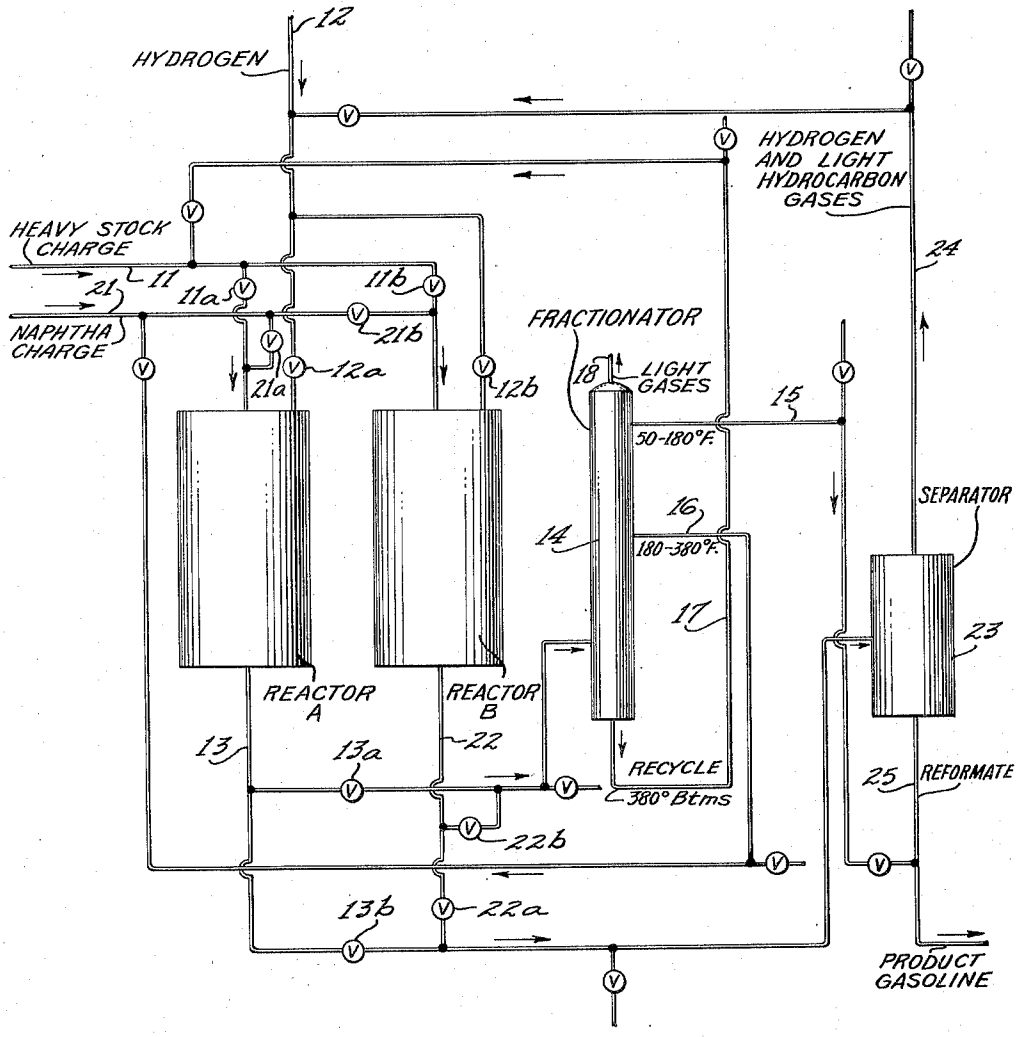
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HYDROGENATIVE CONVERSION OF HYDROCARBONS

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HYDROGENATIVE CONVERSION OF HYDROCARBONS

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This invention relates to the conversion of hydrocarbon materials in the presence of hydrogen, and is particularly directed to conversion of different types of hydrocarbon materials simultaneously within a common system under conditions of heat balance, such that the sensible heat released during an exothermic reaction stage applied to one type of hydrocarbon material in the system is beneficially utilized to supply the heat requirements for an endothermic operation applied to another type of hydrocarbon material undergoing conversion in the system.

