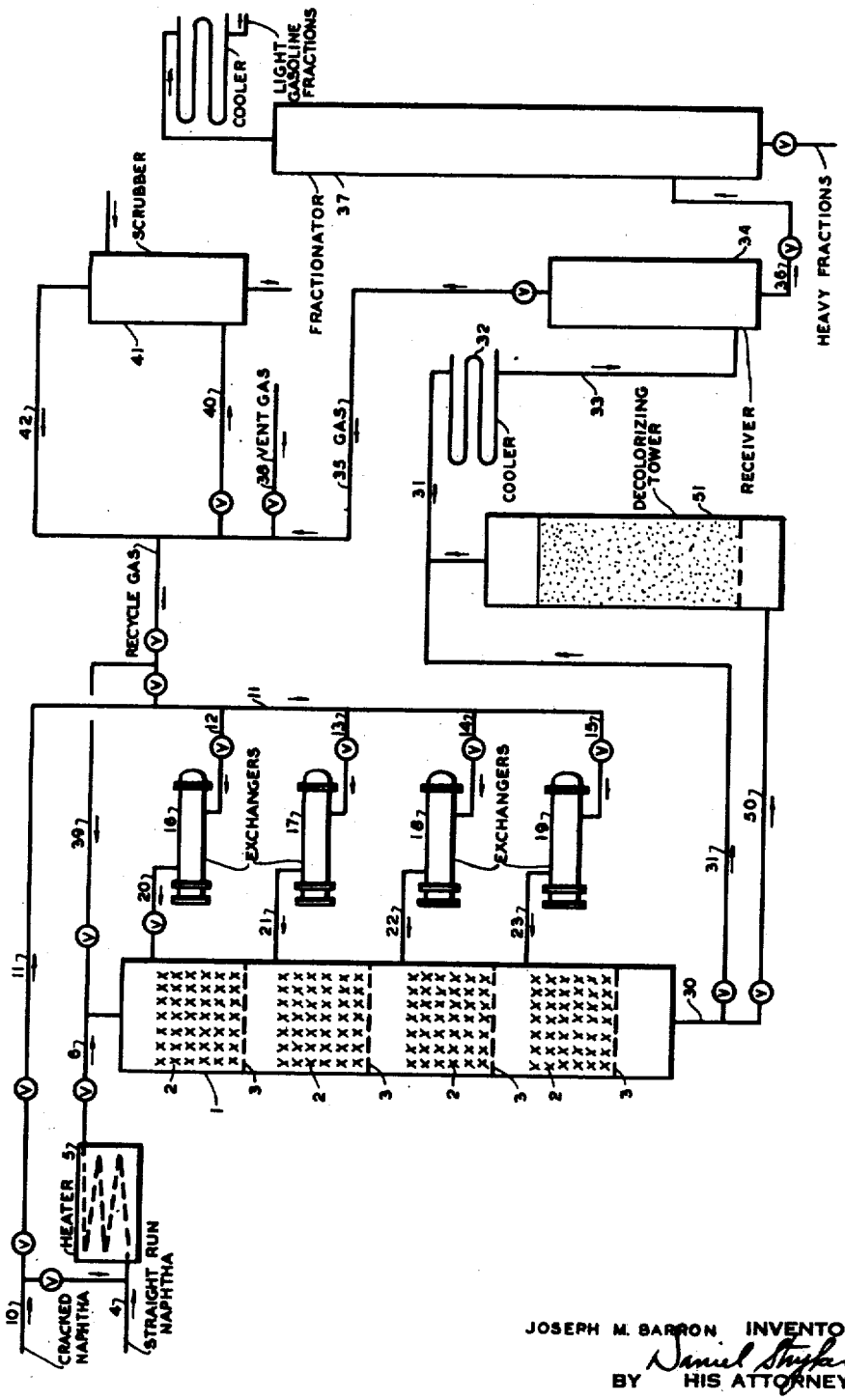
March 4, 1947. J. M. BARRON 2,416,894

COMBINED HYDROGENATION AND DEHYDROGENATION OF HYDROCARBONS

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JOSEPH M. BARRON INVENTOR

BY Daniel Shuman HIS ATTORNEY

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COMBINED HYDROGENATION AND DEHYDROGENATION OF HYDROCARBONS

Joseph Mason Barron, Port Arthur, Tex., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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6 Claims. (Cl. 196—50)

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This invention relates to the manufacture of gasoline to produce gasoline of improved quality from naphtha hydrocarbons.

