

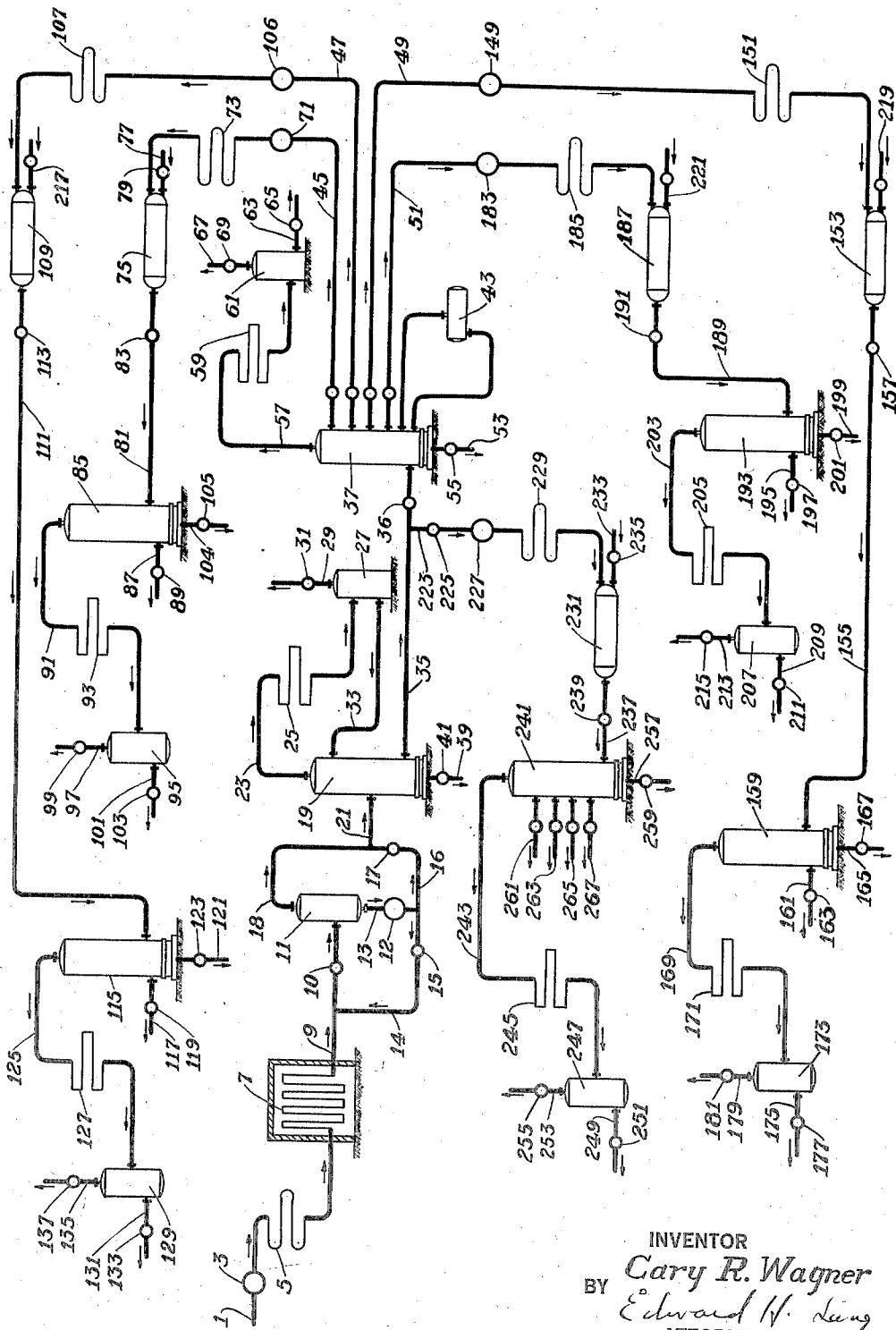
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PREPARATION AND SEPARATION OF AROMATIC HYDROCARBONS

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PREPARATION AND SEPARATION OF
AROMATIC HYDROCARBONSCary R. Wagner, Chicago, Ill., assignor to The
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This invention relates to a method of preparing and stabilizing aromatic hydrocarbons and is more particularly concerned with the preparation and isolation of substantially pure aromatic hydrocarbons.

