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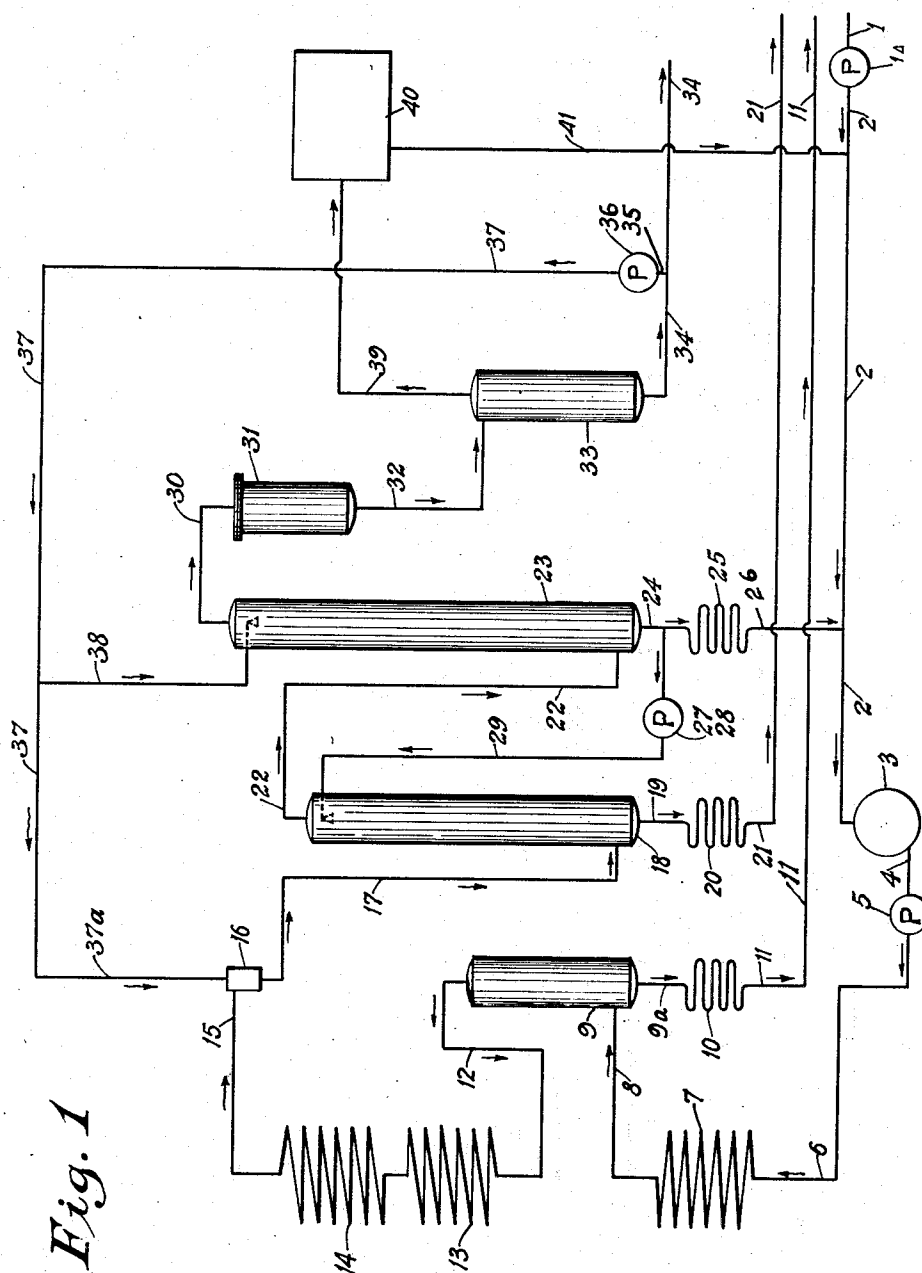
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Filed Dec. 30, 1937

