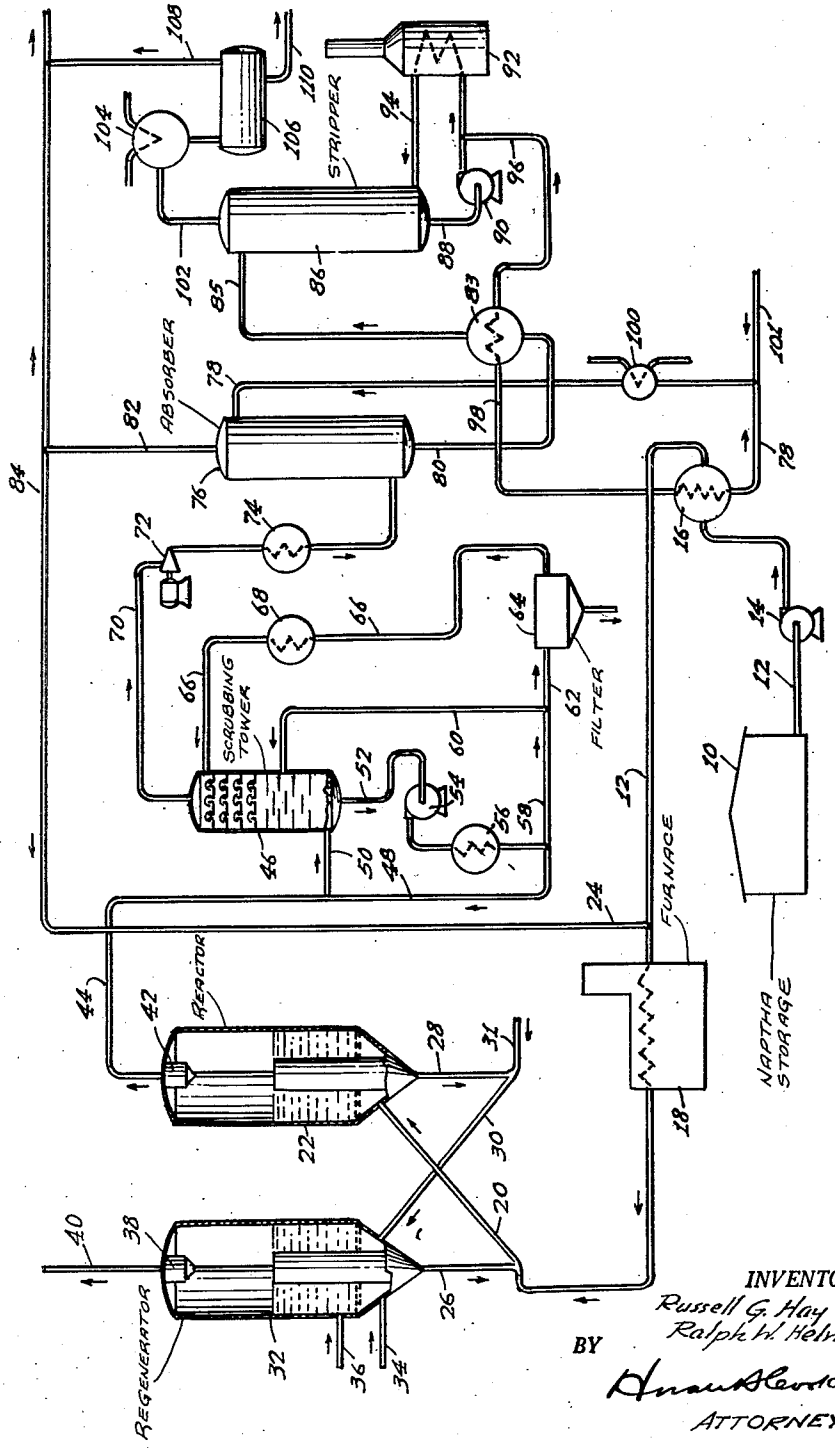
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AROMATIZATION OF NAPHTHA

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AROMATIZATION OF NAPHTHA

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1 Claim. (Cl. 260—668)

This invention relates to the preparation of aromatic hydrocarbons and more particularly to a process for the dehydrogenation of petroleum hydrocarbons to form aromatic hydrocarbons and the recovery of the aromatic compounds from reaction products having lower boiling points.

