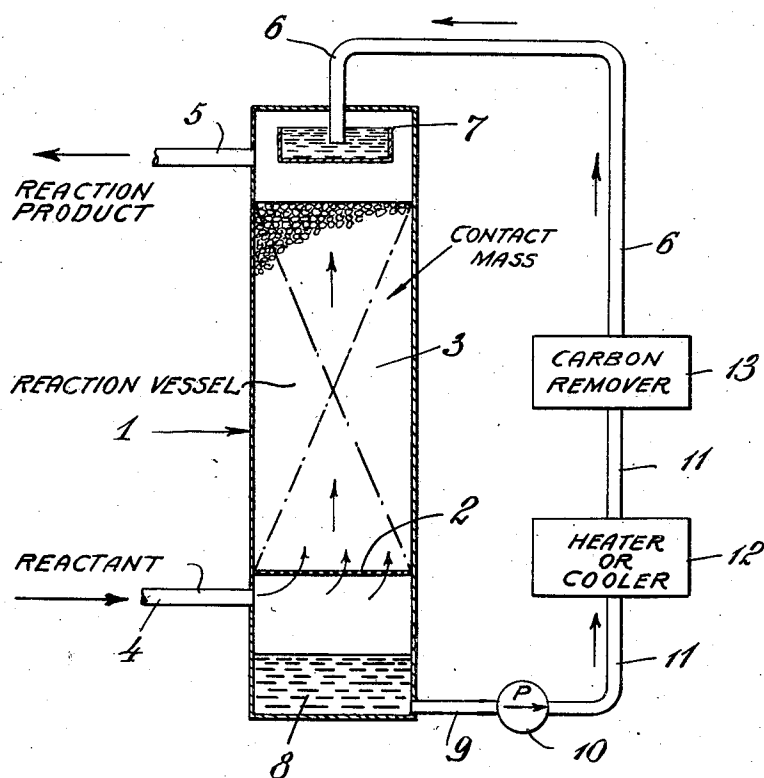


July 25, 1944.

A. J. ABRAMS ET AL
CONVERSION OF HYDROCARBONS

2,354,355

Filed Oct. 22, 1941



INVENTORS
Armand J. Abrams
& Irving H. Welensky
BY
Arthur V. Danner
ATTORNEY

UNITED STATES PATENT OFFICE

2,354,355

CONVERSION OF HYDROCARBONS

Armand J. Abrams and Irving H. Welinsky, Dallas, Tex., assignors to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

Application October 22, 1941, Serial No. 416,018

4 Claims. (Cl. 196—50)

This invention is directed to a method for the conversion of liquid hydrocarbons having a boiling range in or near the gasoline boiling range for the purpose of increasing the anti-knock capabilities of such hydrocarbons. Such a process is usually carried out upon straight run gasolines, natural gasolines, fractions of either natural gasolines or of straight run gasolines, naphthas of either origin which are near to or within the gasoline boiling range, or upon relatively pure hydrocarbon compounds capable of being readily so transformed into gasoline boiling range materials of higher anti-knock value. Any process of this type is known generically by the expression reforming of naphtha, which expression, as used, has a breadth sufficient to embrace processes conducted both thermally and catalytically, and in liquid phase, vapor phase, or mixed phase. The present invention is directed to catalytic reforming of naphtha and in certain respects may be considered a specific invention under the generic invention covered in the co-pending application Serial No. 373,075, filed January 4, 1941.

Catalysts are known for the reforming of naphtha. Thus, for example, silica-alumina and chromic oxide-alumina catalysts have been proposed. This invention is not concerned with a novel catalyst for the process but rather is directed to a method of controlling the temperature in any of these catalytic processes using any solid reforming catalyst. For the sake of simplicity, the invention will be discussed with particular reference to chromic oxide-alumina catalysts. However, it will be apparent, other reforming catalysts may be employed, and it is to be understood that the use of any solid reforming catalyst is considered within the scope of the invention.

Heretofore, for the most part, the catalysts have been used in the form of deep beds which may be stationary or moving, and the naphtha vapors are passed through the bed. The requirements for and the difficult problem of properly regulating or controlling the temperature throughout such beds of catalysts, particularly during regeneration of the catalyst, is well known to everyone versed in the art. Proper temperature control has been attained, however, by the use of internal indirect heat exchange equipment, but such equipment increases the complexity of the apparatus required. Also, chromic oxide-alumina catalysts, which are not so sensitive to heat as, say, alumina-silica catalysts, have been used without any particular temperature con-

trol means, and heat has been supplied solely through the external walls of the converters. We have found, however, that substantially improved results are obtained even with chromic oxide-alumina catalysts where complete and adequate temperature control is provided.