2 Sheets-Sheet 1



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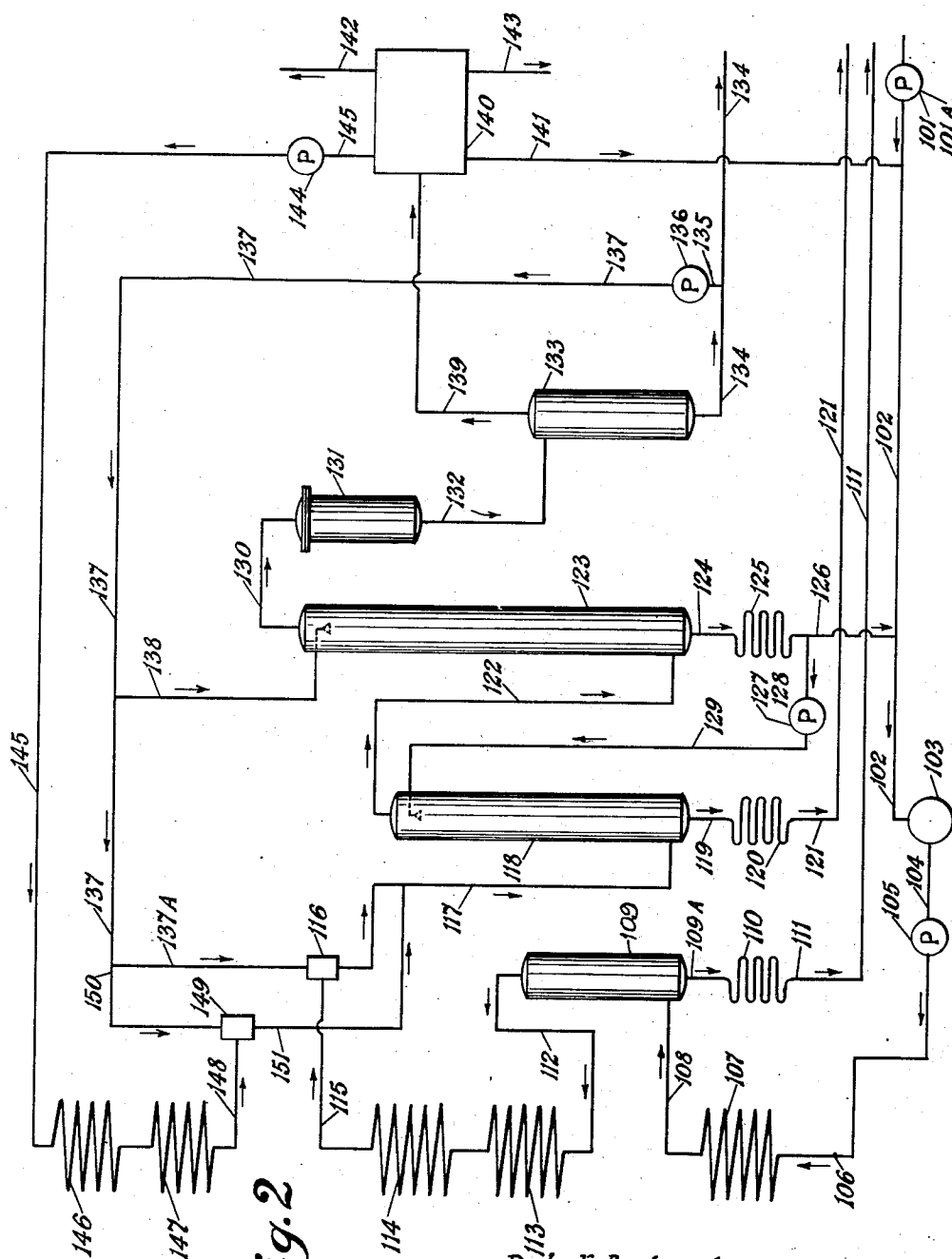
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UNITED STATES PATENT OFFICE

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PROCESS FOR THE PRODUCTION OF OLEFINS AND AROMATIC HYDROCARBONS

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5 Claims. (Cl. 260-668)

This invention relates to the manufacture of low molecular weight olefins and aromatics from petroleum, and more particularly, pertains to the production of normally gaseous olefins such as ethylene and normally liquid aromatics such as benzene, toluene, and xylenes.

The fundamental principles applied by petroleum refiners in producing gasoline and related products from hydrocarbon oils by pyrolysis at elevated temperatures have been known for a long time. It is also well known that most processes which have previously been proposed for making olefins and aromatics by oil cracking, convert relatively small proportions of the oil to olefins or aromatics and yield the latter in a very impure state. It is well known that the effectiveness of many of these processes is based on cracking conditions which are so severe that sustained continuous operation is impossible because of failure of materials of construction or due to blocking of vital equipment parts with carbon. This invention constitutes an improvement over existing methods.

One object of this invention is to provide an effective method for obtaining high yields of olefins, especially ethylene and/or propylene. Another object is the simultaneous conversion of an appreciable portion of a hydrocarbon oil to aromatic compounds and especially to benzene, toluene, and xylenes. A further object is the production of these aromatic compounds in a relatively pure state and in relatively high yields, from which undesirable contaminants can be readily removed. A still further object is the achievement of the above ends under such conditions that continuous operation is possible for long periods of time. Other objects will appear hereinafter.