The invention has to do with the catalytic conversion of naphtha hydrocarbons into gasoline of increased paraffin and aromatic content and of improved octane value. It involves a continuous method for effecting dehydrogenation of straight-run naphtha and hydrogenation of cracked naphtha in a common reaction zone.

More specifically, the invention comprises maintaining a reaction zone containing a mass of solid hydrogenation-dehydrogenation catalyst. Straight-run and cracked naphtha hydrocarbons are passed through the reaction zone in contact with the catalyst during continued onstream operation. Contact between the hydrocarbons and the catalyst is effected at a predetermined elevated temperature within the range about 800 to 875° F. and preferably about 825° F. to 850° F. so that dehydrogenation of hydroaromatic constituents of the straight-run naphtha and hydrogenation of olefinic constituents of the cracked naphtha occur to a material extent without substantial hydrocarbon cracking occurring. In other words, the dehydrogenation and hydrogenation reactions are effected under conditions such that there is no carbonaceous material deposited upon the catalyst, at least to any appreciable extent. The hydrocarbons flow through the reaction zone in the presence of free hydrogen. Periodically, the partial pressure of free hydrogen within the reaction zone is increased, the reaction zone being maintained under operating conditions with the increased partial pressure of hydrogen for a brief period of time, whereupon the partial pressure of free hydrogen is reduced to the normal level.

This periodical increase in partial pressure of free hydrogen may be effected by temporarily charging or recycling additional quantities of free hydrogen without interruption or substantial interruption in the flow of naphtha hydrocarbons through the reaction zone. On the other hand, the passage of unsaturated hydrocarbons to the reaction zone may be interrupted periodically either in part or wholly for brief periods so as to cause temporary increases in the partial pressure of free hydrogen available from the dehydrogenating reaction.

The flow of feed hydrocarbons may be decreased with a corresponding increase in the flow of hydrogen recycle so that the proportion of free hydrogen relative to hydrocarbons flowing through the contact mass is materially increased

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without substantial change in the overall pressure prevailing within the reaction zone.

The invention contemplates periodically increasing for short periods of time the amount of free hydrogen present in the reaction zone during continued onstream operation so as to maintain catalyst activity.

Heretofore, in the catalytic reforming of naphtha, operations have been carried out at a temperature of 900° F. and above using a catalyst of the molybdena-alumina type. In these operations the catalyst becomes deactivated after a period ranging from about 3 to 10 hours, so that it is necessary to interrupt the flow of hydrocarbons through the reaction zone in order to regenerate the catalyst.

The decrease in catalytic activity is the result of carbonaceous deposits formed on the catalyst as a result of hydrocarbon cracking. Deactivation of the catalyst is apparently also due in part to conversion of the metal of the catalyst to oxides or sulfides. It appears that the metal, rather than the oxide or sulfide thereof, is the essential active agent.

Decrease in catalyst activity is evidenced by increase in the bromine number of the effluent hydrocarbon stream.

In accordance with the present invention, the conversion operation is carried out within a relatively narrow and critical temperature range of about 825 to 850° F. and also with a relatively high space velocity. An effective space velocity ranges from about 1 to 5 volumes of naphtha liquid measured at 60° F. per volume of catalyst per hour.

It is important to avoid temperatures above about 875° F. since hydrocarbon cracking will occur with resultant carbon deposition on the catalyst. On the other hand, temperatures below 800° F. are ineffective due to the fact that the rate of dehydrogenation ceases to be practical.

In addition, it has been found that periodically increasing momentarily the partial pressure of hydrogen within the reaction zone permits maintaining the catalyst onstream without interruption for prolonged periods of time. This brief increase in hydrogen concentration effects desulfurization of the catalyst.

