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CATALYTIC HYDROCARBON TREATING

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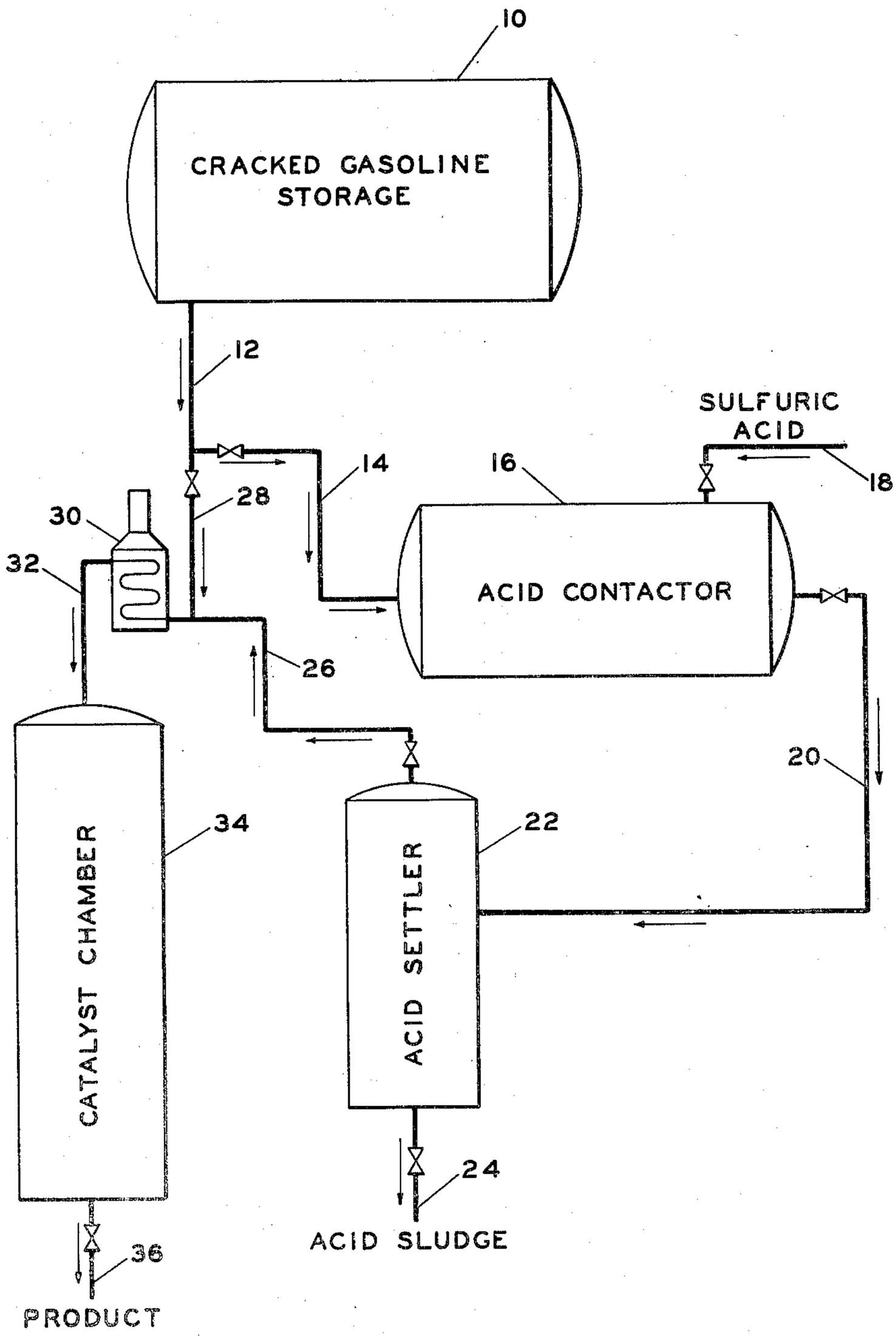

INVENTOR.
C. J. HELMERS

BY Hudson and Young

ATTORNEYS

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CATALYTIC HYDROCARBON TREATING

Carl J. Helmers, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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1

This invention relates to an improved method for treating cracked hydrocarbon material. One embodiment of this invention relates to the treating of cracked hydrocarbon material whereby the antiknock quality of said hydrocarbon material is improved. In one specific embodiment it relates to treating a lesser portion of a stream of a cracked gasoline hydrocarbon material with sulfuric acid, mixing the resulting treated portion with the larger untreated portion of said hydrocarbon material and contacting the resulting mixture with an olefin isomerization type catalyst whereby the octane rating of said hydrocarbon material is improved.

It is a well-known fact that gasolines with a high antiknock rating are superior to gasolines with a low antiknock rating. Present-day automobiles require a comparatively high antiknock rating gasoline and the trend is toward still higher antiknock rating for gasoline. In some cases it is beginning to be a burden for the gasoline manufacturers to supply economically gasoline possessing the proper antiknock rating. Gasoline manufacturers are continually seeking methods by which higher octane number gasoline can be produced more economically.

