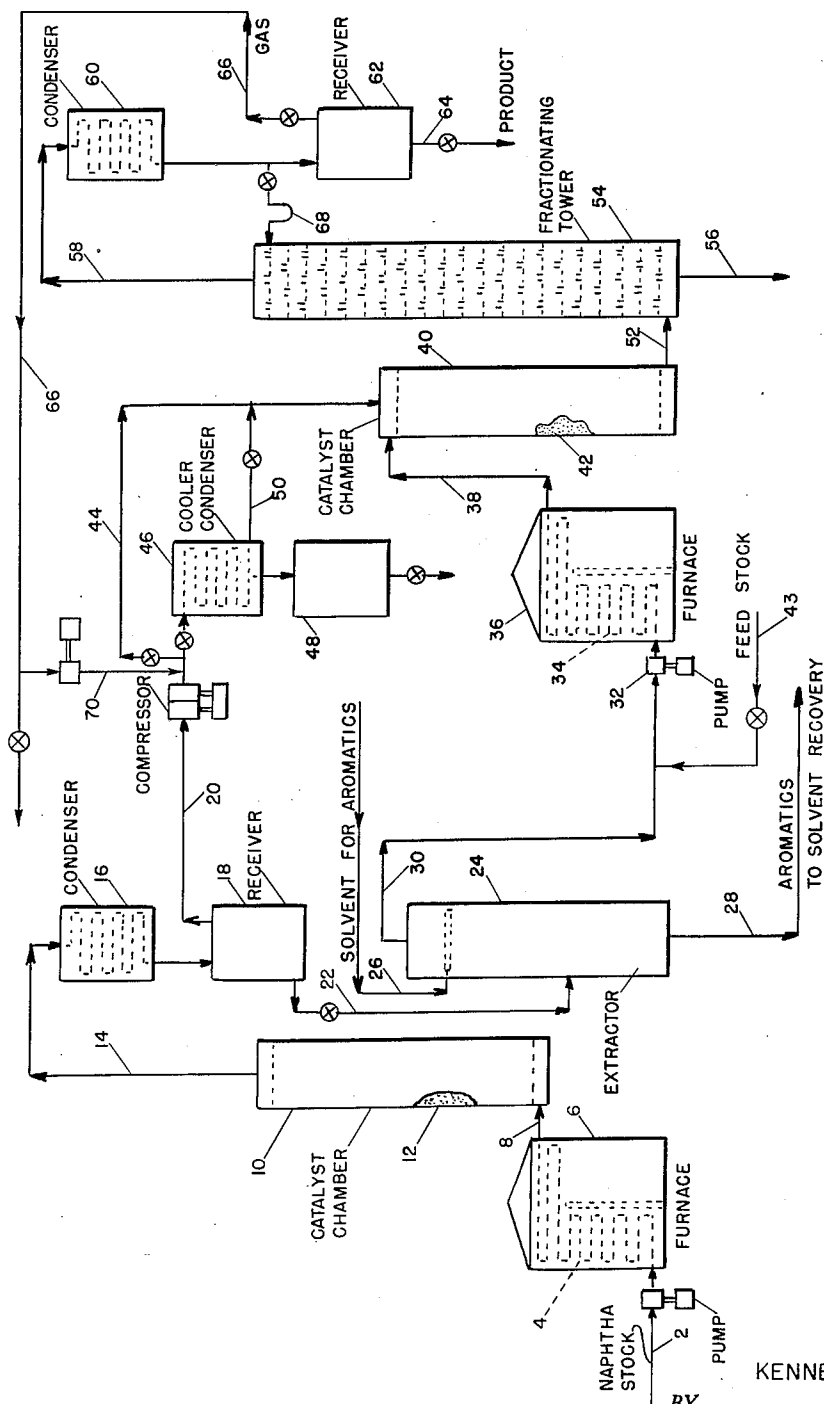


Sept. 19, 1950

K. M. WATSON
CATALYTIC CONVERSION OF NAPHTHA FOR THE
PRODUCTION OF HIGH ANTIKNOCK GASOLINE
Filed June 27, 1947

2,522,696



INVENTOR.
KENNETH M. WATSON

BY
Pauiz, Edwards, Morton & Barrows
ATTORNEYS

UNITED STATES PATENT OFFICE

2,522,696

CATALYTIC CONVERSION OF NAPHTHA FOR
THE PRODUCTION OF HIGH ANTIKNOCK
GASOLINEKenneth M. Watson, Madison, Wis., assignor to
Sinclair Refining Company, New York, N. Y.,
a corporation of Maine

