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CATALYTIC CRACKING TO PRODUCE MOTOR FUELS

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2 Sheets-Sheet 1

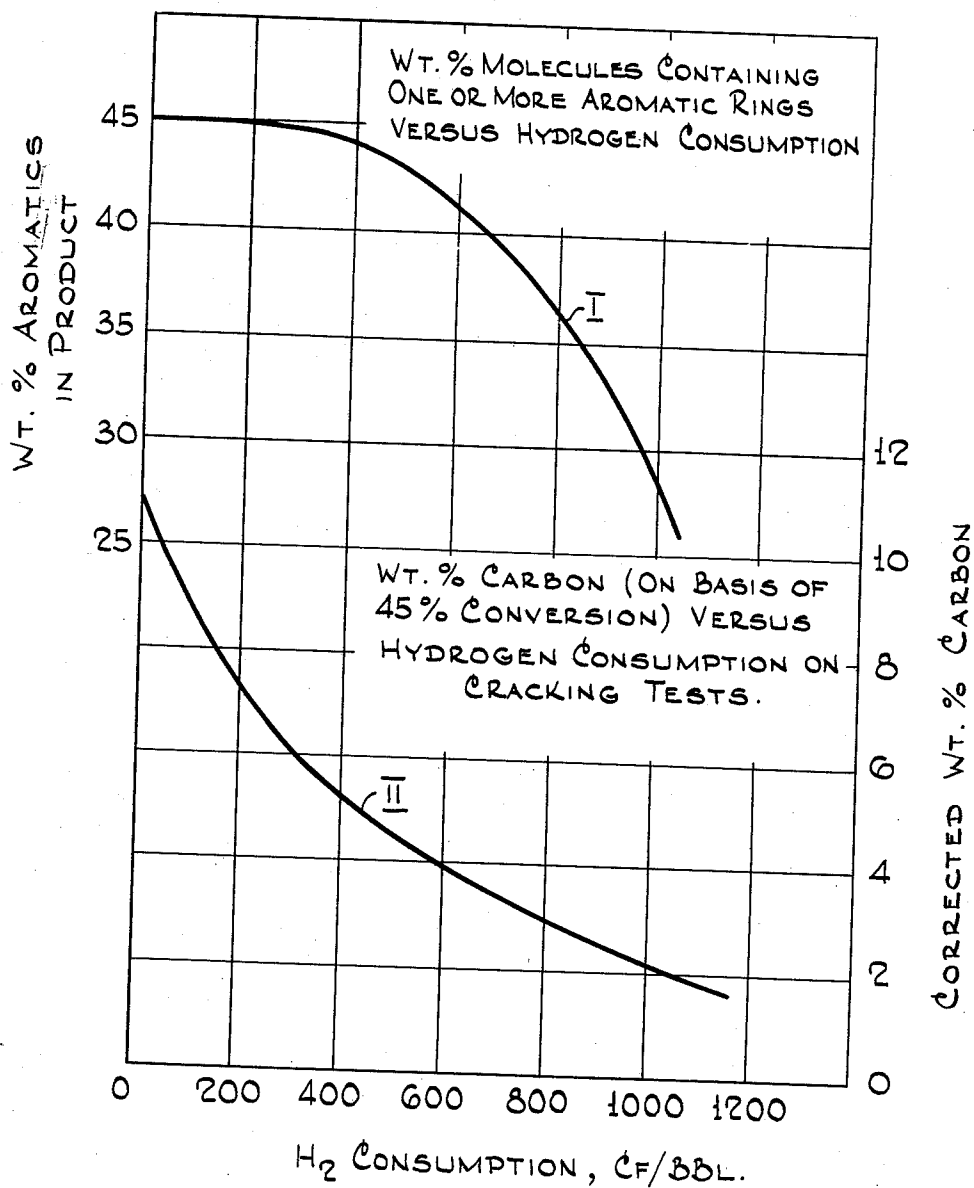


FIG. - 1.

