

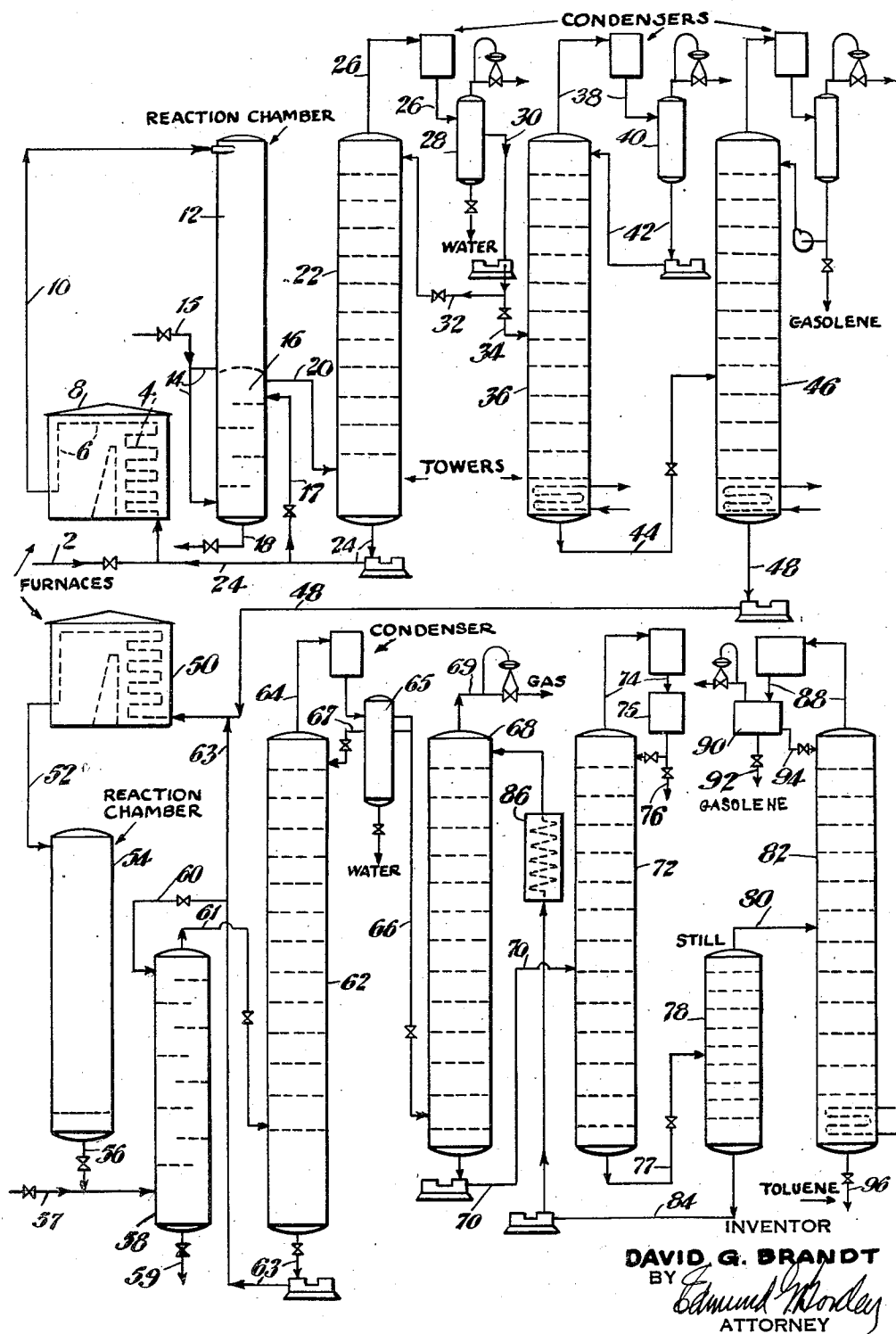
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PROCESS FOR MANUFACTURING TOLUENE

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PROCESS FOR MANUFACTURING TOLUENE

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1 Claim. (Cl. 260-668)

The present invention relates to an improved process for the manufacture of toluene and more particularly to the manufacture of nitration grade toluene from petroleum stock.

Many attempts have been made to manufacture technical benzene, toluene and other aromatic hydrocarbons from petroleum stocks, but for the most part such processes have not been of commercial importance because of various difficulties encountered. On the other hand, petroleum stocks, such as gas oil, have been successfully converted into products containing substantial percentages of aromatic hydrocarbons, portions of which are recovered along with other constituents boiling within the usual gasoline range and used for motor fuel.

