

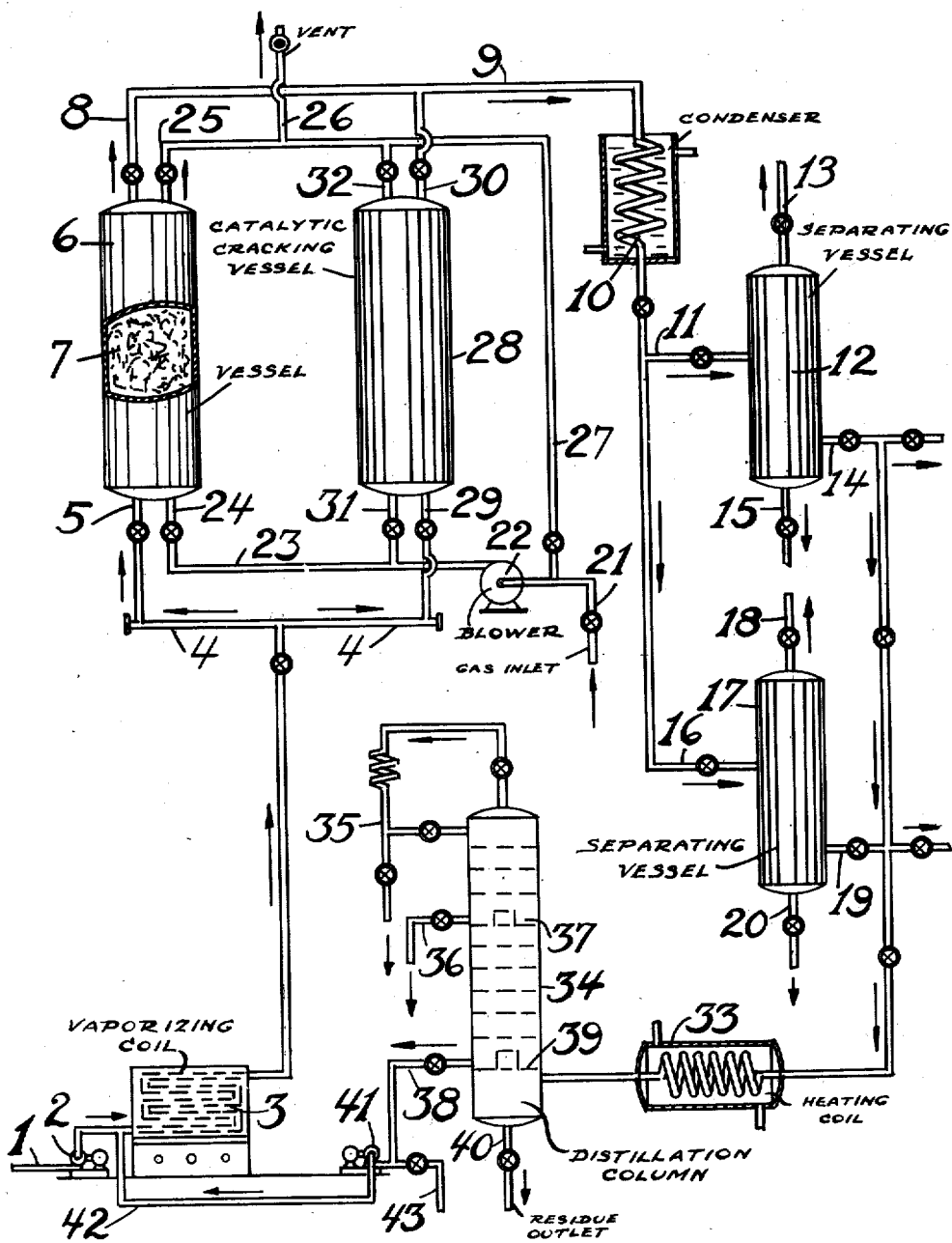
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## CATALYTIC CRACKING PROCESS

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## UNITED STATES PATENT OFFICE

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## CATALYTIC CRACKING PROCESS

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This invention relates to an improved process for the catalytic cracking of hydrocarbons and has particular reference to methods for preparing two or more improved products from a single feed stock.

In the catalytic cracking of hydrocarbons, the process may be carried out in such a manner that both the materials undergoing cracking and the catalyst are passed continuously through the cracking zone. With this type of operation the composition of the cracked products remains substantially uniform for any fixed set of reaction conditions.

