

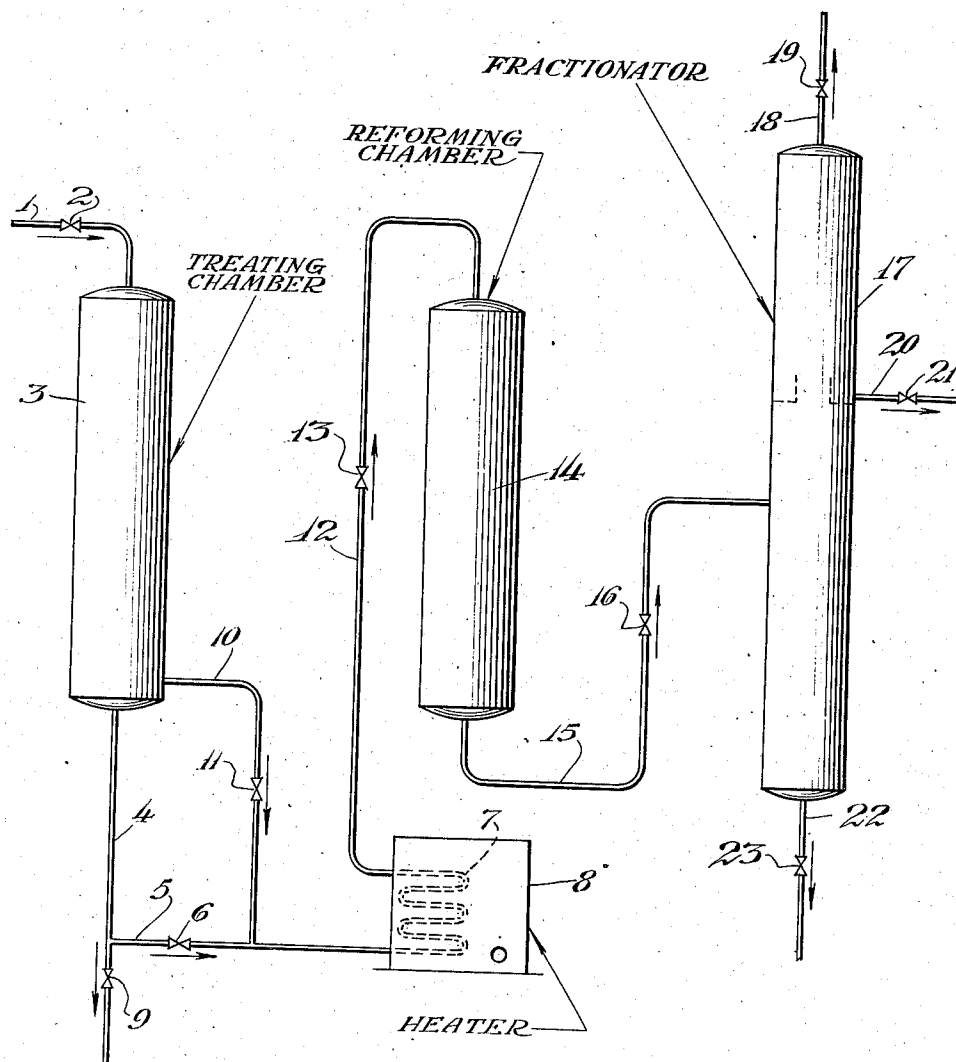
March 20, 1945.

C. H. ALBERDING

2,371,726

CONVERSION OF HYDROCARBONS

Filed Aug. 25, 1941



Inventor:
Charles H. Alberding
By Lee J. Gary
Attorney.

UNITED STATES PATENT OFFICE

2,371,726

CONVERSION OF HYDROCARBONS

Charles H. Alberding, Chicago, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

Application August 25, 1941, Serial No. 408,141

8 Claims. (Cl. 196—52)

This invention relates to an improved process for the treatment of olefinic gasolines and particularly thermally cracked gasolines, in order to improve their properties as regards decreased sulfur content and increased antiknock value. More particularly, the present invention contemplates a two-stage treatment of thermally cracked gasoline in the presence of specific catalysts under controlled conditions of temperature, pressure and time of contact.

