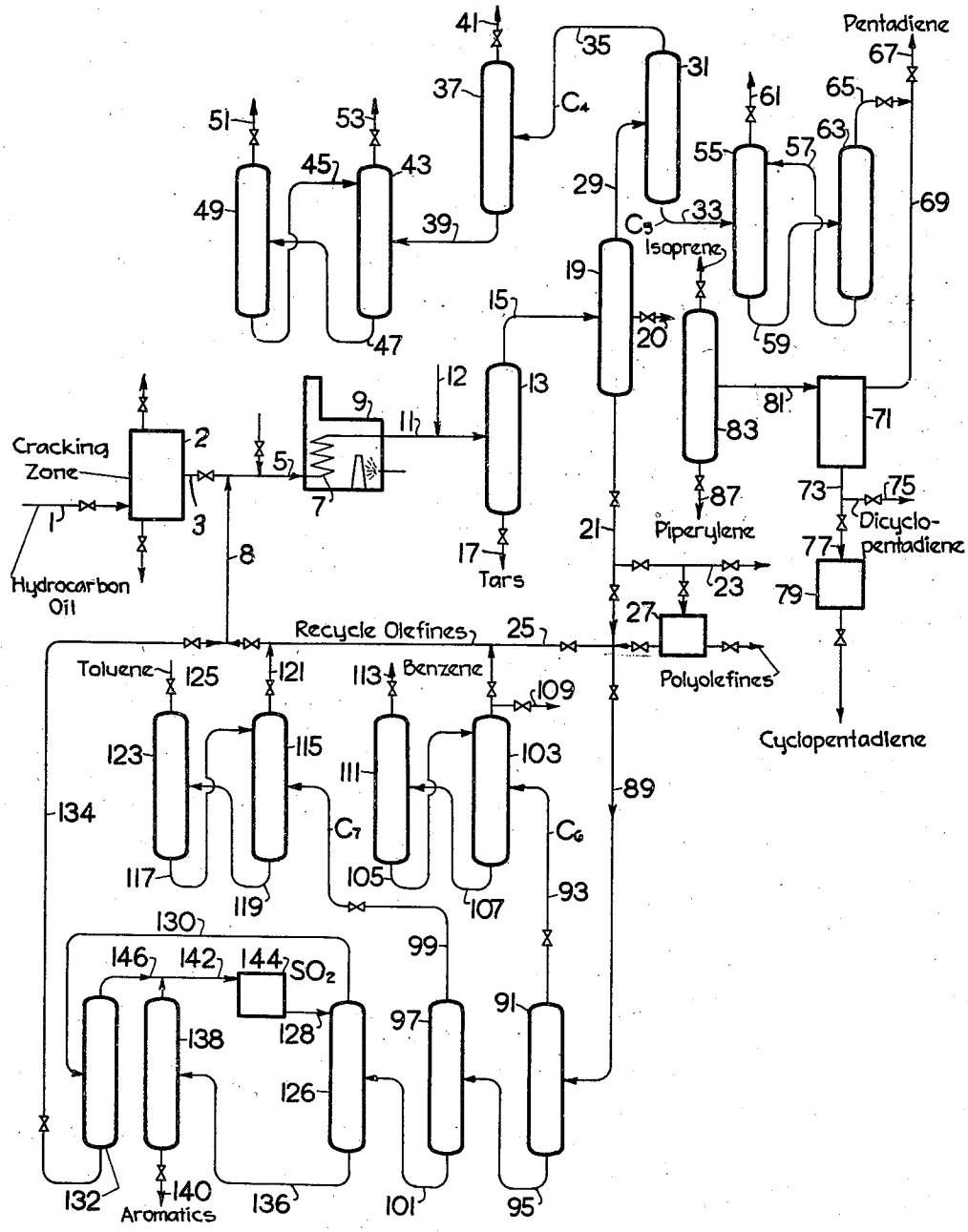
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PRODUCTION OF DIENES

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PRODUCTION OF DIENES

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This invention relates to the art of cracking hydrocarbons, and more especially to the manufacture of diolefines and other valuable products by vapor phase cracking of selected feeds.

Diolefines, and especially butadiene, isoprene and piperylene, are useful as starting materials in the manufacture of elastomers, that is, polymeric materials having elastic properties similar to rubber and finding successful applications in different arts.

It is well known to prepare dienes by dehydrogenation of corresponding olefines, by dehalogenation or dehydrohalogenation of corresponding halogen derivatives, dehydration of corresponding alcohols, etc. These methods, however, have certain disadvantages, for example, the cost involved in preparing the starting materials.