This invention relates particularly to processes in which a hydrocarbon is cracked at high temperature in the vapor phase. In such processes the conversion products are usually separated into gas, light distillate, recycle, and refractory fuel oil fractions. The above mentioned objects are accomplished by the following invention which comprises recovering C_3 or mixtures of C_3 with C_4 and/or higher molecular weight hydrocarbons from the reaction products and especially from the gas fraction, and returning the C_3 alone, or mixed with C_4 and/or higher constituents, usually up to C_7 , to the oil cracking zone with fresh oil and/or recycle stock.

The invention will be more thoroughly understood by reference to the following specification and to the accompanying drawings in which the

preferred arrangements of apparatus for carrying out the invention are illustrated diagrammatically. Figure 1 is a flow sheet in diagrammatical form of a process and apparatus illustrating one embodiment of the invention. Figure 2 is a flow sheet in diagrammatical form of the preferred process and apparatus illustrative of the invention. It is to be understood that details of this equipment which are familiar to those versed in the art have been omitted for the sake of clarity, that modifications in constructional details and in the arrangement of parts may be made without departing from the spirit of the invention, and that said invention is not limited to such factors except as may be required by the claims.

Referring more particularly to the drawing designated as Figure No. 1, raw material, which may for example be gas oil or other petroleum oil, is delivered from a suitable storage through line 1 to pump 1A by means of which it is transferred via pipe line 2 to work tank 3. The fresh, raw material is mixed in work tank 3 with other oil fractions which will be subsequently described. The mixture leaves tank 3 through line 4 and is delivered by pump 5 through line 6 to preheating coil 7. This and other coils are suitably arranged in banks in a furnace setting. The preheating bank is preferably heated by the waste gases discharged from a combustion chamber of the furnace in order that the gases vented to the stack will be at a minimum temperature. The charging stock is forced serially through the tubes of preheating bank 7 in order that the oil may be heated to a vaporizing temperature of approximately 325° to 385° C. Ordinarily, little thermal decomposition of the oil takes place in preheating coil 7.

The material discharged from preheating bank 7 passes by way of pipe line 8 to an evaporator 9 wherein the high boiling constituents, which have remained in a liquid state at the preheater exit temperature, are dropped to the base of the evaporator and withdrawn through outlet 9A and passed, first through cooler 10, and then by means of pipe line 11 to suitable storage tanks. The lighter oils which are in a vaporized state in evaporator 9, pass overhead from the latter through outlet line 12 and are introduced into drying bank 13, which is situated in an intermediate temperature zone in the furnace setting, and, like preheating coil 7, is largely heated by waste products of combustion.

The oil passes serially through the tubes which comprise the drying bank and its temperature

is raised to about 460° to 490° C. The temperature-time relationship in this bank is so adjusted that extensive cracking does not occur. Owing to inefficient separation of mist and vapor in the evaporator and to condensation in transfer line 12, a small amount of liquid oil is sometimes charged to the drying coils. This liquid, however, is effectively evaporated in the drying bank, which discharges a substantially dry vapor.

After being thoroughly dried in coil 13, the hot vapors are introduced into a bank of cracking or conversion tubes 14. These tubes are arranged serially in the radiant section of the furnace setting, preferably around the sides and top wall of the main combustion chamber. It is desirable to raise the temperature of the vapors leaving the drying zone as rapidly as possible to the active conversion temperature, i. e. at least 650° C. and preferably about 690° to about 710° C. The vapors are maintained at this high temperature level in the latter portion or soaking section of bank 14. It will of course be realized that at this high reaction temperature, precautions must be taken to avoid the deposition of carbon in the reaction tubes and to prevent injuries to them. These difficulties are avoided by careful location of the tubes with respect to the furnace setting and burner flames and by maintaining high velocities of oil vapor through the tubes in order that the heat applied to them may be promptly absorbed and carried away.