It is understood that some attempts have been made to manufacture toluene from selected petroleum stocks such as those recovered in the extraction of crude oils, or fractions, with such agents as liquid sulphur dioxide. It is also noted in the literature that toluene, along with benzene, has been produced in certain processes applied to the cracking of kerosene. For example, Kanep (Chem. Abs. 1935, vol. 29, p. 5640), pyrolyzed various kerosene fractions at 700° C., obtaining from about 12% to 21% of aromatic hydrocarbons. He found that the percentage of aromatic hydrocarbons decreased as the boiling range of the kerosene fraction increased, and that in general the proportion of benzene formed was greater than that of toluene.

So far as known, the manufacture of nitration grade toluene from petroleum has not been accomplished, at least on a practical or commercial scale. One of the difficulties encountered, in addition to the fact that relatively low percentages of toluene were produced, is that of recovering nitration grade toluene from the light materials of similar boiling point which are produced along with benzene and other hydrocarbons.

The primary object of the present invention therefore is to overcome the difficulties which have been encountered in previous attempts to manufacture toluene from petroleum and at the same time provide a commercial process in which relatively high percentages of toluene are obtained in conversion operations.

Another object of the present invention is to provide an improved process for the manufacture of nitration grade toluene in which the hydrocarbon constituents of the toluene may be readily separated as a nitration grade product.

Accordingly, the improved process of the pres-

ent invention comprises in general the steps of first producing a particular petroleum stock which may be directly converted into a product containing a high percentage of toluene. This stock is made in accordance with the features of the present invention by starting with a gas oil, kerosene or other suitable petroleum distillate, which may be largely paraffinic, the stock being passed in a confined stream of restricted cross-section through a pipe still furnace and cracked therein at a temperature of about 980° F. This cracking is preferably completed in the pipe still furnace, but may be completed to the desired extent by passing the high-temperature partially converted products from the furnace into an enlarged reaction chamber where a considerable time reaction is allowed for the cracking to take place. At the point where the desired reaction has been completed, the products are immediately and instantly cooled to a temperature below that of further reaction, such, for example, as to a temperature from 600° to 700° F. The resulting vapor products are then subjected to a series of fractionating operations to segregate out a distillate boiling within the range of from about 250° to 500° F.

This distillate having the characteristics described hereinafter, is thereupon subjected to a particular type of conversion operation for converting it into a product containing a substantial proportion of toluene, by passing it in a confined stream of restricted cross section through a heating zone in which it is vaporized and superheated to a temperature of from 800° to 1200° F., and then digested in an enlarged reaction zone, either with or without contact with a catalyst. The resulting products which will be comprised of toluene and high boiling constituents boiling above that of toluene, as well as lower boiling hydrocarbons and gases, are quickly cooled to a low temperature of about 600° F., and then subjected to a fractionation procedure for the recovery of the toluene.

The more important objects and features of the present invention will be appreciated by those familiar with this art from the following more detailed description of the improved process taken in connection with the accompanying drawing, in which:

The single figure is a flow sheet, showing an apparatus in diagrammatic form for carrying out the improved process.

Referring to the drawing, the oil charging stock for the process is introduced into the apparatus at a pressure of from 200 to 500 lbs. per

square inch through a valved charging line 2 and passed in series through banks of heating tubes 4 and 6 mounted in a pipe still furnace 8. The charging stock preferably comprises a petroleum distillate such, for example, as gas oil; but in certain types of operation, lighter distillates, such as kerosene and naphtha may be employed. The charging stock passing through the coil 4 is heated to a temperature of about 900° F. and then further heated to a temperature of from 960° to 1020° F. in passing through the tube banks 6. The resulting highly heated products are conducted from the pipe still furnace through a transfer line 10 and introduced into the upper portion of a vertical reaction chamber 12, where the products are permitted to react for a time sufficient to convert the charging stock into a final product containing a maximum of condensable constituents boiling below about 500° F.

The reaction products reaching the bottom of the chamber 12 are withdrawn through a line 14 and suddenly reduced in temperature by the introduction of a relatively cool fluid such as water through a valved line 15. This cooling operation is preferably sufficient to reduce the temperature of the cracked products to about 700° F., at which temperature they are introduced along with the cooling medium into the lower portion of a vapor separating and scrubbing chamber 16 mounted below the reaction chamber 12. The high boiling constituents are separated out in the bottom of the chamber 16 while the vapors are passed up around baffles therein, and are scrubbed with a regulated proportion of high boiling distillate introduced into the upper part of the chamber 16 through a valved line 17. Some of the distillate introduced through the line 17 is vaporized but the unvaporized portion together with the high boiling liquid constituents collected in the bottom of the chamber 16 are withdrawn as fuel oil through a valved line 18. The vapors remaining uncondensed in the chamber 16, together with vaporized distillate, are discharged through a vapor line 20 at a temperature of from 600° to 700° F. and introduced into the lower portion of a fractionating tower 22.