The first stage of the present invention proposes to refine gasoline by treatment in the presence of clay type catalysts at temperatures of below 800° F. and pressures of atmospheric to 500 pounds, or more. Depending upon the temperature, pressure and time of contact employed in the particular operation, a slight increase in antiknock value, ranging from 1 to 3 octane numbers is usually obtained. It is believed that this increase in octane number is obtained slightly by the conversion of the sulfur compounds and more particularly by isomerization reactions, including conversion from normal or slightly branched chain structure to more highly branched chain structure and the transposition of the double bond from the outer part towards the center of the hydrocarbon molecule. It is not intended to limit the present invention to this explanation since other reactions probably also occur during this treatment.

The second stage of the present invention proposes the treatment of the previously refined gasoline vapors in the presence of synthetically prepared catalysts capable of promoting isomerization reactions, including both the rearrangement of the alkyl radicals and the transposition of the double bonds, at temperatures above 800° F., atmospheric or relatively mild superatmospheric pressures and short times of contact. In this step of the process an increase in the antiknock value of the gasoline may range from 3 to 8 octane numbers, or more. In addition, due to the higher temperatures employed in the second step of the process, some further conversion of the sulfur compounds is effected.

The first stage of the process effects considerable conversion of the sulfur compounds along with improvements in other properties of the gasoline, such as color, gum, etc., but effects a very small increase in antiknock value. On the other hand, the second stage of the process effects a relatively high conversion of antiknock value but effects very little conversion of the sulfur compounds. By the interdependent and related steps of the present invention, a relatively high con-

version of the sulfur compounds and a relatively high increase in octane value are obtained.

As a particular feature of the present invention, the products from the first stage are introduced into the second stage without intervening cooling, thereby effecting an efficient thermal system. The products from the first stage will be withdrawn therefrom at a temperature varying from about 400° to about 800° F. and may be raised to a temperature of about 800° to about 1200° F. prior to being introduced to the second stage of the process. Thus it is readily seen that the invention provides for an economical and practical operation in which cooling of the products between stages is avoided and eliminates the concomitant necessity of heating the products of the first stage from atmospheric temperature to the temperature required in the second stage of the process.

As another particular feature of the present invention, the use of pumps or compressors to convey the products from the first stage into the second stage of the process is avoided. This advantage is very important since difficulty is usually encountered with pumps or compressors operated at the high temperatures prevailing within the system.

As still another feature of the present invention, it has been found that any lighter products formed by decomposition reactions incidental to the primary refining reaction are not detrimental to the synthetically prepared catalysts in the second stage of the process.

In addition, provision is made for the removal of high boiling materials formed in the first stage of the process prior to subjecting the remaining products to conversion in the second stage of the process. The removal of these high boiling materials will avoid contamination of the catalyst in the second stage of the process and increase the life thereof; that is, the catalytic agent may be used for longer periods of time before it is necessary to reactivate the same.

In one specific embodiment, the present invention comprises a process for the conversion of thermally cracked gasoline which consists in subjecting the thermally cracked gasoline to contact with a clay type treating agent at temperatures below 800° F. and pressures above atmospheric, separating higher boiling polymers formed in said treatment, superheating the remaining vapors, without intentional prior cooling thereof, and subjecting the same to contact with a synthetically prepared catalyst having olefin isomerizing properties at a temperature above 800° F. and

at a pressure lower than that employed in the first step of the process.

In another embodiment of the invention, the total products emitting from the first stage of the process may be introduced into the second stage of the process without the intervening separation of the higher boiling polymers therefrom.

The invention will be further explained in connection with the following description and attached diagrammatic drawing illustrating one specific method of operating the process.

