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CATALYTICALLY PROCESSING HYDROCARBON OILS

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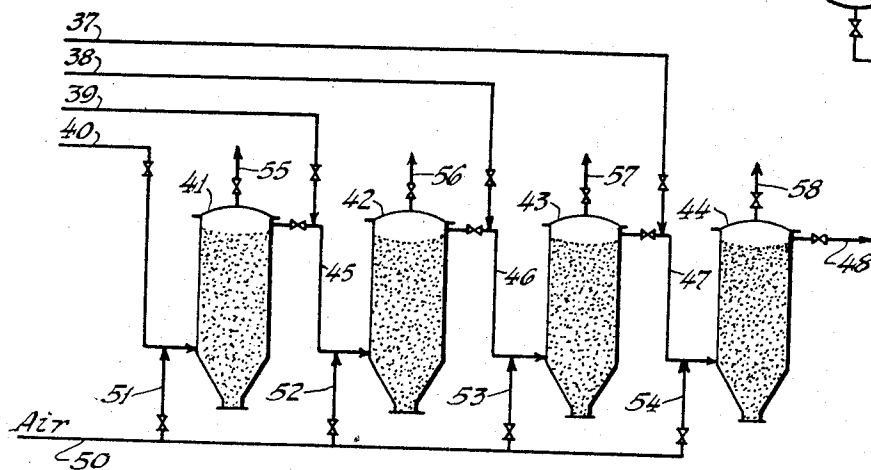
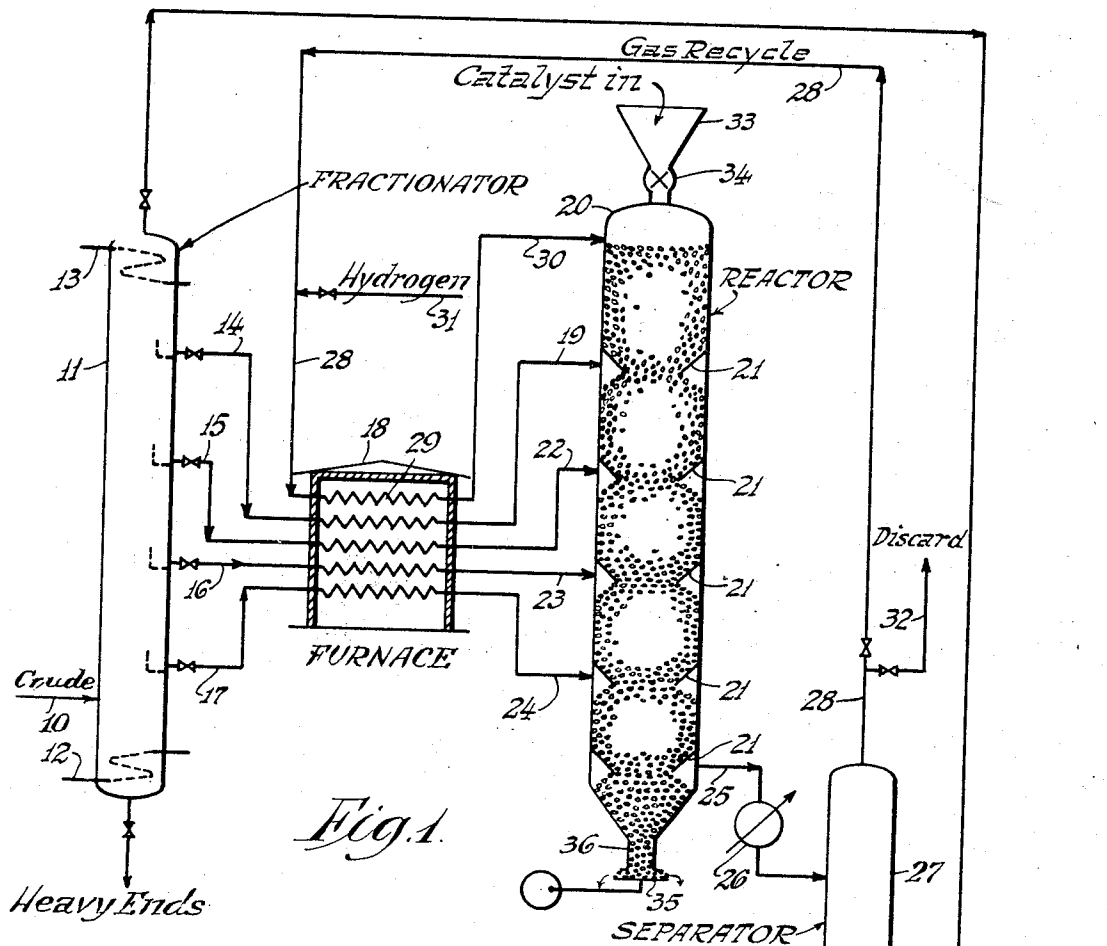


