May 8, 1945. E. G. BORDEN 2,375,464

PRODUCTION OF PURIFIED AROMATIC HYDROCARBONS FROM PETROLEUM

Filed June 20, 1942 2 Sheets-Sheet 1

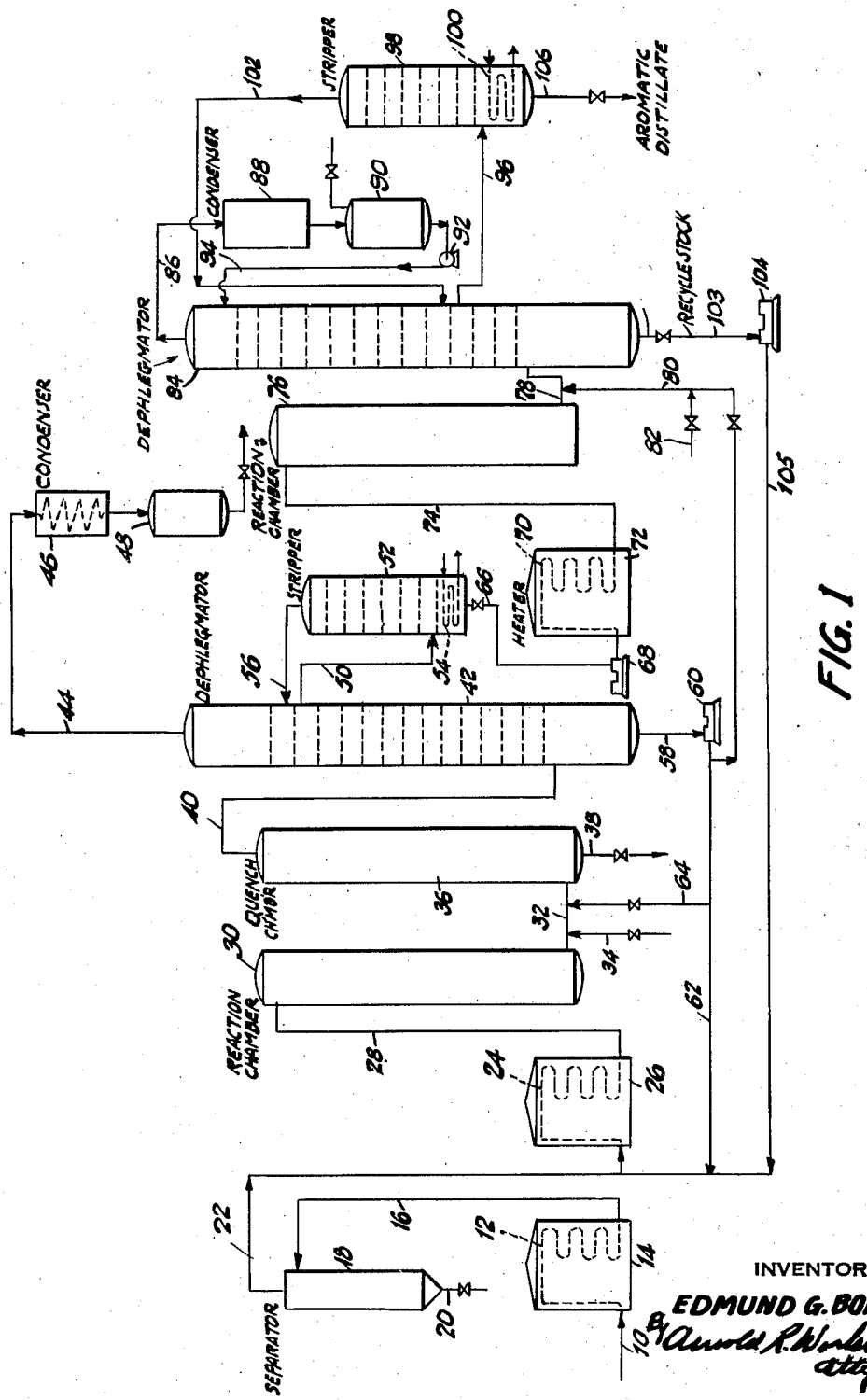


FIG. 1

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Filed June 20, 1942 2 Sheets-Sheet 2