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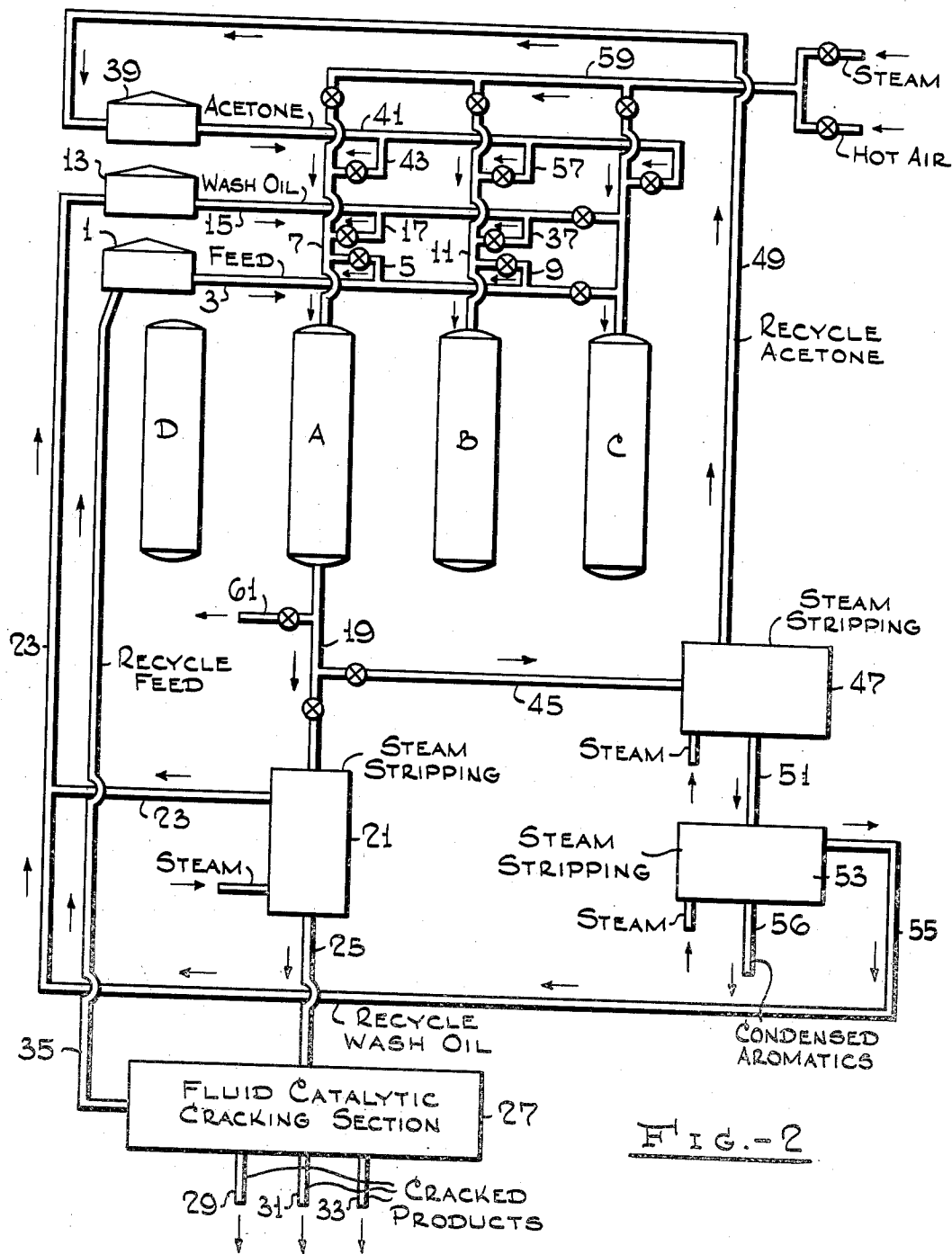
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## PARTIAL HYDROGENATION OF FEED OILS EMPLOYED IN CATALYTIC CRACKING TO PRODUCE MOTOR FUELS

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Application May 26, 1951, Serial No. 228,456

2 Claims. (Cl. 196—50)

The present invention relates to the catalytic conversion of hydrocarbons to produce more valuable hydrocarbons of lower molecular weight. More particularly, the invention pertains to an improved process of producing gasoline range hydrocarbons by catalytically cracking gas oil range feed stocks from which aromatic constituents have been removed. The improvement of the invention is specifically directed to a selective removal of highly condensed aromatic hydrocarbons from the feed stock prior to catalytic cracking.