Therefore, it is an object of this invention to provide a process of reforming hydrocarbons which affords an improved temperature control system for the reaction.

A more specific object is to provide a process of reforming hydrocarbons which is accomplished by flowing the hydrocarbons in vapor phase through a catalytic spreading material in direct contact with a heated, liquid heat transfer medium which flows over the catalytic spreading material without flooding the conversion zone.

In one form of the process described herein, it is proposed to carry out the reforming of naphtha by passing the preheated hydrocarbons and a liquid heat transfer medium, such as, for example, molten metal or molten salt, simultaneously over a bed of a granular reforming catalyst under such conditions of rate and temperature that the necessary heat of reaction will be supplied by the heat transfer medium. The rate of flow and the temperature of the heat-transfer medium can be so regulated that a uniform temperature will result throughout the catalyst bed. At any one time, the bed of catalyst will have the appearance of a tower of catalyst containing a ramification of metal mesh in the form of streams of metal (and/or salt). One distinct advantage associated with this method of supplying heat to a catalytic reaction is that it solves the heat transfer problem attending such reactions and allows the use of relatively large and simple converters. In other words, our process is an improvement upon prior practices in that it solves the heat transfer problem associated with catalytic reactions and at the same time retains the desirable features of simplicity in design and cost of operation.

The process may be readily understood by reference to the drawing attached hereto, the single figure of which shows, in diagrammatic form, a setup of apparatus suitable for accomplishing the process herein described. In this drawing there is a tower, chamber, or housing 1, in which, supported by a grid or screen 2, there is a bed of catalyst 3. Reactant vapors at or near reaction temperature are introduced through pipe 4 and products of reaction are withdrawn through pipe 5. A heated, liquid heat transfer medium is intro-

duced at pipe 6, flows into and through distributor 7, and then through catalyst 3 where it is in direct contact with and giving up heat to both the catalyst mass 3 and the reactant vapors flowing therethrough. The liquid heat transfer medium leaving the catalyst mass 3, is collected in pool 8 at the bottom of the reaction vessel 1 and removed therefrom by pipe 9. This heat transfer medium is then forced through an external circuit by pump 10 wherein it flows through pipe 11 to heat adjuster 12, in which its heat content is restored. Then, if necessary or desirable, the medium flows through some carbon cleaning operation as indicated at 13, after which it is returned to the reaction vessel 1 by pipe 6 to complete a cycle. Obviously, if the catalyst mass requires a regeneration necessitating removal of heat, the same heat control means using a suitable heat transfer medium may be employed for such heat removal, the equipment item 12 in this case acting as a cooler.

A more full and complete description of operations under this general plan of heat control by physical or direct contact with a liquid heat transfer medium, together with many improved forms and modifications thereof, is given in the above-mentioned application Serial No. 373,075, filed January 4, 1941. Therefore, it is to be understood that any of the systems shown in that application may be used for conducting the present process.

Liquid heat transfer media which may be used are molten metals and alloys, fused inorganic salts or mixtures of fused inorganic salts, or, indeed, any material liquid at the temperature of reaction, of low vapor pressure at that temperature, stable at that temperature, and not entering into the reaction being accomplished other than to a catalytic extent. Of these media, the molten metals and alloys are most desirable and preferable. Molten lead is typical of such a heat transfer material, but the invention must be understood as not being limited thereto.

An important discovery of this invention is the fact that the catalyst can be regenerated repeatedly to optimum activity even though it is carrying some lead. Thus, it seems that during the regeneration, the lead on the catalyst is converted to lead oxides; however, as soon as the catalyst is put back on stream, the lead oxide is quickly reduced to metallic lead, and the process goes on with the catalyst at full efficiency.

In order to give a fuller disclosure of the invention, there are set forth below several examples of actual operation, but it is to be understood these specific examples are merely for purposes of illustration.

Example I

A catalyst was prepared by impregnating $\frac{1}{8}$ inch activated alumina pills with a solution of chromic acid. After drying at 250° C. in an atmosphere of hydrogen, the pills contained approximately 15 mol per cent of Cr_2O_3 .

This catalyst was placed in a reactor and a heptane cut (B. P. 96–98.8° C.) from a Mid-Continent natural gasoline containing no olefins or aromatics was passed through it at a temperature of 550° C. and a rate of 0.3 liter of liquid feed per liter of catalyst per hour. The liquid product analyzed 2.5 weight per cent olefins and 17.2 weight per cent of aromatics.