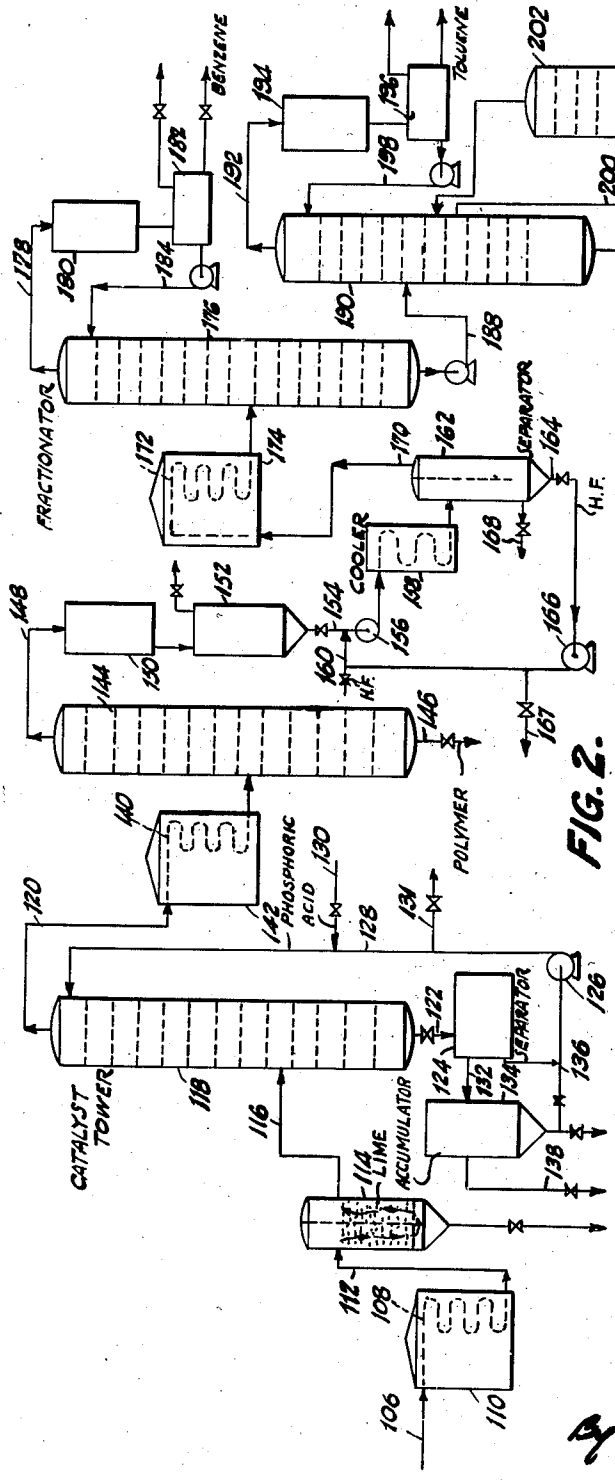


FIG. 2.

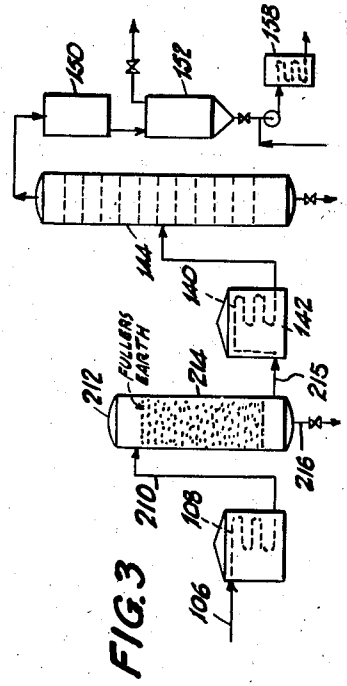


FIG. 3

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UNITED STATES PATENT OFFICE

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PRODUCTION OF PURIFIED AROMATIC HYDROCARBONS FROM PETROLEUM

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Application June 20, 1942, Serial No. 447,788

18 Claims. (Cl. 260—668)

This invention relates to the production of purified aromatic hydrocarbons from petroleum. More particularly the invention relates to the production of commercially pure benzene, toluene and xylene from petroleum.

Aromatic hydrocarbons are now being manufactured extensively from petroleum by thermal and catalytic cracking operations. Aromatic hydrocarbons occur naturally in some petroleums but this invention is concerned principally with those aromatic hydrocarbons which are produced from paraffin and naphthenic base crude petroleum oils. Most of the aromatic hydrocarbons produced from petroleum oils are now used as fuel and solvents, but the present invention contemplates the production of aromatics, such as benzene, toluene and xylene which are sufficiently pure to be satisfactory as nitration grade products suitable for manufacture of explosives or other chemical derivatives therefrom.