Application June 27, 1947, Serial No. 757,642

1 Claim. (Cl. 196—49)

1

My invention relates to improvements in the production of aromatic hydrocarbons and motor fuel gasolines of high anti-knock value by the catalytic conversion of naphtha stocks of relatively high hydrogen content such as straight run naphthas, thermally cracked naphthas or coke still or vis-breaker naphthas. More particularly my invention relates to an improvement in the catalytic hydroforming of such naphthas.

In the hydrocracking of petroleum oil stocks under destructive hydrogenation conditions, it is usually necessary to make and supply hydrogen to the system. In certain instances, tail gases are recirculated directly in the system, but they often contain rather low percentages of hydrogen or are entirely devoid of hydrogen.

I have devised a system for the cracking of naphtha stocks of the type referred to in which the hydrogen is produced directly in the process. In my improved process a naphtha stock is subjected to a catalytic dehydrogenation cracking operation at approximately atmospheric pressure and in the temperature range of from about 900 to 1100° F. These conditions not only produce substantial proportions of hydrogen but also produce aromatic hydrocarbons in substantial proportion. The products of this cracking operation are cooled to condense out the readily condensable constituents as a distillate, which is extracted with a selective solvent, by selective adsorption or by extractive distillation for the separation of aromatic hydrocarbons, or the aromatics are otherwise removed from the distillate. The remaining non-aromatic stock or other suitable stock, together with hydrogen produced in the dehydrogenation operation and separated from the condensable hydrocarbons, is subjected to a catalytic destructive hydrogenation step at a pressure of from about 300 to 3,000 pounds per square inch, at a conversion temperature of from 700° to 1100° F.

In the destructive hydrogenation step, the conditions are controlled so that substantially all of the hydrogen produced in the dehydrogenation step is supplied to the second step in producing lower molecular weight hydrogenated cracked, or hydroformed products of low boiling point and of desirable antiknock properties.

The hydrogen produced in the first part of the naphtha conversion operation along with gaseous hydrocarbons may be used directly as separated from the readily condensable constituents, but it is preferably compressed and cooled so as to condense out the light normally gaseous hydrocarbons present.

2

My invention provides in the combined operations outlined above several special features and combinations of steps which facilitate the conversion of naphthas and the production of aromatic hydrocarbons. The invention, however, will be further described in connection with the single figure of the accompanying drawing, which illustrates diagrammatically and conventionally in elevation, with parts broken away, one form of apparatus which may be appropriately used for carrying out my improved process.

My process is illustrated in connection with the showing in the drawing, in which the charging stock, for example, a straight-run or cracked naphtha of the type described, is introduced into the apparatus through an inlet line 2 and forced at a suitable charging rate and pressure by means of a pump therein through a heating coil 4 mounted in a pipe still furnace 6. The oil in passing through the coil 4 is heated to a temperature of about 1000° F., after which the naphtha stream is conducted through a transfer line 8 into a catalyst chamber 10, carrying a bed of catalyst 12. The highly heated naphtha stock may be introduced either at the bottom or top of the catalyst chamber. A pressure of approximately atmospheric is maintained in the chamber 10 to facilitate dehydrogenation of the naphtha stock, and the conversion of substantial proportions thereof to aromatic hydrocarbons.

The catalyst bed 12 may comprise a dehydrogenation catalyst, such as chromia or molybdena on alumina, or other suitable well known dehydrogenation and cyclicizing catalysts. Furthermore, the catalyst may be used in any other form, such as fluid, granular, or bead.