Accordingly, the feed hydrocarbons are continuously passed through the reaction zone advantageously in the presence of free hydrogen, as evidenced by the maintaining of a predetermined partial pressure of hydrogen in the effluent hydrocarbon stream. The flow, under these con-

ditions, is continued until the bromine number of the effluent hydrocarbons begins to rise or exceeds a predetermined value, such as about 3 or 5. Thus, the flow is continued with the predetermined partial pressure of hydrogen in the effluent stream, usually for a period of from 40 to 100 hours. Thereupon, the partial pressure of the hydrogen is increased substantially for a moment or so or for a few minutes, for example, from about 1 to 10 minutes until the bromine number of the effluent stream decreases to below 3 or 5. Thereupon, fluid flow through the reaction zone is resumed with the normal partial pressure of hydrogen in the effluent stream and continued under these conditions for another period of 40 to 100 hours, after which the partial pressure of free hydrogen is again momentarily increased. The cycle is thus repeated indefinitely so that the catalyst may be maintained onstream indefinitely, for example, a period of several hundred hours without interruption for burning and reactivation.

Thus, the invention involves maintaining a fluid flow during the major portion of the time with the hydrogen partial pressure in the effluent stream ranging from about 20 to 60 pounds per square inch gauge, or amounting to about 10 to 30 per cent of the total pressure within the reaction zone, which pressure may range from about 200 to 500 pounds. Periodically the partial pressure of hydrogen is increased momentarily or for brief periods by as much as 100 to 300 per cent of the normal partial pressure of hydrogen.

While it is contemplated carrying out a continuous operation, without interruption of naphtha hydrocarbon flow, by periodically increasing the hydrogen charged or recycled to the reaction zone, it is also contemplated that the temporary increase in hydrogen partial pressure may be achieved by temporarily discontinuing the flow of unsaturated hydrocarbons or cracked naphtha while continuing the flow of straight-run naphtha. Also, if desired, both straight-run and cracked naphtha components of the feed may be momentarily discontinued or substantially decreased, while continuing the flow of recycled hydrogen gas through the reaction zone either at the same or at an increased rate. In any case, the ratio of free hydrogen to hydrocarbons within the reaction zone is temporarily increased by a substantial amount.

The invention is particularly effective for the conversion of naphtha hydrocarbons, both straight run and cracked, boiling in the range not exceeding about 300° F. and preferably not in excess of about 240 to 250° F.

The cracked naphtha may be obtained from the catalytic cracking of gas oil with an active cracking catalyst of the alumina-silica type, at temperatures in the range about 800 to 900° F., which naphtha is usually characterized by having a relatively high content of branched chain olefins, especially in the fraction boiling up to about 220° F. This cracked naphtha is highly unsaturated, having a bromine number of 100 and above (grams of bromine per 100 grams of hydrocarbon sample). Such naphtha, when converted to a finished gasoline by conventional acid treatment, suffers a treating loss of the order of 15 to 30 per cent, which involves a substantial destruction of olefins.

The present invention involves hydrogenating these olefins with hydrogen evolved in the upgrading of naphthene stock, advantageously boiling below about 300° F., the two reactions being

carried out simultaneously or concurrently under conditions whereby the olefins are converted to paraffins, and naphthenes are converted to aromatics, to the substantial exclusion of other undesired reactions which would result in conversion of the feed hydrocarbons into gaseous and carbonaceous materials.

The naphthene stock is advantageously straight-run naphtha having a high content of C_8 ring naphthene hydrocarbons boiling within the range for aviation gasoline, that is, an end point not in excess of 250 to 300° F. Naphthenic gasoline, having a CRFM octane number of 60 to 70, or in excess of 55, is preferred.

The naphthenic gasoline may amount to about 35 to 50 volume per cent of the combined naphtha charge to the reaction, depending upon the amount of hydrogen required by the acceptor stock and the amount available from the donor stock. At any rate, it is contemplated correlating the proportions of straight-run and cracked naphtha and also the amount of hydrogen recycle so that substantially no hydrocarbon cracking occurs, as evidenced by the securing of a liquid hydrocarbon recovery of at least 98% by weight, and preferably at least about 99%, of liquid feed hydrocarbons. The C_4 hydrocarbons and lighter gas fraction of the effluent stream of reaction products consist of substantially in excess of 95% by weight hydrogen and usually not less than 97%.