It has been found that by means of proper temperature and pressure conditions and the use of catalysts for thermal cracking, condensing and polymerization reactions, that aromatic hydrocarbons can be produced from petroleum oils regardless of the source of the petroleum. That is, the cracking, condensing and polymerization reactions produce aromatic hydrocarbons from other types of hydrocarbons, such as paraffins, naphthenes and olefins. Analyses of products which have been produced by the above-mentioned cracking, condensing and polymerization reactions show that the desired hydrocarbons, such as benzene, toluene and xylene, always have associated with them, other unsaturated hydrocarbons, such as olefins, diolefins and various other alkylated benzenes. The contaminating hydrocarbons are soluble in the desired hydrocarbons and have boiling points very close to the boiling points of the desired hydrocarbons. It is not practicable to separate this hydrocarbon mixture even with the best type of fractionating apparatus to obtain commercially pure desired hydrocarbons.

The primary object of the present invention is to treat the hydrocarbon mixture to be purified to convert the undesired hydrocarbons, without substantially affecting the desired hydrocarbons, into products that can be easily separated from the desired hydrocarbons by decantation and fractional distillation.

The contaminating hydrocarbons produced by the cracking, polymerization and condensing reactions vary quite widely in chemical properties. No single chemical or physical treatment has been found which will convert all of the contaminating hydrocarbons to products which may be easily and effectively separated from the desired hydrocarbons.

Another object of the invention is to provide a process by which the contaminating hydrocarbons in a mixture containing the desired hydrocarbons may be selectively separated in a plurality of separate treatments.

The contaminating hydrocarbons associated with the desired hydrocarbons, i. e., benzene, toluene, and xylene, usually are monoolefins, diolefins, polyolefins and low boiling polymers all of which are unsaturated hydrocarbons. I have found that the polyolefins and low boiling polymers may be polymerized catalytically with clays such as fuller's earth or with phosphoric acid to form tarry sludges that may be easily separated from the desired hydrocarbons by settling and distillation. I have also found that the monoolefins may be catalytically polymerized or catalytically alkylated to produce products which may be easily separated from the desired hydrocarbons by fractionation.

Another object of the invention is to provide a process of purifying aromatic hydrocarbon mixtures by separately removing the polyolefins and the monoolefins prior to fractional distillation of the desired hydrocarbons.

A further object of the invention is to provide a process of purifying aromatic hydrocarbons to separate contaminating hydrocarbons by catalytically converting and separating the polyolefins, thereafter catalytically converting the monoolefins, and separating the conversion products prior to the fractional distillation of the desired hydrocarbons.

A further object of the invention is to provide a continuous process by which different types of unsaturated contaminating hydrocarbons may be separated from desired aromatic hydrocarbons.

In accordance with this object one feature of the invention contemplates a continuous process of catalytically promoting reactions in a hydrocarbon mixture in separate zones at different temperatures and pressures and the separate continuous removal of the contaminating reaction products.

With these and other objects and features in view the invention consists in the process of manufacturing and refining a mixture of aromatic, olefinic and polymerized hydrocarbons to produce commercially pure desired aromatic hydrocarbons as hereinafter described and particularly defined in the claims.

The various features of the invention are illustrated in the accompanying drawings in which—

Figure 1 is a diagrammatic view in the form of a flow sheet illustrating apparatus in which petroleum oil may be cracked to form an aromatic hydrocarbon mixture.

Figure 2 diagrammatically illustrates in the form of a flow sheet an apparatus by which an aromatic hydrocarbon mixture manufactured in the apparatus illustrated in Figure 1 may be refined to separate contaminating hydrocarbons from the desired aromatic hydrocarbons; and

Figure 3 is a diagrammatic view in the form of a flow sheet illustrating one form of apparatus by which the polyolefins which contaminate a desired hydrocarbon mixture may be converted into a product that may be readily separated from the desired aromatic hydrocarbon.

In accordance with the present invention it is desired to manufacture low boiling aromatic hydrocarbons, such as benzene, toluene, and xylene from petroleum hydrocarbons by cracking which may be either thermal cracking, catalytic cracking, or a combination of thermal and catalytic cracking. These cracking operations when carried out under proper pressure and temperature conditions tend to form aromatic hydrocarbons from other types of hydrocarbons, such as paraffins, olefins, naphthenes and cyclic hydrocarbons. Therefore the desired aromatic hydrocarbons can be manufactured from substantially any source of petroleum oil.

