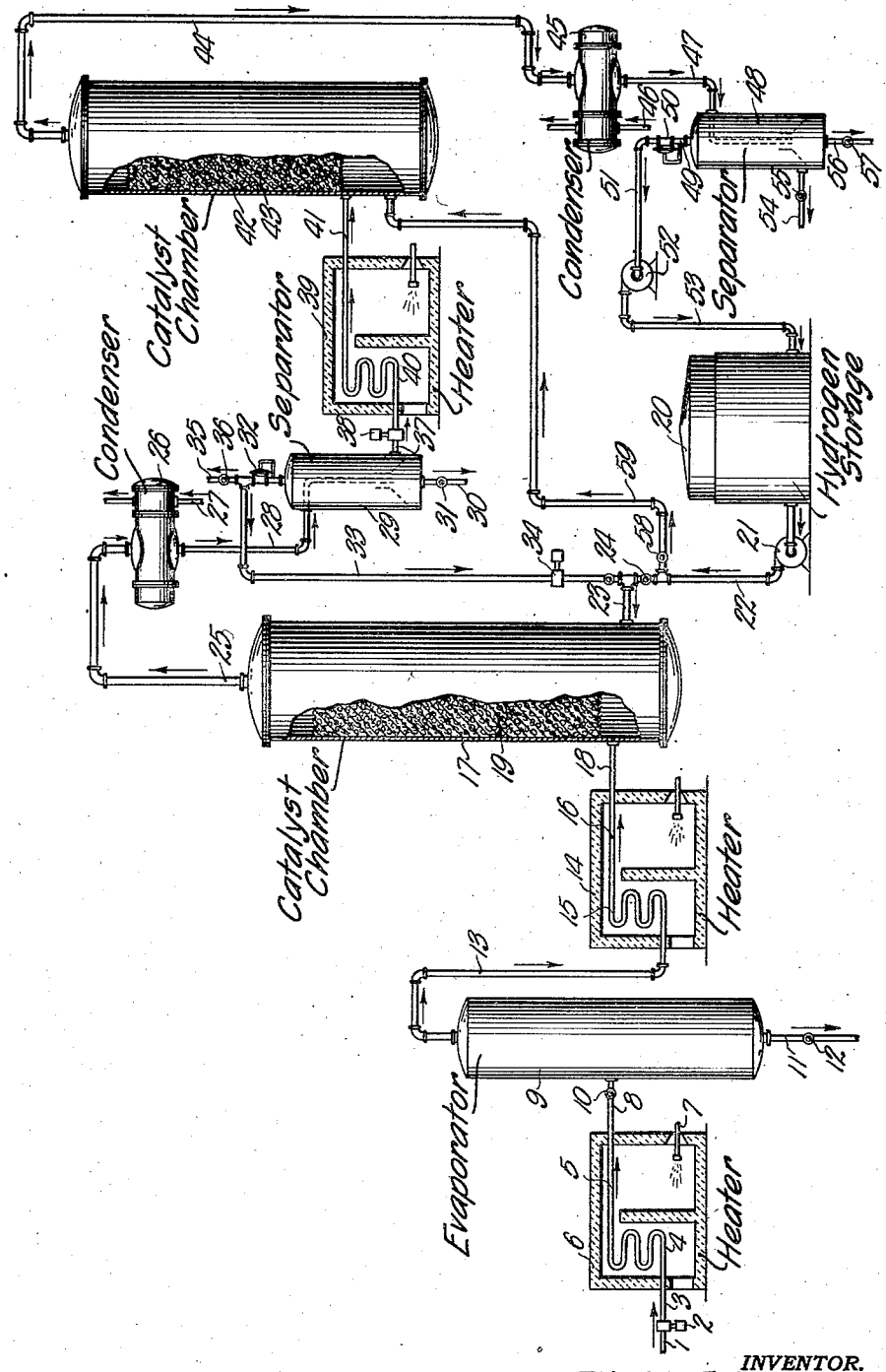
May 30, 1944. E. T. LAYNG 2,349,826

METHOD FOR THE AROMATIZATION OF ALIPHATIC HYDROCARBONS

Filed Oct. 24, 1938



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Patented May 30, 1944

2,349,826

UNITED STATES PATENT OFFICE

2,349,826

METHOD FOR THE AROMATIZATION OF ALIPHATIC HYDROCARBONS

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Application October 24, 1938, Serial No. 236,627