The hot reaction products, which have been held at a substantially constant temperature in the soaking section of 14, are discharged through pipe 15 into arrester 16. The arrester is simply a chamber into which a cold, relatively volatile hydrocarbon fraction is introduced through a suitable spray nozzle. The hot reaction products and the cold spray are intimately mixed; the latter is largely evaporated, and the temperature of the reaction products is dropped almost instantaneously from about 700° to about 250° C. This quenching procedure terminates the cracking reaction abruptly. The mixture of quenched reaction products and vaporized quenching medium leaves the arrester by means of line 17 and passes to the base of flash tower 18. The function of this tower, which may be of any well known design suitable for distillation of hydrocarbon products, is to separate the high boiling constituents formed during the cracking reaction, from unconverted charge and lower boiling materials. The heavy oils and tarry materials, which may find use as fuel oils, are discharged from the base of the tower 18 through outlet 19 and cooler 20 and are finally sent to storage vessels through pipe line 21. The vapors which separate from the hot liquid at the base of tower 18 are scrubbed in the upper portion of the tower by descending, relatively volatile oil which has been introduced into the top of the column as reflux through line 23. The terminal temperature conditions of tower 18 are adjusted by varying the rates of quench liquid to arrester 16 and of reflux to the tower so that the vapors emerging from the top of the column to line 22 are free from heavy, tarry constituents and that the fuel oil fraction discharged at the base is substantially free from volatile constituents which might have further value as cracking stock.

The vapors issuing from the top of tower 18 pass by means of line 22 to the base of tower 23. Its purpose is to separate unconverted raw material or constituents in essentially the same boiling range from lower boiling liquids and fixed

gas. The gas and vapors pass up through and are scrubbed by the liquid on the trays of the fractionating tower. A light distillate having an end point of perhaps 150° to 200° C. is pumped into the top of tower 23 through line 28 to serve as reflux. Sufficient reflux is added in this manner so that the vapors, if cooled to condense constituents boiling in the gasoline range, give a condensate which has an end point of about 190° C. The higher boiling materials descend to the base of the fractionating tower where they are discharged by means of outlet line 24 through cooler 25. A portion of the cooled bottoms from the fractionating tower 23 passes to pump 26 through line 27 and is introduced by way of line 29 into the top of tower 18 to serve as reflux there. The remainder returns by means of lines 26 and 2 to work tank 3 where it is mixed with fresh charge and the steps outlined above repeated to effect further cracking.

The effluent vapors leave tower 23 through outlet 30, pass into condenser 31, and are there cooled to about 30° C. The pressure at this point is about 10 lbs. per sq. in. gauge. Under these conditions an appreciable amount of liquid is formed in the condenser and passes together with uncondensed vapors to a gas-liquid separator 33 by means of line 32. Light distillate is withdrawn from the base of this separator through outlet 34. A portion is delivered through line 35 to pump 36 which forces the material through line 37 and thence through lines 37A and 38 to furnish quenching medium and reflux to the arrester 16 and fractionating tower 23, respectively. The light distillate made above that used for the purposes just mentioned is withdrawn from the system to suitable storage tanks through line 34.

As much as 60% of the vaporized raw material may be converted to gas. Much of this gas is withdrawn from the top of separator 33 through line 39 as a complex mixture containing hydrogen, methane, ethylene, ethane, propylene, propane, butylene, butane, and higher boiling constituents.

The complex gas mixture is processed in recovery plant 40 to separate the high boiling hydrocarbons from lighter constituents. The equipment for achieving this separation is not indicated diagrammatically since it is not a part of this invention. It may be mentioned, however, that the higher boiling materials can be separated from the complex gas mixture by a series of steps involving compression, liquefaction, and rectification procedures or by compression, absorption, and rectification operations. The higher boiling constituents of the gas, which may consist of C₃ and higher hydrocarbons, are returned from recovery plant 40 to work tank 3 via lines 41 and 2. This recovered light distillate is here mixed with fresh charging stock and recycle stock and the mixture subjected to the cracking procedure outlined above.

It has been found that 18 to 20% of the vaporized fresh charge can be converted to ethylene by following the steps indicated above. At the same time, high yields of propylene and of ethane and C₄ hydrocarbons can also be obtained from the complex gas mixture sent to the gas recovery plant. Concurrently, high yields of light distillate containing principally benzene, toluene, and xylenes may be achieved. It has been found that there is a marked increase in yields of normally gaseous products comprising hydrogen to C₃ hydrocarbons, inclusive, and especially of the more

valuable constituents, ethylene and/or propylene, when constituents of higher molecular weight are separated from the gas fraction and recycled to the oil cracking zone, the cracked products being combined with the cracked products from the oil cracking zone. It has been observed that this method of operating not only increases the yields of benzene, toluene, and xylene but also greatly increases their concentration in the light distillate fraction. It is, for example, possible to produce a light distillate by these means in which the benzene, toluene, and xylenes aggregate in excess of 80%.

