

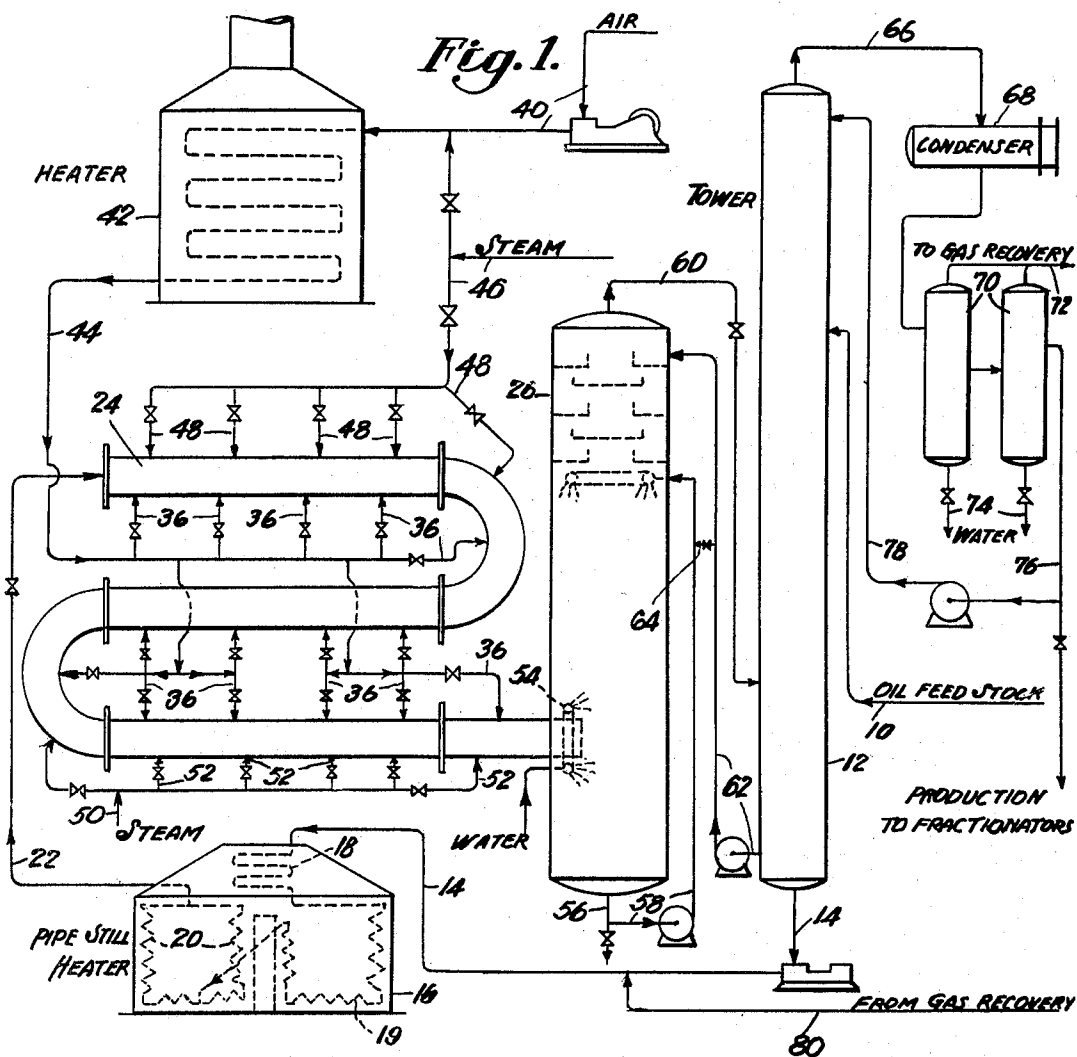
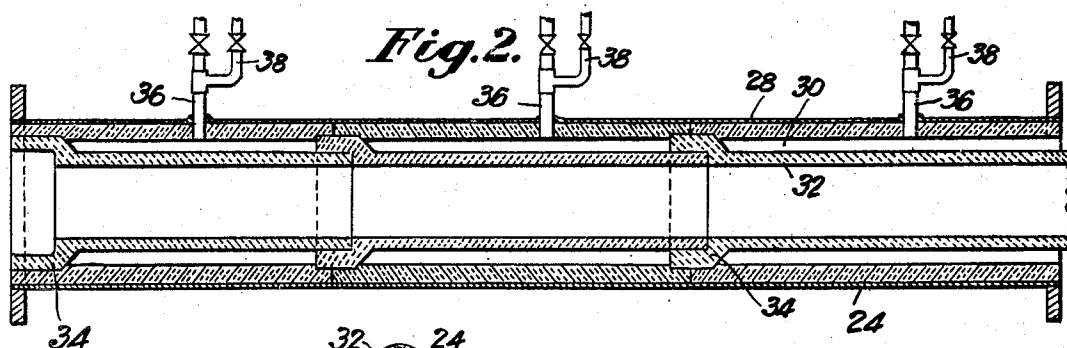
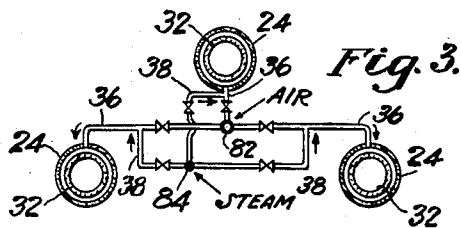
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D. G. BRANDT