It is well-known that heavier hydrocarbons and hydrocarbonaceous materials such as petroleum oils, shale oils, coils, tars and the like can be converted at elevated temperatures and pressures in the presence of hydrogen to obtain, by a process generally known as destructive hydrogenation, yields of lighter boiling hydrocarbons such as those in the gasoline range. Another operation well-known in industry is the reforming of lighter hydrocarbons such as light and heavy naphthas also at elevated temperatures and pressures in the presence of hydrogen to obtain thereby modified hydrocarbon materials having certain desirable attributes such as higher octane numbers, an increased spread through a desired boiling range and other improvements. These two types of conversion are operated at relatively divergent conditions of pressure; the destructive hydrogenation step is highly exothermic while the reforming step is endothermic, thus requiring considerable differences in operating conditions control and procedure. Another general difference apparent with these two types of operation is that the reforming operation is generally performed without the formation in any appreciable amounts of hydrocarbonaceous deposit or coke, whereas destructive hydrogeneration, or hydrogenative cracking or hydrocracking as it may be termed, generally results in the formation of appreciable amounts of coke. Thus, the reforming type of operation, provided sufficient heat is supplied in controlled amounts, can be continued almost indefinitely, at least in so far as the presence of coke inhibiting or stopping the reaction is concerned; whereas with the hydrogenative cracking operation arrangements must be made for the periodic removal of such coke deposit as may be formed in the reactor in or on any surface of such contact mass as may be used in the operation.

It is an object of this invention to provide a system for the simultaneous conversion by hydrocracking and by reforming of the appropriate types of charge stocks. It is a further object of this invention to provide a system in which the exothermic heat of the hydrocracking reaction is efficiently utilized subsequently by the reforming conversion operation while simultaneously utilizing the endothermic phenomenon of the reforming conversion operation to subsequently control within reasonable limits the exothermic heat of the cracking operation. Another object of the invention is to operate this system in such manner that the periodic removal of

hydrocarbonaceous deposit resulting in the hydrocracking operation is efficiently and effectively performed during the reforming operation without any appreciable interruption thereto. Another object is to provide means and apparatus whereby the system may be operated efficiently and economically while obtaining these and other desired results. In accordance with the invention a heavy hydrocarbon charge, which may be a topped or reduced crude petroleum oil, is contacted with catalyst having hydrogen activating properties at elevated pressure and under conditions of temperature to promote hydrogenative cracking of the charge. The reaction being strongly exothermic, sensible heat is stored in the catalyst and the temperature of the catalyst (and of the environment) is accordingly raised, while a small but significant quantity of hydrocarbonaceous deposit is formed in the catalyst. After a predetermined period of such operation, the flow of the heavy charge is discontinued and after suitable adjustment to lower pressure of the reaction zone, the same catalyst is now contacted with a hydrocarbon charge to be reformed. One of the principal reactions reactions taking place in this latter step is dehydrogenation, which is endothermic, and the heat stored in the catalyst during the previous exothermic step is beneficially utilized. During the reforming operation, the temperature of the catalyst and its environment is thus reduced to a suitable level and the hydrocarbonaceous deposit therein is removed to a major extent—seemingly as a result of concomitant hydrogenation thereof taking place—preparing the catalyst and the reaction zone, after a fixed period of operation under reforming conditions, to be used again for hydrocracking of heavy charge, pressure being again adjusted.