It is known that aromatic hydrocarbons may be prepared by conversion of hydrocarbon gases. In my application Serial No. 85,711, filed June 17, 1936, there is disclosed a method for producing hydrocarbons by subjecting olefin containing gases to temperatures of approximately 1100° to 1200° F. under pressures up to approximately 250 pounds per square inch for a period of time ranging from approximately 5 to 30 seconds. When olefinic gases are treated in accordance with the conditions of temperature, pressure and time recited in the aforesaid application, a liquid product is obtained which is a mixture of benzene, toluene, xylene, and heavier aromatic hydrocarbons in which toluene and xylene are present in considerable quantities, together with olefinic and diolefinic hydrocarbons, with possible traces of paraffinic and saturated or partly saturated cyclic hydrocarbons. The liquid may contain from 50 to 80% of aromatics, the major portion of the remaining being diolefins.

The unsaturated, particularly the diolefinic, hydrocarbons present in the liquid mixture, have boiling points so close to those of the several aromatic hydrocarbons present in the liquid that it is impossible to separate them from the aromatic hydrocarbons by fractional distillation or condensation. For example, 2,4-hexadiene boils between 80° and 82° C. and therefore cannot be separated from benzene which boils at 80.1° C. The same applies to 3-methyl-2,4-pentadiene which boils at 76° to 79° C.; 3-methyl-1, 3-pentadiene which boils at 78° to 83° C.; and 1,2-hexadiene which boils at 78° C. Likewise, such compounds as 2,4-heptadiene which boils at 107° C. and 3-methyl-2, 4-hexadiene which boils at 107° to 108° C. are so close to toluene which boils at 110.8° C. that satisfactory separation cannot be obtained by fractionation.

Moreover, the diolefins are unstable and detract from the value of the aromatic hydrocarbons whether used in admixture or separately. It is therefore necessary to separate the diolefins without materially affecting the aromatic constituents present in the mixture.

One of the objects of my invention is to eliminate the olefinic and diolefinic hydrocarbons without changing the aromatic constituents present in the condensate or liquid mixture.

Another object of my invention is to separate

substantially pure aromatic hydrocarbons such as benzene, toluene, xylene, and naphthalene from the liquid mixture.

Other objects of my invention will be apparent from the ensuing description and accompanying drawing of which the single figure is a diagrammatic elevational view of apparatus suitable for carrying out the process.

I have discovered that the undesirable diolefinic hydrocarbons present in the polymer condensate can be converted to saturated compounds by proper hydrogenation so that the resulting product may be used as a motor fuel of high octane value, or the condensate may be fractionated into its various components. The hydrogenation may be carried out as part of a unitary gas conversion and hydrogenation process, or may be carried out separately. In either case, the aromatic condensate, or fractions thereof, resulting from the conversion of the gases are treated with hydrogen at a temperature of about 350° to 800° F. and at pressures up to 100 pounds per square inch, in the presence of a mild hydrogenation catalyst such as nickel or nickel oxide. Under these conditions selective hydrogenation of the olefinic and diolefinic hydrocarbons can be obtained if the quantity of hydrogen used is properly regulated. The amount of hydrogen to be used can be determined by first determining the olefinic and diolefinic content of the polymer condensate and then treating the condensate with hydrogen in slight excess (not substantially above 25% by volume) of the quantity necessary to saturate the olefins and diolefins that are present. The hydrogenation step may be performed either in batch or in continuous manner and either in vapor or liquid phase, depending upon the pressure and temperature conditions used. Preferably, however, the condensate is first heated to a temperature sufficient for reaction and then charged in a stream through the catalyst chamber together with a regulated quantity of hydrogen.