Fig. 2.

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## CATALYTICALLY PROCESSING HYDRO-CARBON OILS

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14 Claims. (Cl. 196—50)

This invention relates to a process of converting aliphatic, open-chain hydrocarbons and naphthenic hydrocarbons into aromatic hydrocarbons by a process of dehydrocyclization. Open-chain hydrocarbons having more than six carbon atoms are simultaneously dehydrogenated and formed into aromatic ring compounds and naphthenic hydrocarbons are further dehydrogenated in the process into aromatic hydrocarbons. An object of the invention is to convert the hydrocarbons of petroleum naphthas into aromatic motor fuels of high knock rating. Naphthas of various boiling ranges may be employed. For example, Pennsylvania, Mid-Continent or East Texas naphthas having a boiling range of about 250 to 450° F. are suitable, or a naphtha having a boiling range of 100 to 300° F. may likewise be employed. In general, it is desirable to employ naphthas having somewhat higher boiling ranges within the limits of 200 to 500° F.

A further object of the process is to convert low knock rating gasoline and naphthas into high knock rating aromatic type motor fuels by passing the vapors of the naphthas in contact with an aromatizing catalyst maintained at an average temperature of about 875 to 1075° F. and more specifically about 950 to 1000° F. The pressure is suitably maintained at about 30 to 450 pounds per square inch gauge and I prefer to employ pressures of about 150 to 250 pounds per square inch. It is also important to employ in the contacting step of my process, hydrogen or hydrogen-containing gas, the hydrogen being present in an amount ranging from about 0.4 to 8 mol ratio of hydrogen to hydrocarbon treated. In a typical case, I may employ a mol ratio of 2 to 3 mols of hydrogen per mol of hydrocarbon.

It is an important feature and object of my process to regulate the time of contact between the catalyst and the hydrocarbon in a specific manner, and a principal object of my invention is to subdivide the naphtha or gasoline undergoing treatment into two or more fractions of different boiling points and to subject the lighter fractions to a longer time of contact in the same operation with the other fractions. I have discovered that those hydrocarbons of higher molecular weight are advantageously subjected to a shorter time of contact than provided for the hydrocarbons of lower molecular weight. The heavier hydrocarbons are more readily converted into aromatic hydrocarbons than are the light hydrocarbons and with excessive treatment, they tend to produce carbon and foul the catalyst. My process is

designed to provide for a more uniform conversion, in a unitary process, of the open-chain hydrocarbons, both light and heavy, into aromatics.

The time of contact employed in my process may be expressed as the "time factor" which term is employed to mean the time in hours required for one volume of naphtha charged in the process to flow through one apparent volume of porous catalyst. The time factors which I prefer to employ lie within the range of 0.1 or 0.2 to 25, depending on the fraction of the oil under consideration, and a time factor of 1 to 2 hours per volume per volume is typical of the operating conditions employed with naphtha of intermediate boiling range.

My process is illustrated by means of drawing in which Figure 1 represents diagrammatically a scheme for continuously treating petroleum naphthas by means of a moving bed catalyst which is continuously removed for regeneration and renewal. Figure 2 represents an alternative arrangement of catalyst chambers in which the catalyst is maintained in fixed beds and is regenerated in situ. Referring to Figure 1 of the drawing, crude petroleum or a distillate from crude petroleum may be introduced by line 10 into fractionator 11 equipped with the usual bubble plates or equivalent fractionating means (not shown) together with a reboiling coil 12 and reflux coil 13. There may be two or more fractions, for example, four fractions, of naphthas as previously described generally boiling within the range of 150 to 500° F.