In the preferred operation, a system of reaction vessels is provided so that the process can be carried out continuously, one or more vessels in the system being switched periodically, so that each vessel operates alternately in hydrocracking and in hydroforming, while the several charges are thus being supplied and treated substantially continuously. In addition to the advantages of temperature control in the process and retarding or preventing the accumulation of hydrocarbonaceous deposit, the reforming and hydrocracking are mutually interrelated in that the hydrogen produced during the reforming step is needed and can be utilized in hydrocracking, while the products from hydrocracking include saturated materials which can be reformed to more valuable products and constitute a desirable charge to the reforming operation.

A more complete understanding of the invention and an appreciation of other advantages thereof will be had from the detailed description which follows read in connection with the accompanyinng drawing illustrating a flow diagram of a typical arrangement for the practice thereof.

With reference to the drawing the general flow pattern of the system in accordance with the preferred embodiment can be followed readily. The operation of the system thus illustrated is as follows: higher boiling hydrocarbon charge is admitted through line 11 to reactor A for hydrogenative conversion at hydrocracking conditions and in contact with a suitable catalyst having the desired activity for the hydrocracking (as well as for reforming) reaction; such catalysts include, for example, platinum supported on silica-alumina, nickel supported on silica-alumina, platinum supported on alumina, molybdena- or tungsten-containing catalysts or other catalysts having hydrogen activating properties. The conditions used for hydrocracking are those familiar for this operation and include liquid hourly space velocity in the range of 0.5 to 4.0 volumes of oil per volume of catalyst and tempera-

tures of 900–1050° F., although temperatures above and below this range are also suitable and dependent to considerable extent on the extent of reaction desired and the type of charge stock admitted for conversion; hydrogen to oil ratios in the order of 3/1 to 10/1 on a molar basis and pressures generally in excess of 75 atmospheres, although lower pressures can be employed; pressure of 100 atmospheres or more is preferred.

The hydrogenative cracking reaction is continued for a predetermined period based on the heat balance of the system, which in a typical operation will be approximately one hour, during which time the temperature rise within the reactor may be approximately 70° with a concomitant deposition on the contact mass of an appreciable amount of hydrocarbonaceous material. Simultaneously and concomitantly, reactor B containing the same type and amount of catalyst as reactor A is operating at reforming conditions with a naphtha charge introduced through line **21**. The temperatures of the several reactions should not be allowed to fluctuate more than 100° during the operating periods which have been described as of approximately one hour's duration but which may be longer or shorter to meet operating requirements.

The conditions of reforming include temperatures of approximately 900–1050° F., pressures less than 100 atmospheres and preferably less than 50 atmospheres, a liquid hourly space rate in the range of 1–6 and hydrogen to oil ratios of 1/1 to 10/1. The catalyst type previously mentioned is used for reforming also. In order to achieve the desired heat balanced arrangement in the several cases, it is necessary to operate the reforming unit over approximately the same temperature range employed for hydrocracking, except that while during the hydrocracking the temperature swing is from the lower to the higher value in this range, during reforming the opposite takes place. In the embodiment under discussion, for instance, if approximately 3,000 bbls. of a typical charge per on-stream day are introduced to the hydrocracking step, the heat evolved thereby is approximately equal to the heat requirement in the reforming of approximately 3 times as much of a typical naphtha stock, or approximately 9,000 bbls. per on-stream day. In view of these charge stock requirements, it is apparent that the products of hydrocracking boiling in the described naphtha range would be insufficient for full charge to the reforming operation; therefore, such charge will preferably comprise in addition material of suitable boiling range, such as naphtha, gasoline, as from catalytic cracking and/or thermal cracking or other suitable sources. The reforming step, in the described relation, is likewise continued for a period of approximately 1 hour with a concomitant temperature drop of approximately 70°.

A typical cyclic operation for the practice of this invention may be of the nature described below.

