

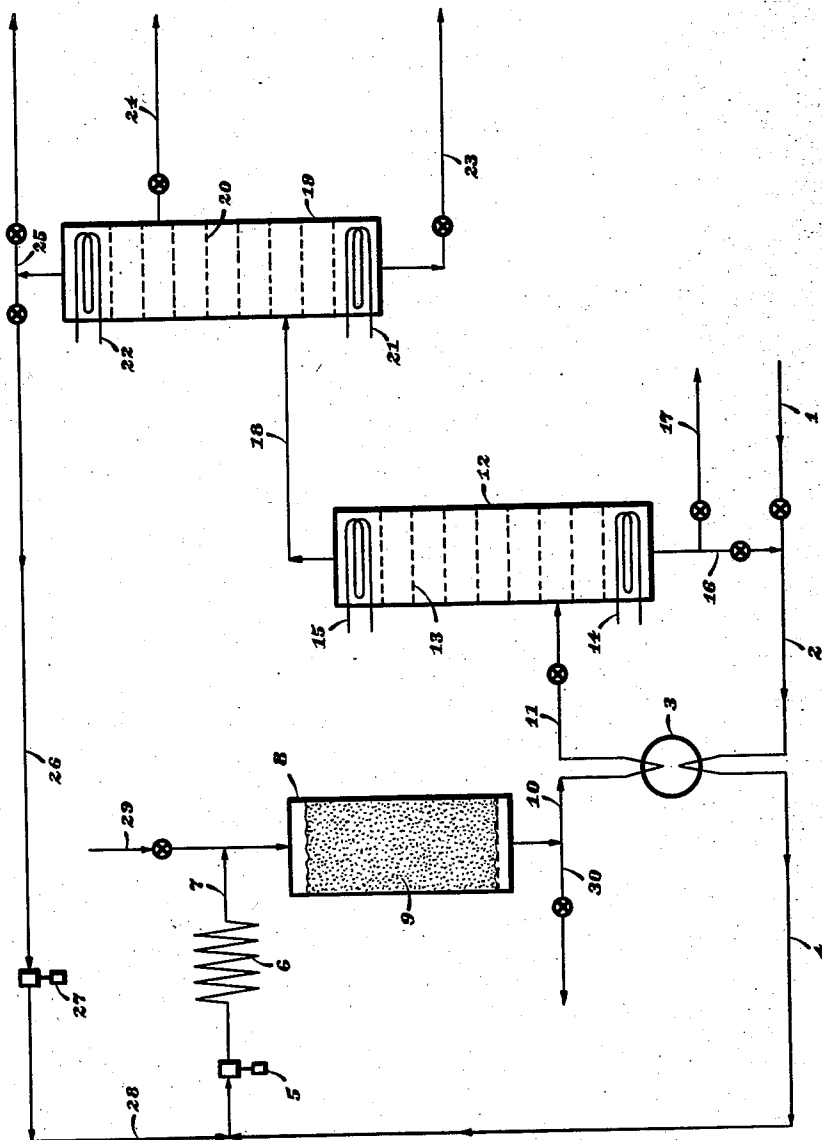
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TREATMENT OF HYDROCARBONS.

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Attest

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## UNITED STATES PATENT OFFICE

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## TREATMENT OF HYDROCARBONS

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The present invention relates to the treatment of hydrocarbons, and more particularly to the conversion of hydrocarbons into more valuable products by catalytic reactions involving cracking, reforming, dehydrogenation and polymerization.

It is an object of this invention to convert high boiling hydrocarbon oils into lower boiling hydrocarbons, particularly gasoline. Hydrocarbon oils such as gas oil, heavy distillates, petroleum residuum, tars, and the like may be advantageously converted in accordance with this invention.

It is a further object of this invention to improve the antiknock qualities of gasoline or naphtha distillate and to increase the lead susceptibility thereof by subjecting such distillates to reforming conditions of temperature and pressure in the presence of a catalyst. Such reforming operation involves essentially a dehydrogenation and structural rearrangement of the distillate molecules, with or without cracking and change in boiling range or volatility of the reformed distillate.

It is a further object of this invention to effect conversion of hydrocarbons in the presence of a catalyst comprising aluminum oxide and an alkali metal borate, such catalyst containing limited amounts of water, preferably from about 5 per cent to about 15 per cent by weight.

It is a further object of this invention to effect conversion of hydrocarbons in the presence of a catalyst comprising aluminum oxide and an alkali metal borate, the moisture content of the hydrocarbons being controlled to provide a charging stock containing not more than about 40 parts per million (0.004 per cent by weight) of water.

I have found that the most effective conversion of hydrocarbons may be obtained when the water content (volatile matter) of the aluminum oxide-alkali metal borate catalyst, and particularly the water content of the aluminum oxide components thereof, is maintained within the range of from about 5 per cent to about 15 per cent by weight, and the water content of the hydrocarbons charged is maintained at not more than about 40 parts per million. Substantial deviation of the water contents of either the catalyst or the hydrocarbons from the range mentioned does not permit optimum conversion of hydrocarbons.

In accordance with the present invention, hydrocarbons containing not more than about 40 parts per million of water are subjected to elevated temperatures, under atmospheric or superatmospheric pressure, in the presence of a catalyst capable of promoting the conversion or reforming reaction, such catalyst comprising aluminum

oxide and an alkali metal borate, and containing from about 5 per cent to about 15 per cent by weight of water in chemical combination. In the conversion of high boiling oils, such as gas oil, into gasoline, temperatures of the order of from about 850° F. to 1050° F. and pressures up to about 3000 pounds per square inch may be employed, while in the reforming of gasoline or naphtha distillates for the improvement of the antiknock quality thereof, temperatures of the order of 975° F. to 1100° F. and pressures of the order of from atmospheric to about 1500 pounds per square inch may be advantageously utilized. The reaction time or space velocity may be varied, depending upon the temperature-pressure conditions and the results desired. In general the contact time may be somewhat longer in the conversion of high boiling oils into lower boiling hydrocarbons such as gasoline, than in the reforming of gasoline or naphtha distillates for the improvement in antiknock quality thereof. For example, in cracking high boiling oils, the space velocity may be of the order of 1 volume of charge oil per volume of catalyst per hour, whereas in the reforming of distillates, the space velocity may be of the order of 1.5 to 4 volumes of charge oil per volume of catalyst per hour.

The catalyst to be employed in accordance with this invention comprises aluminum oxide or bauxite which has been impregnated with an alkali metal borate, said aluminum oxide or bauxite containing from about 5 per cent to about 15 per cent by weight of water, most of which is chemically combined. The water content or volatile matter is found by heating the oxide or bauxite at 1800° F. for 20 minutes, and determining the loss in weight. Such catalyst may be prepared by soaking granular aluminum oxide of proper water content with an aqueous solution or suspension of an alkali metal borate, and thereafter drying the impregnated granular material by heating at temperatures not in excess of about 1000° F. Or, alternatively, finely divided aluminum oxide may be impregnated with an alkali metal borate solution or suspension, and the moist material thereafter granulated or formed into suitable pellets or masses. The quantity of borate to be employed may vary from about 0.1 per cent to 10 per cent or more by weight of the aluminum oxide, quantities of the order of from about 1 per cent to about 5 per cent being preferred. Among the borates which may be utilized are the metaborates, tetraborates, pentaborates, hexaborates, octaborates and dodecaborates of sodium, potassium and lithium.

The water content of the hydrocarbon oil to be converted may be controlled by dehydrating the oil, if the water content is substantially in excess of about 40 parts per million. Oils containing substantially no water, or water in amounts up to about 40 parts per million, are satisfactory. Those containing water in excess of about 40 parts per million are not susceptible of high conversion yields. When necessary, dehydration of the oil to the proper water content may be accomplished by air blowing, or treatment with dehydrating adsorbents or chemical agents commercially available for dehydrating purposes.

My invention may be further illustrated with reference to the accompanying drawing, which shows diagrammatically a system suitable for carrying out my process.

Hydrocarbon oil, such as gas oil having a water content of not more than 40 parts per million, is supplied from a source (not shown) through valve-controlled pipe 1 and is passed by means of pipe 2 to heat exchanger 3, wherein the oil is preheated by indirect heat exchange with cracked products from the catalytic chamber hereinafter described. The preheated oil is passed from heat exchanger 3 through pipe 4 to pump 5, from which it is delivered to the tubular heating coil 6 wherein the temperature of the oil is raised to about 950° F., under a pressure of from about 25 to about 50 pounds per square inch. Higher pressures, of course, may be used. In the coil 6 the oil is vaporized and the heated vapors are passed therefrom by means of pipe 7 into the upper section of catalyst chamber 8 containing a granular catalyst 9 comprising  $\text{Al}_2\text{O}_3$  impregnated, for example, with 1 per cent by weight of sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), and containing from about 5 per cent to about 15 per cent by weight of water. In the chamber 8 cracking of the heated oil in contact with the catalyst takes place, with the production of hydrocarbon gases,  $\text{H}_2$ , cracked gasoline and gas oil, and small amounts of tar. The cracked products, at a temperature of the order of 950° F., are withdrawn from the lower section of chamber 8 and are passed by means of pipe 10 through heat exchanger 3 in indirect heat exchange with relatively cool charge oil introduced through valve-controlled pipe 1 and pipe 2. In the exchanger 3 the hot, cracked products are partially cooled, and thence delivered by valve-controlled pipe 11 to fractionating column 12 provided with contacting plates or trays 13 heating coil 14 and cooling or reflux coil 15. The cracked products are fractionated in column 12 to produce an overhead fraction comprising cracked gasoline and gases, and a bottoms fraction or residue comprising cracked gas oil and small amounts of tar. The cracked gas oil and tar may be withdrawn from the bottom of column 12 by means of valve-controlled pipe 16, and, if desired, a portion thereof may be recycled, with fresh charge oil, to the tubular heating coil 6. The remainder of the cracked gas oil and tar may be withdrawn from the system through valve-controlled pipe 17 and disposed of as desired.

The gasoline vapors and gases are passed from the top of fractionating column 12 and are introduced by means of pipe 18 into a second fractionating column 19 provided with contacting trays 20, heating coil 21, and cooling coil 22. Herein the gases are separated from the gasoline and the latter is stabilized to obtain the desired boiling range and volatility. The stabilized gasoline may be withdrawn from the bottom of the

column and passed by means of valve-controlled pipe 23 to storage (not shown). If desired, a liquid side stream comprising  $\text{C}_3$  or  $\text{C}_4$  hydrocarbons, or a mixture thereof, may be removed from the column through valve-controlled pipe 24, or  $\text{C}_3$  or  $\text{C}_4$  hydrocarbons may be withdrawn with the uncondensed gases, i. e.,  $\text{C}_1$ - $\text{C}_2$  hydrocarbons and  $\text{H}_2$ , from the top of the column by means of valve-controlled pipe 25. If desired, at least a portion of the uncondensed gas or  $\text{C}_3$ - $\text{C}_4$  hydrocarbons may be recycled to the tubular heating coil 6 by means of valve-controlled pipe 26, compressor 27 and pipe 28.

In the operation of the catalyst chamber 8, the activity of the catalyst may be maintained or increased by the introduction of gases such as steam, oxygen, or carbon dioxide, or mixtures thereof, by means of valve-controlled pipe 29. And at such time as the granular catalyst 9 becomes fouled with carbon or tarry matter, the conversion system may be shut down and the catalyst regenerated by contacting with air or steam at elevated temperatures, preferably not in excess of about 1000° F. Such revivifying agents may be introduced into chamber 8 through valve-controlled pipe 29 and may be withdrawn therefrom, together with the matter contaminating the catalyst, by means of valve-controlled pipe 30.

The reforming of gasoline or naphtha distillates for the improvement of antiknock quality may be carried out in a manner similar to that above described in connection with gas oil cracking. In the reforming operation, it is advantageous to employ somewhat higher temperatures, pressures, and rate of flow than are utilized in the conversion of high boiling oils such as gas oil. Depending upon the nature of the distillate to be reformed, the operating conditions may be varied in order to accomplish reforming with a controlled amount of cracking, or with substantially no cracking, as may be desired.

My process may be further illustrated by the following examples, which, however, are not intended as limiting the scope thereof.

The results given in table were obtained by cracking, in a single pass at atmospheric pressure, a petroleum gas oil under the conditions and with the catalysts substantially as set forth. The gas oil employed had an A. P. I. gravity of 31.4°, and a boiling range of 256° F. to 741° F. The borate-containing catalysts were prepared by impregnating granular  $\frac{1}{8}$  mesh  $\text{Al}_2\text{O}_3$  with aqueous solutions of sodium borate and drying the impregnated granules. The gasoline was cut to 400° F. end point.