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PROCESS FOR MANUFACTURING ALKYL BENZENE HYDROCARBONS

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INVENTOR  
DAVID G. BRANDT  
BY *Edmund M. Munday*  
ATTORNEY

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PROCESS FOR MANUFACTURING ALKYL  
BENZENE HYDROCARBONS

David G. Brandt, Westfield, N. J., assignor to  
Cities Service Oil Company, New York, N. Y., a  
corporation of Pennsylvania

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This invention relates to improvements in the manufacture of alkyl benzene hydrocarbons from petroleum oil stocks such as those used in oil cracking processes.

More particularly, the present invention is an improvement over known conversion processes in which certain proportions of aromatic hydrocarbons, such as benzene, toluene, and other alkylated benzene and higher aromatics, are produced by converting oils at relatively high temperatures. Benzene and toluene have been recovered in considerable quantities from gas making processes which are operated at extremely high temperatures adapted for the substantially complete cracking of hydrocarbons to gas and carbon. In one of the conversion processes in which benzene hydrocarbons are produced, the oil is cracked at a temperature of about 1000° F. in a pipe coil heater and then discharged into an enlarged reaction chamber. In this operation a considerable amount of carbon is formed in the coil and in the chamber, and numerous difficulties have arisen because of formation of deposits in the coil and the rapid accumulation of carbon in the chamber.

The primary object of the present invention, therefore, is to provide an improved process for the production of alkyl benzene hydrocarbons in which a relatively high percentage conversion to such compounds is obtained, particularly to compounds in which the alkyl groups include two or more carbon atoms.

A further object of the invention is to provide improved process by which the conversion operation may be carried out without interference by the carbon formed in the reaction.

In general, the improved process of the present invention includes the steps of heating the oil stock to be converted to a temperature in the neighborhood of 1100° F. under conditions adapted to produce a maximum of unsaturated olefin hydrocarbons and a minimum of free carbon, and thereafter passing the high temperature mixture through a tubular reaction zone in which the temperature is raised 200° to 300° F., this operation being carried out in a tubular converter comprising an outer steel casing and a spaced inner tube of porous refractory through which the hydrocarbon products flow. The final conversion of the heated products in the tubular converter is effected by introducing highly heated air of about 1100° F. into the outer steel casing and diffusing it through the porous refractory tube, and thereby preventing the deposit of carbon in the tube, and heating the hydrocarbon

mixture by burning or oxidizing the carbon contacting the tube wall as well as portions of the hydrocarbon mixture.

Other features and advantages of the improved process of the present invention will be apparent to those skilled in the art from the following detailed description of the invention taken in connection with the accompanying drawing which forms a part of this application.

10 In the drawing:

Fig. 1 is an elevational flow diagram of an apparatus particularly adapted for carrying out the improved process.

