_2S to attain the desired concentration. However, where a fresh charge is used which does not contain the requite amounts of sulfur, extraneous hydrogen sulfide will be added in order to attain the desired concentration level. In this case, as well as previously discussed, the use of the recycle hydrogen stream from the effluent from the first stage hydrocracker will result in the recycle of some hydrogen sulfide and ammonia; in this case the recycle hydrogen would be introduced directly into the first stage hydrocracker since there would be no pretreating zone. (There would be no need to hydrotreat the "clean" distillate prior to hydrocracking.)

The products from the first stage hydrocracking zone are fractionated so as to obtain at least an aromatic naphtha product and a heavy bottoms product. The bottoms product is passed into the second stage hydrocracking zone while the aromatic naphtha product is removed for blending or sale. It is also possible to remove an aromatic turbine fuel fraction which can be blended with the low aromatic turbine fuel fraction obtained from the second stage hydrocracking zone. It has been found that all, or a portion of, the aromatic turbine fuel can be blended into the low aromatic turbine fuel product and still obtain a blended product which is suitable for sale as a jet fuel.

The bottoms stream which is passed into the second stage hydrocracker will boil above a cutoff temperature which is determined by whether the aromatic turbine fuel cut is to be passed through the second hydrocracking zone or not. If the aromatic turbine fuel product is to be removed from the hydrocarbon stream before introduction thereof into the second hydrocracking zone, the fractionating cut point will be at about 475° F. to 550° F., whereas if it is to be passed into the second hydrocracking zone, the cut point will be 320° F. to 430° F.

A light paraffins stream may also be withdrawn overhead from the first stage fractionator.

SECOND STAGE HYDROCRACKING ZONE

The second stage hydrocracking zone will employ a hydrocracking catalyst similar to that employed in the first stage. The nature of the hydrocracking catalyst will be more fully spelled out hereinafter. The second stage hydrocracking conditions will include a temperature from 500° F. to 750° F. (preferably 600° F.) and which is approximately 100° F. lower than that employed in the first stage. The hydrocracking conditions will also include a pressure from 1400 to 2000 p.s.i.g. (preferably 1700 p.s.i.g.), a liquid hour space velocity (LHSV) from 1 to 3 v./hr./v. (preferably 1.5 v./hr./v.), a hydrogen treat rate from 2000 to 8000 s.c.f./b. (preferably 5000 s.c.f./b.) a hydrogen uptake from 500 to 1500 s.c.f./b. (preferably about 800 s.c.f./b.) and a conversion of about 20 to 80 volume percent, on the same basis as explained in connection with the first stage hydrocracker. For the production of primarily jet fuel and aromatic naphtha, the second stage hydrocracking reaction will also take place in the presence of from 10 to 500 w.p.p.m. H_2S (based on the hydrogen treat stream being introduced into the second stage hydrocracker). Preferably, 40–50 w.p.p.m. H_2S will be employed. For the production primarily of naphtha, from 100 w.p.p.m. to 2 weight percent (preferably 0.5 to 1.0 weight percent) of H_2S will be employed in the hydrogen treat stream introduced into the second stage hydrocracking zone. Thus, the overall range will be from 10 w.p.p.m. to 2 weight percent H_2S in the treat gas. Hydrogen sulfide is extraneously added in amounts which, when considered in connection with the recycle of hydrogen, are sufficient to maintain the hydrogen sulfide level in the second stage hydrocracking reactor at the required levels.

The products from the second stage hydrocracking zone are removed, the gaseous hydrogen separated from the liquid for recycle, and the liquid products charged into a second stage fractionator.

The second stage fractionator is operated to obtain a low-aromatic naphtha product, a low-aromatic turbine fuel product, and a bottoms stream. The bottoms stream will boil above 500 to 550° F., and is recycled to the second stage hydrocracker. Recycle to extinction is preferred although a bleed stream may be removed if desired.

The low-aromatic turbine fuel will contain from 2 to 20% aromatic hydrocarbons, and will be suitable for use as a turbine fuel. A typical low aromatic turbine fuel product obtained by the present process will have the following inspection data.

