

1

2,965,564

HYDRODESULFURIZATION AND HYDROGENATION WITH PLATINUM-ETA ALUMINA CATALYST

Isidor Kirshenbaum, Union, Arthur W. Langer, Jr., Nixon, and Erving Arundale, Westfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention concerns a novel process for upgrading petroleum fractions boiling in the range of about 300° to 650° F. in a hydrogenation process by the selective hydrogenation of aromatic compounds. The invention is of particular application for processing virgin stocks, but is also applicable and of value in improving catalytically cracked stocks. While this selective hydrogenation of aromatic compounds is valuable for treatment of a number of stocks, this process is of particular value for improving the burning qualities of kerosene, diesel fuel, jet fuel, and fuels for gas turbines.

In accordance with this invention, petroleum fractions containing aromatic hydrocarbons boiling in the range of about 300° to 650° F. are hydrogenated at temperatures of about 500° to 675° F., a pressure of about 100 to 1,000 p.s.i.g., in the presence of about 2000 to 15,000 standard cubic feet of hydrogen per barrel of feed, preferably 5,000 to 8,000 standard cubic feet of hydrogen per barrel of feed, specifically employing a catalyst consisting of platinum supported on eta alumina. The invention resides in use of this particular catalyst at specific hydrogenation conditions with selected feed stocks so as to obtain unique product quality improvements. As indicated, while the invention is of value in the treatment of a variety of feed stocks, it will be described with particular reference to the treating of diesel fuels and kerosenes, including jet fuels and gas turbine fuels.

In the case of diesel fuels and kerosenes, for example, the ignition characteristics and burning characteristics respectively are of particular importance from the viewpoint of product quality. These characteristics are often controlling in refining operations, necessitating specific techniques for improving these properties of these stocks. Burning characteristics of a kerosene may be measured by smoke point tests which can readily be carried out by determining the height of flame obtainable at incipient smoking, with the aim being to obtain kerosenes having the highest values of smoke point. The ignition characteristics of diesel fuels which are pertinent to this invention can be determined by cetane number inspections. These properties of the fuels identified are each dependent on the aromatic content of the fuel. Thus, both kerosene and diesel fuels, which are highly aromatic, are normally deficient in the aforementioned characteristics. To a lesser degree, these characteristics are also related to, and affected by, the naphthene content of the fuel. For these reasons, the present invention is particularly applicable to petroleum fractions boiling within a boiling range of about 300° to 650° F. containing at least 10% and up to about 50% of aromatic hydrocarbons and having a naphthene ring content of less than about 30%. More specifically, the invention is of particular applica-

2

tion to virgin kerosenes boiling in the range of about 300° to 500° F., and to virgin or cracked diesel fuels boiling in the range of 300° to 625° F. This process, is however, applicable but somewhat less efficiently, to feeds containing less than 10% and more than 50% of aromatic hydrocarbons.

In order to improve the burning properties of these fuels, it is necessary to hydrogenate selectively the aromatic compounds present. It is, of course, preferable to obtain complete conversion of all aromatic hydrocarbons, although conversions above about 90%, and particularly above 98% are effective for substantially upgrading these fuels.

The present invention is based on the provision of a suitable process for the conversion of aromatic hydrocarbons present in such stocks as kerosenes and diesel fuels. A particular feature of the invention is the discovery of a catalyst and conditions for using this catalyst which attains the unique objectives which are involved in this problem. These and other features of the invention will be brought out in the description of the invention which follows:

In order to establish the nature and advantages of this invention, reference will be made to some of the critical features involved in upgrading kerosenes and diesel fuels. As a starting point, it must be appreciated that unusual problems are involved in providing a hydrogenation process suitable for hydrogenation of aromatic hydrocarbons while preventing other undesirable results such as hydrocracking. In this connection, in a first step of the study on which this invention is based, a wide variety of hydrogenation catalysts which have proved of value in other types of hydrogenation were evaluated for activity in hydrogenating aromatic compounds. In the specific tests referred to, a low sulfur kerosene derived from Sweden crude was employed. Standard hydrogenation conditions were selected for testing each of the catalysts, and these conditions were a pressure of 800 p.s.i., a temperature of 600° F., and a throughput of 4 v./hr./v.

A commercially available cobalt molybdate alumina catalyst of the nature now used in commercial hydrofining operations was first tested. While this catalyst has excellent activity for conversion of sulfur compounds, and for saturation of olefinic compounds, this catalyst was found to have no activity for the conversion of aromatic hydrocarbons under the conditions of this test. Other catalysts such as a commercially available platinum on alumina catalyst, a commercially available rhodium on alumina catalyst, and other experimental catalysts were found to have substantially no activity for the hydrogenation of aromatic nuclei. One catalyst found to have good activity for this purpose was a commercially available nickel catalyst supported on kieselguhr. However, this nickel catalyst exhibited rapid and serious deactivation in use.