15 Fig. 2 is an enlarged longitudinal sectional view of a portion of the tubular converter showing the construction and arrangement of a preferred form of converter tube particularly adapted for carrying out the improved process of the present invention, but with a modified arrangement for supplying air and steam.

20 Fig. 3 is a cross-sectional view of the improved converter shown in Fig. 1, showing the modified arrangement for supplying air and steam to the tubular converter as in Fig. 2.

25 Referring to Fig. 1 of the drawing, the oil stock to be converted, which may be any one of the distillate stocks used in commercial oil cracking operations, is introduced into the apparatus through a line 10 which discharges the stock into the upper portion of a main fractionating tower 12 in which the stock is used as a cooling and refluxing medium to hold back similar material for recycling. The feed stock, together with such reflux material, flows from the bottom of the tower 12 through a line 14 which includes a pump for forcing the oil at a pressure of from 400 lbs. to 600 lbs. per square inch, through a series of heating coils mounted in a pipe still heater 16. The oil enters the heater 16 through a preheater coil 18 and passes through coils 19 and 20 which are preferably arranged for separate firing so that any desired temperature gradient and final temperature of about 1100° F. may be maintained to produce a maximum of unsaturated or olefinic hydrocarbons and a minimum of coke deposit or carbon formation in the heating coils.

30 The tubes of the pipe still heater 16 are preferably of the usual diameter of from two to five inches, commonly used in cracking furnaces. The cracked products discharged from the coils 20 are conducted through a transfer line 22 into a tubular converter 24 which may be of any suitable length and which may be constructed as a single long tube or as a tube bank in which individual long tubes are connected by return bends

as shown in Fig. 1. The outlet end of the tubular converter extends into the side of a quenching and reflux chamber 26, as shown in Fig. 1.

The tubular converter 24, the structure of which is shown more in detail in Fig. 2, preferably comprises an outer steel casing 28, a relatively thick annular refractory insulation 30 on the inside of the casing 28, and a spaced porous refractory tube or tubes 32 spaced from the inside wall of the insulation 30, so as to provide a series of annular spaces to be supplied with air or steam, as pointed out hereinafter. The porous refractory tube is preferably made up of a series of connected hollow tile members having annular socket or expansion joint projections 34 which rest in the insulation 30 and serve to provide and establish the space between the insulation 30 and the body of the tile members comprising the porous refractory tube 32. Highly heated air is supplied to the space or spaces around the refractory tube 32 through lines 36 which extend through the steel casing 28 and the refractory insulation 30. Steam may be supplied directly to the space around the tube 32, or indirectly through the lines 36 by means of valved connections 38.

The steam and air connections for the tubular converter 24, as shown in Fig. 1, are arranged slightly different from the showing in Figs. 2 and 3. In Fig. 1, air is supplied to the apparatus through a line 40, including a compressor which forces the air at a pressure in excess of the vapor pressure in the tube 32 through an air heater 42 in which the air is raised to the desired temperature, for example, a temperature of about 1100° F., the air being conducted from the heater to a transfer and distributor line 44 from which air may be distributed to the various sections of the tubular converter 24 through the connecting valved branch lines 36. Steam may be supplied to the heater 42 from a steam supply line 46 which connects into the line 40, and steam from the line 46 may also be distributed to all or a portion of the converter 24 through valved branch lines 48. The lower section or length of the converter 24 may be supplied with steam from a line 50 having valved branch lines 52. The return bends of the converter 24 are constructed like the showing in Fig. 2.

The highly unsaturated olefinic mixture entering the inlet of the converter 24 from the transfer line 22, passes through the porous refractory tube 32 and is directly heated and raised in temperature by the heat developed from the air admitted to the space around the tube 32 and diffused therethrough. The air pressure around the tube 32 is maintained above the pressure inside the tube 32, which is preferably about 400 lbs. per square inch, so that air is diffused through substantially the entire area of the tube, and thereby produces an enveloping zone in which the carbon formed in the reaction is burned or oxidized, and in which portions of the hydrocarbons are also oxidized or burned. The air and steam is admitted to the various portions or sections of the converter 24 at such a rate as to produce and maintain any desired temperature gradient throughout the converter and drive off or oxidize any carbon which may approach the inner surface of the tube 32.