Is has also been found that this invention can be advantageously applied to a multistage oil and gas cracking process for manufacturing low molecular weight olefins and aromatics. A better understanding of this application of the invention may be obtained by reference to the drawing designated as Figure No. 2 in which a preferred arrangement of equipment is illustrated diagrammatically. Raw material, which again, for example, may be "gas oil" is subjected to the treatment previously described in detail with reference to Figure No. 1. A complex gas mixture containing hydrogen, methane, ethylene, ethane, propylene, propane, butylene, and higher boiling hydrocarbons is withdrawn from the top of separator 133 through line 139 and passed to recovery plant 140. Here the mixture is separated by liquefaction means into the following fractions: (1) hydrogen and methane, (2) ethylene, (3) a mixture of ethane, C₃ and C₄ hydrocarbons, and (4) higher boiling hydrocarbons. The hydrogen and methane fraction, which may serve as fuel, is discharged from the recovery plant through line 142. Ethylene is released via line 143 to suitable storage or directly to processes in which it may be used as a raw material.

The fraction comprising ethane and C₃ and C₄ hydrocarbons is delivered to pump 144, by means of which it is forced through pipe line 145 and thence into preheating coil 146. This and other gas treating coils are arranged in a furnace setting designed for high temperature service and the preheating coil is preferably situated so that it is heated largely by waste combustion gases. Such portion of the charge as may be in a liquid state under inlet temperature and pressure conditions is completely vaporized as it passes through the tubes of preheating bank 146 in which a final temperature of 650° to 700° C. is attained. The hot gases are then introduced into a bank of cracking or conversion coils 147 and are held at 760° to 790° C. in the latter portion of these coils which are preferably situated in a radiant section of the furnace setting. The time-temperature relationship in this coil is so regulated that about 50% of the incoming ethane, C₃, and C₄ hydrocarbons are converted to other compounds, for example, hydrogen, methane, ethylene, and hydrocarbons in the motor spirit boiling range. The 50% conversion mentioned above refers to the average of ethane, C₃, and C₄ conversions and not to a 50% conversion of each constituent. High vapor velocities are employed in the conversion tubes to prevent excessive tube wall temperatures and to minimize carbon deposition.

The hot reaction products are discharged from conversion zone 147 through line 148 into arrester 149. Arresters 149 and 116 are similar in design. The products of gas cracking are reduced instantly from reaction temperature to about 120° C. by quenching with a volatile fraction which

is withdrawn from line 137, through line 150 to the arrester spray nozzle. The mixture of quenched reaction products and largely vaporized quenching stock leaves arrester 149 by means of exit line 151, and joins a similar mixture discharged from oil cracking arrester 116. The combined, quenched products from oil and gas cracking pass to the base of flash tower 118 via line 117. From this point on the equipment for processing the reaction products is common to both cracking stages and with the exception of recovery plant 140, functions in the manner previously described for the case in which oil only is cracked.

The constituents comprising the higher boiling hydrocarbon fraction which is separated in recovery plant 140 are now obtained from the gas fractions produced by oil and gas cracking operations. This higher boiling mixture is discharged from recovery plant 140 through line 141 to line 102 in which it is returned to work tank 3. It is then mixed and recycled to the oil cracking zone with recycle stock and fresh feed.

As in the case in which oil only is cracked, it has been found that there is a marked increase in yields of gaseous products from hydrogen to C₃ hydrocarbons, inclusive, and of benzene, toluene, and xylenes when C₃ and higher molecular weight constituents are separated from gas produced by combined oil and gas cracking and recycled to the oil cracking zone. It has also been found that this procedure greatly increases the concentrations of benzene, toluene, and xylenes in the aromatic fraction.

Example

A hydrocarbon distillate with characteristics similar to those of the petroleum fraction known to refiners as "gas oil" was used as a cracking stock. This raw material was mixed in a work tank with partially cracked or recycle fractions in the ratio of 52.7 parts by weight of fresh charge to 47.3 parts of recycle stocks. The manner in which these recycle fractions were obtained will be described in detail later.

The above mixture was pumped at the rate of 355 lbs. per hour through a bank of preheating or vaporizing tubes arranged in series. These tubes were so mounted in a furnace setting as to be heated largely by waste gases passing from the main combustion chamber of the furnace to its stack. The oil mixture was heated to 345° to 350° C. in the preheating section and was discharged at this temperature into the lower part of an evaporator. This was a vertically mounted steel vessel with a segment above the oil inlet filled with packing rings. Eighty-two lbs. per hour of steam were also admitted to the evaporator. The high boiling constituents of the hot oil mixture dropped to the base of the evaporator and were withdrawn and cooled at the rate of 33 lbs. per hour. Since the constituents of the recycle stock were relatively low boiling, the evaporator bottoms were mostly uncracked high boiling ends from the fresh charge. The vaporized oil and steam passed overhead through the bed of packing, left the evaporator at 280° C., and then passed serially through the tubes of a drying coil in which the temperature of the vapors was raised to 470° C. After leaving the drying coil, the vapors were transmitted to a bank of cracking or conversion tubes which were arranged in series around the top wall of the main combustion chamber. The temperature of the

vapors was raised rapidly to 700° C. in the cracking zone and was maintained at substantially this temperature in a final or soaking bank which was also situated in the radiant section of the furnace.