As previously stated, under the conditions of hydrogenation above specified, the aromatics remain unchanged but the olefins and diolefins are converted to saturated compounds which boil at temperatures sufficiently different from the boiling points of the aromatic hydrocarbons to enable fractionation of the hydrogenated products into substantially pure benzene, toluene, xylene, naphthalene, etc. to be effected. By saturating 2,4-hexadiene its boiling point is changed from 80°-82° C. to 69° C.; likewise 3-methyl-2,4-pentadiene is changed from 76°-79° C. to 60° C.; 2,4-heptadiene is changed from 107°

C. to 98.4° C.; 3-methyl-2,4-hexadiene is changed from 107°-108° C. to 92° C.; 3-methyl-1,3-pentadiene is changed from 78°-83° C. to 63.2° C.; 1,2-hexadiene is changed from 78° C. to 69° C.

- 5 The character of aromatic polymer distillate will, of course, vary with the temperature and other conditions under which it is prepared. Although temperatures of 1100° to 1200° F., and preferably 1125° to 1150° F. and pressures up to 10 250 pounds per square inch with a reaction period of 5 to 30 seconds are prepared for obtaining large yields of toluene and xylene, it is to be understood that the temperature and pressure as well as time may vary from those given if 15 large yields of toluene and xylene are not desired.

- In order to avoid the likelihood that, upon hydrogenation certain of the diolefins or olefins having boiling points close to a higher boiling aromatic compound, may be converted into saturated compounds having boiling points fairly close to a lower boiling aromatic hydrocarbon, the polymer condensate should preferably first be fractionated into several cuts containing benzene, toluene, xylene, naphthalene, etc., respectively, together with those olefins and diolefins 20 which boil close to the particular aromatics contained in the cut. Each fraction may then be separately subjected to hydrogenation conditions as above set forth, and after hydrogenation, subjected to individual fractionation to separate 30 the saturated olefins and diolefins from the single aromatic hydrocarbon present in the cut. In this manner aromatic hydrocarbons of exceptional purity can be obtained which are valuable 35 in the arts.

- As previously stated, however, if it is not essential to recover pure aromatic hydrocarbons, the total polymer condensate may be subjected to selective hydrogenation to convert the diolefins and to some extent the olefins to saturated 40 hydrocarbons so that the resulting product will be rendered gum and color stable and free from objectionable odor, without detracting from its anti-knock characteristics. The product so 45 treated may be suitably fractionated to obtain a premium motor fuel having an octane rating of approximately 80 to 100.

- In carrying out the process, hydrocarbon gas having an olefin content of approximately 50 40-60% is charged through line 1 by means of compressor 3 into heating coil 5 and reaction zone 7. The gases are heated to reaction temperature in the heating coil, which may be approximately 1100° to 1200° F. under a pressure 55 ranging from atmospheric to approximately 250 pounds per square inch, and then charged under these conditions through the reaction zone, which may be a coil or reaction chamber, in order to give the gas sufficient time to polymerize. From 60 the reaction zone the reaction products pass through outlet 9 controlled by valve 10 in separator 11 and are chilled by a stream of liquid which is pumped from the bottom of separator 11 by means of pump 12 through line 13 and 65 line 14 controlled by valve 15, to the outlet line 9. Pressure on the reaction products may be released at valve 10 below that in the reaction zone. The portion of the liquid which is not used as chilling stock is pumped through line 16 controlled by valve 17 and joins the gas coming off 70 the top of separator 11 through line 18. The mixture of liquid and gas enters the fractionating tower 19 through line 21.