Prior to the present invention, it has been recognized that hydrocarbon oils rich in aromatic constituents are less desirable feed stocks for cracking, particularly catalytic cracking, than strongly paraffinic or naphthenic feed stocks. For a given yield or conversion into gasoline, cracking of aromatic oils produces more coke and gas than cracking of non-aromatic feed stocks, i. e. the production ratio of gasoline to coke or gas is lower in cracking aromatic oils than in cracking non-aromatic oils. High coke formation or a low gasoline to coke production ratio is particularly harmful in catalytic cracking since the coke formed is deposited on the catalyst and must be removed therefrom by combustion to maintain the catalyst active. Coke formation is, therefore, the most important single factor limiting the capacity of catalytic cracking plants.

Numerous proposals have been made heretofore to remove aromatic constituents from catalytic cracking feed stocks by solvent extraction or selective adsorption on solid adsorbents. These processes, so far as known, contemplate the removal of all types of aromatics from the feed and this so completely as is compatible with the economics of commercial operation. The efficiency of most of these processes suffers from the relatively low selectivity of the extractants used for the aromatics removal, which makes a complete removal of aromatics impossible without the simultaneous extraction and loss of substantial proportions of non-aromatic highly desirable feed constituents. The present invention overcomes this difficulty.

In the copending application Serial No. 177,366, filed August 3, 1950, now U. S. Patent No. 2,632,727, of which the present application is a continuation-in-part, a process of improving cracking feed stocks by a total removal of aromatics is disclosed. In this earlier application reference is made to the strong carbon-forming tendency of highly condensed aromatics and to the partial hydrogenation of feed stocks containing such aromatics. The present invention further develops and utilizes these features in an improved manner.

It is, therefore, the principal object of the invention to improve the gasoline yield and the gasoline to coke production ratio of cracking processes, particularly catalytic cracking processes which are based on feed stocks containing aromatic constituents. Other and more specific objects and advantages will appear from the description of the invention given below wherein reference will be made to the accompanying drawing in which

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Figure 1 is a graphical summary of experimental data illustrating the effects of the invention; and

Figure 2 is a schematical illustration of an embodiment of the invention.

It has now been found that the utility of aromatic hydrocarbons as cracking feed stocks, with respect to the gasoline to coke production ratio, decreases as the degree of ring condensation of the aromatic molecule increases. In other words, a feed stock is the less suitable for cracking, particularly for catalytic cracking, the more highly condensed its aromatic constituents and the higher its concentration in highly condensed aromatics. More specifically, it has been found that single ring aromatics, such as benzene and its homologues, are of approximately the same quality with respect to the gasoline to carbon production ratio as are paraffinic and naphthenic catalytic cracking feed stocks while condensed ring aromatics containing 4 or more carbon rings per molecule are extremely strong carbon formers. Aromatics containing two and three condensed rings per molecule are of intermediate quality and may be tolerated in the cracking feed in relatively high concentrations without the danger of an excessive reduction of the gasoline to carbon production ratio.

On the bases of this discovery, the present invention provides for the selective removal, from aromatic-type cracking feed stocks, of condensed-ring aromatic compounds containing 4 or more condensed carbon rings per molecule while leaving less highly condensed aromatics unaffected. The feed stocks so treated are then subjected to cracking at conventional conditions with the result that the capacity of the cracking plant is substantially increased due to the reduced coke formation, and gasoline yields are improved even on the basis of the original untreated total feed stock.