It is known in the art that the antiknock rating of some cracked gasoline hydrocarbon material can be improved by contacting said material with acid treated clay type catalysts at relatively low temperatures. The antiknock improvement which is obtained by this method is thought to be due mainly to the isomerization of the olefins present. Regardless of the mechanism of the reaction, however, improvement in octane rating can be obtained by such a process. I have discovered that if a small part of a stream of cracked gasoline hydrocarbons going to such an isomerization step is by-passed to an acid-treating zone and then directly returned to the main stream of said cracked gasoline hydrocarbons going to the isomerization step, an additional improvement in antiknock rating is obtained and the isomerization catalyst life is prolonged.

One object of this invention is to provide an improved method for treating cracked hydrocarbon material.

Another object of this invention is to provide an improved method for treating cracked gasoline hydrocarbons whereby the octane rating is improved.

Other objects and advantages of the invention will be apparent to those skilled in the art from the accompanying discussion and description.

A further understanding of the invention will

2

be obtained by reference to the accompanying diagrammatic drawing which illustrates one embodiment of the process of my invention. A cracked gasoline hydrocarbon material such as one obtained from a low-pressure thermal cracking unit is pumped from storage **10** through line **12**. At the end of line **12** the stream of hydrocarbon material is divided into two unequal portions; the smaller portion is pumped through line **14** to acid contactor **16** where it is treated with sulfuric acid supplied to the contactor through line **18**. The resulting mixture of acid and said gasoline hydrocarbons is pumped from contactor **16** through line **20** to acid settler **22** where the mixture is separated into an acid phase and hydrocarbon phase. The acid phase may be removed from the system through line **24** for further handling as desired. The hydrocarbon phase is pumped directly, and without intermediate water-washing or other treatment, from acid settler **22** through line **26** to line **28** where it mixes with the untreated main stream of the cracked gasoline hydrocarbon material. The resulting mixture is pumped through line **28** to a heating zone **30** where it is heated to a temperature in the range of about 600 to about 850° F. From heating zone **30** the heated hydrocarbon material flows through line **32** to catalyst chamber **34** where it is contacted with a suitable olefin isomerization catalyst, maintaining the temperature in the catalyst chamber in the range of about 600 to about 850° F. The treated product is withdrawn from the catalyst chamber through line **36**. If desirable, the effluent from the catalyst chamber may be fractionated to remove a small amount of heavy material which may be formed. Though I have illustrated the process of my invention by a continuous operation, it is understood that it is equally applicable to a semi-continuous or a batch-type operation.

In the above-mentioned drawing reference to certain equipment such as pumps, gauges, and the like, which obviously would be necessary to actually operate the process, have been intentionally omitted. Only sufficient equipment has been shown to illustrate the process and it is intended that no undue limitation be read into this invention by reference to the drawing and discussion thereof.

The conditions for carrying out the process of my invention will vary considerably, depending upon the particular cracked gasoline hydrocarbon undergoing treatment, the strength of acid employed, and the particular catalyst employed. In carrying out the process of my invention a

stream of cracked gasoline hydrocarbon material obtained from any suitable source, such as, for example, a low-pressure thermal cracking operation, is split into two unequal portions, the smaller portion usually amounting to between about 5 and 25 per cent of said total original stream. Treating larger portions of said hydrocarbon material with acid offers no significant improvement. This smaller portion is treated with a mineral acid such as sulfuric acid, phosphoric acid, and the like, having a concentration in the range of about 50 to about 90 weight per cent, but preferably with sulfuric acid having a concentration in the range of about 60 to about 75 weight per cent. The acid is contacted with said gasoline hydrocarbon material in an amount in the range of about 2 to about 15 pounds of acid per barrel of gasoline hydrocarbon material, the exact amount depending upon acid concentration and the particular hydrocarbon material undergoing treatment. The temperature of the acid treating step is usually maintained in the range of about 50 to about 100° F., but preferably in the range of about 65 to 85° F. Catalysts which are particularly applicable in my improved process are bauxite, fuller's earth, activated alumina, or the like, but any olefin isomerization catalyst may be employed. The temperature in the catalyst chambers usually ranges from about 600 to about 850° F., but preferably the process is carried out at a temperature in the range of about 700 to about 800° F. and at a pressure in the range of about 0 to about 250 pounds per square inch gauge, however, a pressure in the range of about 25 to 100 pounds per square inch gauge is preferable. The space velocity of the hydrocarbon material through the catalyst chamber is usually in the range of about 0.5 to about 5.0 liquid volumes per volume of catalyst per hour, but a space velocity of about 1.0 to about 3.0 liquid volumes per volume of catalyst per hour is preferable.