The purpose of the fractionating tower 22 is to separate from the vapor constituents the high-boiling hydrocarbons distilling at temperatures above about 500° F. The resulting distillate is preferably used as a recycle stock in the process and therefore withdrawn through a line 24 and forced by means of a pump therein into the line 2 to comprise a portion of the charging stock for the pipe still furnace 8. A portion of the stock in the line 24 may be conducted into the line 17 and used to scrub the vapors in 16. The vapors separated out in the tower 22 are conducted overhead through a vapor line 26, condensed in a condenser therein, and the resulting condensate and uncondensed constituents conducted into a receiver and water separator 28. In this receiver the fixed gases are removed overhead through a pressure valve controlled line, while water is withdrawn through a valved line from the bottom of the receiver. The oil condensate separated out in the receiver 28 is conducted through a line 30 and forced by means of a pump therein (preferably controlled from a float in chamber 28), through a valved line 32 into the tower 22, to control the fractionation therein, and through a valved line 34 into a stabilizer tower 36.

The pressure maintained in the receiver 28 should be at least about 200 lbs. per square inch, so that most of the C₄ hydrocarbons will be con-

densed and not discharged from the receiver with the gas. The pressures in the tower 22 and chambers 12 and 16 will be correspondingly higher, at least sufficient to cause the regular flow of vapors through the apparatus.

The condensable product recovered in the receiver 28 and conducted into the stabilizer 36 through the valved line 34 will include hydrocarbons boiling up to about 500° F. The cracking operation carried out in the pipe still furnace 8 and chamber 12 is preferably controlled, so that the gas oil charging stock, on a once through basis, is converted into a condensable product containing approximately 65% of constituents boiling below about 500° F., such constituents being largely unsaturated olefinic and aromatic hydrocarbons and substantially free of paraffinic hydrocarbons having more than 5 carbon atoms.

The stabilizer 36 is preferably operated at a pressure of about 300 lbs. per square inch, to produce a stable distillate at the bottom of the stabilizer which contains only the desired proportion of C₄ hydrocarbons, and which is substantially free of C₃ and lower hydrocarbons. The overhead vapors from this stabilizer, comprising substantially all of the lower hydrocarbons than C₄, and the undesired C₄, are conducted through a vapor line 38, subjected to condensation in a condenser therein, and the resulting products passed into a receiver 40, which may be used merely for the separation of sufficient condensate to be used as reflux for the control of the stabilizer 36. This reflux is passed from the receiver 40 through a line 42 and a pump therein into the tower 36. The excess of light materials taken overhead from the stabilizer 36 is discharged from line 42 or through a pressure valve controlled vapor line from the receiver 40.

The stabilized distillate produced in the stabilizer 36 is conducted through a valved line 44 and passed into a fractionating tower 46 operated at a lower pressure than that maintained in the stabilizer 36. The stabilized distillate is fractionated in the tower 46 to take overhead a light gasoline fraction and leave a bottoms product having a boiling range of from about 250°-500° F. The light gasoline is taken overhead in vapor form, condensed and collected in a receiver, from which a portion of the condensate may be returned to the upper part of the tower 46, while the light gasoline product is withdrawn to storage for blending purposes.

The bottoms product withdrawn from the tower 46, and which should be substantially free of paraffinic hydrocarbons is conducted through a line 48 and forced by means of a pump therein at a pressure of about 500 pounds per square inch through heating coils mounted in a pipe still furnace 50. The stock passed through this pipe still furnace is preferably heated to a temperature sufficient to vaporize the stock and superheat the vapors to a temperature of from 800° to 1000° F., after which the vapor products are passed through a transfer line 52 into a catalyst chamber 54 in which the vapors pass in intimate contact with a catalyst adapted to convert the constituents of the vapors under cyclization and alkylation conditions into a product containing a maximum proportion of toluene. Activated carbon is a suitable catalytic material and it may be deposited on any suitable refractory material supported in chamber 54. Other catalysts such as the oxides of vanadium, chromium, manganese or cobalt, zinc chloride and others may be used. The catalytic action may be effected in various

other ways, as, for example, by suspending the activated carbon or other catalyst in finely divided form in a stream or body of high-temperature vapors as they are discharged from the furnace 50 through the line 52. Activated carbon containing 10% of a metal oxide or chloride is also suitable.