Considering first reactor A operating at hydro-cracking conditions, the charge stock from a suitable source, not shown, and which may be supplemented by recycle stock, is introduced through suitably valved line **11** for conversion. The proper amount of hydrogen, which may be relatively pure hydrogen from a suitable outside source, not shown, or a mixture of pure hydrogen and recycle gas predominately hydrogen, or a recycle gas such as from the products of dehydrogenation and predominately hydrogen is admitted through line **12** and control valve **12***a* to reactor A. Products of the hydrocracking reaction are removed from reactor A through line **13** and passing through control valve **13***a* enter the fractionator **14** for fractional distillation into suitable fractions. In the illustrated embodiment the fractions are the light gases, i.e., C_4 hydrocarbons and lighter; a 50–180° F. light gasoline cut removed through line **15**; a 180°–380° F. heavy gasoline cut removed through line **16**; and a bottoms fraction boiling above 380° F. and removed through line **17**. The light gases, removed through line **18**, may be sent to any desired usage while the light gasoline fraction is blended with other materials to form part of the final gasoline product, the heavy gasoline is sent as part of the charge to reforming, and the bottoms fraction is recycled to the hydrocracking reaction for further conversion to lighter products.

Considering next the reforming operation occurring in reactor B simultaneously with the hydrocracking reaction in reactor A, the naptha charge, from a suitable source not shown, supplemented by the heavy gasoline fraction from fractionator **14** is introduced through line **21** and valve **21***b* to reactor B. The proper amount of hydrogen-containing gas is admitted to reactor B through line **12** and control valve **12***b*. Products of reforming are removed from reactor B through line **22** and passing through control valve **22***a* enter separator **23** for fractionation into a light gas fraction removed through line **24** and a reformed gasoline removed through line **25** to form at least a portion of the product gasoline.

After the system has operated for a suitable time period in which the temperature in the reaction zone of reactor A has increased as a result of the exothermic nature of the hydrocracking reaction from an initially relatively low temperature to a temperature approximately equivalent to the temperature initially prevailing in reactor B, and the temperature in the reaction zone of reactor B has decreased as a result of the endothermic nature of the reforming reaction from an initially relatively high temperature to a temperature approximately equivalent to the temperature initially prevailing in reactor A, the operation is adjusted to utilize the existing temperature conditions and to obtain a substantial reduction of such coke deposit as formed on the catalyst during the hydrocracking reaction. The adjustment entails switching the reactions so that reactor A previously operating at hydrocracking conditions subsequently operates at reforming conditions and reactor B previously operating at reforming conditions operates at hydrocracking conditions. The charge stocks are likewise shifted to the proper reactors. In the illustrated embodiment the heavy stock charge is discontinued to reactor A by the closing of valve **11***a* and the naphtha charge to reactor B is discontinued by the closing of valve **21***b*. Reactors A and B may be flushed for a short period by the hydrogen admitted through line **12** and the pressure conditions of reactor A are adjusted to that of reforming, i.e., lower pressure, and the pressure in reactor B is raised to the proper pressure for hydrocracking. The closing of valve **13***a* and the opening of valve **13***b* provides for the transfer of the effluent from reactor A to separator **23** instead of to fractionator **14** while the closing of valve **22***a* and the opening of valve **22***b* provides for the transfer of the effluent from reactor B to fractionator **14** instead of to separator **23**. Reactor A is placed on stream by the admission of the naphtha charge through line **21** by the opening of valve **21***a* and reactor B is placed on stream by the admission of the heavy stock charge through line **11** by the opening of valve **11***b* thus providing substantially continuous operation with only a relatively minor interruption of the flow of materials, and the periodic alternation of these switching adjustments provides for cyclic operation substantially continuously.

In reactor A the higher temperatures and the excess hydrogen in addition to the reforming of the charge stock passing therethrough removes by hydrogenation the hydrocarbonaceous, or coke, deposit remaining in the reactor from the preceding hydrocracking step. The temperature effects of each of the several reactions, again continued for approximately an hour, are once again equal but opposite to that occurring in the reactors during the preceding on-stream period and thus the reactors are returned again to the temperature level at the expiration of the on-stream time where, by suitable readjustment of the charge stocks and the related conditions, hydrocracking is again resumed in reactor A and reforming is resumed in reactor B.