Progressively heavier naphtha fractions may be withdrawn by side draws 14, 15, 16 and 17 and these may be subjected to stripping by means not shown. These naphtha fractions are then vaporized in separate coils in furnace 18 and heated therein to a suitable conversion temperature, for example, 975° F. All fractions may be heated to the same temperature but there is often an advantage to heating the separate fractions to a different extent. Thus, the lightest fraction from 14 may be heated to 1025° F. and introduced by line 19 into the upper end of catalyst chamber 20, baffle 21 being provided to maintain a space within the catalyst chamber for introducing the hot vapors.

The next naphtha fraction from 15 may be heated in furnace 18 to a temperature of 1000° F. and then conducted by line 22 into catalyst chamber 20 at a later point. The next fraction from 16 may be heated to a still lower temperature, for example 975° F., and introduced by line 23 into chamber 20. The last fraction from 17

may be heated to about 950° F., and conducted by line 24 to chamber 20. By heating each succeeding heavier fraction to a lower temperature, I avoid the thermal decomposition to which the heavier hydrocarbons are most susceptible. At the same time the introduction of the hydrocarbon vapors into the catalyst chamber at intervals results in a lowering of the vapor velocity at the entering end of the chamber, thus providing a longer time of contact between the catalyst and the vapors of the lighter hydrocarbons. Positive control of the temperature throughout the elongated reaction chamber is also facilitated. As previously indicated, however, all fractions may be charged to the catalyst chamber at the same temperature, although it is usually desirable to employ progressively higher temperatures with the light fractions, in which case the endothermic heat of conversion will produce a gradually diminishing temperature progressively through the reaction chamber 20.

The hydrocarbon vapors in catalyst chamber 20 are conducted therefrom by line 25 leading to condenser 26 and separating drum 27 where fixed gases, including hydrogen, are withdrawn by line 28 and the liquid products are withdrawn by line 29. The fixed gases comprising principally hydrogen and methane with C<sub>2</sub> and C<sub>3</sub> hydrocarbons are conducted by line 28 to a heating coil 29 and thence by line 30 to the upper end of reaction chamber 20. The hydrogen present in the gases facilitates the catalytic reaction apparently by acting on intermediate hydrocarbon products on the surface of the catalyst and preventing their accumulation with consequent loss of catalytic activity. Under the conditions employed, as previously outlined, substantially no hydrogenation of the naphtha occurs, as evidenced by the fact that the products obtained from the process are highly aromatic. For example, the products may contain 40 to 60% or more of aromatic hydrocarbons, including benzene, toluene, and the xylenes, together with ethyl benzene and similar derivatives of benzene. When the amount of hydrogen in the recycle gases is insufficient to accomplish the foregoing purpose or the concentration becomes too low, I may add hydrogen through inlet 31. If desired, the hydrogen may be obtained by purifying gas withdrawn from 32. Excess gases accumulating in the system beyond the amount necessary for recycling may be continuously or intermittently discarded through drawoff line 32. In nearly all cases, there will be a net overall production of hydrogen.

The operation of catalyst chamber 20 is substantially as shown. The catalyst in the form of a granular free-flowing solid is introduced through hopper 33 connected by valve 34 to the upper end of chamber 20. Valve 34 may be operated continuously or intermittently and serves to regulate the rate of flow of catalyst into the chamber 20 while simultaneously preventing the escape of hydrocarbon vapors from said chamber. Chamber 20 is maintained substantially full of catalyst which is permitted to flow through the chamber continuously or intermittently by operating discharge valve 35. Valve 35 may be a vibrating or tipping plate beneath the catalyst discharge spout 36. As the catalyst flows downwardly through the elongated chamber 20, it is directed by baffles 21 to the center of the chamber and thence again to the walls of the chamber, thereby providing the desired amount of mixing of the catalyst and