The hot reaction products from the soaking zone were discharged to an arrester chamber and there intimately mixed with a cold spray of about 550 lbs. per hour of a light, distilled, hydrocarbon fraction. This procedure gave a temperature of about 270° C. at the arrester exit from which the mixture of quenched reaction products and vaporized quenching stock passed to the base of a fractionating tower. The quenched products from a second or gas cracking furnace, to be described later, were also received by the same tower. The heavy, tarry products of oil and of gas cracking accumulated at the bottom of the tower, and 44.9 lbs. per hour, suitable for fuel oil, were withdrawn and cooled. The lower boiling materials, including gas, steam, constituents in the gasoline boiling range, and unconverted charging stock were taken off overhead as vapor and passed into the base of a second fractionating column. Gas, light distillate, and steam were taken off the top of the second tower while higher boiling materials were discharged from its base and cooled. Three hundred and twenty pounds per hour of these cooled bottoms were pumped into the top of the first fractionating tower to serve as reflux there. The remainder was mixed with incoming fresh feed oil and other recycle stock and recharged to the preheating zone of the oil cracking furnace. The overhead vapor from the second fractionator was cooled in a condenser and the resulting mixture of vapor and condensate was discharged to a gas-liquid separating chamber. The two towers and the separator were operated at a pressure of 8 to 10 lbs. per sq. in. gauge. Water, condensed from steam admitted earlier in the process, was released from the base of the separator. Light distillate was pumped from this separator to the top of the second tower as reflux, as well as to the arrester of the oil cracking unit described above and also to that of a gas cracking unit to be described below. The excess, or make of aromatic distillate, was removed from the separator at the rate of 35.5 lbs. per hour.

Gaseous products of oil and gas cracking, amounting to 2,550 cu. ft./hr. (on water free basis at 0° C. and 1 atm. pressure) were vented from the top of the gas-liquid separator and conveyed to a gas recovery plant. The crude gas had approximately the following composition.

	Mol per cent
H ₂	9.9
CH ₄	22.4
C ₂ H ₄	21.9
C ₂ H ₆	9.6
C ₃	19.4
C ₄	5.5
C ₅ and higher	11.3
	100.0

The gas was separated in this plant into the following fractions: (1) hydrogen and methane, (2) ethylene, (3) a mixture of ethane, C₃, and C₄ hydrocarbons, and (4) C₄ and higher boiling hydrocarbons. Fraction 4, consisted chiefly of C₅, C₆, and higher hydrocarbons but also contained butylenes and butadiene. This fraction was sent to the work tank holding charging stock for the

oil cracking operation and was continuously mixed there with fresh feed oil and recycle stock from the base of the second fractionating tower. The composite of the above three stocks made up the charge to the oil cracking unit and was processed in the manner previously outlined. The unsaturated constituents of fraction 4 produced additional gas and liquid products and also underwent polymerization to aromatics when recycled through the oil cracking process. The aromatic compounds in this recycle fraction, however, were more refractory than the olefinic materials and passed through the cracking process substantially unchanged, thus favoring the production of a distillate predominantly aromatic in character.

Fraction 3 above, contained most of the ethane and C₃ and C₄ hydrocarbons present in the raw gas admitted to the gas recovery plant, as well as small percentage of C₅ hydrocarbons. This fraction was vaporized and forced, together with 28 lbs. per hour of steam, into a bank of preheating tubes in a separate gas cracking furnace. The mixture of steam and hydrocarbon vapor was heated to 700° C. in the preheating zone and was then passed serially through the tubes of a cracking or conversion coil in which the vapors reached a temperature of 770° to 780° C. As in the case of the oil cracking furnace, the preheating coil was heated largely by convection and the conversion coil chiefly by radiation. Approximately 50% of the aggregate charge was converted to products other than C₂H₆, C₃, and C₄ hydrocarbons in a single passage through the gas cracking furnace. The temperature of the hot cracked products was dropped almost instantaneously to 115° C. by quenching with cold distillate pumped from the gas-liquid separator into an arrester at the exit of the gas cracking coil. The quenched products joined a similar mixture from the oil cracking operation and both were fractionated into gas, light aromatic distillate, recycle stock, and refractory fuel oil in a common separation system.