The proper charging stock for the cracking reactions is a light gas oil but any type of petroleum oil may be used to secure the desired cracking stock. Referring to Figure 1, a charging stock which may be a kerosene, gas oil, fuel oil, topped crude, or the entire crude, is introduced through a line **10** to a vaporizing coil **12** within a furnace **14**. The temperature and pressure are preferably controlled so that the heated oil which flows through a line **16** into the upper end of a separator **18** will vaporize and the higher boiling point constituents will condense and pass to the bottom of the separator to be withdrawn through a line **20** as a residuum. The vapors which constitute the lower boiling cracking stock pass out of the top of the separator through a line **22** and then pass through a coil **24** in a furnace **26**. The pressure on the vapors passing through the coil **24** may vary from 200 to 600 lbs. and the furnace temperatures are controlled to heat the oil to a temperature of 950° to 1000° F. as it passes through the coils. The heated vapors are transferred through a line **28** to the upper end of a reaction chamber **30**. In the reaction chamber the temperature and pressure is maintained for a sufficient time to complete the initial cracking reaction of the vapors. The length of the coil **24** and the size of the chamber **30** are such that with a temperature of about 980 F. from 55% to 65% of the vapors will be converted into a hydrocarbon mixture which will have a boiling point below 500° F. As the heated vapors leave the bottom of the reaction chamber **30** they are suddenly cooled by means of a large body of oil which is introduced into a transfer line **32** through a line **34**. The mixture of vapors and cooling oil which has a temperature of from 650° to 700° F. passes into a quenching chamber **36** wherein a separation takes place between the vapors and the unvaporized oil. Furthermore the quenching chamber **36** acts partially as a dephlegmator for condensing high boiling hydrocarbons. The high boiling hydrocarbon mixture is withdrawn from the quenching chamber through an outlet **38** as a residue oil substantially as fast as it collects so that an oil body does not accumulate in the chamber. This residue oil may be recharged again if desired through the line **10**. The vapors pass out of the top of the quenching tower **36** through a line **40** and enter the lower portion of a dephlegmating and fractionating column **42**. In the column **42** three products are produced: first—a light hydrocarbon mixture having an end boiling point of about 220° F. which passes overhead through a line **44** to a condenser **46** and is collected in an accumulator **48**. This material may be stabilized for gasoline or fractionated to produce solvents. Second—near the top of the column a distillate is withdrawn from one of the bubble trays through a line **50** and passed into the bottom of a stripping tower **52**. Steam or heated gas may be introduced into the bottom of the stripper through a coil **54** to assist in driving off lower boiling hydrocarbons which may be contained in the distillate. These lower boiling point hydrocarbons pass upwardly through the stripping tower **52** and flow through a line **56** back into the column **42**. Third—the higher boiling point hydrocarbons, which constitute a charging stock of the gas oil boiling point range and which accumulate in the bottom of the column **42**, are withdrawn through a line **58** by a pump **60** and forced by means of the pump through a line **62** back through the coil **24** in the furnace **26**. This recycle stock constitutes the main body of oil being cracked thermally in the coil **24**. If desired this recycle stock may be used as a quenching medium and introduced into the transfer line **32** through a valved line **64**.

The cracking reaction carried out in the coil **24** and in reaction chamber **30** is preferably controlled so that the intermediate distillate which is separated in the stripper **52** will contain a comparatively small amount of paraffin hydrocarbons. The distillate which accumulates at the bottom of the stripper **52** is composed principally of aromatics, mono- and poly-olefinic and naphthenic hydrocarbons, and has a boiling point range of approximately 170° F. to 500° F. Any paraffinic hydrocarbons in this mixture will be converted to unsaturated hydrocarbons in the following cracking operations, but it is desired to have as small an amount of paraffins in this intermediate distillate as practicable because the cracking reaction which follows will produce a higher percentage conversion of unsaturated hydrocarbons to aromatic hydrocarbons if it is not contaminated by a high percentage of paraffins.

The intermediate cut is withdrawn from the stripper **52** through a line **66** and forced by means of a pump **68** through a heating coil **70** in a heater **72**. The heated oil flows from the coil **70** through a transfer line **74** into a reaction chamber **76**. The vapors passing through the coil **70** and reaction chamber **76** are maintained at a pressure of 300 to 600 lbs. per square inch and are heated to a temperature from 1025° to 1125° F. These heated vapors are held in the coil **70** and chamber **76** until from 75% to 93% of the hydrocarbons in the mixture are converted to aromatic hydrocarbons. The heater mixture leaves the bottom of the reaction chamber **76** through a transfer line **78** wherein it is quenched by means of distillate introduced into the transfer line through a line **80**. This distillate may be derived as a recycle stock from the column **42** or may be a cooled distillate, such as kerosene or gas oil, introduced through a line **82**. The mixture of vapors and quench oil which