In carrying out the operations in the converter 24, the high temperature air delivered through the line 44 may contain a regulated proportion of steam admitted to the line 40, so as to control the amount of oxidation effected along the various

sections of the converter 24 and avoid localized overheating. The hydrocarbon reactions taking place in the converter 24 are exothermic in character, and in the formation of alkylated benzene hydrocarbons will produce considerable free carbon. The exothermic reactions may be further controlled by the introduction of steam in regulated quantities through the valved lines 48 and 52, or through lines 38 in the form of arrangement shown in Fig. 3. This steam may be used for diluting the air introduced through the lines 36 or for replacing the use of air in certain portions of the converter in order to maintain the pressure differential between the outside and inside of the tube 32. The proportions of air and steam may be further regulated in a view of temperature changes resulting from carbon oxidation by the water-gas reaction.

The tube 32 may have an inside diameter of from 5" to 8" and may vary from 75 feet to 300 feet in length, or longer, the dimensions being chosen so as to give a very short reaction time which will not be so long as to cause decomposition of the side chains of alkylated benzenes. The converter 24 is suitable for carrying out high temperature high pressure conversions that could not be effected in externally heated metal tubular heaters. The end of the converter 24 projects into the chamber 26, and the products discharged therefrom are quickly cooled with water or other suitable cooling liquid sprayed into the products from a spray head 54 which surrounds the outlet end of the converter in the chamber 26.

The products in the chamber 26 are cooled to a rather low temperature and thoroughly washed with heavy oils, the resulting condensate, carbon slurry, and wash liquid being withdrawn from the bottom of the chamber 26 through a valved line 56. A portion of this withdrawn oil is recirculated through a line 58 which terminates in a spray head in the upper portion of the chamber as shown. The excess of the heavy oil, including carbon, withdrawn through line 56 is discharged to storage or to a coking apparatus. The vapors in the upper part of the chamber 26 are refluxed and further cooled by contact with oil distillates which are largely revaporized in the cooling operation. Vapors at a temperature of about 600° F. are withdrawn from the upper part of the chamber 26 and conducted through a vapor line 60 into the lower portion of the fractionating tower 12 where they are rectified in contact with charging stock and overhead reflux. A portion of the condensate and charging stock reaching the bottom of the tower 12 may be withdrawn through a line 62 and forced by means of a pump therein into the upper portion of the chamber 26 where it flows down over baffles provided therein, as shown. If desired, a portion of this distillate stock may be introduced into the line 58 through a valved branch line 64 to aid in the cooling and washing of the conversion products in the chamber below the baffles. The proportion of oil withdrawn from the tower 12 through the line 62 is preferably controlled so that practically all is revaporized in the chamber 26. The pressure in converter 24 may be controlled by the valves in lines 56 and 60.

The fractionation carried out in the tower 12 is directed mainly to the separation overhead of all desirable aromatic hydrocarbons, particularly the alkylated benzene hydrocarbons, some of which may be of relatively high boiling point. The cut temperature on the tower 12, for example, may be from 400° to 500° F., the vapors

being taken overhead through a vapor line 66, condensed in a condenser 68, and collected in receivers and water separators 70. Non-condensable gases are removed from the separators and sent to a gas recovery system, not shown, through a line 72, water is withdrawn through lines 74, and the condensed hydrocarbon product is withdrawn through a valved line 76. A portion of this product is preferably used as reflux in the top of the tower 12 and may be supplied thereto through a line 78 containing a pump, as shown. The product produced in the conversion operation is withdrawn from the apparatus through the valved line 76 and sent to suitable fractionating apparatus, not shown, for separation of the various alkylated benzene derivatives, and the production of high aromatic high compression motor fuels if desired.