1 Claim. (Cl. 260—673.5)

My invention relates to a method for the aromatization of aliphatic hydrocarbons and more particularly to a process for the catalytic aromatization of aliphatic hydrocarbons in a two stage process.

Currently, the aromatization of hydrocarbons is carried on as a single operation in the presence of a catalyst. The operating conditions vary, depending upon the particular stock being processed. In general, it has been found that temperatures in the vicinity of from 850° F. to 1000° F. and pressures varying from atmospheric to 100 pounds per square inch are satisfactory. Then, too, it is recognized that the degree of conversion is influenced by the contact time. That is, the ratio of the hydrocarbon oil being charged to the volume of catalyst in the reaction chamber exercises considerable influence upon the reaction. The catalysts suitable for the process are known as "aromatizing" or "dehydrogenating-cyclizing" catalysts, and as suitable catalysts, oxides of metals of the third and sixth groups of the periodic table, sulphides of metals of the sixth group of the periodic table, or mixtures of such sulphides and oxides have been used.

Aromatization, as now practiced at elevated temperatures in the presence of a catalyst, is accompanied by several side reactions. One of these side reactions is simple dehydrogenation of paraffins. This results in the formation of olefinic hydrocarbons. The olefinic hydrocarbons formed polymerize, forming higher boiling hydrocarbons which become deposited upon the catalyst rendering it inactive. Another reaction is pyrolytic conversion of the hydrocarbons into lower boiling hydrocarbons commonly referred to as "cracking." Both these reactions are undesirable in an aromatization process. Dehydrogenation and cracking ultimately result in the deposition of carbonaceous materials upon the surface of the catalyst. The deposits of carbonaceous material reduce the activity of the catalyst and ultimately render it inactive.

If the hydrocarbons charged to a one stage aromatization process comprise principally naphthenic stocks, the production of carbon and carbonaceous material is negligible when compared with that produced when the hydrocarbons being charged are predominantly of a saturated or paraffinic nature. For example, I have found that the dehydrogenation or aromatization of a typical naphthene like methyl cyclohexane can be carried out with great efficiency over a long period of time without the formation of deleterious deposits of carbon and carbonaceous materials. On the other hand, the aromatization or dehydrogenation of a typical paraffin hydrocarbon such as normal heptane can be conducted efficiently only for a relatively short period of time.

It has been attempted to overcome the difficulty of carbon deposits with resultant loss in catalyst activity by varying the operating conditions employed. For example, it is obvious that the use of lower temperatures will decrease the rate of carbon formation. Similarly, the use of lower pressures and higher throughputs will achieve the same end. Unforunately, however, all of these expedients lower the yield of the desired aromatic hydrocarbons, since it has been shown that the proportion of aromatic hydrocarbons in the products from such a reaction is increased within rather broad limits by raising the temperature and/or lowering the space velocity. Consequently, it has been necessary to strike a balance in the operating conditions where an optimum ratio of aromatic hydrocarbons and carbonaceous deposits is obtained. Such an arrangement naturally limits the yield per pass to a comparatively low level, since high material loss through carbon formation is not feasible.

Another means of varying the space velocity and therefore the extent to which the reactions occur is to add hydrogen gas to the hydrocarbon feed stock. This has been found to give good results, although as will be apparent later the prior art is by no means the most efficient one. It will also be shown that by my invention the hydrogen is utilized in a most logical and efficient manner so that a high yield of aromatic hydrocarbon is obtainable from a wide variety of charging stocks with a minimum loss through formation of carbonaceous materials.