Aromatic hydrocarbons in the gasoline boiling range are valuable as fuel for internal combustion engines because of their high anti-knock rating, and also are valuable solvents. Specific aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene in substantially pure solutions are important raw materials in the synthesis of plastics and other organic compounds. The aromatization of less valuable hydrocarbons of higher hydrogen to carbon ratio than aromatic hydrocarbons is accomplished by passing the non-aromatic hydrocarbons in contact with a suitable catalyst at an elevated temperature at which dehydrogenation and ring closure, if necessary, occur. For example, it has been suggested in the prior art that the non-aromatic hydrocarbons can be passed in contact with a composite of alumina and chromia at temperatures in as wide a range as 750° to 1200° F. to form aromatic hydrocarbons.

The aromatization of non-aromatic hydrocarbons is a highly endothermic reaction; hence, it is necessary to supply large quantities of heat to the reaction to maintain the optimum reaction temperature. Large volumes of hydrogen are formed in the aromatization reaction, which hydrogen, in addition to the other reaction products, causes high velocities of reaction products and entrainment of substantial amounts of catalyst fines from fluidized catalytic aromatization processes.

This invention resides in a fluidized catalytic process, and apparatus therefor, for the preparation of aromatic hydrocarbons from non-aromatic hydrocarbons of higher hydrogen to carbon ratio, and the separation and recovery of the hydrocarbons boiling in the range of the aromatic hydrocarbons from the entrained catalyst fines and reaction products of lower boiling point. Throughout this specification, the term aromatic hydrocarbons means benzene and alkylated benzenes such as toluene, xylene and ethylbenzene. Aromatic hydrocarbons having more than one benzene ring are not included within the scope of the term aromatic hydrocarbons as herein used.

The single figure of the drawings is a schematic flow sheet illustrating a process and apparatus suitable for use in this invention.

Referring to the drawing, charge stock is delivered from a storage tank 10 through a line 12, pump 14, heat exchanger 16 and furnace 18, to a transfer line 20 from which the charge stock is discharged into a reactor 22 in which a fluidized bed of catalyst is maintained. Suitable charge stocks are normal and branched paraffins and olefins of at least six carbon atoms and naphthenic hydrocarbons preferably having six or more carbon atoms in the naphthenic ring. The charge stock can be substantially a single compound, or a mixture of hydrocarbons having the same number of carbon atoms per molecule for

the preparation of a specific aromatic compound, as in the aromatization of normal hexane and hexene to produce benzene. Also suitable for charge stocks are mixtures of hydrocarbons of hydrogen to carbon ratios higher than those of aromatic compounds having different numbers of carbon atoms per molecule, and particularly mixtures of petroleum hydrocarbons boiling in the gasoline range to produce a mixture of different aromatic hydrocarbons. The term "naphtha" is employed in this specification to designate non-aromatic hydrocarbons of the proper boiling point suitable as charge stocks in the process of this invention.

Recycle gas consisting principally of hydrogen from a line 24 in amounts up to about 6000 standard cubic feet per barrel of naphtha is mixed with the charge stock prior to entrance into the furnace 18, wherein the mixture is heated to approximately the reaction temperature. The charge stock discharged from furnace 18 picks up regenerated catalytic discharged from the bottom of a standpipe 26 and delivers it to the fluid bed within the reactor 22.

The catalyst within the reactor 22 can be any conventional catalyst for conversion of naphtha to aromatic hydrocarbons in finely divided form in which the major weight proportion of the particles falls within the range of about 20 to 100 microns. Examples of suitable catalysts are composites of alumina and chromia and alumina and molybdena. The alumina-chromia catalysts, which are preferred for the preparation of benzene, can be prepared by the impregnation with chromium nitrate of an activated alumina, or an activated alumina impregnated with small amounts of silica, followed by thermal decomposition of the chromium nitrate to form an alumina-chromia composite. Other suitable alumina-chromia catalysts are prepared by coprecipitation of alumina and chromia followed by washing, drying and calcining. Preferred catalysts are alumina-chromia catalysts containing about 5 to 30 percent chromia which are further improved by treatment with sodium hydroxide or potassium hydroxide.