In most instances the high-temperature products passing through the chamber 54 are actually raised in temperature by the catalytic action, and care should be taken to prevent a temperature rise above approximately 1060° F. The pressure in the chamber 54 should be from about 225 lbs. to about 350 lbs. per square inch.

The high temperature conversion products produced in the catalyst chamber 54 are conducted therefrom into a line 56 and instantly chilled to a low temperature of approximately 600° F., by the introduction of a relatively cool fluid, preferably water, through a valved line 57. The resulting relatively cool mixture passes into a baffled separating and scrubbing chamber 58 in which any high boiling materials are separated as liquid and withdrawn through a valved line 59 at the bottom of the chamber. The vapors separated out in the chamber 58, containing the desired toluene and being substantially free of paraffinic hydrocarbons are passed upwardly through the chamber in contact with a high boiling distillate scrubbing oil introduced into the upper part of the chamber from a valved line 60. The oil introduced through the line 60 may be hot, or introduced in small quantity, and not use to reduce the temperature of the vapors much below 600° F. The resulting scrubbed vapors and vaporized scrubbing medium are discharged from the top of the chamber 58 through a vapor line 61 and conducted into a fractionating tower 62 in which most of the hydrocarbons higher boiling than the gasoline range are condensed, although all above the boiling point of toluene may be condensed.

The fractionation carried out in the tower 62 however, is preferably regulated so that all toluene, together with some constituents which boil at about the same temperature and which necessarily must be carried along, are kept in vapor phase. The condensate produced in the tower is withdrawn through a valved line 63 and forced by means of a pump therein into the line 48 leading to the pipe still furnace 50. A portion of this distillate from the bottom of the tower 62 may be used in the top of the scrubber 58 by conducting a regulated portion thereof through the line 60. The distillate in the line 63 is highly unsaturated and contains a considerable proportion of aromatic hydrocarbons, and is therefore very suitable as stock for the furnace 50 and the reactions carried out in the chamber 54.

The toluene and other constituents remaining in vapor form in the fractionating tower 62 are conducted overhead through a vapor line 64, subjected to condensing conditions in a condenser therein, and the resulting condensate and uncondensed gases conducted into a receiver and water separator 65. The water separated out in the receiver is withdrawn through a valved line from the bottom thereof, while the condensate and uncondensed gases are conducted through a line 66 into an absorber 68. A portion of the condensate separated out in the receiver 65 is withdrawn through a valved line 67 and introduced into the upper part of the fractionating tower 62 to control the fractionation therein.

The absorber or absorption tower 68 is operated under temperature and pressure conditions, preferably a pressure of about 250 lbs. per square inch, adapted to liberate all possible normally gaseous hydrocarbons of C₃ and lower, while recovering the C₄ and higher hydrocarbons. The unabsorbed gases in the absorber 68 are discharged from the top of the absorber through a pressure valve controlled line 69 as shown. The absorption medium used in the tower 68 may be any suitable high boiling absorption oil, such as straw oil. The absorption medium is preferably separable from toluene by distillation and is preferably used in sufficient quantity to prevent escape of any toluene with the overhead gases. Back pressure is preferably maintained from the tower 68 through apparatus elements 65, 62, 58, 54 and 50, although considerable pressure drops through these elements may be obtained by the use of the control valves provided. A higher pressure may be used in 68 than in 62 by pumping the materials in line 66 into the absorber 68.

The mixture of absorption medium and distillate collected in the base of the absorber 68, including the toluene and constituents boiling within the range of light gasoline as well as lower boiling normally gaseous hydrocarbons, is conducted through a line 70 and forced by means of a pump therein into a stabilizer tower 72 in which the mixture is stabilized to eliminate overhead any propane and lower hydrocarbons as well as excess C₄ hydrocarbons not desirable in the light gasoline fraction from the standpoint of vapor pressure. The vapor fraction taken overhead from the tower 72 is conducted through a vapor line 74, and a condenser therein, and the mixed products are collected in a receiver 75 from which the gases are discharged through a pressure valve controlled line while the condensate is withdrawn through a valve controlled line 76. A portion of this condensate is introduced into the top of the stabilizer 72 for controlling fractionation as indicated.