As an aid in obtaining this temperature balance, there may be admixed with the catalyst a contact mass of suitable high heat capacity material having the sole purpose of acting as a heat storage or delivery medium whereby the temperature increases are stored therein during the exothermic hydrocracking operation to be subsequently delivered during the endothermic reforming step. Suitable heat capacity materials include alundum, corhart, fused alumina, quartz, and other materials substantially inert and nonreactive at the operating conditions. Heat storage is also provided in part by the reactor walls and related equipment adjacent the reaction zone. In fact, reactors suitable for the high temperatures and high pressures involved are so constructed that an appreciable heat storage capacity is provided by the vessels and internals thereof.

As an aid in determining, but not as limiting, the requirements relative to heat input and the balance of conditions necessary in the reforming operation it can be stated generally that the heat capacities of the reactants are roughly: hydrogen is equal to 3.6 calories per gram per degree C.; the oil is equal to 0.6 calorie per gram per degree C.; and the catalyst of the types described (exclusive of the heat capacity material) is equal to about 0.25 calorie per gram per degree C., all at 900° F. basis. On the basis of charging 2 kgs. of oil per kg. of catalyst per hour at a 10 to 1 hydrogen to oil mol ratio, the heat capacity of the oil is 1200 calories per degree, that of the hydrogen is 1800 calories per degree and that of the catalyst 250 calories per degree; the heat of reforming is approximately 110,000 calories per kg. The exothermic heat of the hydrocracking reaction as previously mentioned is approximately three times that of but opposite to the endothermic heat of reforming thus indicating the necessity of operating hydrocracking with approximately one-third the throughput of the charge stock as that of the charge to reforming; however, this heat relation is not to be construed as absolute inasmuch as differences in charge stocks, particularly for hydrocracking, may alter this such that the exothermic heat may be considerably less than three times that of the endothermic reaction and thus necessitate change in the respective charge rates.

Example

A practical example of an operation in accordance with the foregoing description is as follows. The reforming of hydrocracked naphtha in the reforming section of such system was effected at conditions of 950° F., 600 p.s.i., liquid hourly space velocity of 4 and hydrogen to oil ratio of 4 and using a catalyst of platinum (0.5% wt.) supported on alumina. The naphtha charged to this operation had cut points of 180° and 380° F. and had an octane rating of 60.1 F–1 clear. There was obtained in the products 92 wt. percent C_{5+}, 5.7 wt. percent C_4's and 1.6 wt. percent of dry gas. The liquid product had an octane rating of 86.2 F–1 clear and 97.1 F–1+3 ccs. TEL. The blending of the initial to 180° F. fraction of hydrocracked product with this reformed fraction gave a gasoline material having an F–1 clear rating of 83.6 and an F–1+3 ccs. TEL of 95.2 at 7 lbs. RVP.

Simultaneously in the hydrocracking section utilizing the same type of catalyst, an East Texas gas oil fraction comprising a 56–77% cut and recycle heavy naptha were charged at hydrocracking conditions including temperature of approximately 900° F., 1500#/sq. in. pressure, hydrogen to oil ratio of 6 and liquid hourly space velocity of 2 (including recycle heavy naphta). The yields from such hydrocracking based on the amount of fresh feed to the reactor were 99.1 volume percent of C_{5+} gasoline, 17.8 volume percent of C_4's and 8.3 wt. percent of dry gas. The gasoline was subsequently fractionated into three cuts; namely, initial to 180° F. (30%), 180–380° F. (51.3%) and 380° F. bottoms. The middle cut supplemented with similar material was the charge to the reforming and the light cut was used to blend with reformed products as described above. The heavy cut was recycled to hydrocracking. The hydrocracking operation was accompanied by the deposition on the catalyst of approximately 1.2 grams per liter of hydrocarbonaceous material.