As a result of such studies, it has been found that platinum supported on eta alumina exhibits unique properties for the hydrogenation of aromatics. The catalyst constitutes about 0.001 to 5% of platinum supported on the particular form of alumina known as eta alumina. As now known to the art, eta alumina may be produced by heating alumina beta trihydrate at temperatures of about 500° to 1400° F. In accordance with this invention, this particular catalyst is used for treating petroleum fractions containing aromatic hydrocarbons.

3

The catalyst used in this invention may be prepared in the following manner.

One method of preparing eta alumina is to hydrolyze aluminum alcoholate with an aqueous solution containing ammonium hydroxide. The aluminum alcoholate may be prepared in any suitable manner. One method of preparation of aluminum alcoholate is given in Kiberlin U.S. Patent No. 2,636,865. Aluminum alcoholate is hydrolyzed with good agitation with from about 1 to 10 volumes of ammonium hydroxide per volume of aluminum alcoholate, preferably two to three volumes of ammonium hydroxide per volume of aluminum alcoholate, the concentration of NH_3 being in the range of about 1.8 to 3.4 weight percent. The temperature of hydrolysis is preferably kept within a range of about 35° to 100° F. Upon hydrolysis, an alumina slurry is obtained and this slurry is aged for a period of one to 15 hours, preferably 3 to 8 hours at room temperature. The aging is preferably carried out in the range of about 35° to 80° F.

The alumina slurry contains alumina in the beta trihydrate form and the slurry is first dried at a temperature of about 200° to 400° F. to remove the ammonia and water to recover dry alumina. Crystalline eta alumina is formed by further dehydrating the beta alumina trihydrate and it has been found that the conversion to the eta form is essentially quantitative when the activating temperature is in the range of about 450° to 1100° F. The activation is generally in the presence of air but can be done in the presence of inert gases.

The eta alumina is used as a support for platinum and is impregnated with an aqueous solution of water soluble inorganic platinum containing compounds such as chloroplatinic acid, platinum sulfide, etc. The term "water soluble" also includes platinum-containing compounds which form colloidal solutions.

A preferred solution is one containing 15 grams of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (40% Pt) per liter. This strength of solution can be employed to yield catalysts containing about 0.6% platinum but the strength of the solution may be varied to obtain a catalyst containing about 0.001 to 5% platinum by weight. The alumina support is impregnated with the platinum solution, is then heated to dryness, conveniently at temperatures of about 100° to 600° F., preferably about 250° F., at atmospheric pressure and this results in removal of a substantial portion of the water. Thereafter the catalyst is calcined at a temperature between about 800° and 1250° F., preferably about 1100° F. The calcining step is preferably carried out for about 1 to 24 hours.

Before impregnating the eta alumina base with the platinum compound, it is also within the contemplation of this invention to calcine the eta alumina and this can be done at a temperature between about 800° and 1600° F., preferably about 1100 to 1500° F., for 1 to 24 hours. In some cases it is also desirable to treat the platinum catalyst or the eta alumina base either before or after calcination with an aqueous dilute mixed acid solution such as one containing nitric acid, perchloric acid, or hypochlorous acid, together with a hydrogen halide such as HCl, HF, HI and HBr. The mixture containing nitric acid and hydrochloric acid is preferred. An amount of nitric acid based on the total catalyst of about 0.1 to 8 weight percent on the total catalyst is preferred. The HCl is employed in an amount of about 1 to 30 weight percent based on the total catalyst. The nitric and hydrochloric acids are contained in about 50 to 500 weight percent of water on the total catalyst.

In acid treating the catalyst, the catalyst is mixed with the acid solution, heated on a steam bath at about 150° to 180° F. for at least one hour, the acid solution is then drained off and the catalyst is washed thoroughly with distilled water. The washed catalyst is then dried at about 250° F. and recalcined for about 1 to 4 hours at between about 800° and 1250° F., preferably about 1100° F.

4

In a specific example, the alumina support for a catalyst was obtained by hydrolysis of aluminum alcoholate solution by the method discussed above. The alumina after drying at about 250° F. was pulverized to pass through a 20 mesh screen and was then heated and activated at about 1100° F. for about 4 hours. To each 100 grams of activated alumina was added a solution made by dissolving 1.5 grams of H_2PtCl_6 (40% platinum) in about 65 cc. of distilled water. The composition was well mixed and dried overnight at room temperature. The catalyst was then dried at 250° F., screened and piled. The piled catalyst was calcined for 1 hour at about 1100° F.