Any physical or chemical treatment of the feed stock adapted for the selective removal therefrom of highly condensed aromatics as distinguished from single ring aromatics or aromatics containing less than four condensed carbon rings per molecule may be used for the purposes of the invention. Two methods have been found to be of excellent utility. These are adsorption on suitable adsorbents, particularly alumina gel in carefully controlled amounts and partial hydrogenation to an extent sufficient to hydrogenate the undesirable most highly condensed aromatics while leaving aromatics containing less than four condensed carbon rings unaffected.

When using selective adsorption on such adsorbents as alumina gel the process of the invention may be carried out as follows. The cracking feed may be supplied to the top of a column of adsorbent and washed down this column with a suitable paraffinic or naphthenic solvent in such a manner that only the most highly condensed aromatics which also are the constituents most tenaciously held by the adsorbent will be retained in the column, all other constituents being removed with the solvent. The raffinate is stripped to remove the solvent whereupon the feed stock so stripped is introduced to the cracking stage. The adsorbed extract is washed out with a strongly polar solvent such as ketones, pyridines, etc. and may be recovered therefrom in any conventional manner.

Partial hydrogenation may be used in accordance with the invention by treating the cracking feed stock, preferably catalytically in the presence of such catalysts as the metals of group VI and group VIII of the periodic table, their oxides or sulfides, etc., in an otherwise conventional hydrogenation procedure at a total pressure of about 500–3000 p. s. i. g., and a temperature of about 100°–1000° F., with hydrogen to a hydrogen consumption of about 200–1200 cu. ft. per bbl. of feed, depending on the character of the feed. The higher the content of the feed in highly condensed aromatics, the higher should

be the H<sub>2</sub> consumption within this range. Specific hydrogen consumptions may be determined either by preliminary analysis of the aromatics content of the feed or by a continuous analysis of the hydrogenated product for highly condensed aromatics. An operation of the latter type lends itself readily to automatic process control.

The feed stock treated by either method described above is then ready for use in any conventional catalytic cracking process. The beneficial effects of the process of the invention will be illustrated by the following experiments.

Several different cracking feed stocks including a virgin gas oil and several types of catalytic cycle oils, some of which had been hydrogenated to various degrees, were subjected to catalytic cracking tests. The types of feed, their pretreatment and inspections are summarized in Table I below.

Table I

| Feed No. ....               | Heavy Cycle+Clarified Oil |       |                                                                                       |       | Wide Cut Clarified Oil Hydrogenated at 3000# to H <sub>2</sub> Consumption of— |                 |                   |
|-----------------------------|---------------------------|-------|---------------------------------------------------------------------------------------|-------|--------------------------------------------------------------------------------|-----------------|-------------------|
|                             | Virgin Heavy Gas Oil Feed | Raw   | Hydrogenated at 750# to: H <sub>2</sub> Consumption of 350 C. F. H <sub>2</sub> /Bbl. | Raw   | 450 C. F./ Bbl.                                                                | 800 C. F./ Bbl. | 1,050 C. F./ Bbl. |
|                             | I                         | II    | III                                                                                   | IV    | V                                                                              | VI              | VII               |
| Gravity, °API.....          | 26.4                      | 22.2  | 24.4                                                                                  | 21.6  | 23.9                                                                           | 26.4            | 28.2              |
| Carbon, Wt. Percent.....    | 86.98                     | 88.14 | 87.85                                                                                 | 88.04 | 87.84                                                                          | 87.40           | 87.09             |
| Hydrogen, Wt. Percent.....  | 13.00                     | 11.62 | 12.16                                                                                 | 11.33 | 12.09                                                                          | 12.39           | 13.00             |
| Distillation:               |                           |       |                                                                                       |       |                                                                                |                 |                   |
| Initial, °F.....            | 440                       | 415   | 349                                                                                   | 352   | 346                                                                            | 314             | 340               |
| 50%.....                    | 867                       | 726   | 704                                                                                   | 730   | 717                                                                            | 702             | 694               |
| Final, °F.....              | 1,045                     | 898   | 854                                                                                   | 850   | 852                                                                            | 883             | 844               |
| Recovery, Vol. Percent..... | 94.0                      | 98.0  | 98.0                                                                                  | 98.0  | 98.0                                                                           | 98.0            | 98.0              |

Cracking was carried out in a 200 cc. fixed bed laboratory unit on fresh standard silica-alumina catalyst containing 13% alumina at 975° F. and a feed rate of 1 v./v./hr. in single pass operation with a cycle time of about 2 hours. Typical results of these tests are given in Table II below.