At the end of approximately one hour the charge stock to each of the cases was discontinued and by appropriate manipulation of the feed lines was switched to enter the opposite cases with the conditions of these cases adjusted accordingly in such manner that the case formerly operating at reforming conditions now operated at hydrocracking conditions and the case used for hydrocracking now operated for reforming. The products from each of these reactions were approximately the same as those obtained in the first hour of operation and the coke deposit on the catalyst retained after the original hydrocracking operation was reduced during the on-stream reforming period from 1.2 grams per liter to approximately 0.3 gram per liter. During the course of the reaction in the second hour the temperature in the reaction zone used for hydrocracking rose from about 900° to about 950° F. and the temperature in the reaction zone used for reforming dropped from about 950° to about 900° F. Alternating or switching these reactions periodically after time periods of approximately one hour on-stream permitted continuous operation at relatively uniform temperature conditions and under circumstances at which at no time did the coke deposit on the catalyst exceed 1.5 grams per liter while maintaining an average concentration on the catalyst of less than 0.5–0.7 gram per liter; thus maintaining a system in which temperature balance existed between the two reactions and the coke product of the hydrocracking operation was held in control at relatively low levels by hydrogenative removal during the reforming operation.

The foregoing embodiments are presented as illustrative only and the invention is subject only to such limitations of scope and variations as may appear in the appended claims.

I claim as my invention:

1. The method of hydrogenative conversion of hydrocarbons to more desirable products which comprises effecting hydrogenative conversion of one kind of hydrocarbons in one reaction zone containing catalyst having hydrogen activating properties at exothermic conditions and simultaneously in at least one other separate reaction zone containing catalyst having hydrogen activating properties in the same system effecting hydrogenative conversion of a different kind of hydrocarbons at endothermic conditions differing as to at least one of the variables selected from pressure, space rate, temperature and reactant ratio, switching charges and conditions for each of said reaction zones and thereafter effecting in said second reaction zone the reaction previously conducted in the first reaction zone and simultaneously effecting in said first reaction zone the reaction previously conducted in the second reaction zone, thereby utilizing and controlling the temperature effects of the immediately preceding reaction period, and continuing the cycle operation periodically to utilize and control the temperatures of the several reactions.

2. The process for the hydrocracking of high boiling hydrocarbons to good yields of gasoline range materials and for the reforming of naphthas to improved products simultaneously and in cycle in the same system but in separate reaction zones at different reaction conditions comprising, flowing high boiling hydrocarbon charge to a first reaction zone containing catalyst having hydrogen activating properties for conversion at hydrocracking conditions, flowing naphtha charge to a second reaction zone containing catalyst having hydrogen activating properties for conversion at reforming conditions at a pressure lower than employed in the hydrocracking conditions, continuing such reactions simultaneously for a time period of such duration that the temperature rise from the

exothermic hydrocracking reaction of the high boiling fraction in said first reaction zone approaches the temperature initially obtaining in said second reaction zone while the temperature decrease from the endothermic reforming reaction of naphtha in said second reaction zone approaches the temperature initially obtaining in said first reaction zone, switching charges and conditions for each of said reaction zones and thereafter effecting hydrocracking in said second reaction zone simultaneously with the reforming in said first reaction zone at a pressure lower than employed in the hydrocracking zone, thereby utilizing and controlling the temperature effects of the immediately preceding reaction period, and continuing the cycle operation periodically to utilize and control the temperatures of the several reactions.

3. The process of claim 2 in which said catalyst is platinum supported on silica-alumina.

4. The process of claim 2 in which the temperature rise during hydrocracking is less than 100° F. and the temperature decrease during reforming is less than 100° F.

5. The process of claim 2 in which the initial temperature of hydrocracking is about 900° F. and the initial temperature of reforming is about 970° F.