The conversion products produced in chamber 10 are conducted therefrom through a line 14 into a condenser and cooler 16, which is operated under conditions to condense out substantially all of the readily condensable materials. The hydrogen and liquid products, together with any uncondensable hydrocarbons, are conducted into a receiver 18, in which the hydrogen and other gases are separated out and from which they are removed through a line 20.

The liquid product in the receiver 18 is conducted through a valved line 22 into an extractor 24, where the product is brought into counter-current contact with a selective solvent for aromatic hydrocarbons introduced through a line 26 and distributed into the body of liquid in the extractor 24 at approximately the point shown. The selective solvent, together with the dissolved aromatic hydrocarbons, move downwardly in the

extractor and is discharged through a line 28 and sent to suitable equipment, not shown, for recovering the selective solvent from the aromatic hydrocarbons. The recovered solvent may then be reintroduced into the extractor 24 by the line 26. A phenol-water system or solvent may be used, or other known solvent, for aromatic hydrocarbons. The aromatics may be separated by other means referred to above.

The non-aromatic partially-converted naphtha stock which moves toward the top of the extractor 24 is discharged therefrom through a line 30 and then picked up by a pump 32, placed under a high pressure of approximately 2,000 pounds per square inch and passed through a heating coil 34 mounted in a pipe still furnace 36. The non-aromatic charging stock in the coil 34 is heated to a temperature preferably between 950 and 1050° F., after which it is discharged through a transfer line 38 into the upper portion of a catalyst chamber 40 which carries a bed of catalyst 42 for effecting the hydroforming of the non-aromatic partially-converted naphtha stock.

Other stocks low in hydrogen content may be cracked in the second stage of the process, instead of, or along with, the stock in the line 30, by feeding such stock to the pump 32 through a valved line 43. These stocks may be higher boiling than gasoline and typically be recycle fractions from conventional catalytic cracking operations consisting largely of polycyclic aromatics deficient in hydrogen and difficult to crack without the addition of hydrogen.

The catalyst 42 may comprise one of the typical catalysts used for hydroforming, such as the sulfides of the metals molybdenum, tungsten, iron and the like, for example. A specific metal sulfide deposited on alumina may be used as a catalyst.

The hydrogen for the conversion carried out in the chamber 40 is taken directly from the first step of the process by compressing the hydrogen containing gas in the line 20 up to a pressure in excess of 2,000 pounds per square inch, the resulting compressed gases being conducted directly through a valved line 44 into the top of the chamber 40, where they mingle with the oil products introduced through the transfer line 38. While the gases in the line 44 are rich in hydrogen, they may be further enriched by passing the gases from the compressor through a valved line to a cooler condenser 46, where at the high pressure considerable proportions of any hydrocarbons present are condensed and drawn off into a receiver 48. The greatly enriched hydrogen containing gas is conducted from the condenser 46 through the valved line 50 directly into the top of the catalyst chamber 40. The gas in either lines 20, 44 or 50 may be freed of olefins by contact with concentrated sulfuric acid.

The mixture of hydrogen and partially converted non-aromatic material passing downwardly through the catalyst bed 42 are reacted together at a pressure of approximately 2,000 pounds per square inch so as to consume substantially all of the hydrogen and produce a hydrogenated cracked product comprising a high percentage of low boiling materials of desired antiknock characteristics. The stock subjected to the conversion in chamber 40 is already dehydrogenated and partially converted, so that in the chamber 40 there is considerable molecular breakdown of constituents boiling above the gasoline range to give hydrocarbon molecules containing a smaller number of carbon atoms. Fur-

thermore, considerable proportions of such hydrocarbons are cyclicized and converted to aromatics.

The reaction products at the bottom of the chamber 40, which may carry a relatively shallow or deep bed or beds of the catalyst, are conducted through a line 52 into a fractionating tower 54 where the vapors are cooled and refluxed to condense the small proportion of hydrocarbons boiling above the gasoline or motor fuel range. Such materials are discharged through a valved line 56.