Table II

| Feed No. ....                 | Heavy Cycle + Clarified Oil |      |                                                 |      | Wide-Cut Clarified Oil Hydrogenated to— |                                |                                  |
|-------------------------------|-----------------------------|------|-------------------------------------------------|------|-----------------------------------------|--------------------------------|----------------------------------|
|                               | Heavy Virgin Gas Oil        | Raw  | Hydrogenated to: 350 C. F. H <sub>2</sub> /Bbl. | Raw  | 450 C. F. H <sub>2</sub> /Bbl.          | 800 C. F. H <sub>2</sub> /Bbl. | 1,050 C. F. H <sub>2</sub> /Bbl. |
|                               | I                           | II   | III                                             | IV   | V                                       | VI                             | VII                              |
| Aromatics, Wt. Percent.....   | 31                          | 44   | 40                                              | 45   | 44                                      | 36                             | 25                               |
| Conversion, Vol. Percent..... | 59.0                        | 43.8 | 51.8                                            | 46.8 | 49.2                                    | 56.9                           | 62.7                             |
| Gas, Wt. Percent.....         | 21.2                        | 15.9 | 18.6                                            | 20.3 | 17.5                                    | 20.4                           | 22.3                             |
| Carbon, Wt. Percent.....      | 6.3                         | 10.7 | 9.7                                             | 11.4 | 9.0                                     | 8.0                            | 8.2                              |
| Naphthalene, Wt. Percent..... | 31.4                        | 15.5 | 21.6                                            | 13.6 | 20.2                                    | 27.0                           | 30.6                             |

The second horizontal row of Table II indicates the aromatics content of each of the feeds as determined by adsorption of the total aromatics on silica gel in accordance with the procedure described in the above-mentioned earlier application Serial No. 177,366. In brief, this method involves percolation of an oil sample diluted with normal heptane through a column of silica gel, washing out of non-aromatics with normal heptane and recovering the aromatics by extracting the heptane-washed silica gel with acetone, followed by stripping the non-aromatic and aromatic fractions of heptane and acetone, respectively. This procedure permits a quantitative separation of aromatics from non-aromatics.

The data of Table II show that, in general, the feeds with relatively high aromatic contents produced relatively larger amounts of carbon and gave lower conversions for a given carbon make. For example, the high aromatics

content of the two fairly similar cycle oils (feeds II and IV) resulted in similarly poor cracking characteristics for the two oils with respect to carbon make and conversion.

However, a detailed analysis and correlation of the results of the above cracking experiments indicates that conversion is not a linear function of aromatics content and, also, that the aromatics content is not a linear function of the degree of hydrogenation as determined by H<sub>2</sub> consumption. It has been found that the effect of hydrogenation is not only a reduction of total aromatics content but, in addition, a change in the structure of the remaining aromatics and that this latter effect is responsible to a large extent for the improvement in cracking characteristics obtained by hydrogenation.

More particularly, an analysis of these data indicates that in the hydrogenation of aromatic feed stocks hydrogen is preferentially consumed by at least partial hy-

drogenation of the most highly condensed aromatic ring structures. This result is illustrated by curve I of Figure 1 in which weight percent aromatics (defined as molecules containing one or more aromatic rings) is plotted against hydrogen consumption for feed Nos. IV to VII. It will be seen that "wt. percent aromatics," i. e.

total aromatics, is not reduced appreciably until relatively high hydrogen consumptions (>about 600 cu. ft./bbl.) are reached. This means that the more highly condensed ring structures must have been first partially hydrogenated, resulting in a reduction of the degree of their condensation.