| Gas oil<br>(water<br>content) | Catalyst                                                                                                              | Cracking<br>conditions |                            | Products                              |                           |
|-------------------------------|-----------------------------------------------------------------------------------------------------------------------|------------------------|----------------------------|---------------------------------------|---------------------------|
|                               |                                                                                                                       | Temp.<br>°F.           | Contact<br>time<br>seconds | Vol.<br>per cent<br>yield<br>gasoline | Weight<br>per cent<br>gas |
| 31 P. P. M.                   | Granular $\text{Al}_2\text{O}_3$ +5%<br>$\text{Na}_2\text{B}_4\text{O}_7$ (9.5%<br>water in $\text{Al}_2\text{O}_3$ ) | 1002                   | 6.4                        | 33.0                                  | 20.3                      |
| 37 P. P. M.                   | Granular $\text{Al}_2\text{O}_3$ +5%<br>$\text{Na}_2\text{B}_4\text{O}_7$ (9.5%<br>water in $\text{Al}_2\text{O}_3$ ) | 1002                   | 6.5                        | 32.4                                  | 20.5                      |
| 68 P. P. M.                   | Granular $\text{Al}_2\text{O}_3$ +5%<br>$\text{Na}_2\text{B}_4\text{O}_7$ (9.5%<br>water in $\text{Al}_2\text{O}_3$ ) | 1002                   | 6.0                        | 29.9                                  | 19.8                      |
| 37 P. P. M.                   | Granular $\text{Al}_2\text{O}_3$ +5%<br>$\text{Na}_2\text{B}_4\text{O}_7$ (6.1%<br>water in $\text{Al}_2\text{O}_3$ ) | 1008                   | 7.0                        | 31.4                                  | 19.7                      |
| 37 P. P. M.                   | Granular $\text{Al}_2\text{O}_3$ +5%<br>$\text{Na}_2\text{B}_4\text{O}_7$ (1.5%<br>water in $\text{Al}_2\text{O}_3$ ) | 1009                   | 6.8                        | 27.5                                  | 20.0                      |

From the above results it will be seen that the  $\text{Al}_2\text{O}_3\text{-Na}_2\text{B}_4\text{O}_7$  catalysts containing at least 5 per cent by weight of water, and gas oils containing not more than about 40 parts per million (P. P. M.) of water produce the higher yields of gasoline.

While I have described my invention particularly with respect to the conversion of higher boiling hydrocarbon oils into gasoline, my process is also applicable to the reforming of gasoline to increase the antiknock value thereof, as well as to the dehydrogenation of hydrocarbon gases to produce olefins and aromatics.

I claim:

1. A process for the conversion of a hydrocarbon stock into other hydrocarbons, which comprises contacting said stock with a catalyst comprising aluminum oxide and an alkali metal borate at a sufficiently elevated temperature to effect said conversion, said catalyst containing between 5 per cent and 15 per cent by weight of water.

2. A process for the conversion of a hydrocarbon stock containing not more than about 40 parts per million of water into other hydrocarbons, which comprises contacting said stock with a catalyst comprising aluminum oxide and an alkali metal borate at a sufficiently elevated temperature to effect said conversion.

3. A process for the conversion of a hydrocarbon stock containing not more than about 40 parts per million of water into other hydrocarbons, which comprises contacting said stock with a catalyst comprising aluminum oxide and an alkali metal borate at a sufficiently elevated temperature to effect said conversion, said catalyst containing between 5 per cent and 15 per cent by weight of water.

4. A process for the conversion of high boiling hydrocarbon oil into lower boiling hydrocarbons, which comprises subjecting a high boiling oil containing not more than about 40 parts per

million of water to cracking temperatures in the presence of a catalyst comprising aluminum oxide and an alkali metal borate, said catalyst containing between 5 per cent and 15 per cent by weight of water.

5. A process for the conversion of hydrocarbons containing not more than about 40 parts per million of water into gasoline having improved antiknock qualities, which comprises heating said hydrocarbons to a temperature within the range of from about 950° F. to about 1050° F., in the presence of a catalyst comprising aluminum oxide and an alkali metal borate, and containing between 5 per cent and 15 per cent by weight of water, and separating from the conversion products a fraction boiling within the gasoline boiling range.

6. A process for the conversion of hydrocarbons containing not more than about 40 parts per million of water into gasoline having improved antiknock qualities, which comprises heating said hydrocarbons to a temperature within the range of from about 950° F. to about 1050° F., under superatmospheric pressure, in the presence of a catalyst comprising aluminum oxide and an alkali metal borate, and containing between 5 per cent and 15 per cent by weight of water, and separating from the conversion products a fraction boiling within the gasoline boiling range.

7. A process for the conversion of hydrocarbons containing not more than about 40 parts per million of water into gasoline having improved antiknock qualities, which comprises heating said hydrocarbons to a temperature within the range of from about 950° F. to about 1050° F. under superatmospheric pressure, in the presence of a catalyst comprising aluminum oxide and sodium borate, and containing between 5 per cent and 15 per cent by weight of water, and separating from the conversion products a fraction boiling within the gasoline boiling range.

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