maintaining a more uniformly vapor resistant bed. At the same time baffles 21 maintain annular spaces within the catalyst chamber into which the hydrocarbon vapors are introduced as hereinbefore described. As the catalyst proceeds downwardly through the chamber concurrently with the hydrocarbon vapors subjected to treating, it becomes increasingly deactivated, partly as the result of the deposition of carbonaceous matter thereon. The most nearly deactivated catalyst at the bottom of the reaction chamber is sufficiently active to effect conversion of the heavier hydrocarbon fractions introduced by line 24 whereas the freshest and most active catalyst at the top of chamber 20 is available for converting the lighter naphtha introduced therein. The ratio of hydrogen gas to hydrocarbon oil treated is also the maximum at the top of the chamber, thereby serving to protect the catalyst from too rapid deterioration at the point of maximum activity where deterioration by carbonaceous deposition is most rapid. The catalyst withdrawn from reaction chamber 20 may be regenerated externally by controlled oxidation and then returned to the reactor 20 via hopper 33.

I may also employ a fixed bed type catalyst in my process and an apparatus adapted to this purpose is partly illustrated in Figure 2 by lines 40, 39, 38, and 37, corresponding respectively to lines 19, 22, 23 and 24 in Figure 1. In the fixed bed the catalyst is preferably maintained in a series of interconnected chambers 41, 42, 43 and 44. The vapors entering through 37 pass through chamber 41 and thence by line 45 to chamber 42. After leaving chamber 42 the vapors are further conducted by line 46 to chamber 43. Thence the vapors are further conducted by line 47 to chamber 44. The converted vapors from chamber 44 are withdrawn by line 48 to gasoline recovery means not shown. Thus, the lightest naphtha fraction is introduced by line 40, the next heavier fraction by line 39, the next by line 38 and the heaviest by line 37. It will be observed, therefore, that the lightest fraction introduced by line 40 is subjected to the longest path through the catalyst and hence to the greatest catalyst treating time.

After the catalyst has become exhausted in the reaction chambers 41 to 44, the flow of hydrocarbon vapors is interrupted and the vapors are removed from the catalyst chambers by a current of steam or inert gas. While the catalyst in chambers 41 to 44 is still hot, it may be regenerated by introducing an oxygen-containing gas. For example, air or air-inert gas mixtures, such as air and nitrogen or air and flue gas may be introduced by header 50 leading to valved lines 51, 52, 53 and 54, which supply the oxidizing gas in the desired amount to the catalyst in the reaction chambers. The oxygen combines with and removes the carbon deposited on the catalyst as carbon dioxide and carbon monoxide which escape through lines 55, 56, 57 and 58. The rate of introduction of air and the oxygen concentration therein must be controlled during the regeneration operation to prevent excessive rise of temperature in the catalyst bed. A temperature of 1100° F. may be employed and it is preferred to use temperatures within the range of 1000 to 1100° F. to prevent deterioration of the catalyst. After the catalyst has been regenerated and allowed to cool to the desired reaction temperature, the process of hydrocarbon rearrangement is repeated.

The catalysts which I prefer to employ in my process are the oxides of metals in the left columns of groups IV, V and VI of the periodic system of elements. For example, I may employ oxides of chromium, molybdenum, tungsten, vanadium, titanium, cerium, thorium, etc. In general, I prefer to employ these oxides distributed on a supporting material such as certain of the natural aluminous earths, bauxite, aluminum oxide and particularly aluminum oxide gel prepared from the relatively pure aluminum hydroxide by methods which provide a support having an extensive surface. The oxides of chromium, etc., hereinabove mentioned, may be deposited on the alumina by various means, for example by impregnating the alumina with solutions of the nitrates, followed by thermal decomposition. Ammonium chromate, ammonium vanadate and similar ammonium salts may also be employed in solution as a means of applying the desired oxide, either singly or in combination, to the alumina support. The amount of catalyst oxide employed may suitably be about 1 to 10% and typically 5% is a satisfactory amount. The resulting catalyst may be pelleted or extruded to produce the desired porous form for use in the catalyst chambers. When excessive disintegration of the catalyst to powder occurs in use, it is desirable to remove it and separate the disintegrated material to prevent excessive back pressure in the catalyst bed. Although regeneration temperatures of 1000 to 1100° F. have been mentioned hereinabove, some oxide catalysts may be heated to considerably higher temperatures without material loss of catalytic activity. For example, cerium and thorium oxides on alumina may be regenerated at temperatures as high as 1400 to 1600° F. Intermediate temperatures of 1200 to 1300° F. are satisfactory for different catalysts, depending on their particular composition.