Heretofore, naphtha, boiling up to about 400 and 450° F., has been subjected to catalytic reforming under comparatively drastic conditions of temperature so that considerable cracking occurs, as evidenced by the production of gaseous products amounting to at least 15% of the feed, with a total liquid recovery not exceeding about 80 to 85%. Such reforming involves a large number of separate reactions including cracking of olefins, naphthenes, paraffins and aromatics; polymerization of olefins with subsequent cracking of polymerization products; cyclization of paraffins, and condensation of aromatics. These destructive conversion reactions are so pronounced that even in the conventional hydroforming operation, with a large amount of hydrogen recycle, the catalyst is fouled so rapidly that regeneration is necessary after 10 to 12 hours onstream.

Effective catalysts are those containing a metal selected from the metals of groups 6 and 8 of the periodic system. The catalyst advantageously comprises a supporting material such as alumina or silica-alumina. The catalyst composition may be prepared by mechanical mixing, impregnation or coprecipitation.

The catalyst may contain the active metal agent, mainly in the form of an oxide or sulfide, at least prior to reduction. Catalysts of the alumina-molybdena or alumina-chromia type usually contain the oxide of molybdenum or chromium in amounts ranging from 6 to 40% by weight of the catalyst employed. Upon reduction by treatment with hydrogen, the oxide or sulfide is reduced to the metal form so that about 5 to 25% of the available metal may be present in metal form.

In order to describe the invention in more detail, reference will now be made to the accompanying drawing which is a diagram of flow.

The numeral 1 designates a vertical reaction tower packed with a plurality of relatively shallow beds of dehydrogenating catalyst designated by the numeral 2, each bed being supported by a perforated or porous tray 3. The catalyst may be of the molybdena-alumina type. Straight-run

naphtha, from a source not shown, is conducted through a pipe 4 and a heater 5 wherein it is heated to a temperature of about 850° F. The heated naphtha in vapor phase passes through a pipe leading to the top of the tower 1.

Catalytically cracked naphtha, from a source not shown, is conducted through a pipe 10. It may be commingled, all or in part, with the straight-run naphtha flowing through pipe 4 to the heater 5.

Advantageously, however, the cracked naphtha is introduced to the reaction tower as a plurality of streams entering at succeeding points, intermediate the inlet of straight-run naphtha to the tower and the outlet of the effluent products from the tower. In such case, the cracked naphtha flows through pipe 11 which communicates with a plurality of branch pipes 12, 13, 14 and 15. The branch pipes may lead to individual heat exchangers 16, 17, 18 and 19 respectively, from which the naphtha streams are discharged through pipes 20, 21, 22 and 23 respectively. In this way, the cracked naphtha is introduced at points above each catalyst bed.

Constituents of the straight-run naphtha undergo dehydrogenation during passage through the catalyst beds, and since this reaction is endothermic the reaction temperature tends to decrease. This tendency is offset by adjusting the temperature of the entering streams of cracked naphtha, some of which may enter relatively hot while others enter at a somewhat lower temperature, since the hydrogenation reaction is exothermic. At any rate, it is desired to maintain a temperature of about 825° F. within the reaction tower.

The products of the reaction are continuously discharged from the bottom of the tower through a pipe 30. According to one modification, the discharged products first flow through a pipe 31 to a cooler 32 wherein the gasoline hydrocarbons are condensed.

The cooled stream flows through pipe 33 to a receiver 34, advantageously maintained under substantially the same pressure prevailing within the reaction tower, which pressure may range from about 200 to 500 pounds per square inch gauge.

The reaction products contain free hydrogen and this gas is liberated through the pipe 35. The condensed hydrocarbons are continuously discharged through pipe 36 to a fractionator 37.

The fractionator 37 may be operated to separate the hydrocarbons into any desired fractions.

The liberated gas flows through pipe 35 and may be discharged in part through pipe 38.

However, a suitable proportion of the gas is recycled to pipe 11, by which means it is returned to the reaction tower at any one or more of the succeeding points. Instead, the recycled gas may be recycled through pipe 39 to the top of the tower.

Separate means, not shown, may be employed for heating the recycled gas. Thus, the recycled gas may be heated to a relatively high temperature and used to provide at least the major portion of the heat required for effecting the dehydrogenating reaction.