Another method of catalytic cracking is conducted by passing hydrocarbons through a reaction zone having a cracking catalyst maintained therein and periodically stopping the flow of hydrocarbons and regenerating the catalyst by passing suitable oxidizing gases through the reaction zone. The operation thus comprises a series of cycles of alternate cracking of hydrocarbons and regeneration of the catalyst. It has now been found that the nature of the cracked products changes materially during the cracking cycle in such a "run-blow" operation and that it is advantageous to segregate these products in accordance with their individual fitness for the production of different finished products such as aviation gasoline, Diesel oil, etc., and for further utilization in other processes.

One object of this invention is to provide a process for the catalytic cracking of hydrocarbons by which cracked products of widely different characteristics may be prepared.

Another object of this invention is to provide a catalytic cracking process which is especially adapted for the preparation of improved aviation gasoline.

Another object of this invention is to provide a catalytic cracking process which is especially adapted for the preparation of products of high aromatic hydrocarbon content.

Another object of this invention is to provide an improved process for the catalytic cracking of hydrocarbons by which motor gasoline may be produced with a minimum of refining treatment.

Another object of this invention is to provide an improved process for the catalytic cracking of hydrocarbon oils which is adapted to produce an improved Diesel fuel having a high Diesel index, and which is also especially suitable for the production of high quality kerosene.

Still another object of the present invention is to provide an improved catalytic cracking process which is characterized by the production

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of a gas oil fraction of the cracked products which is especially suitable for further catalytic cracking and which may be used as a cycle stock in the process.

Another object of the present invention is to provide an improved process for the catalytic cracking of hydrocarbons in which there are produced low boiling and gaseous products which are particularly adapted for treatment in other processes involving recovery of hydrocarbons from the cracked gases or the use of the cracked gases for gas reversion, polymerization, the production of specialty products such as alcohols and the like.

Other and further objects of this invention will be apparent from the following description and the drawing.

The drawing is a diagrammatic illustration in partial sectional elevation of an apparatus suitable for carrying out a process involving one modification of the present invention and illustrates the flow of materials.

Turning to the drawing, a suitable hydrocarbon stock for catalytic cracking, such as a petroleum gas oil, is supplied in line 1 and is passed by pump 2 through a vaporizing coil 3 to an inlet manifold 4. Vapors pass from this manifold through line 5 into a vessel 6 which contains a packing or filling of a suitable cracking catalyst 7, such as an active or activated clay or a synthetic gel type catalyst containing oxides of silica, alumina, magnesia or various combinations of such oxides. The catalyst 7 may be disposed in the vessel 6 in any suitable manner, such as by being packed in this vessel or being placed therein on trays, in baskets and the like. Or the catalyst particles may be partially or even substantially completely suspended in a rising stream of gas or vaporous reagents, being thus maintained in the reaction vessel, in a state of limited or vibratory motion. It is desirable that substantially all of the catalyst remain in the reaction vessel and that any carried out of the reaction vessel with the gaseous products be separated therefrom and returned to the reaction vessel or that a relatively stationary mass of catalyst be used to treat the flowing stream of hydrocarbons.

The cracked hydrocarbons leave the vessel 6 by line 8 and are passed through line 9, condenser 10 and line 11 into a separating vessel 12. Uncondensed gaseous products are withdrawn by line 13, liquid products by line 14 and any water present in the cracked products (such as that resulting from the use of steam in the vaporization and/or cracking zones) by line 15.

The cracked products leaving the condenser 10

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may also be passed by line 16 to a second separating vessel 17 provided with a line 18 for taking off uncondensed gases, line 19 for oils and line 20 for water.

Means are also provided for regenerating the catalyst by treatment with air or other suitable oxidizing gases. These comprise a gas supply line 21 from which an oxidizing gas is passed by blower 22 through manifold 23 and line 24 into vessel 6. The regenerating gases leave the vessel 6 by line 25 and may be vented through line 26 or a part thereof may be recycled by line 27 to the blower 22.

One or more alternate catalytic cracking vessels, such as the vessel 28, may be used in parallel connections with the vessel 6 so that one vessel may be used for cracking hydrocarbons while the catalyst in the other vessel is undergoing regeneration. For example, the vessel 28 is provided with a hydrocarbon vapor supply line 29 and cracked products withdrawal line 30, a regenerating gas supply line 31 and a regenerating gas drawoff line 32.