The finely divided catalyst particles are suspended in a fluidized dense phase by the ascending vapors of charge stock, hydrogen-containing gases added to the charge stock, and reaction products. The temperature in the reactor may range from as low as 750° F. to as high as 1200° F.; however, it is preferable that the temperature within the reactor be within the range of 900° to 1150° F., and still more desirably between 950° and 1100° F. The pressure is maintained as low as possible consistent with the maintenance of satisfactory throughputs through the reactor to improve the yield of aromatic hydrocarbons. Pressures below about 25 p. s. i. g., and preferably about 5 p. s. i. g., are employed. The space velocity of the charge stock is between 0.1 volume of liquid feed per volume of catalyst per hour and 10 volumes per volume per hour.

Deactivated catalyst is withdrawn from the reactor 22 through a standpipe 28 and discharged into a transfer line 30 in which the catalyst is transported by a stream of air introduced through a supply line 31 from a source, not shown, to a regenerator 32. A fluidized bed of catalyst particles suspended by air and flue gases is maintained in the regenerator in which carbonaceous deposits on the catalyst particles are oxidized. Oxidation air, in addition to that used to transport the catalyst through transfer line 30, can be added to the regenerator through a line 34. Because of the endothermic nature of the aromatization reaction, the carbonaceous deposits on the catalyst ordinarily will not supply all of the heat required to maintain the fluid bed within reactor 22 at the desired temperature. Additional heat is supplied by the introduction of fuel, such as fuel oil, into the regenerator through a line 36

to heat the regenerated catalyst to a temperature sufficiently high to convey substantial heat to the reactor in the form of sensible heat of the catalyst. The temperature in the regenerator is maintained at 950° to 1250° F. Flue gases from the regenerator pass through a cyclone separator 38, in which entrained catalyst particles are separated and returned to the fluid bed, and are discharged through line 40 to a stack.

Gaseous reaction products from the fluid bed within reactor 22 pass through a separator 42, in which the larger of the entrained catalyst particles are separated from the reaction products, and then are delivered through line 44 to a scrubbing tower 46. Prior to their introduction into the scrubbing tower 46, the reaction products are quenched with a relatively cold stream of quench oil from line 48. The mixture of quench oil and reaction products enters the bottom of scrubbing tower 46 through a line 50. The reaction products, which remain in the gaseous phase, flow upwardly through the scrubbing tower in countercurrent contact with descending scrubbing oil which cools the reaction products to a temperature suitable for further processing and removes entrained catalyst fines from the reaction products. The scrubbing tower is provided with suitable apparatus such as the bubblecap trays and disk and doughnut trays indicated diagrammatically for improving the contact between quench oil and ascending gaseous reaction products.

The quench oil and catalyst fines are discharged from the bottom of scrubbing tower 46 through a line 52 and are circulated by means of a pump 54 through a cooler 56. A portion of the cooled quench oil discharged from cooler 56 returns via line 48 for quenching reaction products. A second portion of the cooled quench oil passes through lines 58 and 60 to a point at approximately the middle of the scrubbing tower 46 to provide a downward flow of liquid in the tower to scrub the reaction products. A third portion of the quench oil passes through line 62 to a continuous filter 64, or other suitable apparatus, in which the entrained catalyst particles are separated from the quench oil. The filtered quench oil is returned through lines 66 and cooler 68 to the top of the scrubbing tower 46. The quench oil introduced into the top of the scrubbing tower 46 provides catalyst-free reflux in the top of the scrubbing tower which further cools the gaseous reaction products and cleans traces of catalyst which may be present from the gases.