A duplicate experiment carried out with lead passing over the catalyst under non-flooding conditions yielded a liquid product which analyzed 7.3 weight per cent olefins and 34.8 weight per

cent aromatics. Distillation data proved that the aromatics were mainly toluene. This very significant increase in yield must be attributed to the uniform temperature conditions which prevail in the catalyst bed while lead is passing through it.

Example II

An essentially depentanized Mid-Continent natural gasoline containing no olefins or aromatics was passed over a catalyst, prepared as in Example I, at a temperature of 550° C. and a rate of 1.6 liters of liquid feed per liter of catalyst per hour. The liquid product (82.6 weight per cent of feed) analyzed 10.3 weight per cent olefins and 28.2 weight per cent aromatics. The gaseous product contained 84.7 volume per cent hydrogen.

A duplicate experiment carried out with lead passing over the catalyst under non-flooding conditions yielded a liquid product (84.8 weight per cent of feed) which analyzed 20.9 weight per cent olefins and 34.9 weight per cent aromatics. The gaseous product contained 87.0 volume per cent hydrogen.

Here again, the higher yields of olefins, aromatics and hydrogen illustrate how the process with lead passing over the catalyst is more efficient. Furthermore, after each run, the catalyst was regenerated with oxygen-containing gases, and the continuation of reaction in each case demonstrated that the catalyst was brought back to initial activity, thereby establishing that regeneration of the catalyst in the presence of lead is not harmful.

Example III

An essentially depentanized Mid-Continent natural gasoline which showed an A. S. T. M. octane number of 54.7 was reformed in a manner similar to that described in Example II. The product showed an A. S. T. M. octane number of 71.8.

It will, of course, be realized that when regeneration of the catalyst is appropriate to provide a unitary process that such regeneration is contemplated as a part of the process herein disclosed as has been indicated above.

We claim:

1. The process of catalytically reforming aliphatic hydrocarbons of approximately gasoline boiling range to provide aromatic hydrocarbons of gasoline boiling range which comprises passing the hydrocarbon charge stock in vapor form through a bed of catalyst under reforming conditions in direct contact with molten lead as a heat transfer medium which is flowed through the catalyst bed in insufficient amount to flood the voids therein, removing liquid heat transfer medium from the catalyst bed, eliminating carbonaceous matter from said removed liquid medium and adjusting its heat content for re-use in the catalyst bed, and returning the thus treated liquid heat transfer medium to the catalyst bed.

2. The process of catalytically reforming hydrocarbons of boiling range similar to gasoline to produce hydrocarbons of gasoline boiling range and enhanced antiknock capability which comprises passing the hydrocarbons in vapor form under reforming conditions through a bed of a regenerable, inorganic catalytic material, maintaining the catalyst bed and the hydrocarbons at the desired reaction temperature by directly contacting said catalyst bed and said hydrocarbons with molten lead as a heat transfer medium, and supplying the necessary heat

to said heat transfer medium when the heat transfer medium is out of contact with the catalyst bed.

3. The process of catalytically reforming hydrocarbons of boiling range similar to gasoline to produce hydrocarbons of gasoline boiling range and enhanced antiknock capability which comprises passing the hydrocarbons in vapor form under reforming conditions through a bed of a regenerable, inorganic catalytic material, maintaining the catalyst bed and the hydrocarbons at the desired reaction temperature solely by flowing a heated, normally solid melt, which is substantially inert under the reaction conditions, as a heat transfer medium downwardly through said catalyst bed in direct contact with said hydrocarbons at a rate insufficient to flood the voids therein, and supplying the necessary heat to said heat transfer medium when the heat transfer medium is out of contact with the catalyst bed.

4. The process of catalytically reforming hydrocarbons of boiling range similar to gasoline

5 to produce hydrocarbons of gasoline boiling range and enhance antiknock capability which comprises passing the hydrocarbons in vapor form under reforming conditions through a bed of regenerable, catalytic material, supplying all of the necessary heat to maintain the hydrocarbons and catalyst bed at a desired reaction temperature by flowing hot molten metal downwardly through said catalyst bed in direct contact with said hydrocarbons at a rate insufficient to flood the voids therein, removing the molten metal from the bottom of said catalyst bed, supplying the necessary heat to said molten metal and recirculating it through said catalyst bed, and regulating the rate of admission of hydrocarbons to the catalyst bed so that the over-all heat losses are at a rate substantially equal to the heat input supplied by the molten metal whereby a substantially constant temperature gradient is maintained in the catalyst bed.

ARMAND J. ABRAMS.
IRVING H. WELINSKY.