

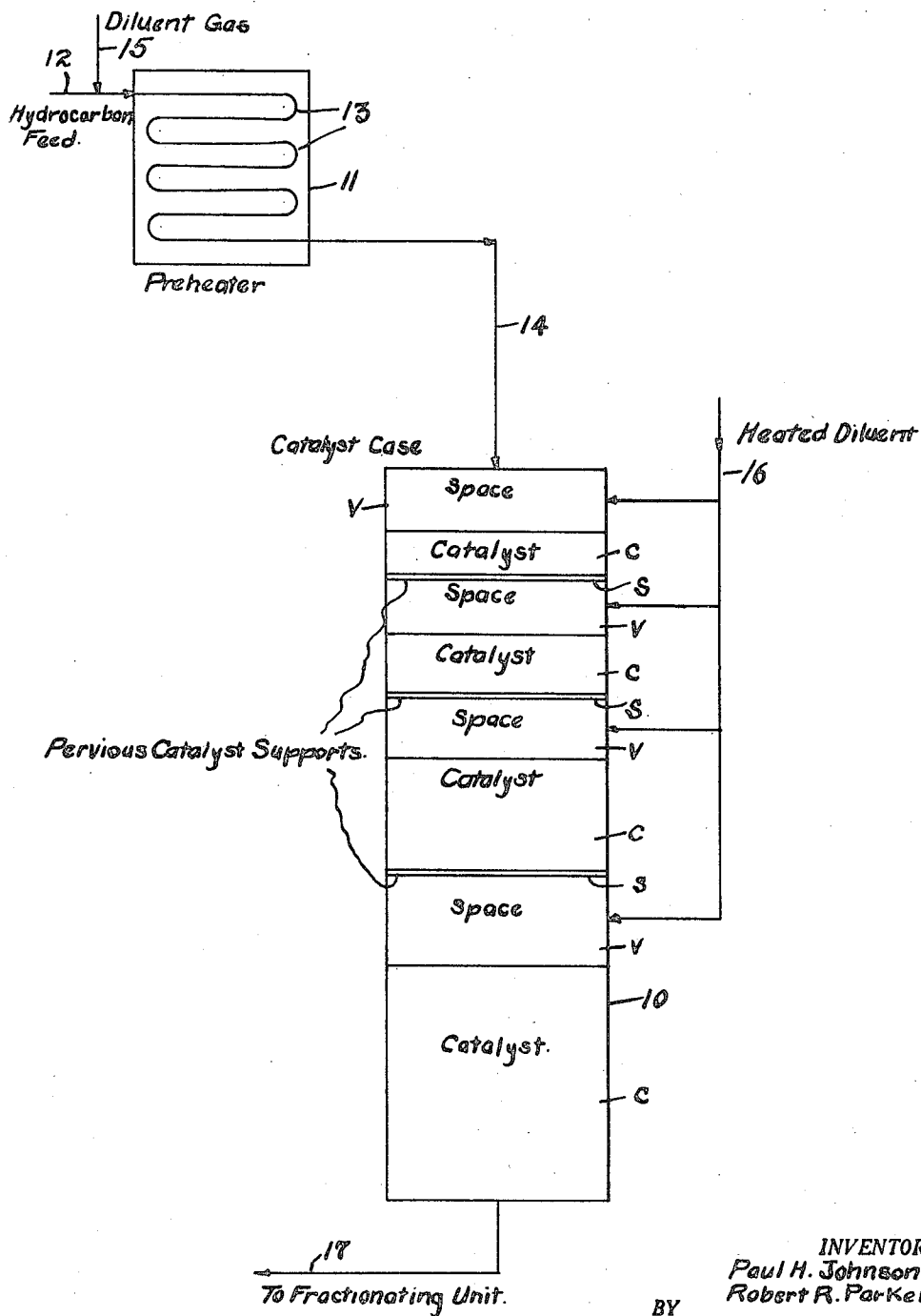
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METHOD OF PRODUCING AROMATIC HYDROCARBONS

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METHOD OF PRODUCING AROMATIC
HYDROCARBONS

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This invention relates to a new and commercially practicable method of treating hydrocarbon oils by a series of reactions to increase the content of aromatic hydrocarbons therein.

It is known that increasing the aromaticity of paraffinic motor fuel fractions will result in an increase in the octane number thereof. This has been accomplished either by incorporating aromatic materials boiling in the motor fuel range or by converting a portion of the paraffinic material in the motor fuel or material from which it is derived, to aromatics boiling in the motor fuel range. In order to convert paraffinic materials to suitable aromatic compounds it is usually necessary to carry out a series of complex thermal and/or catalytic reactions and as a necessary consequence thereof certain losses occur due to carbonization and conversion into products which are outside of the desired boiling range. Certain other disadvantages result from the necessity for carrying out these reactions at elevated temperatures and the necessity for supplying or abstracting heat in these reactions. Applicants have now discovered a method for increasing the aromaticity of paraffinic materials in a simple and economic manner.