The charging stock to the process preferably comprises olefinic gasoline such as that produced in the non-catalytic cracking of higher boiling oils, the polymers produced by the polymerization of propylene and/or butylene gases, etc. When the charging stock comprises thermally cracked gasoline it may advantageously be supplied directly from the fractionator of the cracking plant. Regardless of the source of the charging stock, it is preheated to a temperature of 400° to 800° F., by well known means not illustrated, and introduced to the process at a pressure of above atmospheric and up to 500 pounds or more per square inch, through line 1 and valve 2 to treating chamber 3. Treating chamber 3 preferably contains a bed of suitable refining agents such as clays, bauxite, fuller's earth, etc., which may be either of natural or synthetic origin. It is of course understood that these alternative treating agents will not necessarily be equivalent in the results obtained. Instead of one treating chamber as illustrated in the drawing, two or more treating chambers may be employed within the scope of the present invention. The treating chamber is maintained at a temperature of between about 400° to about 800° F. at any pressure above atmospheric and usually within the range of 50 to 200 pounds or more. It is within the scope of the invention to employ vapor phase, liquid phase or mixed phase conditions in the treating chamber.

The products from the treating chamber may be withdrawn therefrom in total through line 4 and directed through line 5 and valve 6 to heating coil 7 in furnace structure 8. Preferably, however, any high boiling products formed in treating chamber 3 are separated from the vaporous products therein, by any well known method not illustrated. The higher boiling products may then be withdrawn through line 4 and valve 9 to storage or elsewhere as desired, while the vaporous products are withdrawn from chamber 3 through line 10 and valve 11 and supplied through line 5 to heating coil 7.

Since treating chamber 3 is maintained at a higher pressure than that employed in the subsequent steps of the process, the products emitting from chamber 3 may be conveyed through heating coil 7 and through the subsequent reforming chamber without the necessity of utilizing any pumps or compressors. The reforming chamber is preferably operated at atmospheric or mildly superatmospheric pressures up to 50 pounds per square inch, although higher or lower pressures may be employed. The products supplied to coil 7 are heated therein to a temperature of between about 800° to about 1200° F., and are directed therefrom through line 12 and valve 13 to reforming chamber 14. Preferably a short time of contact or high space velocity is employed in the reforming chamber in order to produce only a minimum amount of lighter products. The term "space velocity" is intended to mean the volume of liquid charging stock per hour per unit

volume of catalyst. Space velocities of about 5 to about 25 or more are preferably employed. It is believed that the relatively low conversion of sulfur compounds effected in this step of the process is probably due to the relatively high space velocities employed. On the other hand, if lower space velocities were employed, the isomerization reaction would be accompanied by the excessive production of lighter boiling products as well as excessive coke formation.

Reforming chamber 14 contains a bed of synthetically prepared catalytic material capable of effecting isomerization of the olefinic hydrocarbons introduced thereto. Due to the higher temperatures employed in the second step of the process, other reactions will be effected along with isomerization and it is not intended to limit the present invention to any particular reaction or reactions. It is believed, however, that the isomerizing reaction will predominate in this zone. In any event, the products emitting therefrom will be of higher octane number than the products introduced thereto.

The preferred synthetically prepared catalysts comprise silica composited with alumina. These catalysts may or may not contain other oxides such as zirconia, thorium or the like. The catalysts may be prepared by separate or simultaneous precipitation and usually are treated to remove alkali metal compounds. It is also preferred to calcine these catalysts at high temperatures prior to their use.

In addition to these catalysts, there are other synthetically prepared catalysts which are suitable for use in this step of the process, and include, for example, aluminum sulfate-containing catalysts, phosphates of certain metals such as aluminum, magnesium, etc., fluorides of certain metals such as aluminum, magnesium, etc., phosphoric acid-containing catalysts, and others. It is of course understood that these catalysts are not necessarily equivalent in promoting the desired reactions.