6. The process for the hydrocracking of high boiling hydrocarbons to good yields of lower boiling hydrocarbons and for the reforming of naphthas to improved products including high octane gasoline in heat balanced relationship within the same system but in separate reaction zones by continuous cycle comprising, introducing high boiling hydrocarbon charge to the system in a first reaction zone for conversion at hydrocracking conditions including temperatures of 900–1050° F., pressure in excess of 75 atmospheres, added hydrogen in mol ratio to the oil charge of 3 to 10 to 1 and liquid hourly space velocity in the range of 0.5 to 4.0, and in the presence of a platinum catalyst supported on silica-alumina, said catalyst having hydrocracking and reforming activity, effecting hydrocracking with attendant temperature elevation from about 900° F. to less than 1000° F. and deposition of inactivating amounts of coke on the catalyst, terminating said hydrocracking in said first reaction zone by discontinuing the introduction of high boiling hydrocarbon charge to said first reaction zone; introducing naphtha charge to the system to a second reaction zone for conversion at reforming conditions including temperature of 900–1050° F., pressure below 75 atmospheres, added hydrogen in mol ratio to the naphtha charge of 1 to 10 to 1, and liquid hourly space velocity in the range of 1–6, and in the presence of a platinum catalyst supported on silica-alumina, said catalyst having hydrocracking and reforming activity, effecting reforming with attendant temperature decrease from about 950° F. to a temperature greater than 850° F., terminating said reforming in said second reaction zone by discontinuing naphtha charge to said second reaction zone simultaneously with said termination of said hydrocracking in said first reaction zone; introducing said high boiling hydrocarbon charge to said second reaction zone having lower temperature and effecting hydrocracking therein similar to that previously effected in said first reaction zone; introducing said naphtha charge to said first reaction zone having higher temperature and effecting reforming therein similar to that previously effected in said second reaction zone and simultaneously removing substantial amounts of said coke from said catalyst to effect substantial reactivation thereof; and periodically alternating said hydrocracking and said reforming reactions in said first and said second reaction zones to maintain heat balance and catalyst reactivation.

7. The process of claim 6 in which the initial temperature of hydrocracking is about 900° F. and the initial temperature of reforming is about 950° F.

8. The process for the production of good yields of high octane gasoline by hydrocracking high boiling hydrocarbons and reforming naphthas simultaneously and in cycle in the same system but in separate reaction zones comprising, subjecting high boiling hydrocarbon charge stock to hydrocracking in a first reaction zone containing catalyst having hydrogen activating properties, simultaneously subjecting naphtha charge stock to reforming in a second reaction zone containing catalyst having hydrogen activating properties; passing products of said hydrocracking to fractionation into at least three fractions comprising a light gasoline, a heavy gasoline and a higher boiling fraction, recycling said higher boiling fraction as part of said charge to said hydrocracking, passing said heavy gasoline as part of said naphtha charge to said reforming, and recovering said light gasoline as part of said high octane gasoline; passing products of said reforming to separation into a light gas fraction and a gasoline fraction, recovering said gasoline fraction as part of said high octane gasoline, recycling said light gas fraction to said hydrocracking and said reforming as at least a portion of the hydrogen-containing gas supplied thereto; and periodically alternating said hydrocracking and said reforming between said first reaction zone and said second reaction zone when the temperature of said hydrocracking reaches the temperature initially prevailing for said reforming and the temperature of said reforming reaches the temperature initially prevailing for said hydrocracking.

9. The process of claim 8 in which said high octane gasoline product is a blend of reformate from said reforming and of light gasoline fraction of the product of said hydrocracking.

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CERTIFICATE OF CORRECTION

Patent No. 2,902,436 September 1, 1959

George Alexander Mills

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 28, for "coils" read -- coals --; column 2, line 22, strike out "reactions", second occurrence; column 5, line 67, for "naphta" read -- naphtha --; column 7, line 5, after "of" insert -- the --.

Signed and sealed this 9th day of February 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents