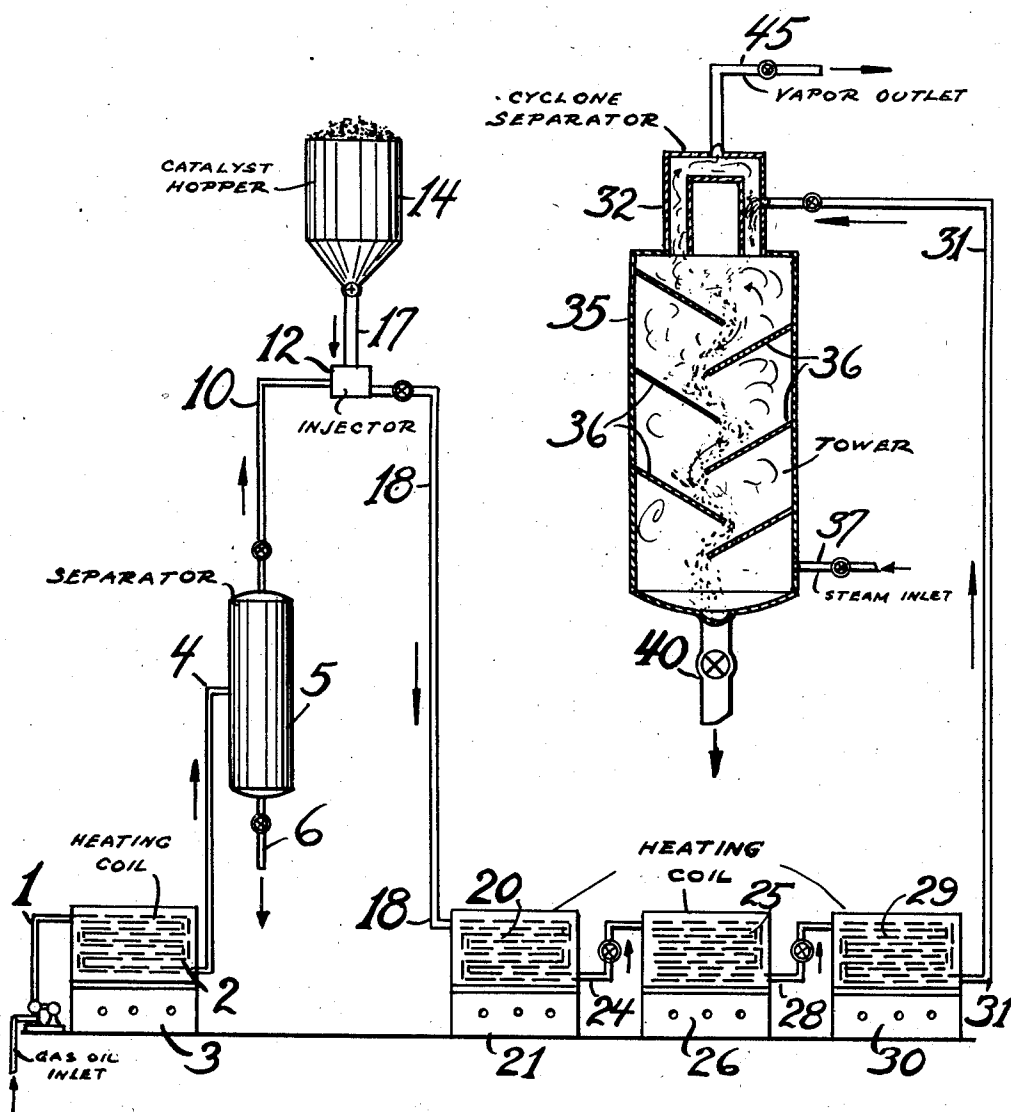


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J. S. WALTON
TREATING OILS TO PRODUCE ANTI-KNOCK GASOLINES
OR AROMATIC TYPE LIQUIDS
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Jesse S. Walton Inventor
By *R. Young* Attorney

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TREATING OILS TO PRODUCE ANTIKNOCK
GASOLINES OR AROMATIC TYPE LIQUIDSJesse S. Walton, Westfield, N. J., assignor to
Standard Oil Development Company, a corpora-
tion of Delaware

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The present invention relates to the art of treating hydrocarbon oils. More particularly, the present invention relates to the production of aromatic hydrocarbons from paraffinic hydrocarbons in a multi-step process fully disclosed herein.

It is a principal object of this invention to treat paraffinic hydrocarbons in the vapor phase to crack the said hydrocarbons to produce a mixture of saturated and unsaturated hydrocarbons, i. e., olefins and paraffins, to cause cyclization to take place to form cyclo-olefins and cyclo-paraffins, and thereafter to dehydrogenate the cyclo-olefins and cyclo-paraffins to form aromatic hydrocarbons.

It is a specific object of this invention to crack paraffinic hydrocarbons boiling within the kerosene and gas oil range by first vaporizing the oil, preferably in the presence of 1-2% water or steam where a catalyst is employed, and then subjecting the vapors to cracking conditions to form olefins and paraffins having from 6-8 carbon atoms, then treating the olefins and paraffins under such conditions as to form ring compounds and finally dehydrogenating said ring compounds to form aromatics.