has a temperature of from 650° to 700° F. flows into the bottom of a dephlegmator 84 wherein the vapors and oil are separated into three cuts. Light vapors pass up through the dephlegmating bubble tower and leave through a vapor line 86 by which they are conducted into a condenser 88 and receiver 90. Part of the distillate recovered in the receiver 90 may be passed by means of a pump 92 through a line 94 back into the top of the deplegmator to assist the fractional distillation. This light cut may be stabilized and used as a motor fuel or it may be fractionated to produce a solvent. It has a boiling point range of from 75° to 250° F. An intermediate fraction is withdrawn from the dephlegmator through a line 96 and passed into a stripping tower 98. Superheated steam or preheated gas is introduced into the bottom of the stripper 98 through a coil 100 to assist in removing low boiling point vapors. The low boiling vapors and gas pass up through the top of the tower and out through a vapor line 102 to pass back into the dephlegmator 84. A condensed hydrocarbon mixture which is a distillate in the boiling range of kerosene and gas oil accumulates in the bottom of the dephlegmator 84. This product is desirable as a cracking stock and is passed through a line 103 by means of a pump 104 and forced through a line 105 back to the transfer line 22 to be recracked.

The conversation of a cracked distillate into aromatic hydrocarbons may be advantageously carried out by catalytic cracking. To accomplish this a catalyst is supported in the reaction chamber 76 on suitable trays and the preheated vapors from the heating coil 70 are passed through and into contact with the catalyst in the chamber. By means of the catalyst the temperature may be maintained of from 100° to 300° F. lower than when the conversion is carried out thermally. Suitable catalysts are the oxids of vanadium and chromium that are preferably deposited in a porous bed of alumina. The oxids of manganese also may be used. Zinc chlorid, phosphorus pentoxide and silica gel all have catalytic properties which tend to produce aromatic hydrocarbons.

The liquid distillate collecting in the bottom of the stripper consists of a mixture of aromatic hydrocarbons with some unsaturated hydrocarbons. This distillate constitutes the main product from which the desired benzene, toluene and xylene hydrocarbons are manufactured. It is withdrawn from the bottom of the stripper 98 through valve line 106.

The refining of the cracked distillate to make the desired hydrocarbons is carried out more particularly in apparatus of the type illustrated in Figures 2 and 3. Referring to Figure 2, the aromatic hydrocarbon distillate is pumped through the line 106 into a heating coil 108 in a furnace 110 and heated to a temperature of from 400° to 600° F. to be vaporized. The vapors pass from the coil 108 through a line 112 into a lime treating tower 114. A baffle is located in the center of the tower 114 by which the vapors are required to pass downwardly and then upwardly through two bodies of lime for the purpose of removing sulfur from the vapors, particularly any hydrogen sulfid. The sulphurized spent lime may be withdrawn from time to time through the bottom of the tower 114. The purified vapors pass from the tower 114 through a line 116 into the intermediate portion of a catalyst tower 118 wherein the vapors are treated catalytically with phosphoric acid for the purpose of polymerizing the diolefins and polyolefins which contaminate the aromatic hydrocarbons to convert the contaminating hydrocarbons into tars and higher boiling products which can be separated from the aromatic hydrocarbons by gravity settling and distillation. The phosphoric acid is maintained in a liquid state as a series of bodies of liquid through which the hydrocarbon mixture bubbles. The vapors pass upwardly through the catalytic tower and flow out of the top of the tower through a line 120. The tower 118 is held under pressure to assist in condensing polymerized hydrocarbons and the temperature in the tower is maintained at from 250° F. at the top to 400° F. near the entrance of vapors in line 116 in order to condense the polymers and carry the polymers along with the acid to the bottom of the tower. The temperature at the top of the tower may vary from 175° to 250° F. in accordance with the material being treated while the temperature at the entrance through the line 116 is preferably held around 400° F. The temperature at the bottom of the tower 118 is approximately 350° F. The mixture of acid and polymer is withdrawn from the bottom of the tower through a valved line 122 into a separator 124. The phosphoric acid settles to the bottom of the separator 124 and is forced by means of a pump 126 through a line 128 back to the top of the tower 118 to be recirculated. Fresh phosphoric acid may be added from time to time to the line 128 through a valved line 130 and spent acid may be removed through valved line 131. The polymer overflows from the top of the separator 124 through a line 132 and passes into an accumulator 134. The accumulator may further act as a separator so that acid may be withdrawn from a line 136 and polymer through a line 138. The acid withdrawn from the line 136 may be returned to the pump 126 to be recirculated back to the tower or may be discarded.