It is also known that cracking of hydrocarbons often yields minor proportions of dienes, particularly of butadiene. The proportion of the diene in the cracked products is, however, small and it is associated with major amounts of saturated and ethylenic hydrocarbons having nearly equal vapor pressures. Thus, the recovery of the dienes is difficult and their yields are small.

It is an object of this invention to provide a process for the manufacture of valuable hydrocarbons, especially dienes and particularly butadienes, by cracking a selected hydrocarbon stock which is readily available. Another object is to produce hydrocarbon fractions rich in di- and mono-olefines and aromatic hydrocarbons, from which the dienes can be separated in a simple manner. Another purpose is to pyrolyze, i. e., to crack, selected cracked naphthas in order to raise their octane numbers and to produce large amounts of normally gaseous diolefines rather than mono-olefines. Still further objects include simplified procedures, decreased cost in the manufacture of dienes, and other improvements found hereinafter.

We have found that when pyrolyzing cracked gasoline distillates in the vapor phase at temperatures above 600° C., gases may be obtained which contain very large proportions of dienes, much larger than those obtainable by cracking under similar conditions of straight-run hydrocarbon oils including gasolines, and that selected fractions of such gases may comprises almost 50% pentadienes.

Accordingly, our invention comprises pyrolizing cracked gasoline distillates so as not only to raise materially the octane numbers of resulting pyrolyzed fractions boiling within gasoline boiling range over those of the feeds, but also simultaneously to produce normally gaseous fractions which are exceedingly rich in diolefines. Our complete process calls for a pre-cracking by conventional cracking methods of straight-run hydrocarbon oils such as naphthas, kerosene, gas oils, etc., at temperatures below 600° C., separating from the cracked product a gasoline distillate and further pyrolyzing the latter in the vapor phase at temperatures above 600° C.

The pre-cracking may be conducted either in the liquid, mixed or vapor phases, depending on the results desired. Suitable pre-cracking temperatures should be below 600° C. and may in general be between 400° and 600° C. Pressures may range from atmospheric to 5000 p. s. i. and more. If desired, the cracking may be conducted in the presence of catalysts, preferably catalysts which do not promote cyclization of olefines such as activated alumina, zeolites, silicates, etc.

Cracked gasolines always contain olefines and aromatic hydrocarbons in amounts which vary with the conditions of cracking. The number of olefinic double bonds may be estimated by the bromine number which is determined, for example, by the method of Uhrig and Levin, Industrial and Engineering Chemistry, Analytical edition, 13 90, 1941. The content of aromatics may be calculated from its bromine number and specific dispersion by a method such as that described by Grosse and Wackher, Industrial and Engineering Chemistry, Analytical edition, 11 614, 1939.

In general, higher cracking temperatures and pressures, and particularly higher residence times favor the production of aromatics. Under more moderate conditions of temperature, time and pressure, mono-olefines are formed in larger amounts. Thus cracking at relatively low temperatures, i. e., below about 540° C. (1000° F.), gives in general relatively low proportions of aromatics but may result in high contents of olefines. Therefore, cracked gasoline distillates obtained in this way are in general preferred over those originating by cracking at temperatures above about 540° C.

As indicated above, we prefer to re-crack gasoline distillates containing substantial amounts of mono-olefines, such distillates yielding, on cracking at temperatures above 600° C., particularly large amounts of dienes and especially of pentadiene. Thus gasoline distillates having bromine numbers above 40, and preferably above 60, are especially suitable as the feed which is re-cracked.

The presence of aromatic hydrocarbons in the pre-cracked gasoline distillate does not by itself reduce its suitability. However, aromatics are normally formed at the expense of olefines and thus a high content of aromatics is usually accompanied by a relatively low content of olefines. Moreover, aromatics do not on cracking contribute to the formation of diolefines. Therefore, pre-cracked distillates having aromatic contents below about 30%, and preferably below about 15%, are particularly suitable.

Relatively low boiling lean distillates, particu-

larly those boiling up to about 120° C., are preferred, as they give in general higher yields of dienes than higher boiling distillates from the same source. This may be due to the fact that in general relatively low boiling fractions have higher bromine numbers, i. e., higher olefine contents than the heavier fractions from the same source.

Suitable pre-cracked gasoline distillates may contain minor proportions of C_4 and C_5 hydrocarbon, but the main portions should consist of C_6 and higher hydrocarbons which yield C_4 and C_5 dienes by breaking of carbon-carbon bonds, rather than by dehydrogenation, the latter requiring conditions different from those necessary for optimum diene production by carbon-carbon scission.