It is an object of this invention to pass a preheated hydrocarbon charge through a catalyst chamber having a plurality of appropriate catalyst beds separated by thermal cracking zones to cause successive thermal and catalytic reactions in the charge to increase the aromatic hydrocarbon content thereof.

A more specific object of this invention is to subject heated hydrocarbon oils to alternate thermal and catalytic reactions under conditions where the paraffin content of the charge is converted to olefins, the olefins reacted to form aromatics, the mixture again treated to form additional olefins which again are reacted to form aromatic hydrocarbons, and these reactions alternately caused to take place in a continuous flow of hydrocarbons to substantially increase the aromatic content of the original charge.

Another object of this invention is to provide a method which takes advantage of the fact that the reaction of the olefins to form aromatics is an exothermic reaction and the formation of olefins from paraffins is an endothermic reaction and thus each reaction may be carried out in a manner which will wholly or partially compensate for the temperature change occurring in the other. Further advantage is taken of the fact that the aromatics which are formed are relatively stable under the conditions where the ole-

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fins are formed from unreacted paraffins so that the addition of successive increments of aromatics is effected without destruction of the aromatic compounds formed during previous reactions.

Other and more detailed objects of this invention will be apparent from the following disclosure of one method of practicing it.

This invention resides in the steps and series of steps of the method herein disclosed.

In general the charge stocks converted in the present process are highly paraffinic materials, the aromaticity of which it is desired to increase. Such materials include light naphthas boiling in the range of, say, 200 to 400° F., straight run gasolines, and highly paraffinic fractions from various sources such as the C₇ and higher materials fractionated from natural gasoline. In accordance with applicants' invention these materials are subjected to alternate thermal and catalytic reactions in a series of zones located within the same reaction chamber or in contiguous or heat exchange relationship. In the thermal zones dehydrogenation of paraffinic materials to olefins occurs as a primary reaction and these olefinic materials are successively aromatized by catalytic reaction to form aromatics. At the same time some cracking, particularly of heavier paraffins, also occurs. The dehydrogenation-cracking reaction to form olefins is endothermic while that for the conversion of olefins to aromatics has been found to be exothermic.

The invention may be carried out by arranging in a reaction chamber a series of alternate thermal and catalytic zones. The thermal zones may be open spaces or may contain relatively inert contact material of the nature of firebrick, Alundum, or silicon carbide. These zones should be of sufficient dimension to provide the desired contact time necessary to effect thermal dehydrogenation and cracking at the flow rate of charge which is used. The catalyst zones contain a desired catalyst for effecting aromatization and this catalyst should be one which would be specific enough for aromatization and polymerization reactions to result in a net exothermic effect. Such catalysts include bauxite, silica-alumina, and chromium oxide alone or preferably activated by admixture with oxides of aluminum, iron, molybdenum, thorium and the like. Heavy metal salts may also be used. Among these may be mentioned the molybdates and tungstates of nickel, vanadium, chromium and iron. In particular it has been found that the use of bauxite will result in a substantial exothermic reaction at the tem-

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peratures and under the conditions described herein and that this exothermicity may under the proper conditions be of the same order as the temperature drop occurring to the endothermic reaction which takes place in the thermal zones.

In view of the fact that in accordance with this invention both endothermic and exothermic reactions are taking place, it is intended that advantage of this fact may be taken in order to permit mutual compensation for heat loss or rise in the respective zones. Thus if the thermal conversion zone is of such dimensions as to permit a temperature drop of 50° F. to take place, the catalyst and dimensions of the catalytic zone are so selected as to permit a temperature rise in that zone of approximately 50° F. so that when the effluent from that zone enters the next thermal conversion zone it will have been elevated to the desired initial conversion temperature. The temperature drop in this next thermal conversion zone may be compensated for by the temperature rise which occurs in the succeeding catalytic zone. Thus the two reactions may be carried out without the necessity for supplying additional heat to the endothermic zones or removing heat from the exothermic zones.

Further control of temperature or reaction time in the respective zones may be obtained by the use of an inert diluent such as steam which may, if desired, be heated to an extent sufficient to provide for removing or supplying the desired amount of heat to or from the respective zones. Thus in case the temperature drop or temperature rise, as the case may be, in any zone is insufficient to compensate for the change in temperature of the preceding or succeeding zone, the deficiency may be compensated for by the use of heated diluent. Inasmuch as the use of diluent will decrease contact time it may be desirable to compensate for this decrease by increasing the depth of the successive zones in proportion to the concentration of diluent. It is also frequently desirable to add diluent to the feed entering the thermal conversion zones in order to maintain the contact time therein sufficiently low to promote olefin formation. This will of course necessitate an increase in the depth of the catalyst zones in order to provide a sufficient contact time to permit substantial aromatizing to take place.