The phosphoric acid catalytic polymerizing treatment of the distillate is an important feature of the invention in that the acid has a selective polymerizing reaction to polymerize the diolefins, polyolefins, and low boiling unsaturated polymers and place them in a condition whereby they may be effectively separated from the aromatic hydrocarbon distillate. The concentration of the acid is not important, although it is preferred to use 100% phosphoric acid. If more dilute acid is used the water will be distilled out of the acid and it will soon reach 100% concentration. In the operation a predetermined amount of the phosphoric acid will be withdrawn from the apparatus through the line 136 as the polymer tends to contaminate the acid. The acid withdrawn through the line 136 is replaced by the acid introduced into the system through the line 130.

The aromatic hydrocarbon distillate passing through the top of the tower 118 contains some polymerized polyolefins which are dissolved in the aromatic hydrocarbons, but these are preferably separated from the aromatic hydrocarbons by distillation. To accomplish this the vapors pass through a line 120 into a heating coil 140 located in a furnace 142. The vapors are heated to a temperature of 300° to 500° F. in the coil 140 and enter the mid portion of a fractionating column 144. A simple distillation is carried out in the column 144 to separate the polymerized hydrocarbons from the aromatic hydrocarbons which also contain the olefinic hydrocarbons. The polymer is withdrawn from

the bottom of the tower through a line 146 and the aromatic vapors pass through a line 148 into a condenser 150. The condensed vapors pass into an accumulator 152 and flow from the accumulator through a line 154 into a pump 156 by which they are circulated through a cooler 158. As the distillate flows through the line 154 hydrofluoric acid is introduced into the distillate through a line 160. The cooled mixture flows into a reaction and separating tower 162 where the hydrofluoric acid acts catalytically to polymerize the olefins. A temperature of from 30° to 70° F. is maintained in the cooler 158 and tower 162 to provide the proper conditions for reacting on the olefinic hydrocarbons to separate them from the aromatics. If the temperature is maintained around 30° F. an alkylation reaction will be carried on whereby the olefins will react with part of the aromatic hydrocarbons to form higher boiling alkylates that can be separated by distillation. On the other hand if the temperature is held between 35° and 70° F. the hydrofluoric acid acts as a catalyst for polymerizing the olefins to produce a sludge polymer that can be separated partially by gravity and partially by distillation from the aromatic distillate. The hydrofluoric acid and polymer accumulates in the bottom of the tower 162, the acid being withdrawn through valved line 164 and passed by means of a pump 166 back to the line 160. Spent hydrofluoric acid may be withdrawn from the system from time to time through valved line 167. Polymer may be withdrawn from the bottom of the tower 162 through a valved line 168. The aromatic distillate in liquid form passes out of the top of the tower 162 through a line 170 from which it passes into a coil 172 mounted in a furnace 174. In the furnace 174 the oil is heated to a temperature of from approximately 300° to 450° F. to provide sufficient temperature to fractionate the product for the purpose of separating the benzene, toluene, and xylene. Preheated vapors enter a midportion of a fractionating tower 176 wherein the temperatures are maintained at a sufficient degree to cause the benzene vapors to flow overhead through a vapor line 178 into a condenser 180. The benzene condensed in the container 180 flows into an accumulator 182. A portion of the benzene may be pumped through a line 184 back into the tower to secure proper fractionation of the distillates. The hydrocarbon mixture containing toluene and xylene accumulates in the bottom of the tower 176 and is pumped through a line 188 into the intermediate portion of a second fractionating tower 190. The temperatures maintained in the tower 190 are such that toluene vapors pass off from the top of the tower through a vapor line 192 and flow through a condenser 194 to be condensed. The condensate collects in an accumulator 196. Toluene from the accumulator may be pumped through the line 198 back to the top of the tower for refluxing to secure the proper fractionation. An intermediate cut is withdrawn from the tower through a line 200 and passes to the bottom of a stripping tower 202. Steam introduced through a coil 204 in the bottom of the stripping coil acts to force lower boiling points vapors up through the tower and out through a line 206 back to the tower 190. The steam introduced in the stripping tower 202 tends to fractionate the xylene and this product is withdrawn from the bottom of the stripper through a valved line 206. Any high boiling point oil or polymer that contaminated the aromatic hydrocarbon passing through the heating coil 172 accumulates in the bottom of the fractionating tower 190 and is withdrawn through a valved line 208.