Stated otherwise, it is an object of this invention to form from paraffinic hydrocarbons, aromatic hydrocarbons which may be blended with gasoline or motor fuel of relatively low octane number to increase materially, the octane rating of the motor fuel.

Other and further objects will appear from the ensuing description.

The single figure of the drawing represents diagrammatically, a combination of apparatus elements in which the present invention may be carried into effect.

Referring in detail to the drawing, a gas oil having an A. P. I. gravity of about 32°-46° and boiling within the range from 350° F.-850° F. is introduced into the system through line 1 and thence discharged into a heating coil 2 disposed in a furnace setting 3 where the said oil is vaporized, thence withdrawn through line 4 and discharged into a separation drum 5 where any unvaporized product may be withdrawn through line 6. The vapors, on the other hand, are withdrawn through line 10 and admixed in an injector 12 with a powdered catalyst, comprising clay or elements of the third and sixth group of the periodic system, including aluminum, chromium, and molybdenum or their oxides, or mixtures of these elements or their oxides, withdrawn from some source 14 and discharged into the injector

12 through line 17. The amount of catalyst admixed with the vapors may vary within rather wide limits. Good results are obtained by mixing from 2-5 lbs. of catalyst per cubic foot of oil vapors measured under the conditions of temperature and pressure prevailing in the injector 12. The suspension is withdrawn from the injector 12 through line 18 and then passed through a reaction zone which may be in the form of a tank, but preferably is in the form of a coil 20 disposed in the furnace setting 21 where more heat may be added to the suspension if desired. The temperature prevailing in coil 20 should preferably be within the range of from 800° F. to 975° F. and best results are obtained by maintaining a pressure of about 40 lbs. per square inch gauge in this coil. The hydrocarbons undergo cracking in the coil to form substantially equal amounts of olefinic and paraffinic hydrocarbons and under best conditions contain a large preponderance of hydrocarbons having from 6-8 carbon atoms. From coil 20 the total product is withdrawn and passed into a third coil 25 disposed in a furnace setting 26 where the temperature of the vapors is increased to a temperature within the range of from 900° F. to 1050° F., the pressure conditions being about the same as in coil 20. In this furnace the principal reaction is one in which the olefins formed in coil 20 are converted into cyclo-olefins or cyclo-paraffins, and the paraffins formed in coil 20 along with unreacted feed stock are further converted into olefins, cyclo-olefins or cyclo-paraffins. From coil 25, the total product is withdrawn through line 28 and discharged into a fourth coil 29 disposed in a furnace setting 30, where the hydrocarbons are subjected to severe conditions, such as temperatures in the range of from 925° F. to 1450° F., and under pressures such as the order of those prevailing in coils 20 and 25. In this coil the hydrocarbons, that is to say, the cyclo-paraffins and cyclo-olefins are dehydrogenated and converted to aromatic compounds and then the product is withdrawn through line 31 and discharged into cyclone separator 32 where the catalyst is removed from the vapors and passed by gravity into a baffle tower 35 having inclined baffles 36, as shown. Steam or some other gas, such as CO₂, nitrogen, flue gas, and the like, heated to approximately 825° F., more or less, may be introduced into the bottom of the tower through line 37 and permitted to flow upwardly against the downcoming catalyst to remove the volatile constituents. The catalyst is then withdrawn from the bottom of the tower and may be delivered to a

regeneration system (not shown) for revivification, according to known methods, for reuse in the process.

Meanwhile, the vapors are withdrawn overhead through line 45 and may then be passed to a fractionating tower to recover desired products, namely, aromatic hydrocarbons.

It will be understood, of course, that instead of using a powdered catalyst type of operation hereinbefore described, good results are obtained by using beds of stationary catalyst, that is to say, coils 20, 25 and 29 may be substituted by cylindrical chambers containing continuous beds or separated bodies of catalyst in granular or lump form supported on perforated trays. The vapors to be treated would be caused to flow through the bed or beds of catalyst.

To recapitulate, the present invention relates to improvements in the production of hydrocarbons having relatively high octane ratings and which are particularly suitable for blending with motor fuels of relatively low octane value to produce a fuel of satisfactory performance. The particular advantages of this invention are believed to lie in the capability of controlling closely, the type of reactions which occur in each of the various steps and by thus controlling the temperature, time and pressure under which the reactions are carried out, it is possible to minimize undesirable and co-occurring side reactions.

In order to give further information regarding my invention, the following specific example is set forth:

Example

A gas oil fraction, largely paraffinic and having an A. P. I. gravity of 43.5° and boiling within the range from 300° F. to 600° F. was treated according to the foregoing process whereupon 14% paraffinic hydrocarbons and 86% aromatic and naphthenic products were found present in the product. In this treat, the temperature in coil 28 was from 800° F. to 950° F., and the time the material was resident therein was about 15 seconds. In the operation carried out in coil 25 the temperature therein was within the range of from 900° F. to 1050° F., and the vapors were resident therein for about 10 seconds. In the operation carried out in coil 29, the temperature therein was within the range of from 925° F. to 1450° F., and the vapors were resident therein for about 8 seconds.