The gaseous reaction products from scrubbing tower 46 flow through line 70 to a compressor 72 in which the pressure on the gases is raised to a pressure which will facilitate the absorption of the aromatic hydrocarbons in an absorber oil. A pressure in the range of 35 to 75 p. s. i. is preferred. The compressed reaction products are then cooled in a heat exchanger 74 and introduced into the bottom of an absorption tower 76. A stream of lean absorber oil is introduced into the top of the absorber tower through line 78 and descends through the tower countercurrently to the gaseous reaction products. The descending absorber oil extracts a higher boiling fraction, herein designated as the aromatic fraction, which includes the aromatic hydrocarbons and other hydrocarbons of approximately the same boiling point as the aromatic hydrocarbons, from the reaction products of lower boiling point, and is discharged as a rich oil from the bottom of absorption tower 76 through a line 80. The reaction products which are not absorbed by the absorber oil, and which largely consist of hydrogen, are discharged from the top of the absorption tower 76 through line 82 into a gas line 84. The gas line 84 is connected with line 24 for the recycle of hydrogen to the reactor. Absorption tower 76 is provided with bubblecap trays, perforated trays, or other apparatus such as packing, to improve the contact between the liquid and gaseous phases therein.

Rich absorber oil is directed through line 80 to a heat exchanger 83 in which it is heated by heat exchange with lean absorber oil and a then delivered through a line 85 into the top of a stripper 86. Stripper 86 is equipped with bubble cap trays, perforated trays, packing, or other means for providing efficient contact between the descending rich oil and ascending gases which strip the aromatic fraction from the rich oil. Lean absorber oil is discharged from the bottom of the stripper 86 through a line 88 to a pump 90. A portion of the lean oil is pumped through a heater 92, which serves as a boiler, and then back to the stripper 86 through line 94. Heater 92 provides the heat necessary for the vaporization of the absorbed aromatic fraction from the rich oil. Another portion of the lean oil passes from pump 90 through a line 96, and heat exchanger 83, wherein it gives up a portion of its sensible heat to the rich absorber oil, and then passes through a line 98 to heat exchanger 16 in which the lean oil is further cooled by heat exchange with the charge stock. The cool lean oil from heat exchanger 16 is further cooled in a cooler 100 and delivered through line 78 to the top of the absorber 76 for the absorption of the aromatic fraction from the lower boiling point reaction products. Makeup absorber oil is added to the system as required through line 101.

Gaseous reaction products stripped from the absorption oil in stripper 86 are discharged from the top of the stripper through a line 102 and pass through a cooler 104 to an accumulator 106. Gases separated from the reaction products in the accumulator 106 are delivered through line 108 to the gas line 84. Liquid reaction products are removed from the accumulator 106 through a line 110 and delivered to apparatus, not shown, for separation of the aromatic hydrocarbons from non-aromatic hydrocarbons of substantially the same boiling range. The non-aromatic hydrocarbons separated from the aromatic hydrocarbons may be recycled through the reactor 22, if desired.

The following specific embodiment of this invention is described in detail to illustrate the process of this invention for the preparation of benzene from a specific charge stock.

A charge stock consisting of approximately 80 percent by volume of normal hexane, 13½ percent by volume methylcyclopentane, 5 percent by volume isohexanes, and 1½ percent by volume benzene is heated to a temperature of 1022° F. and is introduced into a reactor which is maintained at the same temperature. The charge stock is passed through the reactor at a liquid space velocity of 1.0 volume per volume of catalyst per hour. The pressure in the reactor is regulated at 5 p. s. i. g. Hydrogen is recycled to the reactor by introduction into the charge stock at the rate of 1500 standard cubic feet per barrel of charge prior to final heating of the charge to the reaction temperature. A fluidized bed of coprecipitated alumina-chromia catalyst containing approximately 80 percent alumina and 20 percent chromia is maintained in the reactor.

Gaseous reaction products together with entrained catalyst fines are withdrawn from the reactor at approximately the reaction temperature and quenched with a quench oil at a temperature of 150° F. to produce a mixture at a temperature of approximately 500° F. The quench oil is a gas-oil of approximately 200 molecular weight. The quenched mixture is introduced into a tower in which it is scrubbed with additional quench oil. Gaseous reaction products pass upwardly through the scrubbing tower and are discharged therefrom at 130° F. Quench oil and entrained catalyst fines are withdrawn from the bottom of the tower and are cooled at approximately 150° F. A portion of the cooled quench oil withdrawn from the bottom of the tower is recirculated continuously through the scrubbing tower. The gaseous reaction products are also washed with a catalyst-free quench oil for further cooling and scrubbing of the reaction products.