One object of my invention is to provide a method for the catalytic aromatization of hydrocarbons in which the formation and deposit of carbonaceous material is substantially minimized.

Another object of my invention is to provide a method for the aromatization of hydrocarbons in which a static body of catalyst may be employed with efficiency.

Other and further objects of my invention will appear from the following description.

The accompanying drawing which forms part of the instant specification and is to be read in conjunction therewith, is a diagrammatic view of one form of apparatus capable of carrying out the process of my invention.

In general, my invention contemplates a meth-

od in which the aromatization is carried out in two zones. The catalyst employed may be the same in both zones. If desired, one catalyst may be employed in one zone and a different catalyst in the other zone. In the first zone, I employ conditions of moderate pressure as for example in the vicinity of 100 pounds per square inch and carry on the aromatization reaction in the presence of an excess of hydrogen. These operating conditions direct the reaction so that predominantly naphthenic hydrocarbons are formed. In the second zone, I employ a lower pressure and a lower hydrogen concentration. Lower pressures and lower hydrogen concentrations in the second zone are adapted to convert naphthenic hydrocarbons produced in the first zone into aromatic hydrocarbons. The carrying on of aromatization according to my method, minimizes the formation of undesirable products and prolongs the life of the catalyst.

In order that a more complete understanding of the nature of my method may be gained, let us review the reactions which ordinarily occur under the usual conditions for dehydrogenation. They are as follows:

(1) Paraffin=olefin+H_2

(2) Paraffin=naphthene+H_2

(3) Olefin=naphthene

(4) Naphthene=aromatic+$3H_2$

All of the foregoing are equilibrium reactions and are thermodynamically favorable to varying degrees under the conditions of my process. By way of example and not by way of limitation, if, in reaction (1) normal heptane is the paraffin hydrocarbon and heptene is the olefin formed, calculations will show that, at equilibrium, 26 percent of the heptane is converted according to the reaction at a process temperature of 1000° F. and a process pressure of one atmosphere. Reaction (2) is much more favorable in a forward direction. Calculations show that approximately 92 percent of the heptane is converted under the same equilibrium conditions. Similarly, in reaction (4), calculations show that essentially all of the naphthene is converted into the corresponding aromatic. The calculations were checked in the laboratory, using heptane, heptene, methyl cyclohexane and toluene.

The same type of calculations may be made for reaction (3), but as will hereinafter be shown more fully, these need not be considered in the instant process.

On the basis of equilibrium considerations, it will be readily apparent that the use of either higher pressures or an excess of hydrogen will force reactions (1), (2) and (4) in the reverse direction while reaction (3) will be unaffected. For example, a pressure of 100 pounds per square inch gauge decreases the conversion of heptane in reaction (1) from 26 percent to 9 percent. In other words, an increase in pressure from atmospheric to 100 pounds per square inch decreases the formation of olefinic hydrocarbons about 58 percent. Similarly, the addition of 4 mols of hydrogen for each mol of heptane reduces the conversion of heptane from 26 percent to 7 percent or a reduction of 73 percent. The application of an increased pressure of 100 pounds, together with the addition of 4 mols of hydrogen reduces the conversion of heptane from 26 percent to one percent or a reduction of 96 percent. It will be readily apparent that for practical purposes the use of an increased pressure and an excess of hydrogen practically prevents the operation of reaction (1).

In reaction (2), the application of an increased pressure of 100 pounds, using heptane by way of example, reduces the conversion of heptane from 92 percent to 66 percent or a reduction of about 28 percent. The addition of 4 mols of hydrogen reduces the conversion of heptane in reaction (2) from 92 percent to 87 percent or a reduction of about 5½ percent. The simultaneous use of increased pressure and added hydrogen reduced the conversion of heptane only to 49 percent.