TABLE II

Low Aromatic Jet Fuel

Balance number	1803	1804	1807	1808
Jet fuel quality:				
API gravity	43.3	45.6	45.2	45.4
Aniline pt., ° F	154.0	152.5	156.0	156.5
Freeze, pt., ° F	−43.6	−40.0	−27.4	−27.4
Smoke pt., mm	27.0	33.0	34.0	28.0
Luminometer No.	66.6	66.8	66.4	68.5
FIA-9, vol. percent:				
Aromatics	5.3	5.1	3.9	5.4
Saturates	92.9	93.4	94.2	94.1
Unsaturates	1.8	1.5	1.9	0.5
D-158:				
IBP, vol. percent	343	292	302	306
5%	370	338	341	339
10%	376	346	346	348
20%	382	358	359	360
30%	390	370	372	373
40%	398	380	384	386
50%	408	392	401	401
60%	420	406	417	418
70%	435	422	438	441
80%	454	444	463	467
90%	480	470	493	499
95%	494	488	511	521
FBP	533	522	538	540
Percent rec	98.0	98.0	98.0	98.0
Percent res	2.0	2.0	2.0	2.0

The present invention preferably will produce about 1 volume of low-aromatic turbine fuel from the second stage fractionator per volume of aromatic turbine fuel produced from the first stage fractionator. These volumes are such that they can be blended to obtain a suitable jet fuel. The aromatic turbine fuel from the first stage fractionator will contain about 50% aromatics.

Where the production of aromatic naphtha is to be optimized, the segregation of the lower aromatic product from the second stage allows it to be reformed for an increase in aromatics. The prior art methods do not segregate the products, so it is not possible separately to treat this lower aromatic naphtha product.

In the jet fuel mode, the aromatic naphtha from the first stage will contain about 25% aromatic hydrocarbons and will have a Research Octane Number at 3 cc. TEL of about 96. The low-aromatic naphtha from the second stage reactor will contain 10% aromatics and will have a Research Octane Number (3 cc. TEL) of about 81. About 1.7 volumes of aromatic naphtha are obtained from the first stage fractionator per volume of low-aromatic naphtha obtained from the second stage fractionator.

Thus, it is seen that by the present invention both an aromatic naphtha product and a low-aromatic turbine fuel can be obtained from an aromatic distillate, while employing hydrogen sulfide and ammonia in the first stage

hydrocracking reactor and hydrogen sulfide in the second stage hydrocracking reactor to control the hydrogenation activity of the hydrocracking catalyst.

HYDROCRACKING CATALYST

Any of a number of commercially available hydrocracking catalysts can be utilized in the present process. A preferred hydrocracking catalyst, however, is a crystalline aluminosilicate zeolite catalyst which is well known in the art and extensively described in the patent literature. These catalysts are characterized by highly ordered crystalline structure and uniformly dimensioned pores and have an aluminosilicate anionic cage structure wherein alumina and silica tetrahedra are intimately connected to one another so as to provide a large number of active sites, with the uniform pore openings allowing the entry of molecular structures having small cross-sectional diameters. For the purpose of the present invention, the crystalline aluminosilicate zeolites should have effective pore diameters within the range from 6 to 15 A. units, preferably 7 to 13 A. units. Such "large pore" crystalline zeolites are exemplified by the naturally occurring minerals faujasite and mordenite. Because of availability, only mordenite may be employed practically. Synthetically produced aluminosilicate zeolites having large pore diameters are also available and will be preferred in the present invention. In general, all crystalline alumino zeolites, in natural or synthetic form, contain a substantial portion of alkali metal oxide (normally sodium oxide) which is substantially removed by ion exchange. The ion exchange substitutes for the sodium either a metal cation or a hydrogen containing NH_4+ so as to reduce the sodium oxide content to less than about 10 weight percent and preferably to 1 to 5 weight percent based on the zeolite. The anhydrous form of the base-exchanged crystalline aluminosilicate zeolite prior to compositing with a platinum group metal may be generally expressed in terms of mols by the formula:

$$0.9 \pm 0.2\ \frac{Me_2}{n}O : Al_2O_3 : xSiO_2$$

wherein Me is selected from the group consisting of hydrogen and metal cations so that the Na_2O content is less than 10 weight percent of the zeolite, n is its valence and x is a number which is at least 3, preferably 3 to 10, and most preferably 4 to 6. Crystalline zeolites having these ratios have been found to be highly active, selective, and stable. However, zeolites having higher or lower silica-to-alumina ratios may in some cases be employed quite advantageously. A suitable commercial product is known as the "Type Y" molecular sieve.