The  $C_2$ ,  $C_3$  and  $C_4$  hydrocarbons recovered in the gas recovery apparatus or from the fractionators handling the final product withdrawn through the line 76 may be returned to the conversion apparatus by a supply line 80 which leads directly to the coils of the pipe still heater 16. These returned hydrocarbons may be both paraffinic and olefinic, and the ones returned will depend on the market or other uses for various materials such as butane, isobutane, the butenes, propane, propene, ethane, and ethylene. Any of such hydrocarbons from an outside source may be used. It has been found that the introduction of  $C_3$  and other light hydrocarbons increases the production of aromatic hydrocarbons. The process may be operated as a once-through process by introducing all of the stock through the line 80, including hydrocarbon gases.

In Fig. 3, the converter 24 is shown in cross-sectional view with a slightly modified arrangement of the lines for supplying air and steam. Each of the three sections of the converter 24 are shown with the air distribution lines 36 connected directly into a main air supply line 82 which corresponds to the line 44 in Fig. 1. In Fig. 3 the steam is distributed to the lines 36 through valved distributor lines 38 from a main steam supply line 84. The line 84 is used in place of lines 46 and 50 in Fig. 1 and provides a simplified means for supplying steam to all of the sections or lengths of the converter. It is to be understood that the arrangement shown in Fig. 3 may be used in apparatus of Fig. 1, and that steam may be supplied to the central section of the converter 24, although for simplicity in the showing, this is not indicated in Fig. 1.

The operation carried out in the converter 24 involves a relatively close control of the pressure around the tube 32, so that it always equals or exceeds the pressure of the hydrocarbon vapors in the tube. Furthermore, air or oxygen or other combustion supporting gas, at a temperature of about 1100° F. aids in controlling the temperature in the converter since no heat is lost in raising the temperature of the air from atmospheric temperature to 1100° F. This reduces the air required by about 20%, and also reduces vapor consumption in tube 32. The entering vapors, consisting largely of the primary products of cracking in the coils 20, are quickly raised to a temperature of from 1350° F. to 1450° F., and maintained at this temperature while at the same time preventing the deposition of carbon on the inside wall of the tube 32. The operation is such that the vapors entering the converter 24 practically proceed through an annular layer or envelope of

burning carbon and gases along the inside wall of the tube 32. The oxygen in the air reacts with or burns hydrogen in the vapor stream to produce water, and burns the free carbon to form carbon monoxide. Some air is preferably supplied throughout the length of the converter 24 even though in some sections in the converter it may be necessary to supply some steam to prevent a runaway temperature condition caused by the exothermic reactions taking place, for example, in the first section of the converter. In fact, the air heated in the heater 42 may be diluted to a substantial extent with steam but not sufficient to interfere with the attainment of the high temperatures in the initial stages of the operation. The steam introduced through lines 48, 52 or through lines 38 (Figs. 2 and 3), will be a relatively low temperature, depending on the pressure, so that it will have a very substantial cooling effect when introduced into the tube 32 from the space between the tube 32 and the refractory insulation 30.

The improved process of the present invention may be illustrated in connection with the conversion of a paraffinic gas-oil stock which is introduced into the apparatus either through the line 10 or the line 80, until the apparatus is on stream, when, of course, the stock would be fed through the line 10 into the tower 12, unless a once-through operation is desired. In either case the gas-oil stock is supplied at a pressure of about 600 lbs. per square inch through the line 14 to the furnace 16, and therein heated and cracked at a final temperature of about 1100° F. The cracking in the coils 20 is preferably of such length as to produce substantially only primary cracking to olefins which comprises most of the vapors conducted through the line 22. The stream of vapors passed into the converter 24 is rapidly raised to a temperature of approximately 1350° F. and subjected to conversion for a period of approximately eleven seconds, at a pressure of about 400 lbs. per square inch, after which it is quickly cooled as it enters the chamber 26.