Reaction (4) is so favorable thermodynamically under all conditions that the conversion in all cases approaches 100 percent. It will be seen that the presence of 4 mols of hydrogen and 100 pounds pressure renders reaction (1) virtually impossible. These conditions, too, reduce reaction (3) since substantially no olefins will be produced in the reactions, under conditions of elevated pressure and an excess of hydrogen. Therefore, any olefins which may be present in the charge will be converted into paraffins by the reverse of action (1), or under special circumstances may be converted to naphthenes via reaction (3).

It follows that, if the process is so conducted, that is, in the presence of an excess of hydrogen and under elevated pressure, the formation of carbonaceous deposits will practically cease due to the fact that at no time will there be an appreciable concentration of olefins. It is believed that it is the polymerization of olefins which produces the major proportion of carbonaceous material in the process as previously conducted.

Despite the fact that reaction (1) and possibly reaction (3) practically cease under the conditions of increased pressure and added hydrogen, reaction (2) still proceeds to the extent of about 50 percent. In other words, the production of the naphthene continues unaccompanied by undesirable side reactions. This formation of naphthenes is represented in the first zone of the process. The naphthenes are then converted to aromatics chiefly in the second zone of the process, though of course some conversion of naphthenes to aromatics will take place in the first zone.

It will be readily apparent to those skilled in the art that the process conditions will vary greatly depending upon the character of the charging stock. In general, the use of elevated pressures and added hydrogen in the first zone and the employment of pressures in the neighborhood of atmospheric without additional hydrogen in the second zone, is characteristic. It will be understood, of course, that hydrogen may be added in the second zone of the process if the character of the stock makes this desirable.

The above examples have been given by way of illustration and not by way of limitation. It should be borne in mind that my process is in no sense a hydrogenation process and should not be confused with these. In hydrogenation, the necessary hydrogen is obtained from an extraneous source. In the instant case, the hydrogen produced in the second stage is more than adequate to supply the needs of the first stage. The process is merely one of controlling the flow of gas produced in the second zone so that all or part of it can be recycled through the first zone with a fresh charge, the excess of hydrogen acting as a reaction control.

More particularly referring now to the drawing, the hydrocarbons to be aromatized are charged from any suitable source through pipe 1, and pumped by pump 2 through pipe 3 through

convection heated coil 4 and radiantly heated tubes 5 of the heater 6 which is fired by any suitable burner 7. The hydrocarbons are heated to vaporizing temperature and pass from the heater 6 through transfer line 8 into an evaporator 9, past valve 10. In the evaporator 9 the heated hydrocarbons are flashed into vapors and unvaporized oil. The unvaporized oil is withdrawn from the process through pipe 11 controlled by valve 12. The vapors pass through pipe 13, through a heater 14 and are heated in convection heated coil 15 and radiantly heated tubes 16 to the desired temperature which may be between 850° F. and 1000° F. The superheated vapors enter a catalyst chamber 17 through a transfer pipe 18. The catalyst chamber contains a suitable catalyst 19 which may be an oxide of a metal of the third or sixth group or a sulphide of a metal of the sixth group, of mixtures thereof. Hydrogen from hydrogen storage tank 20 is pumped by pump 21 through pipe 22 and passed through pipe 23 into the bottom of the catalyst chamber, it being understood that valve 24 is open. The catalyst chamber is maintained under a pressure of about 100 pounds per square inch. It is understood, of course, that the pressure may be varied within suitable limits, depending upon the charging stock being employed. Similarly, the quantity of hydrogen being passed into the catalyst chamber may be varied.