Many modifications of my invention within the spirit thereof will occur to those skilled in this art who have read the present disclosure.

The invention claimed is:

1. A process for the production of aromatic hydrocarbons from hydrocarbon oils predominantly non-aromatic in character, such as kerosene or gas oil which comprises vaporizing said oil in a vaporizing zone, mixing the oil vapors with a finely-divided conversion catalyst selected from the group consisting of clay, elements of the third and sixth group of the periodic system and oxides of elements of the third and sixth group of the periodic system, passing the mixture of oil vapors and finely divided catalyst under superatmospheric pressure through an initial conversion zone maintained at an active conversion temperature of from about 800° F. to 975° F., keeping said mixture within said conversion zone for a period sufficient to obtain a substantial conversion of the initial oil into paraffinic hydrocarbons of lower molecular weight and olefinic hydrocarbons, passing the reaction mixture from said initial conversion zone to a second conversion zone main-

tained at a materially higher temperature of up to 1050° F. than was maintained in said first conversion zone, keeping said reaction mixture under superatmospheric pressure in said second conversion zone for a period sufficient to obtain further formation of olefinic hydrocarbons and cyclization of olefinic hydrocarbons, passing the reaction mixture from said second conversion zone into a third conversion zone maintained at a materially higher temperature of up to 1450° F. than was maintained in said second conversion zone, keeping said reaction mixture under superatmospheric pressure in said third conversion zone for a period sufficient to cause conversion of the major portion of the hydrocarbons present into aromatic hydrocarbons and withdrawing conversion products and finely-divided catalyst from said third conversion zone.

2. A process for the production of aromatic hydrocarbons from hydrocarbon oils predominantly non-aromatic in character, such as kerosene or gas oil which comprises vaporizing said oil in a vaporizing zone, mixing the oil vapors with a finely-divided conversion catalyst selected from the group consisting of clay, elements of the third and sixth group of the periodic system, and oxides of elements of the third and sixth group of the periodic system, passing the mixture of oil vapors and finely divided catalyst under superatmospheric pressure through an initial conversion zone maintained at an active conversion temperature of from about 800° F. to 975° F., keeping said mixture within said conversion zone for a period sufficient to obtain a substantial conversion of the initial oil into paraffinic hydrocarbons of lower molecular weight and olefinic hydrocarbons, passing the reaction mixture from said initial conversion zone to a second conversion zone maintained at a materially higher temperature of up to 1050° F. than was maintained in said first conversion zone, keeping said reaction mixture under superatmospheric pressure in said second conversion zone for a period sufficient to obtain further formation of olefinic hydrocarbons and cyclization of olefinic hydrocarbons, passing the reaction mixture from said second conversion zone into a third conversion zone maintained at a materially higher temperature of up to 1450° F. than was maintained in said second conversion zone, keeping said reaction mixture under superatmospheric pressure in said third conversion zone for a period sufficient to cause conversion of the major portion of the hydrocarbons present into aromatic hydrocarbons, separating the finely divided catalyst from the conversion products and recovering a product rich in aromatic hydrocarbons.

3. The process as defined in claim 2 wherein the superatmospheric pressure maintained in the several conversion zones is about 40 lbs./sq. in.

4. A process for the production of aromatic hydrocarbons from a gas oil fraction having an A. P. I. gravity of 43.5° and boiling within the range of 300° F.-800° F. which comprises vaporizing said oil in a vaporizing zone, mixing the oil vapors with a finely divided conversion catalyst consisting of a mixture of chromium oxide and aluminum oxide, passing the mixture of oil vapors and finely divided catalyst through a first conversion zone maintained at an active conversion temperature of from about 800° F. to 975° F., keeping said mixture under a pressure of about 40 lbs./sq. in. in said conversion zone for about 15 seconds to convert a substantial proportion of the initial oil into paraffinic hydrocarbons of lower

molecular weight and olefinic hydrocarbons, passing the reaction mixture from said initial conversion zone into a second conversion zone maintained at a materially higher temperature of up to about 1050° F. than was maintained in said first conversion zone, keeping said reaction mixture under a pressure of about 40 lbs./sq. in. in said second conversion zone for about 10 seconds to effect formation of additional olefinic hydrocarbons and cyclization of olefinic hydrocarbons, passing the reaction mixture from said second conversion zone into a third conversion zone maintained at a materially higher temperature

of up to 1450° F. than was maintained in said second conversion zone, keeping said reaction mixture under a pressure of about 40 lbs./sq. in. in said third reaction zone for about 8 seconds to cause conversion of the major portion of the hydrocarbons present into aromatic hydrocarbons, withdrawing the reaction mixture from the third conversion zone, separating the finally divided catalyst from the reaction mixture and recovering from the conversion products a fraction rich in aromatic hydrocarbons.

JESSE S. WALTON.