The motor fuel vapors and the gases are discharged from the tower 54 through a line 58, condensed in a condenser 60 and recovered in a receiver 62. The product is withdrawn from the receiver through a valved line 64, while the normally gaseous hydrocarbons, including hydrogen, are withdrawn through a valved line 66. The desired reflux ratio is maintained on the tower 54 by returning a part of the condensate from the condenser 60 through a valved return line 68.

In my process the naphtha stock either for the first or second cracking zones may be heated in any other manner than that described above, and the stock may be contacted with the catalyst either in countercurrent or concurrent flow, and in either cracking zone the catalyst may be one of the fluid type, a bead type catalyst or a granular catalyst, or in the form of an aerogel. It is generally understood how these different forms of catalysts are employed in conversion operations, and therefore that procedure need not be described in detail. If catalyst chambers such as 10 and 40 are employed, they may be operated in duplicate or triplicate, so that the catalyst bed of one chamber may be regenerated while another chamber is being used to carry out the conversion operation.

The non-aromatic naphtha stock, recovered from the extractor 24 and used as the charging stock in the second cracking zone, is preferably handled so that a very large percentage of it is converted to high anti-knock constituents within the gasoline boiling range. Constituents of boiling points intermediate between the gasoline produced in the second stage and the heaviest fractions withdrawn through line 56 are advantageously recycled for retreatment in the second stage by withdrawing a side-stream from tower 54 and returning it to the suction of pump 32 by means of a line not shown.

The conditions employed in the second conversion zone in chamber 40 are preferably such that substantially all of the hydrogen introduced therinto from the first conversion zone is free to enter into the hydroforming reactions, and therefore the hydrogen introduced into the chamber 40 is preferably free of olefins which would take up hydrogen. However, a portion or all of the gases, including hydrogen, discharged through the line 66 are advantageously recycled to the top of the reaction chamber 40 to augment the hydrogen ratio and further the hydroforming reactions therein, the gases being drawn from the line 66 by a compressor in a line 70, discharging into the line 20 beyond the compressor therein.

The operation in the dehydrogenation zone is correlated with that in the hydrocracking zone so that adequate hydrogen is produced for the hydrocracking reactions.

The aromatic hydrocarbons recovered in the extractor 24 may be blended with the product recovered in receiver 62 so as to increase the octane value and power factor of the gasoline

5

product. On the other hand, the aromatics from the extractor 24 may be fractionated and used for various other purposes as desired. The liquid product recovered in the receiver 48, which is at a pressure higher than that employed in the chamber 40, may be fractionated to recover the various individual or groups of hydrocarbons.

I claim:

In the production of high anti-knock gasoline by the catalytic conversion of naphthas in the presence of hydrogen, the improvement which comprises contacting a naphtha of relatively high hydrogen content with a dehydrogenation catalyst at a temperature of from 900° to 1100° F. in a first cracking zone in which a pressure of approximately atmospheric is maintained, producing substantial proportions of aromatic hydrocarbons and hydrogen in said zone, continuously removing the hydrogen and products of conversion from said zone, separating out the hydrogen substantially free of hydrocarbons, separating the aromatic hydrocarbons from the converted naphtha stock to provide a substantially non-aromatic cracked naphtha stock, subjecting such naphtha stock while substantially free from aromatic hydrocarbons to cracking conditions in a second cracking zone in a continuous

6

operation in the presence of the hydrogen produced by the dehydrogenation in said first zone by contacting the non-aromatic stock and hydrogen with a hydrogenating cracking catalyst at a temperature of from 700° to 1100° F. and a pressure of from 300 to 3,000 pounds per square inch, introducing a cracking stock difficult to crack and deficient in hydrogen into the second cracking zone in addition to the non-aromatic stock from the first zone, and recovering a high anti-knock gasoline product from the cracking of the non-aromatic stock and the additional cracking stock in the presence of hydrogen.

KENNETH M. WATSON.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,202,401	Rosen	May 28, 1940
2,241,430	Snow	May 13, 1941
2,289,716	Marschner	July 14, 1942
2,292,677	Thomas	Apr. 11, 1942
2,389,176	Anderson	Nov. 20, 1945
2,407,492	Hall et al.	Sept. 10, 1946