The cracked products collected in vessels 12 and 17 may be subjected to any suitable rectification and refining treatments to prepare aviation gasolines, motor gasolines, kerosene, burning oil distillates, Diesel oils, fuel oils and the like as may be desired. For example, the liquid condensate received in vessel 17 may be passed by line 19 through heating coil 33 into a distillation column 34 which may be operated to separate cuts or distillate fractions of any desired volatility. For example, a column may be operated so as to take off the overhead distillate through line 35, a heavy naphtha fraction through line 36 from the trapout tray 37, a gas oil by line 38 from the trapout tray 39 and a residue by line 40. The gas oil may be used as cycle oil in the process and may be recycled by pump 41 and line 42. It may also be withdrawn by line 43 for treatment by any other suitable process, such as cracking, catalytic cracking or destructive hydrogenation.

The condensate collected in vessel 12 may also be fractionated in the tower 34 or in a separate tower, it being preferred to keep the condensates in vessels 12 and 17 separate in the distillation and refining treatment until substantially ready for blending into finished products.

The catalytic cracking operations of this invention are preferably conducted at elevated temperatures, such as for example, from 600 to 1200° F., preferably between about 650 and 1000° F., and with the hydrocarbons substantially completely in the vapor phase. The time of treatment should be adjusted in regard to the cracking temperature, catalyst activity and other factors, so as to secure a conversion of about 25 to 65% of hydrocarbons boiling below 400° F. from the heavier hydrocarbons passed through the cracking zone. The feed rate will ordinarily be between the limits of about 0.1 and 20 volumes of oil (liquid basis) per volume of cracking zone per hour and the operation is preferably conducted with a feed rate below about 5.0. The length of the cracking cycle will also depend largely on the activity of the catalyst and may range from 10 minutes to about 12 hours, and cycles of longer than about 20 minutes each are generally preferred.

Following the cracking cycle, the catalyst is regenerated by treatment with suitable oxygen-containing gases, such as air, air diluted with nitrogen or steam, flue gas and the like. The temperature of regeneration should be sufficiently

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high to remove carbonaceous material from the catalyst, but should not be permitted to rise at any time high enough to injure the activity of the catalyst. The regeneration temperature is preferably maintained between about 800 and 1100°, and temperatures exceeding 1200° will generally be found harmful to the activity of the silica-alumina type of cracking catalysts.

The operation of the apparatus illustrated in the drawing will now be described in connection with an example illustrating a suitable manner for conducting the process of this invention.

#### EXAMPLE 1

A petroleum gas oil distillate fraction boiling between about 500 and 700° F. and having a density of 33° A. P. I. and an aniline point of 174° F. is supplied as the feed stock and is heated rapidly in the vaporizer 3 to a temperature of about 910° F. as rapidly as possible in order to avoid the formation of coke. Any unvaporized material may be separated from the products leaving the vaporizer 3 and the vapors are then passed through manifold 4 and line 5 into vessel 6 which contains a fresh or freshly regenerated cracking catalyst at a temperature of about 850° F. Hydrocarbon vapors are passed through the cracking vessel 6 at a rate of about 0.3 volume of hydrocarbon (liquid base) per volume of the catalytic cracking zone per hour. The cracked products are withdrawn from vessel 6 through lines 8 and 9 and are passed through condenser 10 into the separating vessel 12 by line 11. After the cracking vessel has been in use for a time the activity of the cracking catalyst undergoes a change which is evidenced by changing characteristics in the cracked products. The separating vessel 12 is then shut off and the cracked products are passed from the condenser 10 through line 16 into vessel 17. After further use the activity of the cracking catalyst decreases to the extent that further operation is undesirable and the supply of hydrocarbon vapors is shut off in line 5 and is diverted through the manifold 4 and line 29 to vessel 28 which at this time contains a fresh or freshly activated cracking catalyst and which may be operated under the same conditions just described for cracking vessel 6. The cracked hydrocarbon products leave the vessel 28 by line 30 and, during the initial stages of the cracking cycle, are passed through line 9, condenser 10 and line 11 into vessel 12. During the latter stages of the cracking cycle these cracked products are diverted through line 16 into vessel 17, the vessels 12 and 17 thus serving to receive cracked products from the initial and final portions, respectively, of the cracking cycle from each of the cracking vessels.

While the vessel 28 is being used on the cracking cycle, the catalyst in vessel 6 may be undergoing regeneration. This is accomplished by forcing an oxidizing gas such as air, which is preferably diluted with steam, nitrogen, flue gas or the like, in order to avoid too rapid oxidation of the catalyst, by means of a blower 22 through the manifold 23 and line 24 into the vessel 6. The regenerating gas is preferably supplied in manifold 23 at a temperature of about 700-800° F. and at such a rate and oxygen content that the temperature of the catalyst 7 does not rise above about 1100° F. at any time during the regeneration. When the catalyst is substantially regenerated, as indicated by a dropping off in the oxides of carbon in the used regenerating gases leaving vessel 6 by line 25 and by decreasing

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catalyst temperatures, the vessel 6 is ready for use again in cracking hydrocarbons. The regenerating gas may then be cut off, the catalyst purged with steam or inert gas to remove oxygen, and hydrocarbon vapors may be again supplied by line 5, thus starting a fresh cracking cycle for this vessel. The cracked products obtained in the initial stages of this cycle are passed to vessel 12 and those from the latter stages of the cycle to vessel 17 as before. The catalyst in vessel 28 may similarly be regenerated during the carrying out of the cracking cycle in vessel 6.

It will be understood that the process may be conducted with any additional number of reaction vessels as may be desired and that these can be used in parallel with vessels 6 and/or 28 or in any intermediate stages between these vessels in the cracking and regenerating cycles. Provision should be made for segregating the products obtained in the initial and final stages of the cracking cycle from all such vessels, which may be done by connecting their cracked products outlet lines to vessels 12 and 17.

It will also be understood that provision may be made for segregating the products obtained in any desired number of portions of the cracking cycle, for example, other receiving vessels may be connected to receive cracked products in parallel with vessels 12 and 17, and the products of any intermediate portion of the cracking cycle may be separately collected in any of such vessels.

In carrying out the process of this invention as described in the above example, it has been noted that the products obtained in the initial

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C<sub>4</sub> hydrocarbons were produced during an entire four hour cracking cycle, while in the first thirty minutes of this cycle 4.5% by weight of dry gas and 7.5% by weight of C<sub>4</sub> hydrocarbons were produced. Of the C<sub>4</sub> hydrocarbons produced during the first thirty minutes, 32% were unsaturated, while 41% of the C<sub>4</sub> hydrocarbons produced during the entire four hour cycle were unsaturated. Thus it is desirable to segregate the gas produced during the different stages of the cracking cycle in accordance with its intended use. The gas from the initial stages of the cracking cycle is advantageously segregated for use in gas reversion-catalytic cracking processes or where the recovery of the entire C<sub>4</sub> cut is desired, while the gases from the latter portion of the cycle may be used for the production of a C<sub>4</sub> cut which is intended for polymerization or for the production of specialty products such as alcohols.

#### EXAMPLE 2

There is presented in the following table an outline of the operating conditions used and of the results obtained in catalytic cracking of an East Texas petroleum gas oil distillate fraction of 33.3° A. P. I. over an activated clay cracking catalyst at a feed rate of 0.3 vol. of oil per volume of catalyst per hour. The products from six consecutive periods of six cracking cycles were separately collected and composited for each period, each composite product then being distilled for maximum workings of aviation gasoline, heavy naphtha and 12# Reid vapor pressure, 400° F. end point gasoline.