As an example of the results obtainable by my process, I may process a Mid-Continent heavy naphtha of 45 to 55 octane number C. F. R. motor method in the manner hereinabove described employing a molybdenum oxide on alumina catalyst at 1000° F., a pressure of 250 pounds per square inch, a time factor of 0.5 to 2 hours, and a hydrogen ratio of about 2 mols per mol of hydrocarbon treated, with the production of a highly aromatic gasoline of 83 octane number C. F. R. motor method. In general, the products obtained by my process possess knock ratings within the range of 75 to 85 octane number C. F. R. motor method and excellent motor fuels having knock ratings of about 80 C. F. R. motor method are readily obtained in good yield when processing paraffinic stocks such as Pennsylvania or Michigan naphthas which possess extremely low knock ratings before processing.

Having thus described my invention what I claim is:

1. The method of aromatizing petroleum naphtha which comprises fractionating said naphtha into lighter and heavier fractions, separately heating the fractions to a high conversion temperature above 875° F., contacting the lighter fractions with a solid aromatizing catalyst in an elongated conversion zone in the presence of hydrogen under non-hydrogenating conditions, commingling the vapors of said heavier fractions in said conversion zone with the vapors of said lighter fractions and with catalyst after said lighter fractions have undergone substantial conversion by the action of said catalyst, continuing

the conversion of said combined lighter fractions and heavier fractions, withdrawing the combined vapors of lighter and heavier naphtha fractions from said conversion zone, and condensing and separating liquid motor fuel products from hydrogenous gases associated therewith.

2. The method of aromatizing petroleum naphtha which comprises fractionating said naphtha into lighter and heavier fractions, separately heating the fractions to a high conversion temperature above 875° F., contacting the lighter fractions with a solid aromatizing catalyst in an elongated conversion zone in the presence of hydrogen under non-hydrogenating conditions, commingling the vapors of said heavier fractions in said conversion zone with the vapors of said lighter fractions and catalyst after said lighter fractions have undergone substantial conversion by the action of said catalyst, continuing the conversion of said combined lighter fractions and heavier fractions, meanwhile causing said catalyst to flow concurrently through said zone with vapors of said naphtha fractions while said fractions are undergoing conversion, withdrawing the combined vapors of lighter and heavier naphtha fractions from said conversion zone, and condensing and separating liquid motor fuel products from hydrogenous gases associated therewith.

3. In a process for converting open-chain hydrocarbons of petroleum naphtha into aromatic hydrocarbons useful for the production of motor fuel of high knock rating wherein vapors of petroleum naphtha are subjected to the action of a solid aromatizing catalyst at a temperature within the range of 875° to 1050° F., a pressure of about 30 to 450 pounds per square inch and in the presence of added hydrogen at a concentration of about 0.5 to 8 mols per mol of hydrocarbon treated, the improvement comprising initially fractionating said naphtha into lighter and heavier fractions before subjecting it to the action of said catalyst, disposing said catalyst in an extended path through which said hydrocarbon vapors are conducted, conducting said lighter fraction through the full extent of said vapor path, conducting said heavier fraction through a lesser extent of said vapor path wherein it is commingled with said light fraction, withdrawing the commingled vapors of the lighter and heavier fractions from said catalyst and separating a liquid aromatic motor fuel fraction therefrom.

4. The process of claim 3 wherein said catalyst is disposed in a series of separate beds through which said vapors are passed serially.

5. The process of claim 3 wherein said catalyst is disposed in an elongated upright zone and wherein it is caused to flow downwardly through said zone during said hydrocarbon conversion operation.