As indicated in the drawing, provision may be made for scrubbing hydrogen sulfide from the recycled gas when operating on stocks of high sulfur content. In this case, the recycled gas is diverted through a pipe 40 to a scrubber 41 wherein it may be scrubbed with a suitable reagent to effect removal of hydrogen sulfide, at least in substantial amount. The scrubbed gas is then piped through pipe 42 for return to the reaction tower.

The scrubbing step may be desirable in the case of high sulfur feed stocks, that is, stocks containing more than about .05% sulfur, basis the combined naphtha mixture. Ordinarily, however, the bulk of the hydrogen sulfide formed in the reaction remains dissolved in the condensed hydrocarbons removed from the receiver 34, which is maintained under elevated pressure. In this way, build-up of hydrogen sulfide in the recycled gas is avoided.

Also, as indicated in the drawing, the effluent stream of hydrocarbon products from the reaction tower may be subjected to a decolorizing treatment. In this case, the products are passed through a pipe 50 to a tower 51, which may be packed with activated clay. The hydrocarbon vapors pass through the clay bed at substantially the temperature prevailing within the reaction tower 1, and thus undergo decolorization to produce a color stable gasoline.

In the case of naphthas obtained by cracking high sulfur oil such as California gas oil, the sulfur content of the naphtha fraction boiling up to about 220° F. may be about one-third of that of the fraction boiling about 220° F. Thus a light fraction may be obtained having a sulfur content not in excess of about 0.2 and such when mixed with the straight-run stock will not exceed about 0.05% for the mixture, so that desulfurizing prior to conversion is unnecessary.

If desired, the cracked naphtha may be treated to remove diolefins, as for example, by contact with clay at elevated temperatures.

It is contemplated that the feed hydrocarbons may be subjected to any type of pretreatment effective to render the hydrocarbons more suitable or more susceptible to the hydrogen transfer conversion.

By way of example, straight-run naphtha derived from naphthene base crude is blended with catalytically cracked naphtha in the proportion of about 35% cracked naphtha to 65% straight-run, both naphtha components boiling in the range below about 300° F.

This mixture is passed in a continuous stream through a heater wherein it is vaporized and heated to a temperature of about 850° F. The vapor stream is passed continuously through the reaction tower under pressure of about 200 lbs. per square inch gauge and at a space velocity of about 2 (volumes of liquid naphtha per volume of catalyst per hour). The flow is continued for a period of about 40 hours employing a recycle hydrogen gas rate of about 2500 cu. ft. per bbl. of naphtha, the gas being measured at standard conditions.

Under these conditions the partial pressure of hydrogen in the effluent stream leaving the reaction tower is about 140 lbs. per square inch gauge.

After about 40 hours onstream the bromine number of the effluent stream rises, increasing from about 1 or 2 to a value of about 5 to 10, this increase taking place rather rapidly and within a matter of a few hours. Upon observing this pronounced rate of increase in the bromine number of the effluent stream the recycle gas rate is increased without susbtantial change in the rate of hydrocarbon flow so that the partial pressure of hydrogen in the effluent stream is increased to about 500 lbs.

Operations at the increased level of hydrogen partial pressure are continued for about 5 to 10 minutes during which period the bromine number of the effluent stream declines to below 2. Thereupon the hydrogen gas recycle rate is restored to its original rate thereby reducing the partial pressure of free hydrogen to the normal level. Operations are then continued for another 40-hour period or until the bromine number of the effluent stream begins to rise appreciably whereupon the cycle is repeated.

The following tabulation affords a comparison of the characteristics of the feed naphtha and the product obtainable during continued operation over a period of several hundred hours, the product amounting to about 98.5% by weight of the total naphtha charged.

	Straight run	Cracked naphtha	Blend of straight run and cracked	Product
Gravity, API	57.4	67.7	62.3	62.5
Bromine No.	0.6	105	35	1
Distillation:				
IBP	150	140		168
10%	180	146		
50%	217	150		193
90%	260	158		255
EP	299	196		300
Weight, per cent aromatics		196	8.9	85.4
Octanes:				
AFD-1C—clear	71.2	72.4		
AFD-1C+4 cc. TEL	88.0	82.0	85	87.3

While a stationary mass of solid catalyst in particle form has been described, it is contemplated that a fluidized mass of such catalyst may be used, wherein the bulk of the catalyst is confined within the reaction zone as a fluidized mass due to the flow of vapors and gas therethrough at high velocity.