As described above phosphoric acid may be used for the polymerizing of the polyolefins to separate them from the aromatic hydrocarbons. In place of phosphoric acid the catalytic polymerization of the polyolefins may be effected by means of fuller's earth. An apparatus for accomplishing this is illustrated in Figure 3. The aromatic hydrocarbon passes through the line 106 into a heater 108 where the distillate is heated to a temperature of 475° to 650° F. to be vaporized. The heated vapors pass through a line 210 into the upper portion of a catalytic treating tower 212. In the main portion of the tower 212 is located a granular body of fuller's earth 214. As the vapors pass through the fuller's earth the temperatures vary from 475° at the top to 250° F. at the bottom. The vapors pass downwardly through the fuller's earth and leave the bottom of the tower through a transfer line 215 from which they pass into the heating coil 140. The vapors are heated to a temperature of 300° to 500° F. in the heater 140 and then flow into the intermediate portion of the column 144. From the column 144 the aromatic vapors flow through a cooler 150 into an accumulator 152 from which they pass into the catalytic apparatus for further treatment with hydrofluoric acid. It will be noted in Figure 3 that the furnace 108 and the furnace 142 correspond to the same parts of Figure 2, the distinction between the apparatus illustrated in Figures 2 and 3 being the use of a fuller's earth catalytic treating tower 212 in Figure 3 in place of the phosphoric acid treating tower 118 of Figure 2. The fuller's earth acts to selectively polymerize the diolefins and the polyolefins as well as some of the low boiling unsaturated polymers in the aromatic distillate and this material partially condenses in the body of the fuller's earth and drains to the bottom of the tower. This polymer may be withdrawn from the bottom of the tower through a valved line 216. Some polymer may be dissolved in the aromatic hydrocarbons and this polymer is separated in the bottom of the fractionating tower 144.

In the past it has been customary to refine aromatic distillates to produce commercially pure aromatic hydrocarbons with strong sulfuric acid. The strong sulfuric acid has many disadvantages in that it acts as an oxidizing agent and it acts as a sulfonating agent by reacting with the aromatic hydrocarbons. This entails a loss of aromatic hydrocarbons as well as a loss of acid. On the other hand the hydrofluoric acid treatment of the aromatic distillate gives an accurate control by which the olefins contaminating the aromatic distillate may be selectively polymerized in order to separate them from the distillate. Furthermore if some of the olefins produce polymers which are difficult to separate from the aromatic distillate these olefins may be alkylated by carrying on an alkylating reaction between the olefins and the aromatics to convert the olefins into products having boiling points that will permit the reaction products to be separated from the desired aromatic hydrocarbons. The hydrofluoric acid does not have an oxidizing reaction and by controlling the temperatures the hydrofluoric acid does not react with the hydrocarbons to form esters. Furthermore the hydrofluoric acid catalytic re-

actions may be carried on at temperatures of 30° to 70° F. while sulfuric acid reactions require very low temperatures, that is from 30° to −20° F. in order to protect the aromatics and prevent the sulfonating reactions.

Hydrofluoric acid may be used in concentrations of 80% to 100% and still give effective results. Furthermore the acid is heavy which assists materially in effecting a gravity separation between the acid, the hydrocarbon and the polymers. Hydrofluoric acid has a sufficiently high boiling point so that it may operate in the temperature range of 30° to 60° F. without the disadvantage of volatilization. Furthermore hydrofluoric acid has a freezing point of minus 83° C. which adapts it for operation at low temperatures.

It has been found furthermore that the selective separation of the diolefins and the monoolefins from the aromatic hydrocarbons provides a process by which the contaminating hydrocarbons may be effectively separated without the use of excess acid or entailing the loss of aromatic hydrocarbons. The phosphoric acid and fuller's earth treatments are very effective in separating the olefins and places the distillates in a condition so that the monoolefins may be easily polymerized to be separated from the aromatic distillates.

The preferred form of the invention having been thus described, what is claimed as new is:

1. The process of purifying a hydrocarbon distillate containing desirable aromatic hydrocarbons and contaminating hydrocarbons such as monoolefins and polyolefins, which comprises heating the said distillate and passing it into a reaction zone in contact with a catalyst adapted to selectively polymerize the polyolefins, separating the resulting polymers from the distillate containing the aromatic hydrocarbons and monoolefins, passing the purified distillate into a second reaction zone in contact with a hydrofluoric acid catalyst under conditions adapted to polymerize the monoolefins, and fractionally distilling the resulting treated distillate to separate the olefin polymers from the desired aromatic hydrocarbons.