For hydrocracking use, the zeolite is preferably base exchanged with a hydrogen-containing cation and or a metal cation to reduce the soda content to below 10 weight percent. Suitable metal cations include ions of metals in Groups I to VIII and rare earth metals, preferably metals in Groups II, III, IV, VI-B, VII-B, VIII and rare earth metals, most preferably Groups II and VIII. Mixtures of these various cations can be employed. Where a hydrogen-containing cation is used to replace the sodium, the hydrogen form of the zeolite is produced. A convenient method of preparing the hydrogen form is to subject the zeolite to base exchange with an ammonium cation solution, followed by controlled heating at elevated temperatures, such as 600 to 1000° F. to drive off ammonia and water. The crystalline aluminosilicate zeolite can also be impregnated with a platinum type metal, e.g., so as to contain from 0.1 to 1.0 weight percent palladium.

PREFERRED MODE

Referring now to the drawing, a preferred mode of carrying out the present invention is set out whereby both a low aromatic jet fuel and a high aromatic naphtha are recovered. The feedstock of the present process is introduced by way of line **100** into a hydrotreating zone **102**, along with a hydrogen stream **104**. The hydrogen and aromatic distillate are passed over a suitable catalyst such as 2 to 5 weight percent cobalt oxide on a silica alumina support (the support containing 1.5 weight percent silica), under conditions including a temperature of about 700° F., a pressure of about 1700 p.s.i.g., a LHSV of about 0.8 v./hr./v. and a hydrogen treat rate of about 5000 s.c.f./b. Under these conditions, there is a hydrogen uptake of about 500 s.c.f./b. and from 95 to 99.5% of the combined sulfur is converted into hydrogen sulfide and from 94 to 99.5% of combined nitrogen is converted into ammonia.

The total effluent, including the liquid and vapor, is passed from the hydrotreating zone **102** by way of line **106**, and is then introduced into the first hydrocracking zone **108**. In the hydrocracking zone the liquid is contacted, along with the vaporous constituents, with a hydrocracking catalyst which is suitably a Type Y crystalline silica-alumina zeolite containing from 0.1 to 1.0 weight percent palladium, under hydrocracking conditions including a temperature of about 700° F., a pressure of about 1700 p.s.i.g., an LHSV of about 1.5 v./hr./v., and a hydrogen treat rate of about 5000 s.c.f./b. Under these conditions there is a hydrogen uptake of about 800 s.c.f./b. and a conversion (single pass) of about 50 volume percent of materials boiling above 520° F. into materials boiling below 520° F. The hydrogen sulfide concentration is about 0.5 weight percent and the ammonia concentration is about 0.05 weight percent, based on the liquid feed into the first hydrocracking zone. The effluent from the first hydrocracking zone is removed by way of line **110**, passed through a cooler **112** and flashed in the zone **114** in order to remove the recycle hydrogen stream. The recycle hydrogen stream is directed by way of lines **116** and **104** into the hydro-treating zone as a source of hydrogen. A certain amount of hydrogen sulfide and ammonia will also be recycled, typically the recycle hydrogen stream comprising about 0.4 volume percent H_2S, 5 p.p.m. NH_3 and 80 volume percent hydrogen. Makeup hydrogen is introduced into the system by way of line **118**, and a bleed stream of hydrogen may be withdrawn if required. The liquid product from the first stage hydrocracker is passed by way of line **120** into the first stage fractionator **122**. From the first stage fractionator **122** are withdrawn overhead a light paraffins product stream **124** and an aromatic naphtha product **126**. An aromatic turbine fuel product stream is withdrawn by way of line **128** and a bottoms stream **123** is withdrawn for submission into the second stage hydrocracking zone.