Curve II correlates carbon formation upon catalytic cracking on the basis of equal conversion (45%) to hydrogen consumption in the hydrogenating pretreatment for feeds Nos. II-VII. It will be seen that the rate of reduction of carbon formation (downward slope of curve II) is substantially greater within the range of low H<sub>2</sub> consumption (<about 600 cu. ft./bbl.) than at higher H<sub>2</sub> consumptions. It follows that the highest rate of carbon make reduction (as shown in curve II) coincides with the preferential hydrogenation of the most highly condensed aromatics (as shown in curve I) and that the

selective hydrogenation of these highly condensed aromatics from catalytic cracking feed stocks affords substantial advantages.

These findings are fully borne out by analysis of the ultraviolet absorption spectra of the seven feed stocks used. Also, additional cracking experiments carried out with relatively pure aromatic compounds isolated from feed No. I, as the cracking feed further prove the advantage of a selective removal of the more highly condensed aromatics. In these experiments the total aromatic fraction obtained by silica gel percolation as described above was vacuum distilled at absolute pressures of 0.08–0.15 mm. Hg in a column designed to have two theoretical plates to obtain seven different, approximately equal fractions. Each of these cuts was diluted with 100 vol. percent of n-heptane and further fractionated by selective adsorption on an alumina gel column consisting of ten superimposed sections each 25 mm. in diameter and six inches long, separated from each other by glass frits. In all cases, the charge to the top of the column was 50 cc. of a heptane-diluted distillation cut which was fed at a pressure of about 2–6 p. s. i. g. After the charge had entered the column, the column was washed through with about 300 cc. of n-heptane until aromatics had spread down into the bottom section, as indicated by an abrupt rise in the refraction index of the liquid dripping from the bottom of the column. At this point, the column was disassembled and the aromatic fraction was removed from each section separately by desorption with approximately 80 cc. of acetone which was subsequently stripped from the aromatic fraction. In this manner, each of the distillation cuts of the aromatic materials was separated into 10 narrow fractions on the alumina column, approximating closely pure aromatic compounds whose structure was determined by their refractive indices, boiling points and ultraviolet spectra. Thus, the original feed stock was analyzed as to its content in specific aromatic compounds and these compounds were isolated from the feed.

The aromatics content of feed stock No. I was found to be 31% and to be composed as follows:

| Compound type:                        | Weight percent of total aromatics |
|---------------------------------------|-----------------------------------|
| Benzenes                              | 30                                |
| Naphthalenes                          | 30                                |
| Phenanthrenes and anthracenes         | 20                                |
| Condensed 4-ring aromatics            | 10                                |
| Condensed 5-ring and higher aromatics | 10                                |

A sample of each of the compounds so isolated was diluted with non-aromatics obtained from feed stock No. I to an aromatic content of 25% and subjected to a cracking test of the type described above. The results were compared with those obtained by cracking feed stock No. I, a dilution thereof to an aromatics content of 25% and the non-aromatic portion of feed stock No. I, at comparable conditions. In the comparison the carbon yield of original feed stock No. I was given a base value of 100 and the carbon yields of the other feeds were correlated to this base value. Typical data so obtained are summarized in Table III below.

Table III

| Feed Stock                                               | Conversion | Carbon Yield |
|----------------------------------------------------------|------------|--------------|
| Feed No. I                                               | 59         | 100          |
| Feed No. I Diluted to 25% Aromatics                      | 63         | 95           |
| Non-aromatics from Feed No. I                            | 73         | 30           |
| Aromatics (25% Blends in Non-aromatics from Feed No. I): |            |              |
| Benzenes                                                 | 73         | 37           |
| Naphthalenes                                             |            | 180          |
| Phenanthrenes and Anthracenes                            | 56         | 118          |
| 4-Ring Aromatics                                         | 56         | 170          |
| 5-Ring+Compounds                                         | 54         | 183          |

<sup>1</sup> Estimated.

From the above data it will be noted that the cracking characteristics of the benzenes fraction are far superior to those of the total feed stock No. I as well as to those of the diluted total feed stock and about equivalent to those of the non-aromatic portion of feed stock No. I with respect to conversion and carbon make. Phenanthrenes and anthracenes, i. e. compounds containing three condensed aromatic rings are of about the same quality as the total original feed stock, while the higher condensed aromatics form about 70–80% more carbon than the total original feed and about five times as much as the benzenes. It will be readily appreciated, therefore, that significant benefits may be derived from the selective removal of these highly condensed aromatics from the feed stock prior to cracking in accordance with the present invention.