The piled and calcined catalyst was then treated with a solution containing 7 weight percent on catalyst of concentrated HCl and 4 weight percent on catalyst of concentrated HNO_3 and 200 weight percent on catalyst of distilled water. The catalyst pills were slurried in the acid solution on a steam bath for about one hour. The temperature of the solution was about 150° to 190° F. The acid solution was then drained off and the catalyst washed with distilled water. The washed catalyst was dried at 250° F. and calcined at 900° to 1100° F. for one hour.

In a first experiment conducted, a platinum on eta alumina catalyst not acid treated, was employed in the hydrogenation of a xylene fraction constituting mixed xylenes, although predominating in meta xylene. A temperature of 615° F., a pressure of 400 p.s.i.g., a feed rate of 1 v./v./hr. and 7000 cubic feet of hydrogen per barrel of feed were employed. It was found that the product obtained showed a 96% conversion of the mixed xylenes to dimethyl-cyclo hexanes and tri-methyl cyclo pentanes. Other experiments conducted with substantially pure aromatic hydrocarbons boiling in the range of about 430° to 650° F., supported these results in showing the practicality of hydrogenating aromatic hydrocarbons with this specific catalyst.

Other tests which were conducted to demonstrate the process of this invention employed a commercial kerosene having the inspections shown in Table I.

TABLE I
Kerosene inspections

50	Gravity, ° API.....	42.6	ASTM Distillation	
			Percent O.H.	Temp. ° F.
55	Specific Gravity 60/60.....	0.813		
	Aniline Point, ° F.....	148	IBP	319
	Smoke Point, mm.....	21.5	10	382
	FIA, vol. percent.....	17.8(15.9)	20	400
	Aromatics.....	5.3	30	414
	Olefin.....	76.9	40	425
	Saturates.....	0.023	50	435
	Sulfur, Wt. percent.....	1.77	60	445
	Bromine No., cc. Br ₂ /gm.....	1.4460	70	456
60	Refractive Index, 20° C./D.....	11.2	80	469
	Viscosity at -30° F., cs.....	-42	90	484
	Freezing Point, ° F.....	134	95	498
	Flash Point, ° F.....		FBP	516

A variety of tests for the hydrogenation of this kerosene and additional tests for the hydrogenation of xylene, are summarized in Table II. These tests were conducted in a continuous hydrogenation operation at a pressure of 400 p.s.i.g., and 0.8 to 1.0 v./hr./v., employing a platinum on eta alumina catalyst containing 0.6% of platinum which was diluted with an equal amount of tabular alumina. Temperatures of 500°, 600° and 675° F. were studied and hydrogen dilutions ranging between

6,000 to 7,500 standard cubic feet per barrel were employed. Table II summarizes the results of these tests:

temperature of about 900° F. to 1100° F. for about 1 to 8 hours. Pressure during regeneration may be that

TABLE II
Hydrogenation of aromatics over platinum on eta
alumina catalyst

[0.6% Pt. on Al₂O₃; 400 p.s.i.g.]

Feed	Hour on Feed	Temp., °F.	V./Hr./V.	H ₂ , M. S.C.F./Bbl.	Refractive Index 20° C./D	Smoke Pt., mm.	FIA		
							Arom.	Olefins	Sats.
Xylene ¹	1	610	1.06	3.0	1.4951	—	100	0	0
	2	610	0.90	7.0	1.4288	28.0	5.4	1.5	93.1
	3	675	0.90	6.5	1.4258	31.5	2.4	1.7	95.9
	4	600	0.96	6.0	1.4298	24.0	9.4	2.3	88.3
	5	500	0.92	6.0	1.4490	21.5	17.8	5.3	76.9
	6	600	0.98	6.0	1.4407	29.0	10.7	5.5	83.8
	7	600	0.98	6.0	1.4424	25.5	14.0	2.7	83.3
	Regeneration	(9)	0.89	6.0	1.4438	27.0	13.4	3.5	83.1
	8	675	1.00	6.0	1.4440	25.0	15.8	3.0	81.2
	9	675	0.80	7.0	1.4412	28.0	11.2	2.1	86.7
	10	675	0.86	6.5	1.4438	25.5	15.8	2.8	81.4
Kerosene ¹	11	675	0.90	6.5	1.4441	24.0	15.8	3.6	80.6
	Regeneration	(9)	0.90	6.5	1.4440	24.0	16.1	2.6	81.3
	12	675	0.88	6.5	1.4447	24.0	16.3	3.3	80.4
	13	675	0.88	6.5	1.4450	—	—	—	—
	14	500	0.90	6.5	1.4417	28.0	10.9	3.9	85.2
	15	500	0.86	6.5	1.4440	—	—	—	—
	16	500	0.91	6.5	1.4441	27.0	14.6	5.2	80.2
	Regeneration	(9)	—	—	—	—	—	—	—
	17	600	0.85	6.7	1.4402	30.5	8.7	4.0	87.3
	18	600	0.84	6.5	1.4410	—	—	—	—
	19	600	0.75	* 7.5	1.4412	30.0	9.1	5.4	85.5
	20	500	0.80	* 7.0	1.4410	29.5	13.2	5.3	81.5
	21	500	0.79	* 7.0	1.4422	27.0	13.7	5.2	81.1
	22	500	0.44	* 13.0	1.4422	—	—	—	—

¹ Mallinckrodt A. R. Xylene, 0.003% S.