- The incondensable constituents in the mixture 75 pass overhead from the fractionating tower 19

through line 23 and condenser 25 to accumulator and gas separator 27. The uncondensed constituents leave the top of the separator 27 through line 29 controlled by valve 31, and may be withdrawn from the system. The condensed 5 constituents are recycled from the separator 27 through line 33 to the top of the fractionator 19 to act as reflux. The unvaporized products may be withdrawn from the lower part of the fractionator 19 through line 35 controlled by valve 10 36 and passed into a second fractionating tower 37. Any tarry material that may collect in the fractionator 19 may be withdrawn from the bottom thereof through the line 39, controlled by valve 41. 15

The liquid in the fractionating tower 37 may be heated by reboiler 43 to a temperature sufficient to vaporize benzene, toluene, xylene, naphthalene and other hydrocarbons boiling within the range of these constituents. The 20 benzene, toluene, xylene and naphthalene are withdrawn as side cuts from the fractionating tower 37 through valve-controlled lines 45, 47, 49, and 51 respectively. Any material boiling above naphthalene may be withdrawn from the 25 fractionating tower 37 through the line 53 controlled by valve 55. Those constituents boiling below benzene may be withdrawn from the top of the fractionating tower 37, through line 57, and passed through condenser 59 into accumulator 61, from which the liquids may be withdrawn through lines 63 controlled by valve 65, and any gaseous material may be withdrawn through line 67 controlled by valve 69. If desired, the pressure on the fractionating system may be 35 maintained at super-atmospheric pressure sufficiently high to enable the several cuts to be charged to the subsequent hydrogenation steps without the necessity of pumping. In that case the pumps may be dispensed with or by-pass 40 lines provided around the pumps.

The benzene cut which may have a boiling range of from approximately 165° F. to approximately 181° F., may be charged through line 45 by means of pump 71 to heating coil 73 wherein 45 it is heated to a temperature of approximately 350° to 800° F. and then fed into the reactor 75 which contains the hydrogenating catalyst. Hydrogen, or a gas rich in hydrogen, is fed into the reactor through line 77 controlled by valve 79. 50 The products leave the reactor 75 through line 81 controlled by valve 83 and pass into a fractionating tower 85, wherein the benzene is separated from contaminating constituents. The benzene may be withdrawn as a side stream 55 through line 87 controlled by valve 89; overhead products may be withdrawn through line 91, condenser 93, to a separator 95, from which gases are withdrawn through line 97, controlled by valve 99, and condensate is withdrawn through 60 line 101 controlled by valve 103; and constituents heavier than benzene are withdrawn through line 104 controlled by valve 105.

The toluene cut having a boiling range between about 227° F. and 235° F., is similarly 65 charged from line 47 by means of pump 106 through heating coil 107, reactor 109, line 111 controlled by valve 113, to fractionator 115. The toluene is withdrawn from the fractionator as a 70 side stream through line 117 controlled by valve 119. The fractions boiling above toluene are withdrawn from the fractionating tower 115 through line 121 controlled by valve 123, and the fractions lighter than toluene are withdrawn 75

through line 125, condenser 127, into separator 129. The liquid collected in separator 129 is withdrawn therefrom through line 131, controlled by valve 133, and the gases are withdrawn through line 135 controlled by valve 137.

The xylene cut having a boiling range between about 267° F. and 282° F., is charged from line 49 by means of pump 149 into heating coil 151 through reactor 153, line 155, controlled by valve 157, to fractionator 159. The xylene is withdrawn as a side stream from fractionator 159 through line 161 controlled by valve 163. Constituents boiling above xylene are withdrawn from the fractionator through line 165 controlled by valve 167, and the constituents boiling below xylene are withdrawn from the fractionator through line 169 and condenser 171 into separator 173. The liquids collected in 173 may be withdrawn therefrom through line 175 controlled by valve 177. Gases may be withdrawn from the separator 173 through line 179 controlled by valve 181.

The naphthalene cut is charged from line 51 by means of pump 183 through heating coil 185, reactor 187, line 189 controlled by valve 191, into fractionator 193. The naphthalene may be withdrawn from the fractionator 193 as a side cut through line 195 controlled by valve 197. Fractions heavier than naphthalene may be withdrawn from the fractionator through line 199 controlled by valve 201. Fractions boiling below naphthalene may be withdrawn from the fractionator through line 203 and condenser 205 into separator 207. Liquids may be withdrawn from the separator through line 209 controlled by valve 211, and gases may be withdrawn through line 213 controlled by valve 215. Hydrogen, or gas rich in hydrogen, may be fed into the reactors 109, 153, and 187 through valve-controlled lines 217, 219, and 221 respectively.