In the second stage hydrocracking zone the first stage fractionator bottoms product is contacted with hydrogen and a hydrocracking catalyst similar to that employed in the first stage hydrocracker. From 10 to 100 p.p.m. H_2S (based on the second stage hydrogen treat stream) is charged into the second stage hydrocracker, representing both the recycle stream and extraneous H_2S which is added. The conditions in the second stage hydrocracker utilize a temperature of about 600° F., a pressure of about 1700 p.s.i.g., an LHSV of about 1.5 v./hr./v., and a hydrogen treat rate of about 5000 s.c.f./b. These conditions are so correlated that a hydrogen uptake of about 800 s.c.f./b. and a conversion of 50 volume percent materials boiling over 520° F. in the materials boiling below 520° F. is obtained. The effluent from the second stage hydrocracker **130** is withdrawn by way of line **132** and passed through a cooler **134** from whence it is introduced into a separation zone **136** where the hydrogen gas is removed for recycle by way of line **138**. The recycle hydrogen may be supplemented by makeup hydrogen introduced by way of line **140** and hydrogen sulfide may be added by way of line **142**.

The liquid product of the second stage hydrocracking zone is withdrawn from the separation zone **136** by way of line **144** and introduced into the second stage fractionator **146**. In the second stage fractionator, an overhead light paraffins stream is withdrawn by way of line

148, a low-aromatic naphtha is withdrawn by way of line 150, a low-aromatic turbine fuel is withdrawn by way of line 152 and a bottoms recycle stream is withdrawn by way of line 154.

The low-aromatic turbine fuel product in line 152 is suitably combined with all or a portion of the aromatic turbine fuel in line 128 so as to obtain a blended jet fuel shown in line 156.

Typical yields of the process are shown below in Table III.

TABLE III

Yields on Fresh Feed, Volume Percent

	Feed	First stage	Second stage	Overall
C_4		8.4	4.7	13.1
C_5/180° F		17.0	8.1	25.1
180/290° F		18.3	16.1	34.4
290/320° F		4.8	3.7	8.5
320/525° F	33.0	[1] 33.7	42.2	42.2
525° F.+	67.0	[1] 33.3		
		Product qualities		
Naphtha Octane Numbers (RON + 3 cc.):				
C_5/180° F		100.0	95.7	
180/290			82.7	
180/320		95.0		
Jet fuel properties:				
290/525° F				
Freeze point, ° F			−35.0	
Luminometer No			67.0	
Aromatics, vol percent			5.4	
320/525° F				
Freeze point, ° F		−42.0		
Luminometer No		17.8		

[1] Sent to second stage.

Having disclosed the present invention and a preferred mode of carrying it out, what is to be covered by Letters Patent should be determined not by the specific examples herein given but rather by the appended claims.

I claim:

1. A two-stage process for hydrocracking an aromatic hydrocracking stream which comprises in a first hydrocracking zone, contacting said aromatic hydrocarbon stream with hydrogen in the presence of a palladium supported on a crystalline zeolite having the formula:

$$0.9 \pm 0.2\ \frac{Me_2}{n}O : Al_2O_3 : x SiO_2$$

wherein Me is selected from the group consisting of metal cations and hydrogen, n is the valence of Me, and x is a number which is at least 3, and wherein the Na_2O content is less than 10 weight percent of the zeolite, hydrocracking catalyst in the presence of from 0.2 to 1.0 weight percent of H_2S and from 0.02 to 0.2 w.p.p.m. of ammonia (based on liquid feed), under hydrocracking conditions including:

a temperature from about 600° F. to about 850° F.,
a pressure from about 1400 p.s.i.g. to about 2000 p.s.i.g.,
a LHSV from about 1.0 v./hr./v. to about 3.0 v./hr./v.,
a hydrogen treat rate from about 2000 s.c.f./b. to about 8000 s.c.f./b., and
a hydrogen uptake from about 500 s.c.f./b., to about 1500 s.c.f./b.,
all of said conditions being correlated to obtain a single-pass conversion of about 20 to 70 volume percent of 520° F.+ materials into 520° F.− materials,
fractionating the reaction products from said first hydrocracking zone to obtain at least an aromatic naphtha product and a first bottoms stream,
in a second hydrocracking zone, contacting said bottoms stream with hydrogen in the presence of a palladium supported on a crystalline zeolite having the formula:

$$0.9 \pm 0.2\ \frac{Me_2}{n}O : Al_2O_3 : x SiO_2$$

wherein Me is selected from the group consisting of metal cations and hydrogen, n is the valence of Me, and x is a number which is at least 3, and wherein the Na_2O content is less than 10 weight percent of the zeolite, hydrocracking catalyst under hydrocracking conditions including:

a temperature from about 500° F. to about 750° F.,
a pressure from about 1400 p.s.i.g. to about 2000 p.s.i.g.,
a LHSV from about 1 v./hr./v. to about 3.0 v./hr./v.,
a hydrogen treat rate from about 2000 s.c.f./b. to about 8000 s.c.f./b., and containing from 10 w.p.p.m. to 2 weight percent of H_2S, and
a hydrogen uptake from about 500 s.c.f./b. to about 1500 s.c.f./b.,
all of said conditions being correlated to obtain a single-pass conversion of about 20 to 80 volume percent of 520° F.+ materials into 520° F.− materials, and the temperature in the second hydrocracking zone being approximately 100° F. lower than that in the first hydrocracking zone,
fractionating the reaction products from said second hydrocracking zone to obtain at least a low aromatic turbine fuel product and a second bottoms stream, and
recycling at least a portion of said second bottoms stream as a part of the feedstock to said second hydrocracking zone.

2. A process in accordance with claim 1 further comprising the steps of:
recovering from the reaction products from the first hydrocracking zone, an aromatic turbine fuel product, and
blending at least a portion of said aromatic turbine fuel product with said low aromatic turbine fuel product.

3. A process in accordance with claim 1 wherein the first hydrocracking zone conditions are about as follows:
temperature—700° F.
pressure—1700 p.s.i.g.
LHSV—1.5 v./hr./v.
hydrogen treat—5000 s.c.f./b.
hydrogen uptake—800 s.c.f./b.
conversion—50%
and the second hydrocracking zone conditions are about as follows:
temperature—600° F.
pressure—1700 p.s.i.g.
LHSV—1.5 v./hr./v.
hydrogen treat—5000 s.c.f./b.
hydrogen uptake—800 s.c.f./b.
conversion—50%.

4. A process in accordance with claim 1 wherein the feedstock into the first hydrocracking zone is obtained by catalytically hydrotreating an aromatic hydrocarbon stream containing at least 20% aromatic hydrocarbons and charging the total gaseous, vaporous and liquid effluent from said hydrotreating step into said first hydrocracking zone.

5. A process in accordance with claim 4 wherein the hydrotreating catalyst is chosen from the group consisting of the oxides or sulfides of at least one Group VI–B metal and at least one Group VIII metal and the hydrotreating conditions include:
a temperature from about 550° F. to about 850° F.,
a pressure from about 1400 to about 2000 p.s.i.g.,
a LHSV from about 0.3 to about 1.5 v./hr./v.,
a hydrogen treat rate from about 2000 to about 8000 s.c.f./b., and
a hydrogen uptake from about 200 to about 1000 s.c.f./b.,
whereby from 95 to 99.5 weight percent of the combined sulfur and from 94 to 99.5 weight percent of the combined nitrogen in the liquid feedstock are converted respectively to H_2S and NH_3.

6. A process in accordance with claim 5 wherein the aromatic hydrocarbon feedstock into the hydrotreating zone has the following characteristics:

a boiling range from about 470° F. to about 735° F.,
an API gravity of about 25.8,
a nitrogen content of about 314 p.p.m., and
a sulfur content of about 0.36 weight percent.

7. A process in accordance with claim **6** wherein the hydrotreating catalyst is a cobalt molybdate catalyst containing from 1 to 10 weight percent cobalt oxide and from 5 to 40 weight percent molybdenum oxide on 70 to 88 weight percent of a silica-alumina support containing from 1.5 to 5 weight percent silica.

8. A process in accordance with claim **1** wherein the H_2S concentration in the second stage treat gas is from 100 w.p.p.m. to 2 weight percent, and wherein a lower aromatic naphtha stream is recovered from the second stage fractionator.

9. A process in accordance with claim **1** wherein the H_2S concentration in the second stage treat gas is from 10 to 500 w.p.p.m.

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