Cracked gasolines, unless refined, generally contain highly unstable components, such as those known as gum-forming compounds, e. g., polyolefines, certain branched and other highly reactive olefines, styrenes, etc., which, upon re-cracking, are apt to form tars and coke. Likewise, nitrogen, sulfur, oxygen, etc., derivatives, particularly the so-called petroleum bases, may also favor coke formation if present in excessive amounts. These objectionable components may be removed by any suitable means prior to re-cracking, such as by extraction with a liquid having greater solvent power for aromatics than for paraffinic hydrocarbons, for example, liquid SO_2, nitrobenzene, phenol, cresol, methyl acetate, phenyl acetate, methyl or ethyl cellosolve, furfural, acetone, aniline, cresylic acids, dichlorethyl ether, etc., alone or in combination with an anti-solvent such as propane, under conditions to cause mono-olefines to remain in the resulting raffinate; or by treatment with adsorption agents such as clay, bauxite, fuller's earth, diatomaceous earth, silica gel, etc., preferably at elevated temperatures below incipient cracking; or by sulfuric acid or phosphoric acid treatment at suitable concentrations to produce a sludge containing the undesirable constitutents which can be separated without materially affecting mono-olefines, etc.

When compared with the vapor phase cracking above 600° C. of straight-run gasolines, it is found that the described pre-cracked gasolines give a much larger yield of diolefines, and particularly pentadienes.

When compared with the vapor phase cracking of heavier-than-gasoline hydrocarbons, our process gives a higher concentration of dienes in the C_4, and particularly in the C_5, fraction and, furthermore, coking and carbon formation is greatly decreased so that the cracking operation is very appreciably facilitated.

Thus, according to this invention, a cracking stock consisting mainly of cracked gasoline distillates, and preferably a mixed phase cracked gasoline having a bromine number above 40 and containing less than 30% aromatics, is cracked in the vapor phase at temperatures above about 600° C. and pressures not substantially above atmospheric for a time to gasify and transform in one or several passes a major portion of said gasoline into normally gaseous products.

The vapor phase cracking to produce the dienes is conducted so as to gasify 15%–85% of the feed per pass. We define as gasified that part of the cracked products which consists of molecules having less than six carbon atoms. The cracking temperature, i. e., the maximum temperature to which the cracking stock is heated, is above 600° C., preferably 650°–850° C.

The resulting cracked products are rapidly quenched and then fractionally distilled, preferably under conditions to produce separate C_4 and C_5 fractions, and from them the dienes, which constitute substantial proportions thereof, are isolated by conventional methods. Other products obtained in this process include, besides the dienes, tar, tar-free naphtha or middle oil, or both, and gases lighter than naphtha containing high percentages of mono-olefines.

These products may be withdrawn, treated and used as may be convenient. Certain portions of them may, however, advantageously be utilized within the process.

The composition of the cracked naphtha obtained in this process varies with the intensity of the cracking, i. e., it may substantially retain the composition of the cracking feed, or it may have become much more aromatic.

If the cracking is relatively superficial, i. e., the gasification per pass is of the order of 15%–50%, the ungasified portion of the cracking stock is but little aromatized, and may therefore be re-cracked and treated like the original cracking stock, for example, by recirculation as part of said stock. Or else a reformed gasoline of high octane number may be recovered from it.

If the cracking is deep, i. e., the gasification is of the order of 50%–85%, the naphtha fraction of the cracked products may contain large amounts of aromatic hydrocarbons which are formed by secondary reactions such as polymerization, condensation, cyclization, etc., of the primary products. In this case, it is advantageous to separate valuable aromatic hydrocarbons such as benzene, toluene, styrene, etc., from the naphtha fraction and then, if desired, to further crack remaining non-aromatic components. This latter procedure, i. e., the deep cracking, is often preferable because the yields of diolefines in the gaseous products are higher and, simultaneously, liquid products are produced which are valuable per se. However, if it is not desirable to recover aromatics, the former procedure, i. e., superficial cracking, is often preferable.

The cracking may also be conducted for intermediate gasification, such as about 40%–50%, to produce a relatively large proportion of gasoline of high octane number. Aromatics are thereby formed in small though appreciable amounts which are sufficiently large to be objectionable in further cracking, yet not large enough to make their recovery desirable.

The naphtha fraction may also contain polyolefines having six and more carbon atoms. These hydrocarbons may be desirable in themselves. On the other hand, they may interfere, for example, in the cracking because of their tendency to polymerize, or in the recovery of aromatics with the aid of selective solvents because of their solubility therein which comes close to that of aromatics. It is thus often desirable to separate and eliminate them.