If it is not desired to separate the several cuts prior to hydrogenation, the polymer condensate may be withdrawn from fractionator 19 through line 35 and charged through line 223 controlled by valve 225, by means of pump 227, into the heating coil 229 and catalyst chamber or reactor 231. Hydrogenating gas may be fed into the reactor through line 233 controlled by valve 235. The reaction mixture is discharged from the reactor through line 237 controlled by valve 239, into fractionator 241. The reaction products may be fractionated in 241 in order to obtain an overhead distillate suitable as motor fuel, which may be withdrawn through line 243, through condenser 245, into accumulator and separator 247. From the accumulator 247 the finished motor fuel may be withdrawn through line 249 controlled by valve 251, and the gases may be withdrawn through line 253 controlled by valve 255. Liquids heavier than those suitable for motor fuel may be withdrawn from the fractionator 241 through line 257 controlled by valve 259.

If it is desired to separate benzene, toluene, xylene, and naphthalene, or any one of them, these compounds may be separated as side streams from the fractionating tower through the valve-controlled side stream withdrawal lines 261, 263, 265, and 267 respectively.

The apparatus shown and described herein is for the purpose of illustration only. It will be understood that the method may be carried out in any suitable apparatus and that the polymerization of the gases to liquid may be carried out as a separate and distinct operation from the hydrogenation and fractionation of the resulting products.

In accordance with my invention, I am enabled to increase the yield of high octane gasoline without destroying the anti-knock rating thereof and at the same time obtain a product which is stable as to gum and color and free of objectionable odor; or as an alternative I am enabled to produce substantially pure aromatic hydrocarbons without decreasing the quantity thereof present in the original mixture.

I claim as my invention:

1. The method of preparing substantially pure aromatic hydrocarbons from mixtures containing predominantly aromatic liquid hydrocarbons produced by subjecting olefin-containing hydrocarbon gases to temperatures of approximately 1100° to 1200° F. at pressures up to approximately 250 pounds per square inch for a period of time ranging from approximately five to thirty seconds, which comprises separating the mixtures into a plurality of fractions each having a narrow boiling range closely approaching the boiling point of an aromatic hydrocarbon, separately subjecting said fractions to selective hydrogenation under conditions whereby to hydrogenate unsaturated non-aromatic compounds contained therein in order to lower the boiling points of said compounds without substantially affecting the aromatic hydrocarbons and separately fractionating the hydrogenated products to obtain substantially pure aromatic hydrocarbons.

2. Method in accordance with claim 1 in which the hydrogenation is carried out at temperatures between 350° and 800° F. and under pressures up to 100 pounds per square inch in the presence of a mild hydrogenating catalyst.

3. The method of preparing substantially pure aromatic hydrocarbons from mixtures containing predominantly aromatic liquid hydrocarbons produced by subjecting olefin-containing hydrocarbon gases to temperatures of approximately 1100° to 1200° F. at pressures up to approximately 250 pounds per square inch for a period of time ranging from approximately five to thirty seconds, which comprises separating the mixtures into at least three fractions having boiling ranges between approximately 165–181° F., 227–235° F. and 267–282° F., respectively, separately subjecting each fraction to selective hydrogenation at temperatures between 350–800° F. and under pressures up to 100 pounds per square inch in order to convert non-aromatic hydrocarbons having boiling points closely approaching that of the aromatic hydrocarbons in the particular fraction into hydrocarbons whose boiling points differ more widely from that of the aromatic hydrocarbons, and subjecting the hydrogenated fractions to careful fractionation in order to separate the aromatic from the non-aromatic hydrocarbons.

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