6. The process of claim 3 wherein said lighter naphtha fraction is heated to a different temperature than that to which said heavier naphtha fraction is heated.

7. The process of obtaining more uniform aromatization of the constituents of petroleum naphtha subjected to the action of a solid aromatizing catalyst at an elevated temperature above 875° F. in the presence of hydrogen, comprising separating lighter hydrocarbons from heavier hydrocarbon constituents of said naphtha, subjecting said lighter hydrocarbons to an initial aromatization with said catalyst, commingling the vapors of said heavier hydrocarbons with said lighter hydrocarbons following said pre-

liminary treatment, contacting said commingled hydrocarbons with additional catalyst, removing said hydrocarbons from said catalyst and recovering the desired aromatic hydrocarbon motor fuel therefrom.

8. In a process for converting an aliphatic hydrocarbon oil into high knock rating aromatic type gasoline wherein said oil is vaporized and the vapors are subjected, in the presence of added hydrogen, to the action of a porous solid dehydrogenating and cyclizing catalyst in a vertically elongated reaction zone into which fresh catalyst is continually added at the top and from which spent catalyst is continually removed at the bottom, at a conversion temperature within the range of 875 to 1050° F. and at a pressure of about 30 to 600 pounds per square inch, the improvement comprising fractionating said aliphatic hydrocarbon oil into at least two fractions, vaporizing and heating the vapors of said fractions to the desired temperature, introducing the lightest of said fractions into contact with the fresh catalyst in the upper part of said reaction zone and introducing successively heavier fractions at successively lower points in said reaction zone, withdrawing the combined vapors of said fractions from the bottom of said reaction zone and separating from them the desired aromatic gasoline.

9. The process of claim 8 wherein hydrogen is introduced into said reaction zone in contact with the fresh catalyst at a point above the point of introducing said lightest fraction.

10. The process of claim 8 wherein hydrogenous gases are separated from said reaction products and recycled to said reaction zone.

11. A method of catalytically aromatizing hydrocarbon naphtha which comprises initially contacting a light naphtha fraction with an aromatizing catalyst under aromatizing conditions to produce part of the desired aromatization, admixing a heavier naphtha fraction with the partially aromatized light fraction and subjecting the mixture to further contact with an aromatizing catalyst under aromatizing conditions to complete the desired aromatization of said light fraction and simultaneously to aromatize said heavier fraction.

12. A method of obtaining more uniform cata-

lytic aromatization of the constituents of a hydrocarbon naphtha which comprises separating relatively light hydrocarbon constituents of a naphtha from the remainder and catalytically

5 aromatizing them, recombining remaining constituents with said lighter constituents after the latter have undergone some aromatization and catalytically aromatizing said remaining constituents while the desired aromatization of said  
10 lighter constituents is being completed.

13. In a method of catalytically aromatizing hydrocarbon naphtha in the vapor phase at a temperature between about 875° and 1050° F. under  
15 superatmospheric pressure and in the presence of added hydrogen, the improvement which comprises causing a vaporized light naphtha fraction to flow through an elongated confined zone in contact with an aromatizing catalyst maintained  
20 under said aromatizing conditions to effect aromatization of said light fraction, introducing a vaporized heavier naphtha fraction into said zone at a point intermediate the path of said light fraction therethrough, and causing said heavier  
25 naphtha vapors to flow concurrently and in admixture with said light vapors while contacting said catalyst to promote the aromatization of both of said fractions.

14. In a method of catalytically aromatizing hydrocarbon naphtha in the vapor phase at a  
30 temperature between about 875° and 1050° F. under superatmospheric pressure and in the presence of added hydrogen, the improvement which comprises causing a vaporized light naphtha fraction to flow through an elongated confined  
35 zone in contact with an aromatizing catalyst maintained under said aromatizing conditions to effect aromatization of said light fraction, causing said aromatizing catalyst to move through said zone concurrently with said light fraction,  
40 introducing a vaporized heavier naphtha fraction into said zone at a point intermediate the path of said light fraction therethrough, and causing said heavier naphtha vapors to flow concurrently and in admixture with said light vapors while  
45 contacting said catalyst to promote the aromatization of both of said fractions.

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