The stabilized mixture collected in the base of the tower 72 including the absorption medium, toluene and light gasoline, is conducted through a valved line 77 at substantially reduced pressure into a still 78 in which the toluene and light gasoline product is vaporized and separated from the absorption medium which may include all possible constituents boiling above the boiling point of toluene under the conditions. Such constituents for example may include hydrocarbons boiling in the higher boiling range portion of gasoline, in fact gasoline range material boiling above toluene may be used as absorption media. The vaporized materials including the toluene are conducted from the still 78 through a vapor line 80 into a fractionating tower 82, while the absorption medium is withdrawn from the still 78 through a line 84 and forced by means of a pump therein through a cooler 86 mounted in the line, and then into the upper portion of the absorption tower 68. Excess material in line 84 over that required in 68 may be used as gasoline blending stock or sent to the furnace 50.

The fractionation carried out in the tower 82 is preferably conducted in such a manner that the light gasoline boiling range materials boiling below the boiling point of toluene are taken overhead while the toluene is held back in the tower. The vapors from the tower 82 are conducted through a vapor line 88, subjected to condensation by means of a condenser therein, while the resulting product is collected in a receiver 90,

from which any normally gaseous uncondensed hydrocarbons are removed through a pressure valve controlled line as shown, while the stabilized light gasoline boiling range product is withdrawn through a valved line 92. The fractionation and rectification in tower 82 is aided by refluxing the top of the tower with a portion of the overhead product introduced through a valve controlled line 94.

The toluene product produced in the operation and which may include some constituents of substantially the same boiling point is withdrawn from the tower 82 through a valved line 96. The relatively pure toluene withdrawn through the line 96 will be almost entirely free of paraffinic hydrocarbons which normally cause considerable trouble in the fractionation of toluene made from coal. The product, however, may contain small percentages of unsaturated olefinic type hydrocarbons having about the same boiling point as toluene, and these may be effectively removed by contacting the toluene product (in a well-known manner not shown) with sulfuric acid of from 64 to 66 Bé. gravity containing from 0.5 to approximately 1% of nitric acid. The product is preferably refractionated after acid treatment, and such refractionation may be effected in the presence of a selective solvent or carrier agent. Toluene to be used for nitration purposes should be free of unsaturated olefinic type hydrocarbons, have a boiling point of about 110° C., with an initial not below 108.5° C., and distilling completely at a temperature below 111° C. For certain purposes the toluene fraction removed through the line 96 may be used directly, preferably after acid treatment.

The charging stock for the pipe still furnace 50, as stated above, should be substantially free of paraffinic hydrocarbons. It preferably comprises a mixture of unsaturated olefinic and aromatic hydrocarbons of which about 20% are aromatics, although the proportion may run as high as 35%. While this stock may possibly be secured from other sources than by the method of production described above, no present source of such material is known. The charging stock for pipe still furnace 50 therefore is preferably made in the manner described above. The light gaso-

line in the tower 46 may be conveniently used for blending with straight run gasoline or other suitable heavy gasoline stock, as for example that from still 78.

From the foregoing description of the improved process of the present invention, it will be readily apparent that certain modifications may be made therein without departing from the spirit and scope of the invention as defined in the claim.

Having described the invention in its preferred form, what is claimed as new is:

A process for the manufacture of toluene, which comprises passing a hydrocarbon charging stock in a confined stream of restricted cross-section through a conversion zone and therein subjecting it to non-catalytic cracking conditions at a temperature in the neighborhood of 1000° F. for a sufficient time to produce substantially a maximum of condensable constituents boiling below a temperature of about 500° F. which is substantially free of paraffin hydrocarbons having more than five carbon atoms to the molecule, quenching the resulting high temperature conversion products and fractionating the same to recover the constituents boiling between about 250° and 500° F. as a separate fraction consisting essentially of olefines and aromatic hydrocarbons, passing this separate fraction through a separate heating and conversion zone maintained at a pressure of from 225 to 350 lbs. per square inch and subjecting the fraction to conversion conditions at a temperature in the neighborhood of 1000° F. for a sufficient time to convert said fraction into a product containing a relatively high proportion of toluene, cooling the said conversion product containing toluene to condense high boiling constituents, subjecting the remaining vapors containing the toluene and lower boiling constituents to a fractionating operation in the presence of an absorption medium to eliminate C₃ and lower hydrocarbons, distilling the mixture comprising the toluene and absorption medium to separate the toluene including toluene boiling range constituents and substantially only lower boiling constituents therefrom, and fractionating the latter to separate out a fraction high in toluene content.

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