The improvements afforded by the present invention are generally similar to, through quantitatively less pronounced than, those of total aromatics removal by silica gel adsorption in accordance with the procedure disclosed and claimed in the above-mentioned earlier application Serial No. 177,366. However, the process of the present invention, particularly that embodiment thereof which involves partial hydrogenation of the feed stock lends itself more readily to continuous operation in commercial plants of even the largest size. The great significance of the improvement of the gasoline to carbon ratio in accordance with the present invention lies in the fact that the selective removal of the highly condensed aromatics will result in a substantial increase of the gasoline producing capacity of the cracking unit, particularly in fluid operation. Conventional fluid catalytic cracking units are "carbon balance" units, i. e. the capacity for burning carbon off the catalyst limits the conversion permissible. By increasing the gasoline to carbon production ratio, the present invention, therefore, permits a substantial increase in the feed rate to the plant and in total conversion to gasoline at the same carbon formation and carbon combustion capacity.

The invention will be further illustrated by a description of the system shown in Figure 2.

Referring now to Figure 2 there are shown four columns A, B, C, and D filled with a heat-activated alumina gel which are used in a cyclic type of operation involving four cycles, namely (1) charging of the feed, (2) introduction of wash oil, (3) desorption of the aromatics and (4) regeneration of the adsorbent. Each column is used successively to carry out cycles 1, 2, 3, and 4 in the order named, operation of the four columns being properly staggered to provide a continuous flow of treated feed stock to the cracking plant. The four cycles will be briefly described with reference to their sequence in a single column, column A being used as an example.

In operation, the catalytic cracking feed, such as a virgin gas oil, cycle oil, or heavier feed stock, may be supplied at atmospheric pressure and temperature from tank 1 through lines 3, 5 and 7 to the top of column A in an amount of about 0.5–7 lbs. per lb. of alumina gel of about 50–250 mesh particle size in the column depending on the concentration of highly condensed aromatics in the feed. When this amount of feed is introduced into column A, cycle (1) is completed. The valve in line 5 is closed and feed is supplied through lines 9 and 11 to column B in the same manner.

Returning now to column A, a wash oil, such as n-heptane, is introduced from tank 13 via lines 15, 17 and 7 into the top of column A. The wash oil is passed through column A until all aromatics except those having four or more condensed carbon rings per molecule have been washed out of column A, which may be readily determined by continuous ultraviolet spectrophotometric analysis of the effluent of column A. This effluent is passed via line 19 to steam stripping zone 21 wherein the wash oil is removed from the feed raffinate by steam stripping. The wash oil strippings are returned via line 23

to tank 13 after water removal in any conventional manner (not shown). The amount of wash oil needed depends on the composition of the feed in tank 1. For most feeds, about 3-12 bbls. of n-heptane per bbl. of feed is sufficient. The steam stripped feed raffinate now free of wash oil and highly condensed aromatics is passed via line 25 to a fluid catalytic cracking plant schematically indicated at 27. Cracked products may be recovered via lines 29, 31 and 33, as desired. Recycle oil may be returned via line 35 to tank 1 at a ratio of about 0.5-3 or higher. This concludes the second cycle of the process, the valve in line 17 being closed and wash oil being passed through lines 15 and 37 to column B.

In the third cycle of the process, a highly polar solvent, such as acetone, is introduced from tank 39 via lines 41, 43 and 7 into column A until the adsorbed extract consisting of highly condensed aromatics is removed. In most cases about 1-4 bbls. of acetone per bbl. of feed is sufficient for this purpose. The acetone extract is passed through lines 19 and 45 to a steam stripping vessel wherein the acetone is taken overhead to be returned via line 49 to tank 39. The material free of acetone is passed via line 51 to a second steam stripping zone 53 wherein residual heptane is taken overhead to be returned via line 55 to tank 13. Highly condensed aromatics are recovered via line 56 for the production of carbon black, chemicals, etc. This completes cycle 3 of the process. The valve in line 43 is closed and acetone is passed via lines 41, 57 and 11 to column B.