Segregation of Products from Portions of the Cracking Cycle

|                                                    | Part of cracking cycle |           |           |           |           |           |
|----------------------------------------------------|------------------------|-----------|-----------|-----------|-----------|-----------|
|                                                    | 1                      | 2         | 3         | 4         | 5         | 6         |
| Length, hrs.                                       | 0-0.25                 | 0.25-0.50 | 0.50-1.00 | 1.00-2.00 | 2.00-3.00 | 3.00-4.00 |
| Operating conditions:                              |                        |           |           |           |           |           |
| Temperatures, ° F.—                                |                        |           |           |           |           |           |
| Reactor inlet                                      | 904                    | 907       | 910       | 910       | 911       | 911       |
| Catalyst—top                                       | 861                    | 851       | 842       | 842       | 846       | 849       |
| Catalyst—middle                                    | 858                    | 877       | 853       | 834       | 832       | 836       |
| Catalyst—bottom                                    | 873                    | 874       | 860       | 839       | 829       | 832       |
| Catalyst—average                                   | 872                    | 867       | 852       | 838       | 834       | 839       |
| Reactor outlet                                     | 844                    | 846       | 847       | 829       | 822       | 822       |
| Yields on oil fed:                                 |                        |           |           |           |           |           |
| 12# R. V. P.—400° F. E. P. gasoline, per cent vol. | 50.5                   | 46.6      | 41.1      | 35.1      | —         | 29.1      |
| Aviation gasoline, per cent vol.                   | 29.8                   | 25.9      | 23.0      | 20.3      | —         | 16.4      |
| Heavy naphtha, per cent vol.                       | 14.2                   | 14.7      | 13.0      | 11.1      | —         | 9.5       |
| Aviation gasoline inspections:                     |                        |           |           |           |           |           |
| Acid heat, ° F.                                    | 24                     | 29        | 37        | 47        | —         | 60        |
| Aniline point, ° F.                                | 111                    | 117       | 115       | 108       | —         | 104       |
| Heavy naphtha inspections:                         |                        |           |           |           |           |           |
| Acid heat, ° F.                                    | 11                     | 10        | 12        | 13        | —         | 19        |
| Aniline point, ° F.                                | 30                     | 54        | 59        | 68        | —         | 73        |
| 12# R. V. P.—400° F. E. P. gasoline inspections:   |                        |           |           |           |           |           |
| Acid heat, ° F.                                    | 28                     | 33        | 40        | 46        | —         | 57        |
| Bottoms or cycle stock inspections:                |                        |           |           |           |           |           |
| Acid heat, ° F.                                    | 11                     | 10        | 10        | 9         | —         | 7         |
| Aniline point, ° F.                                | 126                    | 135       | 145       | 154       | —         | 158       |
| Gravity, ° A. P. I.                                | 25.1                   | 28.2      | 30.4      | 31.6      | —         | 32.4      |
| C <sub>4</sub> cut inspections:                    |                        |           |           |           |           |           |
| Total unsaturates, per cent.                       | 27.2                   | 34.6      | 41.2      | 47.3      | —         | 48.3      |
| Isobutylene, per cent.                             | 7.2                    | 8.9       | 10.9      | 12.9      | —         | 16.8      |

stages of the cracking cycle are quite different from those obtained in the latter stages and that very great advantages may be secured by segregating these products. For example, more hydrocarbons of 4 carbon atoms per molecule are formed at the beginning of the cycle than at the end, while those produced at the end of the cycle contain the greater proportion of unsaturates. For example, operating under conditions similar to those described in the above example, 3.5% by weight (based on the feed to the cracking zone) of dry gas (free of C<sub>4</sub> and heavier hydrocarbons) and 2.7% by weight of

It will be seen from the above table that the distillate fractions of the cracked products boiling in the motor fuel range are characterized by an increase in the unsaturate content and a decrease in the aromatic content as the cycle progresses. It is desirable to segregate the distillate from the first part of each cracking cycle for the production of aviation gasoline. Finished aviation gasoline should have a low acid heat representing a low content of olefinic hydrocarbons. The aviation gasoline produced in catalytic cracking operations usually has an excess of such unsaturates, and in finishing the gasoline to aviation

specifications, these unsaturates must be removed. Refining losses are decreased and the refining process simplified by selecting the distillate fractions of the first portions of each cracking cycle for the production of aviation gasoline. In an illustrative process conducted as described in the above example, the acid heat of the aviation gasoline distillate fraction produced during the first fifteen minutes of the cracking cycle was 24° F., while the acid heat of the aviation gasoline produced during the third hour of the cracking cycle was 60° F.

The aromatic content of the distillate fraction of the cracked products is also greatest at the beginning of the cracking cycle and the segregation of this first distillate for the production of aromatic solvents and of even more highly concentrated aromatic hydrocarbons is also advantageous. For example, the heavy naphtha distillate fraction boiling between about 300 and 400° F. of the products obtained during the first fifteen minutes of the cracking cycle under operations similar to those described in the above example had an aniline point of 30° F. and an acid head of 11° F., while the heavy naphtha distillate fraction produced during the third hour of the cracking cycle had an aniline point of 73° F. and an acid heat of 19° F. Aromatic solvents of high purity are thus prepared by any suitable treatment, such as by extraction of the naphtha fraction of the products of the early portion of the cracking cycle with liquid sulfur dioxide, phenol or other selective solvents, to concentrate the aromatic hydrocarbons therein.