Mention has been made of treating catalytically cracked naphtha. However, the invention may be applied to the treatment of unsaturated naphtha derived from other sources such as that obtained by the hydrogenation of carbon monoxide. It is contemplated that the process may have application to the treatment of unsaturated hydrocarbons derived from other sources and also to the treatment of other unsaturated materials such as contained in fatty oils and fatty acids or derivatives thereof obtained from vegetable, animal or fish oil sources. Thus the process may be used for effecting saturation of these unsaturated fatty oil or fatty acid substances by reaction with naphthenic hydrocarbons derived from straight-run naphtha.

It may also be applied to the treatment of stock containing a substantial amount of sulfur compounds so as to effect desulfurization concurrently with the hydrogen transfer reaction.

Obviously many modifications and variations of the invention as above set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of converting naphtha, composed mainly of hydrocarbons boiling below about 300° F. and containing olefins in substantial amount, which comprises passing a stream of said naphtha, in the presence of naphthene hydrocarbons consisting essentially of a C_6 ring cyclo paraffin boiling below 250° F. to 300° F., in contact with a mass of solid hydrogenation-dehydrogenation catalyst in a reaction zone during continued onstream operation for a prolonged period of time, effecting said contact at a temperature in the range about 825 to 850° F., such that naphthene hydrocarbons are dehydrogenated to produce aromatics and liberate hydrogen, and olefin hydrocarbons are hydrogenated with said liberated hydrogen without substantial hydrocarbon cracking, maintaining the proportion of naphthenes present in the reaction zone such that a predetermined and minimum partial pressure of available hydrogen is continuously present in the reaction zone in excess of that required for said hydrogenation of olefins and periodically increasing substantially above and then reducing substantially to said minimum the partial pressure of said available hydrogen within the reaction zone with continued flow of hydrocarbons through the reaction zone during said continued onstream operation such that catalyst activity is maintained, each period of increased hydrogen partial pressure having a duration not exceeding a few minutes.

2. The continuous method of preparing gasoline, rich in aromatic hydrocarbons and saturated aliphatic hydrocarbons, from straight-run and cracked naphtha hydrocarbons, said gasoline being characterized by a predetermined low bromine number, which comprises maintaining a reaction zone containing a mass of solid hydrogenation-dehydrogenation catalyst, passing said straight-run and cracked naphtha hydrocarbons through the reaction zone in contact with the catalyst during continued onstream operation, effecting said contact at an elevated temperature not less than about 800° F. and not in excess of about 875° F., such that dehydrogenation of naphthenic constituents of the straight-run naphtha and hydrogenation of olefinic constituents of the cracked naphtha occur without substantial hydrocarbon cracking, causing the hydrocarbons to flow through the reaction zone in the presence of a predetermined partial pressure of free hydrogen, continuing said flow until the bromine number of the effluent stream exceeds said predetermined value as a result of decreased catalyst activity, then increasing substantially the partial pressure of said free hydrogen within the reaction zone with continued flow of hydrocarbons through the reaction zone, maintaining said increased partial pressure for a brief period of time sufficient to restore catalyst activity and reduce the bromine number of the effluent hydrocarbon stream to not in excess of said predetermined value, thereafter reducing the hydrogen partial pressure to substantially said predetermined partial pressure, continuing the operation with said reduced partial pressure and repeating the cycle when the bromine number of the effluent stream exceeds said predetermined value.