It has been previously mentioned that the bottoms obtained from the evaporator used in the oil cracking operation were substantially unvaporized fresh feed oil. The following yields were obtained based on 100 parts by weight of vaporized fresh feed:

H ₂	10.9
CH ₄	16.5
C ₂ H ₄	28.3
Aromatic distillate	23.0
Refractory fuel oil	29.1
	97.8

¹ Prior to losses in gas recovery plant.

The aromatic distillate contained approximately 37% benzol, 26% toluol, and 20% xylenes. It should be understood that the successful application of this invention is not limited to the use of a single raw material. The use of gas oil has been mentioned but other stocks such as crude petroleum and topped or reduced crude may also be employed. A "viscosity breaking" operation may be used to advantage in conjunction with the oil cracking step if the raw material has a high pour point and high viscosity.

Steam was used to adjust the contact time in the cracking sections of the oil and gas furnaces mentioned in the foregoing example. The process, however, will function adequately without steam and its use is optional.

The invention pertains to improving the yield of olefins and aromatic hydrocarbons and is applicable to any cracking process where these products are obtained. In the cracking of hydrocarbons at temperatures in excess of 600° C. olefins and aromatic hydrocarbons are produced in substantial quantities, this invention is particularly applicable in such instances. The upper temperature limit of the cracking reactions in which olefins and aromatic hydrocarbons are produced depends upon the length of time the hydrocarbons to be cracked remain under the cracking conditions. The shorter the time of cracking the higher the temperature that can be used thus temperatures of about 900° C. have been used and it is possible to use even higher temperatures if the length of time of cracking is properly adjusted. In the tubular type cracking unit it is preferable to operate the gas cracking step at higher temperatures than the oil cracking step, usually at least 50° C. higher. When the oil vapor is cracked in the tubular type units described herein the cracking step may be carried out at 650° to 750° C., preferably at 690° to 710° C. and the time-temperature relationship is so adjusted that 40 to 60% of the total vaporized oil charge is cracked in a single passage through the cracking zone. It is also desirable to operate the gas cracking step in such a way that a per pass conversion of the same order of magnitude is achieved. It is possible that the gas cracking step could be carried out at a temperature the same as or lower than the oil cracking step provided that the length of time of cracking in the gas cracking step is properly adjusted to produce olefins and aromatic hydrocarbons.

It is desirable to maintain high vapor velocities in the high temperature zones to avoid overheating of cracking tubes and deposition of coke. It is also important from the standpoint of continuity of operation to effect an efficient separation between cracked tar and lower boiling materials. The necessity of avoiding carbonaceous material in recycle stocks is familiar to those versed in the cracking art.

The production of ethylene has been emphasized in the earlier description but other hydrocarbons, such as the lower olefins, can also be readily produced. For example, any part or all of the propylene in the raw gas may be separated in the gas recovery plant and withdrawn from the process. In this case, C_2H_6 and C_4 hydrocarbons, and any C_3 hydrocarbon not removed serve as charging stock for the gas cracking operation. The process is equally flexible as regards the production of ethane or of C_4 hydrocarbons. The production of an aromatic distillate rich in benzene, toluene, and xylenes has been particularly mentioned but higher aromatics, including naphthalene, may be obtained by operating the fractionation equipment so that distillate of a higher end point is produced.

It has been pointed out that yields of aromatics and of gaseous products of lower molecular weight than C_4 hydrocarbons can be improved by re cracking C_5 and higher hydrocarbons recovered from the raw gas produced by oil or oil and gas cracking. It is also advantageous to include some C_4 hydrocarbons in the recycle mixture, especially if these are rich in butylenes and butadiene. Another satisfactory method is as follows: (1) the high boiling hydrocarbons are recovered from the raw gas, such as obtained from the gas and liquid separator 33 or 133, (2) the C_5 and higher constituents, which are pre-

dominantly aromatic in character, are separated and withdrawn from the process, and (3) the C_5 or C_6 and some C_4 hydrocarbons which are predominantly olefinic, are recycled for further cracking and polymerization. An alternative procedure is to recover the high molecular weight constituents of the raw gas, such as obtained from the gas and liquid separators 33 or 133, and separate from this fraction and from light distillate from the gas-liquid separator, a C_5 and higher fraction rich in aromatics and a lower boiling fraction rich in olefins. The latter, which may contain chiefly C_5 or C_6 and C_4 hydrocarbons, is recycled to the oil cracking operation. The former fraction is withdrawn and processed to recover benzene, toluene, xylenes, etc. These modifications in character and methods of obtaining the light recycle fraction are equally applicable to single stage oil cracking or multiple stage oil and gas cracking.