The products from the reforming chamber are withdrawn therefrom through line 15 and are directed through valve 16 into fractionator 17. The products introduced into fractionator 17 are fractionated therein to separate any light gases formed in the process. The light gases are removed through line 18 and valve 19 to storage or elsewhere as desired. The unvaporized products in fractionator 17 may be further separated therein into a fraction having an end boiling point of about 400° F. and may be removed therefrom through line 20 and valve 21 to storage or elsewhere as desired. Any higher boiling products may be removed from fractionator 17 through line 20 and valve 21 to storage or elsewhere as desired.

The following example illustrates one specific operation which may be conducted in accordance with the features of the present invention. It is not presented with the intention of unduly limiting the broad scope of the invention.

The charging stock comprises gasoline produced by the non-catalytic cracking of a Texas topped crude. The properties of the charging stock are given below in the following table. In the first step of the process, the charging stock is contacted with attapulgus clay at a temperature of about 650° F. and a pressure of about 20 pounds per square inch. In the second step of the process the products from the first step are contacted with a catalyst containing silica, alumina and zirconia at a temperature of about

950° F., approximately atmospheric pressure and space velocity of about 5. The products which may be obtained from each of the steps of the process are indicated below:

	Charging stock	Products from the first step	Products from the second step
A. P. I. gravity.....degrees.....	56	55	55
Total sulfur.....per cent.....	0.53	0.35	0.25
Color.....deg. Saybolt.....	0	25	-----
Copper dish gum.....mg.....	217	12	-----
Oxygen bomb induction.....minutes.....	325	910	-----
Octane number, motor method.....	69	70	76
Initial boiling point.....° F.....	102	115	105
End boiling point.....° F.....	398	398	400

I claim as my invention:

1. A process for the treatment of thermally cracked gasoline which comprises subjecting said gasoline to contact with bauxite at a temperature of between about 400° F. and about 800° F. under a superatmospheric pressure of between about 50 and about 200 pounds per square inch, superheating the products therefrom without intentional prior cooling thereof and subjecting the same to contact with a synthetically prepared catalyst containing silica and alumina at a temperature of between about 800° F. and about 1200° F., under a pressure of substantially atmospheric to about 50 pounds per square inch and with an hourly liquid space velocity of between about 5 and about 25.

2. The process defined in claim 1 wherein said synthetically prepared silica-alumina catalyst also contains another metal oxide.

3. The process defined in claim 1 wherein said synthetically prepared catalyst comprises silica-alumina-zirconia.

4. A process for improving the characteristics of olefinic gasolines which comprises desulfurizing the olefinic gasoline in the presence of a desulfurizing catalyst at a temperature of from about 400 to about 800° F., passing resulting ole-

finic conversion products, while retaining heat from the desulfurizing operation and without prior cooling to a heating step and therein heating the same to a temperature of from about 800° F. to about 1200° F., subjecting the thus heated products to the action of an olefin isomerizing catalyst different from said desulfurizing catalyst, and adjusting the time of contact so that a substantial portion of the olefinic products are isomerized.

5. The process of claim 4 further characterized in that said olefinic gasoline comprises a cracked gasoline.

6. The process of claim 4 further characterized in that said olefinic gasoline comprises a thermally cracked gasoline.

7. A process for improving the characteristics of olefinic gasolines which comprises desulfurizing the olefinic gasoline in the presence of a desulfurizing catalyst at a desulfurizing temperature, passing resultant conversion products, without intentional prior cooling to a heating step and therein heating the same to an olefin isomerizing temperature which is substantially greater than said desulfurizing temperature, and isomerizing the thus heated products in the presence of an olefin isomerizing catalyst different from said desulfurizing catalyst.

8. A process for improving the characteristics of olefinic gasoline which comprises desulfurizing the olefinic gasoline in the presence of a desulfurizing catalyst under desulfurizing conditions and subjecting resultant conversion products, without intentional prior cooling to the action of an olefin isomerizing catalyst different from said desulfurizing catalyst at a temperature of from about 800 to about 1200° F., a pressure of from about atmospheric to about 50 pounds per square inch and for a time of contact corresponding to a liquid hourly space velocity of from about 5 to about 25.

CHARLES H. ALBERDING.