² Inspections, Table I

³ Alternate feed + H₂ strip 10 min.

⁴ Alternate feed 10 min., H₂ strip 5 min.

⁵ H₂, 900° F., 3 Hours.

Referring to the data of Table II, it will be seen that in every run reported, substantial conversion of aromatic compounds was obtained. However, the data shows that particularly good results were obtained in hydrofinishing kerosene at 600° F., serving to reduce aromatics from 17.8% to 8.7% and improving smoke point from 21.5 mm. to 30.5 mm. Included in Table II are data showing the effect of regenerating the catalyst used in a hydrogen regeneration treatment. It is shown that contact of spent catalyst with hydrogen at 900° F. for three hours is effective for regenerating the catalyst. Also, as shown by hours 20 to 22, however, intermittent hydrogen stripping at 600° F. is also particularly effective in maintaining good catalyst activity.

These and other tests which were conducted establish that platinum on eta alumina catalyst may be used in the process of this invention at temperatures in the range of 500° to 675° F., with about 600° F. being a preferred temperature for operation. Non-regenerative operations may be conducted at temperatures in the upper portion of this range, particularly when employing intermittent hydrogen stripping which may be conducted by periodically cutting off hydrocarbon feed at intervals of about 5 to 180 minutes. Hydrogen stripping will be carried out at about 500° to 800° F., preferably for about 5 to 60 minutes. However, somewhat lower temperatures better favor aromatic conversion, although necessitating regeneration of the catalyst. Pressures to be employed in this invention are selected from the broad range of 100 to 1000 p.s.i.g., although pressures of about 200 to 400 p.s.i.g. are preferred. Use of higher pressures in the range stated are favorable for aromatics conversion.

As stated, the present invention may be conducted as either a non-regenerative process, or a regenerative process. Conventional techniques for catalyst regeneration may be employed. The preferred procedure, however, is to employ high temperature hydrogen regeneration entailing hydrogen contact with the catalyst at a

maintained during the hydrotreating process; that is, about 200 to 1000 p.s.i.g.

Alternatively, an oxidative regeneration may be conducted. In this case the catalyst is first purged of hydrocarbons employing an inert gas such as nitrogen. Thereafter air diluted with nitrogen or other inert gas is contacted with the catalyst to secure combustion of carbonaceous deposits on the catalyst while holding the temperature below about 1050° F. After an initial period of regeneration with dilute air, the oxygen content may be increased to that of undiluted air, preferably including exposure of the catalyst to air at about 950° F. to 1175° F. at reaction pressure for an hour or more, preferably four or more hours.

As described, the process of this invention concerns the hydrofinishing of petroleum fractions for product quality improvement by the conversion of aromatic hydrocarbons. The invention has been described with particular reference to the treatment of diesel fuel in kerosene, but is also of application in the treating of jet fuels and gas oils. In the latter connection, for example, the hydrotreating process of this invention can desirably be used for the upgrading of catalytic cracking feed and cycle stocks by conversion of the aromatic hydrocarbons present in such stocks.

While the invention has been described with particular reference to fixed bed operation, it is apparent that the fluidized technique or moving bed principles may be employed. Again, while the invention has been described as a single stage treatment with platinum on eta alumina, staged operations or combinations with other treating processes may be used. For example, in the case of high sulfur content feed stocks, it may be desirable to employ a desulfurization step prior to the use of the process of this invention. Hydrodesulfurization using a catalyst such as cobalt molybdate can desirably be used for this purpose. These and other variations and modifications of the invention may be employed.

What is claimed is:

1. A process for upgrading petroleum fractions containing aromatic and sulfur compounds boiling in the range of about 300° to 650° F., which consists of hydrogenating said fractions to obtain substantial hydrogenation of aromatics and removal of sulfur at a temperature of about 500° to 675° F., at a pressure of about 100 to 1000 p.s.i.g., in the presence of about 5,000 to 8,000 standard cubic feet of hydrogen per barrel of feed in contact with a catalyst comprising platinum supported on eta alumina. 5 10

2. The process defined by claim 1 in which the said petroleum fraction is selected from the group consisting of kerosene, diesel fuel, gas oil, and jet fuel.

3. The process defined by claim 1 in which the said catalyst contains 0.001 to 5.0% of platinum. 15

4. The process defined by claim 1 in which the said catalyst contains 0.05 to 1.0% platinum.

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