3. A continuous method of preparing gasoline, rich in aromatic hydrocarbons and saturated aliphatic hydrocarbons from straight-run and cracked naphtha hydrocarbons, which comprises maintaining a reaction zone containing a mass of solid hydrogenation-dehydrogenation catalyst, passing said straight-run and cracked naphtha hydrocarbons through the reaction zone in contact with the catalyst during continued onstream operation for a prolonged period of time, effecting said contact at an elevated temperature not in excess of about 850° F., such that dehydrogenation of naphthenic constituents of the straight-run naphtha and hydrogenation of the olefinic constituents of the cracked naphtha occur without substantial cracking, causing the hy-

drocarbons undergoing treatment to flow through the reaction zone in the presence of free hydrogen, continuously discharging an effluent stream of treated hydrocarbons containing free hydrogen, separating from the effluent stream a gaseous fraction consisting essentially of hydrogen, recycling said gaseous fraction, at least in part, to the reaction zone and periodically and temporarily increasing the ratio of recycled gas to naphtha feed so as to temporarily increase the partial pressure of free hydrogen within the reaction zone during continued passage of hydrocarbons through the reaction zone, the number of said periodic increases and the duration thereof being such that the bromine number of the effluent hydrocarbon stream during said onstream operation does not exceed about 5.

4. The method according to claim 3 in which said periodic and temporary increase in hydrogen partial pressure is effected without substantial change in the total pressure prevailing within the reaction zone.

5. The method according to claim 3 in which said periodic increase in pressure is effected by temporary reduction in the rate of feed hydrocarbon flow to the reaction zone.

6. The continuous method of preparing gasoline rich in aromatic hydrocarbons and saturated aliphatic hydrocarbons, from straight-run and cracked naphtha hydrocarbons boiling below about 300° F., said gasoline being characterized by a bromine number below a predetermined limit not substantially exceeding about 5, which comprises maintaining a reaction zone containing a mass of solid hydrogenation-dehydrogenation catalyst, passing said straight-run and cracked naphtha hydrocarbons through the reaction zone in contact with the catalyst at a temperature of about 825° F. to 850° F., such that dehydrogenation of naphthenic constituents of the straight-run naphtha and hydrogenation of olefinic constituents of the cracked naphtha occur without substantial hydrocarbon cracking, causing the

hydrocarbons to flow through the reaction zone in the presence of free hydrogen such that a predetermined partial pressure of hydrogen is maintained in the effluent hydrocarbon stream from the reaction zone, continuing said flow until the bromine number of the effluent stream exceeds said predetermined limit, then increasing substantially the partial pressure of free hydrogen within the reaction zone such that the partial pressure of free hydrogen in the effluent hydrocarbon stream is from 100–300% greater than said predetermined partial pressure, maintaining said increased partial pressure, with continued flow of hydrocarbons through the reaction zone, for a brief period of time sufficient to reduce the bromine number of the effluent hydrocarbon stream to not in excess of said limit, thereafter reducing the hydrogen partial pressure to substantially said predetermined partial pressure, continuing the operation with said predetermined partial pressure and repeating the cycle when the bromine number of the effluent stream exceeds said limit.

JOSEPH MASON BARRON.

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

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Number	Name	Date
2,143,364	Taylor	Jan. 10, 1939
2,241,393	Danner	May 13, 1941
2,251,554	Sabel et al.	Aug. 5, 1941
2,297,773	Kanhofer	Oct. 6, 1942
2,317,494	Thomas	Apr. 27, 1943
2,322,863	Marschner et al.	June 29, 1943
2,268,187	Churchill	Dec. 30, 1941

FOREIGN PATENTS

Number	Country	Date
423,001	British	Jan. 23, 1935

Certificate of Correction

Patent No. 2,416,894. March 4, 1947.

JOSEPH MASON BARRON

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 6, line 28, for "about" read *above*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of May, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.

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hydrocarbons to flow through the reaction zone in the presence of free hydrogen such that a predetermined partial pressure of hydrogen is maintained in the effluent hydrocarbon stream from the reaction zone, continuing said flow until the bromine number of the effluent stream exceeds said predetermined limit, then increasing substantially the partial pressure of free hydrogen within the reaction zone such that the partial pressure of free hydrogen in the effluent hydrocarbon stream is from 100–300% greater than said predetermined partial pressure, maintaining said increased partial pressure, with continued flow of hydrocarbons through the reaction zone, for a brief period of time sufficient to reduce the bromine number of the effluent hydrocarbon stream to not in excess of said limit, thereafter reducing the hydrogen partial pressure to substantially said predetermined partial pressure, continuing the operation with said predetermined partial pressure and repeating the cycle when the bromine number of the effluent stream exceeds said limit.

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