Ordinarily, the dehydrogenation reaction is conducted at a slightly higher temperature than the aromatizing reaction, for example, with a temperature in the range of about 1000 to 1200° F. for the thermal dehydrogenation reaction is purely thermal, so that the aromatization reaction will be conducted at a slightly lower initial temperature due to the temperature drop in the preceding zone. Because of practical considerations the extent of this temperature drop should preferably not be greater than about 100° F. In order to obtain substantial olefin formation in the dehydrogenation zone a contact time of 0.05 to 1 second may be used, while in the aromatization zone a contact time of 0.5 to 2 seconds may be provided.

In the accompanying drawings the single figure is a diagrammatic illustration of an apparatus suitable for illustrating the procedural steps of the method herein claimed.

In accordance with this invention a catalyst chamber or case 10 is employed of any suitable and well known construction in which a plurality of catalyst beds C of suitable catalyst are supported on perforated or permeable supports S in spaced relation, as shown in the drawing, to

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form spaces or voids V between the catalyst beds. Thus it is clear from the drawing, in relation to the flow path of the charging stock, that it passes alternately through the voids or spaces and the catalyst beds as it progresses from the inlet of the catalyst case to the outlet.

The charging stock is preheated before delivery to the catalyst case in a preheater 11 of any suitable construction. The charging stock is supplied from the source through the line 12 to the heating coils 13 of the preheater and from there through the line 14 into one end of the catalyst case 10. As will be described later, a suitable diluent may be added to the charging stock through the line 15 for admixture therewith before preheating and/or the same or a different diluent may be introduced into the charging stock at one or more reaction zones in the catalyst case through the line 16 and its branches. The reacted fluid is withdrawn from the catalyst case 10 and delivered to any suitable separating or fractionating equipment, not shown, by the line 17. The contemplated reactions are carried out in the catalyst case under pressures from 0 to 200 pounds per square inch, and therefore, the various lines are suitably valved and controlled in an obvious manner to maintain the selected operating pressure.

In one actual demonstration of this process, the hydrocarbon oil charging stock, which was a light naphtha containing mainly paraffins, some olefins, some aromatic hydrocarbons and other cyclic compounds such as cycloparaffins, was supplied to the preheater 11 where its temperature was raised to approximately 1140° F. The charge stock had a boiling range of about 200-400° F. In this operation the charging stock was diluted with steam in the weight ratio of oil to steam of about 6 to 1, and the mixture was fed at the rate of 8 to 10 barrels of oil per hour.

The catalyst employed was 10-20 mesh granular bauxite although other catalysts as described may be used in this process. In the particular operation described the catalyst beds were about 3 feet in diameter and progressively increased in depth from 2 feet at the top to 4 feet at the bottom. The thermal spaces varied in depth from 2 feet at the top to 3 feet at the bottom.

Olefins are formed in the mixture while in the first space V and under the temperature and pressure conditions and flow rate noted. Some olefins, of course, may be formed in the preheater and in the line 14 on the way to the catalyst case. The mixture then proceeds through the first catalyst bed C where a portion of the olefins present in the mixture is converted into aromatic hydrocarbons. During the reaction in the first space, which is a thermal reaction, heat is absorbed since this is an endothermic reaction. However, during the reaction in the catalyst bed, which is of course a catalytic reaction, heat is given off since this is an exothermic reaction. Therefore the temperature of the mixture in the catalyst bed rises. When the mixture proceeds to the next space V further olefins are formed and the temperature falls to be followed by an increase in temperature of the mixture during the formation of additional aromatic hydrocarbons from the olefins just formed. These alternate reactions continue as the mixture moves through the catalyst case and the percentage of aromatic hydrocarbons present gradually increases in view of the fact that under the conditions noted previously formed aromatic hydrocarbons are stable during

the subsequent reactions and particularly during the thermal reaction resulting in the formation of olefins. As shown, provision is made for the introduction of heated diluent into the thermal spaces to supply additional heat in the event sufficient exothermic heat is not developed in the catalytic zones.

In the example being given there was a net production of 11.15% of aromatic hydrocarbons.

The resulting mixture was then passed through the line 17, first, to suitable separating equipment to remove the diluent steam therefrom, and then to suitable fractionating equipment of conventional form to fractionate the product in accordance with the uses to which it was to be put. The resultant product in this case is very valuable as an ingredient of high-octane high-rich rating aviation gasoline.