The re cracking of C_5 or mixtures of C_5 with C_4 and/or higher molecular weight hydrocarbons recovered from products of cracking increases the yields of gaseous olefins and of aromatics. It also greatly increases the concentration of benzene, toluene, and xylenes in the crude aromatic product and produces this fraction in a relatively pure state from which undesirable contaminants can be easily removed by well known methods. A very important advantage of this invention is that the above results are obtained under such conditions that continuous operation is possible for long periods of time. It has, for example, been found extremely difficult, when the recycling feature outlined above is not employed, to obtain an aromatic fraction in equivalent yields and quality without encountering one or more of the following difficulties: (1) choking of equipment with coke, (2) overheating and burning out of cracking tubes, (3) an excessive production of hydrogen and methane at the expense of more valuable olefins, and (4) the production of heavy tar which is unsuitable for fuel oil. This invention effects marked improvements in yields and quality of valuable products and, at the same time, avoids all of the above, well known difficulties.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is not intended to be limited except as indicated in the appended claims.

We claim:

1. In the process of cracking at temperatures between 650° and 750° C. the vapors of hydrocarbon oil boiling within the range of gas oil so as to produce ethylene and aromatic hydrocarbons, the method of improving the yield of said ethylene and aromatics which comprises adding to the hydrocarbons to be cracked a hydrocarbon fraction comprising essentially a mixture of C_4 , C_5 , C_6 , and C_7 hydrocarbons.

2. In the process of cracking the vapors of a hydrocarbon oil boiling within the range of gas oil so as to produce lower olefins and aromatic hydrocarbons by passing hydrocarbon oil vapor through a cracking zone at a temperature between 650° and 750° C., the method of improving the yield of said lower olefins and aromatics which comprises separating from the cracked gaseous product a fraction consisting of a mixture of C_4 , C_5 , C_6 , and C_7 hydrocarbons, and returning at least a portion of same to the oil cracking zone.

3. In the process of cracking at temperatures

between 650° and 750° C. the vapors of hydrocarbon oil boiling within the range of gas oil so as to produce lower olefins and aromatic hydrocarbons, the method of improving the yield of said lower olefins and aromatics which comprises separating the desired lower olefins and aromatics from the cracked gases and then separating two hydrocarbon fractions, one comprising essentially a mixture of C₂, C₃, and C₄ hydrocarbons, and the other comprising essentially a mixture of C₄, C₅, C₆, and C₇ hydrocarbons, cracking at least a portion of the C₂ to C₄ fraction at a temperature higher than the temperature used in the first cracking step and returning at least a portion of the C₄ to C₇ hydrocarbon fraction to the first cracking step.

4. A process for the production of ethylene and aromatic hydrocarbons which comprises cracking at a temperature between 650° and 750° C. normally liquid hydrocarbons of petroleum oil boiling within the range of gas oil so as to produce ethylene and aromatic hydrocarbons, cracking in a separate step at a higher temperature ethane and C₃ and C₄ hydrocarbons, separating into separate fractions from the products of both cracking steps a hydrocarbon fraction consisting of a mixture of ethane and C₃ and C₄ hydrocarbons and another fraction consisting of a mixture of C₄, C₅, C₆, and C₇ hydrocarbons, returning at least a portion of the first-mentioned fraction to the last-mentioned higher temperature cracking step and recycling at least a portion of the

last-mentioned fraction by admixing same with the fresh feed to the first-mentioned cracking step.

5. A process for the production of ethylene and aromatic hydrocarbons which comprises removing from a normally liquid hydrocarbon fraction higher boiling tarry materials that may be contained therein, cracking the hydrocarbon fraction at temperatures between 650° and 750° C. so as to form ethylene and aromatic hydrocarbons, separating from the cracked products the heavy oils and tarry materials produced, then separating the unconverted raw material and materials in approximately the same boiling range, also separating a light aromatic distillate fraction, and finally separating the resulting cracked gaseous products into the following fractions—a fraction containing hydrogen and methane, a second fraction containing ethylene, a third fraction containing the aromatic hydrocarbons, a fourth fraction containing predominantly ethane and C₃ and C₄ hydrocarbons, and a fifth fraction consisting of a mixture of C₄, C₅, C₆, and C₇ aliphatic hydrocarbons; cracking at a higher temperature the fourth fraction and recovering from said cracked fraction additional ethylene and aromatic hydrocarbons, and returning to the first cracking step the fifth fraction together with the unconverted raw material and constituents in approximately the same boiling range.

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