The segregation of the motor fuel distillate fractions produced during the various stages of the cracking cycle is also advantageous in that the degradation of the gasoline and the treating costs are decreased. In the finishing of the motor fuel distillates to motor gasoline specifications, the motor fuel distillate fractions produced in the early stages of the cracking cycle are quite stable and in many cases will be found to be suitable for use directly as gasoline or after a very slight refining treatment to remove any mercaptans present. The motor fuel distillate fraction produced during the mid portion of the cracking cycle is somewhat less stable and usually requires a mild refining treatment, while the motor fuel distillate fractions produced in the last part of the cracking cycle are relatively unstable and require more severe refining treatment.

Also, the gasoline produced in the early part of the cycle usually is sweet, but, especially with high sulfur feed stocks, there is a tendency for the gasoline produced during the latter stages of the cycle to become slightly sour. In this case, the first gasoline produced may by-pass the sweetening treatment and thus save considerable handling expense.

The heavier fractions of the cracked products boiling above the motor fuel range are characterized by a decrease in the content of aromatic hydrocarbons and an increase in the unsaturate content as the cracking cycle proceeds. The gravity and aniline point of these heavy fractions produced during the last part of the cracking cycle are higher than those of the heavy fractions produced during the first part of the cycle; the Diesel index is therefore greatest for the heavy fractions of the cracked product produced in the latter stages of the cracking cycle. The segregation of these heavy fractions for the production of Diesel fuels is thus advantageous. Similarly, the fractions boiling in the kerosene or burning oil range of the cracked products ob-

tained in the latter stages of the cracking cycle are particularly suited for the production of kerosene. Aromatic and unsaturated hydrocarbons are both undesirable in kerosene used for lighting purposes. The unsaturates may be readily removed by treating, but the removal of aromatic compounds is much more difficult. Thus it is preferred to segregate the kerosene distillate fractions of the cracked product of the latter stages of the cracking cycle and to subject this to suitable refining treatments for the production of water white kerosene.

The heavy fractions of the cracked products not used to produce Diesel oils, fuel oils or kerosene as described above may be subjected to further cracking or other destructive treatments to produce motor fuels. The entire heavy fractions may be used as cycle stock in the process of this invention. However, it is preferable to segregate the heavy fractions produced during the latter portion of the cracking cycle and to use it as cycle stock in this process, as this portion of the heavy fractions has a higher aniline point and higher gravity than that produced during the first part of the cracking cycle and is better adapted to cracking for maximum yield of gasoline. The heavy fractions obtained in the early stages of the cracking cycle are relatively more aromatic in character and are less suitable for catalytic or non-catalytic cracking. These fractions, however, may be subjected to destructive hydrogenation under conditions suitable for the production of gasolines high in aromatic content, and form a desirable feed stock for such treatment.

This invention is not to be limited by any specific examples or explanations presented herein, as all such are intended solely for purpose of illustration. It is the applicants' intention to claim their invention as broadly as the prior art permits.

We claim:

1. A hydrocarbon oil conversion process which comprises providing a bed of fresh cracking catalyst and maintaining said bed at catalytic conversion temperature during a period of processing, continuously passing a stream of hydrocarbons through the catalyst bed during the processing period and converting a substantial portion of the hydrocarbons into gasoline in said bed, said stream being introduced to said bed at a substantially uniform conversion temperature throughout the processing period, whereby the activity of the catalyst is gradually diminished by deposition of carbonaceous matter thereon, producing from the hydrocarbons a substantially saturated gasoline during the initial portion of the processing period when the catalyst bed is in a state of high activity and an unsaturated gasoline during a subsequent portion of said period when the catalyst bed is in a state of diminished activity, and separately collecting said substantially saturated gasoline and said unsaturated gasoline.

2. A hydrocarbon oil conversion process which comprises providing a bed of fresh cracking catalyst and maintaining said bed at catalytic conversion temperature during a period of processing, continuously passing a stream of hydrocarbons through the catalyst bed during the processing period and converting a substantial portion of the hydrocarbons into gasoline in said bed, said stream being introduced to said bed at a substantially uniform conversion temperature throughout the processing period, whereby the

activity of the catalyst is gradually diminished by deposition of carbonaceous matter thereon, producing from the hydrocarbons a substantially saturated gasoline during the initial portion of the processing period before there has been deposited on the catalyst bed a sufficient quantity of carbonaceous matter to materially impair the catalytic activity of the bed, condensing and collecting the saturated gasoline thus formed, pro-

5 ducing from the hydrocarbons an unsaturated gasoline during a subsequent portion of the processing period when the catalyst bed has received a sufficient deposit of carbonaceous matter to substantially reduce its catalytic activity, and condensing and collecting said unsaturated gasoline independently of said saturated gasoline.

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