2. The process of producing commercially pure aromatic hydrocarbons from petroleum comprising, cracking petroleum at a high temperature to produce a product having a high unsaturated content, fractionating the cracked product to separate a distillate in the boiling point range of kerosene and light gas oil, cracking the distillate in the vapor phase to obtain a high conversion to unsaturated hydrocarbons containing aromatics and olefins while substantially eliminating paraffins and naphthenes, fractionating the cracked distillate to obtain an aromatic distillate in the boiling point range of the desired aromatic hydrocarbons, heating the aromatic distillate and passing it into contact with a catalyst to polymerize diolefins, separating the diolefin polymers, passing the distillate into contact with a hydrofluoric acid catalyst to polymerize monoolefins, and fractionating the treated distillate to separate polymer from the desired aromatic hydrocarbons.

3. The process defined in claim 2 in which the kerosene and light oil distillate is cracked by means of a catalyst to provide an aromatic distillate.

4. The process defined in claim 2 in which the kerosene and light gas oil distillate is cracked by contact with a heated catalyst comprising an oxide of one of the metals of the 5th group deposited on alumina.

5. The process of purifying a hydrocarbon distillate containing desired aromatic hydrocarbons and contaminating hydrocarbons, such as monoolefins, polyolefins, and unsaturated polymers, comprising heating said distillate and passing it into contact with a catalyst to selectively polymerize polyolefins and unsaturated polymers, separating the polymers from the distillate, passing the purified distillate containing monoolefins into contact with a hydrofluoric acid catalyst to polymerize monoolefins, and fractionally distilling the distillate to separate polymers from the desired aromatic hydrocarbons.

6. The process of purifying a hydrocarbon distillate containing desired aromatic hydrocarbons and contaminating hydrocarbons such as monoolefins, polyolefins and unsaturated polymers, which comprises heating said distillate and passing it into contact with a catalyst adapted to selectively polymerize the polyolefins and the unsaturated polymers, separating the resulting polymers from the treated distillate, passing the resulting purified distillate containing monoolefins into contact with an alkylation catalyst at an alkylating temperature adapted to alkylate a part of the aromatic hydrocarbons with the monoolefins to form an alkylate having a boiling point different from the boiling points of the desired unalkylated aromatic hydrocarbons, and fractionating the treated distillate to separate the alkylate from the desired unalkylated aromatic hydrocarbons.

7. The process defined by claim 1 in which the hydrogen sulfide content of the distillate to be treated is removed therefrom prior to passing the distillate into the first-mentioned reaction zone.

8. The process defined in claim 5 in which the polymerization of the polyolefins is promoted by the catalytic reaction of phosphoric acid.

9. The process defined in claim 5 in which the polymerization of monoolefins is promoted with the hydrofluoric catalyst at a temperature between 35° and 60° F.

10. The process defined in claim 5 in which the polymerization of the polyolefins is promoted by phosphoric acid at a temperature between 170° and 350° F.

11. The process defined in claim 5 in which the polymerization of the polyolefins is promoted by means of fuller's earth.

12. The process defined in claim 5 in which the polymerization of polyolefins is promoted in the vapor phase by fuller's earth at temperatures from 250° to 475° F.

13. The process defined in claim 5 in which the polyolefins are polymerized with 100% phosphoric acid and monoolefins are polymerized with 90% to 100% hydrofluoric acid.

14. The process defined in claim 1 in which the polyolefins are polymerized in the vapor phase with fuller's earth and monoolefins are polymerized in the liquid phase with 90% to 100% hydrofluoric acid.

15. The process as defined by claim 6 in which the polyolefins are polymerized in the vapor phase with phosphoric acid and in which the alkylation operation is carried out with hydrofluoric acid as a catalyst at a temperature of from 30° to 40° F.

16. The process defined in claim 5 in which the aromatic distillate is treated in the vapor phase by passing the vapors through a bed of lime to

remove sulfids prior to polymerizing the polyolefins with a catalyst.

17. The process of purifying hydrocarbon distillates containing desired aromatic hydrocarbons and contaminating hydrocarbons such as monoolefins, polyolefins and unsaturated hydrocarbon polymers, which comprises heating said distillate and passing it into a reaction zone in contact with a phosphoric acid catalyst to selectively polymerize polyolefins and unsaturated polymers, separating the resulting polymers from the treated distillate, passing the purified distillate containing monoolefins into a second reaction zone in contact with a different catalyst adapted to polymerize monoolefins, polymerizing the monoolefins in contact with said catalyst in said second reaction zone, and fractionally distilling the resulting treated distillate to separate monoolefin polymers from the desired aromatic hydrocarbons.

18. The process defined in claim 17 in which the distillate to be treated is passed in contact with an alkaline material to separate hydrogen sulfide from the distillate prior to passing it into said first-mentioned reaction zone in contact with the phosphoric acid catalyst.

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