In the catalyst chamber 17 the paraffin and olefin hydrocarbons will be converted chiefly into naphthenic hydrocarbons, due to the use of increased pressure and added hydrogen. The products of the reaction are withdrawn from the chamber 17 through pipe 25 and passed through a condenser 26 which is supplied with a cooling medium through pipe 27. The condensate and uncondensed gases are withdrawn from the condenser through pipe 28 and pass into a separator 29. If desired, a portion of the liquid products may be withdrawn through pipe 30 controlled by a valve 31 and recycled. A back pressure controlled valve 32 maintains the desired elevated pressure upon the first catalyst zone. The gases withdrawn from the separator will be preponderantly hydrogen. These may be passed through pipe 33 and pumped by pump 34 through pipe 23 back to the catalyst chamber to supply the excess of hydrogen desired. A portion of the gases may be vented through pipe 35 by opening valve 36. The hydrocarbons formed, which will be principally naphthenic hydrocarbons, are withdrawn from the separator 29 through pipe 37 and pumped by pump 38 through the heating coil 40 of heater 39. The heated hydrocarbons are withdrawn from heater 39 through transfer pipe 41 and passed into a second catalyst chamber 42 containing a suitable catalyst 43. The temperature existing in the second catalyst zone may be between 850° F. and 1000° F. The pressure existing in the second catalyst zone is considerably lower and may be as low as atmospheric. In the second reaction zone, the naphthenes will be converted into aromatic hydrocarbons accompanied by the evolution of hydrogen. The reaction products are withdrawn from the catalyst chamber 42 through pipe 44 and passed through a condenser 45 which is supplied with a cooling medium through pipe 46. The condensate and incondensable gases leave the condenser through pipe 47 and pass into a separator 48. The incondensable gases which are chiefly hydrogen, are withdrawn from the separator through pipe 49 and past back pressure controlled valve 50 into pipe 51 from which they are pumped by pump 52 through pipe 53 into the hydrogen storage tank 20. Back pressure controlled valve 58 determines the pressure which exists in the second catalyst zone 42. The desired aromatic hydrocarbons are withdrawn from the separator through pipe 54, controlled by valve 55. If desired, a portion of the hydrocarbons may be withdrawn from the separator through pipe 56, controlled by valve 57 and recycled either to the second heater 14 or the third heater 39. If the conditions are such that an excess of hydrogen is desired in the second catalyst zone, valve 58 may be opened and a portion of the hydrogen from pipe 22 may pass through pipe 59 along with the heated hydrocarbons entering the second catalyst zone through pipe 41.

It will be observed that I have accomplished the objects of my invention. I have provided an aromatization process in which a static body of catalyst may be employed and long runs be obtained by minimizing the deposition of carbonaceous materials. Not only are long runs obtained, but the avoidance of the formation of carbonaceous materials produces higher yields of the desired aromatics. The employment of such a two stage process will also lengthen the life and permit the reduction in rate of flow of a moving catalyst when used.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of the claims. It is obvious that various changes may be made in the operating conditions within the scope of the claims without departing from the spirit of the invention. It is therefore understood that the invention is not limited to the specific details shown and described.

Having thus described my invention, I claim:

In a method of producing aromatic hydrocarbons and hydrogen by contacting aliphatic hydrocarbons of six or more carbon atoms in a straight chain at an elevated temperature within the range of about 850° F. to 1000° F. with a dehydrogenating-cyclizing catalyst comprising a compound selected from the oxides and sulfides of the metals included within the sixth group of the periodic table, the improvement which consists in effecting such contact in an initial stage by passing said hydrocarbons in contact with the catalyst at superatmospheric pressures of the order of about 100 lbs. and in the presence of added hydrogen in amount such that the aliphatic compounds are converted largely to cyclic compounds with minimized formation of olefinic compounds and consequent deposition of carbonaceous material on the catalyst, cooling and separating the reaction products into normally gaseous products and a condensate containing the liquid conversion products, thereafter vaporizing and contacting said condensate in a second stage with the catalyst at a pressure and with a quantity of added hydrogen substantially lower with respect to the pressure and quantity of added hydrogen than that utilized in the initial stage, and recycling hydrogen produced in the process to supply said added hydrogen.

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