Example I

Two runs were made treating a cracked gasoline over bauxite at a temperature of 765° F., at a pressure of 35 p. s. i. g., at a space velocity of 1.5 liquid volumes per volume of catalyst per hour and for a process period of 16 hours. In the first run the gasoline was treated as received; in the second run 10 per cent of the gasoline was first treated with 5 pounds of 60 weight per cent sulfuric acid per barrel of gasoline treated and then recombined with the untreated portion. The specifications on the two products as well as those of the original gasoline are tabulated below.

	Cracked Gasoline	Bauxite Treated	Acid and Bauxite Treated
ASTM Distillation, ° F.:			
IBP	121	113	116
5%	170	173	174
10%	198	197	198
50%	301	299	300
90%	386	392	391
95%	400	416	416
EP	416	472	471
Gravity, 60° F., °API	51.5	51.0	50.8
Reid Vapor Pressure, pounds	4.25	4.65	4.15
Sulfur, Wt. Per cent	0.017	0.0140	0.0140
ASTM Octane Number:			
0 ml. TEL	58.5	63.3	64.7
1 ml. TEL	67.7	72.3	73.1
3 ml. TEL	74.9	78.0	78.5
Research Octane Number:			
0 ml. TEL	64.0	69.5	71.2
1 ml. TEL	72.8	78.4	78.8
3 ml. TEL	80.8	84.6	85.1

The bauxite treatment alone raises the octane rating of this cracked gasoline about 5 units and the preliminary acid treatment increases the octane ratings by an additional 1.5 units on both the ASTM and Research ratings.

Example II

Two runs were made treating a cracked gasoline over bauxite under substantially the same conditions as given in Example I, except that the acid treated portion of the second run was washed with water, then with an aqueous solution of sodium carbonate before it was recombined with the untreated portion. The octane number and tetraethyl lead response of the two treated products as well as the original gasoline are given in the following table.

	Cracked Gasoline	Bauxite Treated	Acid-treated, Washed, and Bauxite Treated
ASTM Octane No.:			
0 ml	59.3	63.6	64.0
1 ml	64.7	70.5	70.5
3 ml	70.3	76.1	76.1
Research Octane No.:			
0 ml	62.9	66.9	67.3
1 ml	70.0	74.8	75.2
3 ml	76.8	82.3	82.7

The product containing the acid-treated, water and sodium carbonate washed portion showed substantially no improvement over the straight bauxite treated product.

It is to be understood that this invention should not be unnecessarily limited to the above discussion and description and that modifications and variations may be made without departing from the invention or from the scope of the claims.

I claim:

1. A process for improving the antiknock rating of a cracked gasoline hydrocarbon material, which comprises dividing a cracked gasoline hydrocarbon material into two unequal portions; each of said two unequal portions having the same physical and chemical characteristics, treating the smaller portion in a contact zone maintained at a temperature in the range of 50 to 100° F. with a mineral acid of a concentration in the range of 50 to 90 weight per cent in the amount of 2 to 15 pounds of acid per barrel of said hydrocarbon material; separating the effluent mixture from said contact zone into an acid phase and a hydrocarbon phase in a separation zone, mixing the resulting acid treated portion with the untreated main portion, heating the resulting mixture in a heating zone to a temperature in the range of 600 to 850° F., passing said heated mixture maintained at a temperature in said range through a catalyst zone containing a solid olefin isomerization catalyst; maintaining the pressure in said catalyst zone in the range of 0 to 250 pounds per square inch, maintaining a space velocity through said catalyst zone in the range of 0.5 to 5.0 liquid volumes per volume of catalyst per hour, and withdrawing the product from said catalyst zone.

2. A process for improving the antiknock rating of a cracked gasoline hydrocarbon material, which comprises dividing a cracked gasoline hydrocarbon material into two unequal portions; each of said two unequal portions having the same physical and chemical characteristics, the smaller portion amounting to between 5 and 25

per cent of the total of said hydrocarbon material, treating said smaller portion in a contact zone maintained at a temperature in the range of 50 to 100° F. with sulfuric acid of a concentration in the range of 50 to 90 weight per cent in the amount of 2 to 15 pounds of acid per barrel of said hydrocarbon material; separating the effluent mixture from said contact zone into an acid phase and a hydrocarbon phase in a separation zone, mixing the resulting acid-treated hydrocarbon material without intermediate treatment directly with the untreated main portion of the original cracked gasoline hydrocarbon material, heating the resulting mixture in a heating zone to a temperature in the range of 600 to 850° F., passing said heated material maintained at a temperature in said range through a catalyst zone containing bauxite at a pressure in the range of 0 to 250 pounds per square inch, maintaining a space velocity through said catalyst zone in the range of 0.5 to 5.0 liquid volumes per volume of catalyst per hour.

3. A process as in claim 1 where the acid used is phosphoric.

4. A process as in claim 1 where the olefin isomerization catalyst used is fuller's earth.

5. A process as in claim 1 where the olefin isomerization catalyst used is activated alumina.

CARL J. HELMERS.

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