In the fourth and last cycle, the adsorbent is regenerated. This may be accomplished by passing first steam and then hot air from line 59 via line 7 through column A at a temperature of about 100°-500° F. to remove adhering acetone. The column effluent from this stage may be removed via lines 19 and 61 and, if desired, passed to any suitable equipment for acetone recovery (not shown). This completes the last cycle. The valve in line 7 is closed and regeneration gas is introduced via line 11 into column B. Thereafter column A is ready for a fresh charge of oil feed.

In place of the cyclic batch type operation described, continuous operation may be employed involving continuous circulation of the adsorbent successively through an adsorption tower, a wash tower, a desorption tower, and a regeneration tower and back to the adsorption, as will be understood by those skilled in the art.

Fluid catalytic cracking which is the preferred cracking operation for the purposes of the invention is, as such, well known in the art. Briefly, this operation involves the use of finely divided catalysts, such as various activated clays or composites of silica gel with alumina, magnesia and/or boria having particle sizes of about 50-400 mesh. The catalyst is maintained in separate cracking and regenerating vessels in a dense, turbulent, fluidized state by gaseous media passing upwardly through the beds at linear superficial velocities of about 0.3-5 ft. per sec. The catalyst circulates continuously between the reactor and regenerator, heat for cracking being generated by burning carbon from the catalyst in the regenerator. Conventional conditions include cracking temperatures of about 800°-1000° F., regeneration temperatures of about 950°-1200° F., pressures of from sub-atmospheric to 500 p. s. i. g. or higher, total oil feed rates of about 4-5 w./hr./w., catalyst to oil ratios of about 6-10

and oil recycle to fresh feed ratios of about 0.5-5 on a weight basis.

When employed in the present invention, the fresh feed and/or the recycle stream are continuously subjected to a selective removal of the most highly condensed aromatic ring compounds either by partial hydrogenation or selective adsorption on alumina gel as described above. The oil feed rate may then be increased to about 6-10 w./hr./w. and a catalyst/oil ratio of about 11:1-17:1. Recycle ratios may be increased over conventional operation without the deleterious effect of increased carbon formation which normally accompanies high recycle ratios.

While operations of this type are preferred for the purposes of the invention, marked improvements may also be secured when fixed bed, moving bed or suspensoid systems are used. The gasoline yields and gasoline to carbon ratio may likewise be improved when employing thermal cracking in the cracking stage of the invention. The treatment of the feed stock in accordance with the invention not only reduces carbon forming tendencies by aromatics removal, but it prevents cracking catalyst contamination by removal of nitrogen, oxygen and sulfur compounds and removal of ash contents, such as metallic salts, from the oil. Moreover, when employing selective adsorption for the aromatics removal, the aromatic extract is of unusual nature. This pure concentrate of high boiling aromatic oils is a valuable source of chemicals for such by-products of the oil industry as carbon black, plasticizers, detergents, weed killers, wood preservatives, solvents, etc.

The foregoing description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. The process of cracking hydrocarbon oils, which comprises subjecting a gas oil range hydrocarbon oil boiling substantially above the motor fuel range and containing aromatic constituents to partial hydrogenation, securing a hydrogen consumption less than about 600 cubic feet per barrel of oil until at least a substantial portion of the aromatic constituents containing at least four condensed aromatic rings per molecule are selectively hydrogenated, without substantial hydrogenation of aromatic constituents containing less than four condensed aromatic rings per molecule and without any substantial reduction in the total aromatic content of the said hydrogenated oil, and thereafter cracking the oil so treated in the presence of a cracking catalyst at conditions conducive to the formation of motor fuel range hydrocarbons.

2. The process of claim 1 in which said cracking is carried out in the presence of a dense, turbulent, fluidized mass of subdivided cracking catalyst.

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