The reactions effected in the converter appear to be a combination of polymerization, cyclization, alkylation, isomerization and dehydrogenation reactions, which lead to the production of various cyclic and aromatic hydrocarbons, particularly relatively high boiling benzene hydrocarbons containing one or more side chains of from 2 to 6 carbon atoms. Some dialkyl benzene derivatives are formed and some alkylated benzenes having relatively long branched side chains, all of which as far as known have high antiknock values. Practically all of these hydrocarbons are recovered overhead from the tower 12 and subjected to fractionation in fractionating equipment, not shown. The toluene content of the overhead mixture recovered from tower 12 may be fractionated, for example, to produce various relatively pure fractions, such for example as a relatively pure fraction of toluene which may be treated with sulfuric acid or extracted with a selective solvent in the usual way and refracted to produce nitration grade toluene. Side chain aromatic hydrocarbons, such as toluene, the xylenes, ethylbenzene, n-propylbenzene, isopropylbenzene, and other related compounds, have very high critical compression ratios. Therefore, the aromatic production withdrawn through the line 76 may be used for the manufacture of aromatic motor fuels, or certain fractions thereof may be used for increasing the critical compression ratio of other motor fuels.

The process of the present invention may be varied in some respects, as for example by converting individual olefins, such as heptene or octene in the converter 24, but such materials are relatively expensive, and it is preferred to operate on relatively inexpensive stocks, such as gas-oil, kerosene, naphtha and similar materials alone or with hydrocarbon gases. The process may be carried out on a combination of stocks comprising liquid hydrocarbons introduced through the line 10, and normally gaseous hydrocarbons of the type referred to above, introduced through the line 20. A residual stock may be used by inserting a residuum separator between coils 19 and 20. Different stocks may require different temperatures and different operations for the furnace 10.

The converter 24 may be operated at any selected pressure from atmospheric to 400 lbs. and above, and at high temperatures which could not be used in pipe still heaters with metal tubes. Modifications of the type referred to, as well as others coming within the scope of the invention, are intended to be covered by the accompanying claims.

Having thus described the invention, what is claimed as new is:

1. In a process for manufacturing side chain benzene hydrocarbons in which a petroleum oil distillate stock low in aromatic hydrocarbons is cracked at a temperature of about 1100° F. in a cracking zone to produce a vapor mixture consisting largely of unsaturated olefinic hydrocarbons, the improvement which comprises passing the vapor mixture directly from the cracking zone into a tubular porous refractory converter through which the vapor mixture passes as a stream and is heated rapidly by an annular envelop of burning carbon, hydrogen and hydrocarbons produced by separately heating air to a high temperature and diffusing it while in a highly heated condition through the wall of said tubular converter around the stream of vapors passing therethru, said vapor mixture being heated in said converter to a temperature of from 1350° to 1450° F. for a matter of seconds, whereby hydrocarbons of said vapor mixture are converted to side chain benzene hydrocarbons and controlling the final temperature attained

by said vapor mixture in said converter by diffusing steam through the porous wall thereof.

a process for manufacturing side chain benzene hydrocarbons as defined by claim 1 in which the air is supplied to said converter at a temperature of approximately 1100° F.

3. In a process for the production of aromatic hydrocarbons and aromatic type motor fuels from petroleum stocks, the improvement which comprises superheating the vapors of the petroleum stock to a high temperature of about 1100° F., passing the superheated vapors into a tubular conversion zone in which the vapor mixture is further heated and raised in temperature to about 1350°-1450° F. by an annular envelop of burning carbon, hydrogen and hydrocarbons which envelop is produced by diffusing highly heated air through the wall of said tubular conversion zone around the stream of vapors therein, and controlling the final temperature attained by the vapor mixture by diffusing steam through the wall of said tubular conversion zone.

4. In a process for manufacturing aromatic hydrocarbons from petroleum oil stocks, the improvement which comprises passing a mixture of the petroleum oil stock to be converted with a substantial proportion of hydrocarbon gases into and through a pipe still furnace in which the mixture is vaporized and the vapors cracked at temperature of about 1100° F., passing the high temperature products from the pipe still heater into and through a tubular conversion zone in which the products are heated to a temperature of from about 1350° to 1450° F. by supplying a combustion supporting gas at high temperature to the outer surface of the stream in said conversion zone whereby portions of the stream are burned and deposition of carbon in the conversion zone is prevented, controlling the temperature attained by the products by admixing steam with said combustion supporting gas, passing the products from said conversion zone into a chamber and rapidly cooling them to a temperature of from 600° to 700° F., and passing the vapors from said chamber into a fractionating tower for the recovery of the desired aromatic hydrocarbons.

DAVID G. BRANDT.