The scrubbed gaseous reaction products are compressed

to a pressure of approximately 40 p. s. i. g. and cooled to a temperature of 130° F. The aromatic fraction of the reaction products is absorbed in a light gas-oil of approximately 200 molecular weight. A portion of the unabsorbed gases, which consists principally of hydrogen, is recycled to the charge stock at the rate set forth above.

The rich absorption oil is heated to a temperature of approximately 250° F. and introduced into a stripper tower operated at a pressure of approximately 10 p. s. i. g. A reboiler at the bottom of the stripper provides the heat required for stripping the aromatic fraction from the absorber oil.

The quenching of the reaction products not only cools the reaction products to a temperature suitable for further processing, but provides an efficient separation of entrained catalyst fines from the very large volume of gaseous reaction products. Recirculation of cooled quench oil countercurrent to the flow of gaseous reaction products thoroughly scrubs the gases prior to their discharge from the scrubbing tower. Erosion of the equipment in which the catalyst fines are separated from the reaction products, as well as cooling and other processing equipment, is minimized by the quenching and scrubbing procedure.

The details of the process have been set forth with respect to an embodiment of this invention for the purpose of illustrating a process in detail. It will be appreciated that specific operating conditions will depend at least in part upon the details of the design of the equipment. Specific operating conditions will be dependent in some instances upon other operating conditions. For example, the temperature employed in the absorber and stripper will depend upon the operating pressure of those units and their fractionating efficiency. This invention is not limited to such details except as set forth in the appended claim.

What we claim is:

A process for the preparation of aromatic hydrocarbons comprising mixing a recycle gas consisting principally of hydrogen with a naphtha consisting essentially of non-aromatic hydrocarbons having at least 6 carbon atoms per molecule in a ratio of about 1500 to 6000 standard cubic feet of recycle gas per barrel of naphtha to form a charge stock, passing the charge stock through a heated coil to heat the charge stock to a temperature of 900 to 1150° F., introducing hot regenerated aromatization catalyst particles from a regenerator into the heated charge stock to form a suspension of the catalyst in the charge stock, delivering the suspension of the catalyst in the charge stock into the lower end of a reactor containing a fluidized bed of the aromatization catalyst maintained at a temperature of 900 to 1150° F. and a pressure below about 25 p. s. i. g., withdrawing a stream of aromatization catalyst from the fluidized bed in the reactor and transferring it to a regenerator, burning carbonaceous deposits from the catalyst in the regenerator, the temperature in the regenerator being higher than the temperature in the reactor and in the range of 950 to 1200° F. to supply heat to the reactor upon transfer of the regenerated catalyst to the reactor, withdrawing reaction products from the upper surface of the fluidized bed and passing them through a separator in which entrained catalyst particles are separated from the reaction products and returned to the fluidized bed, passing the reaction products from the separator through a line into a scrubbing tower adapted for countercurrent contact of gas and liquid and maintained at substantially atmospheric pressure, withdrawing a slurry of quenching oil and catalyst from the bottom of the scrubbing tower, cooling the withdrawn slurry, discharging a first portion of the cooled slurry into the line for admixture with the reaction products between the separator and the scrubbing tower, returning a second portion of the cooled slurry into the scrubbing tower above the point of admission of the reaction products, further cooling the quenching oil in a third portion of the cooled slurry, separating catalyst from the third portion of the cooled slurry to form a substantially catalyst-free stream of quenching oil, introducing the catalyst-free quenching oil into the scrubbing tower at a point higher than the point of introduction of the second portion of slurry to provide clean reflux further cooling and cleaning the gaseous reaction products in the scrubbing tower, discharging gaseous reaction products from the upper end of the scrubber and compressing them to a pressure in the range of about 35 to 75 p. s. i. g., cooling the compressed gaseous reaction products and passing the min countercurrent contact with an absorber oil to strip aromatic hydrocarbons from the recycle gas, returning recycle gas for admixture with the naphtha, and stripping aromatic hydrocarbons from the absorber oil.

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