As noted in the example above, no additional heated diluent was added to the spaces through the line 16 and its branches but where it is desired to vary the reaction time this can be controlled by the volume of the heated diluent introduced directly into the spaces through the line 16 or its branches, either as an addition to that added to the mixture through the line 15 or as an alternative thereto. Thus reaction time as well as temperature may be controlled in whole or in part by the use of diluent at a predetermined volume or temperature. It is to be noted that in addition to steam other inert gases such as nitrogen or methane can be used for the same purpose. It is also within the purview of this invention to employ heating coils in the spaces V for supplying heat to the thermal reaction and thereby controlling the reaction time.

To be more specific with regard to the example described above, the following observation temperatures are noted remembering that the charge stock was delivered into the reaction chamber at a temperature of 1140° F. The temperature in the first catalyst bed averaged about 1100° F. and in the first space below it about 1075° F. The temperature of the mixture in the upper part of the second catalyst bed was 1090° F. and in the lower part 1100° F. The temperature in the next space V was 1080° F. and in the upper part of the next catalyst bed 1077° F. At about the center of this bed it was 1076° F. In the next, that is the last space V, the temperature was 1087° F. In the upper part of the last catalyst bed it was 1095° F., at the center 1097° F. and near the bottom 1093° F. Thus it will be seen that by alternate thermal and catalytic reactions there was very little total loss of heat in the charge as between the top of the first catalyst bed and the bottom of the last one.

From the above description it will be apparent to those skilled in the art that the method herein disclosed is capable of some variation within the novel scope thereof without departure from the true subject matter of the invention. We do not, therefore, desire to be strictly limited to the illustrative example herein given but rather by the limitation of the appended claims.

What is claimed is:

1. A process for converting a paraffin hydrocarbon material boiling in the gasoline range to aromatic hydrocarbons, which comprises heating such a material to a temperature in the range of 1000 to 1200° F. and maintaining same within this temperature range in an endothermic conversion

zone and in the absence of any catalyst for a time of 0.05 to 1 second, passing the resulting material containing olefins so produced into contact with a mass of solid granular catalyst which promotes exothermic aromatization and polymerization reactions for a reaction time of 0.5 to 2 seconds to effect an exothermic hydrocarbon reaction, passing hydrocarbons effluent from said catalyst mass through a second endothermic conversion zone in the absence of a catalyst for a reaction time of 0.05 to 1 second, passing the resulting material containing olefins so produced into contact with a second mass of solid granular catalyst which promotes exothermic aromatization and polymerization reactions for a reaction time of 0.5 to 2 seconds to effect an exothermic hydrocarbon reaction, each of said endothermic reactions being carried out without addition of heat from an outside source, and recovering from effluents of the last said zone an aromatic hydrocarbon material boiling in the gasoline range so produced.

2. A process for converting a paraffin hydrocarbon material boiling in the range of 200 to 400° F. to aromatic hydrocarbons, which comprises heating such a material to a temperature in the range of 1000 to 1200° F. under a pressure not greater than 200 lbs. sq. in. and maintaining same within this temperature and pressure range in a subsequent endothermic conversion zone and in the absence of any catalyst and added heat for a time of 0.05 to 1 second and such that a temperature fall of not more than 50° F. takes place, passing the resulting material containing olefins so produced into contact with a mass of solid granular catalyst which promotes exothermic aromatization and polymerization reactions for a reaction time of 0.5 to 2 seconds and such that a temperature rise of not more than 50° F. takes place in the absence of added heat to effect an exothermic hydrocarbon reaction, passing hydrocarbons effluent from said catalyst mass through at least one additional series of endothermic and subsequent exothermic conversion zones operated under the same conditions as those just recited, and recovering from effluents of the last exothermic conversion zone an aromatic hydrocarbon material boiling in the gasoline range so produced.

3. A process according to claim 2 wherein the aromatization catalyst is bauxite.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,847,238	Frey et al.	Mar. 1, 1932
2,124,566	Grosse	July 26, 1938
2,167,602	Schulze	July 25, 1939
2,251,571	Howard	Aug. 5, 1941
2,271,646	Kassel	Feb. 3, 1942
2,301,044	Heard et al.	Nov. 3, 1942
2,315,839	Burk et al.	Apr. 6, 1943
2,322,366	Kassel	June 22, 1943
2,327,746	Schultz	Aug. 24, 1943
2,342,881	Mekler	Feb. 29, 1944
2,353,509	Schulze et al.	July 11, 1944
2,366,567	Schultz	Jan. 2, 1945
2,375,940	Nitescu	May 15, 1945
2,378,651	Matuszak	June 19, 1945