The cracking in this process is conducted at pressures of about atmospheric or below, and preferably not substantially above 100–150 lbs. p. s. i. Thus, pressures above atmospheric sufficient to overcome the resistance of conduits, condensers and other equipment which follow the cracking zone may be maintained therein. If desired, the cracking may be conducted in the presence of steam, nitrogen and other substantially inert gases and the concentration of

such gases may vary from traces up to 80% of the mixture.

The heating of the hydrocarbons to the cracking temperature may be achieved by contact with a heated surface, for example, in an externally heated coil, or in a preheated brick checker work; or by admixture of hot, substantially inert gases; or by a combination of both methods. The rate of heating should be as high as possible to avoid undesirable side reactions at the intermediate temperatures. In order to avoid destruction of dienes formed in the cracking, the cracked product should be quenched rapidly from the cracking temperature down to safe temperatures, preferably below about 400° C.

In order to prevent excessive coke formation in the cracking zone, it is often preferred that this zone be constructed of non-ferrous metals or alloys containing less than predominating amounts of iron. Materials which do not cause rapid coke formation, such as copper-containing alloys, e. g., aluminum- or phosphor-bronze, or refractory ceramics, are thus preferred in the construction of surfaces which are exposed to hydrocarbons at cracking temperatures.

The velocity at which the gases pass through the cracking zone depends on the exact result desired, the temperature and pressure of cracking, and the dimensions of the cracking zone. The space velocity necessary to produce the desired degree of gasification increases rapidly as the cracking temperature is raised. The real velocity of the gaseous hydrocarbons in the cracking zone is very difficult to determine accurately because the volume of the cracking stock changes rapidly under the cracking conditions. Therefore, in defining this invention, we prefer to utilize the concept of liquid space velocity which is the liquid volume of the feed delivered to the cracking zone per volume of said zone per hour. The cracking zone is defined as the space occupied by gas in which the temperature is within 20° C. of the maximum cracking temperature. Liquid space velocity can be accurately measured and, for a given pressure, temperature and dilution, determines the real space velocity of the vapors.

Our process is illustrated in the accompanying drawing which represents a simplified flow diagram of an embodiment of this invention.

For simplicity, the drawing does not show pumps, tanks, heat exchangers, valves, by-passes, vents, reboilers, condensers, coolers, and other auxiliaries, the proper placement of which will be at once evident to those skilled in the art.

A hydrocarbon oil is introduced from storage, not shown, through line 1 into cracking and distilling zone 2, wherein a cracked gasoline distillate is prepared and withdrawn through line 3. The cracked gasoline so obtained is preferably refined in refining zone 4 where it is treated to remove gum-forming and non-hydrocarbon components. The refined cracked gasoline distillate is then withdrawn through line 5. Suitable recycle stock obtained in the process as hereinafter described may be admitted through line 8 into line 5.

The mixed liquids are led through line 5 into cracking coil 7 in furnace 9 in which the desired conditions of temperature, pressure and residence time are maintained, for example, at 700° C., atmospheric pressure and a liquid space velocity of 300, so as to effect a gasification of about 25%.

The cracked products which leave reaction coil 7 through line 11 are quenched with suitable quenching fluid introduced through line 12 from a source not shown, and are separated from tars and other relatively heavy materials in fractionator 13. The lighter products, including gases and naphtha, are taken overhead through vapor line 15. The heavier products are withdrawn from the system through line 17.

The products in line 15 pass into stabilizer 19, wherein an overhead fraction consisting essentially of C_5 and lighter components is separated from a heavier naphtha fraction; the latter, substantially free of C_5 and lighter components, is taken through line 21 and may go through line 23 to storage not shown, or preferably may serve as recycle stock which is returned through lines 25 and 8 to the cracking coil 7. If the cracking stock is composed of hydrocarbons substantially heavier than C_5, it is advantageous to also eliminate from the recycle stock those components formed during cracking which are lighter than the original cracking stock. This can be done by withdrawing an appropriate side stream from fractionator 19 through line 20.

If desired, the polyolefines contained in this naphtha fraction may be separated in zone 27, for example, by extraction with a suitable complex-forming reagent, e. g., $CuCl_2$, AgCl, SO_2, etc., or by polymerization with or without suitable catalysts such as poly-oxy acids, e. g., H_2SO_4, H_3PO_4, etc., or Friedel-Crafts catalysts, or by the Diehls-Alder reaction involving the use of maleic anhydride-type reagents, etc.

The overhead C_5 and lighter fraction from stabilizer 19 is taken through conduit 29 to a fractionating system wherein it is subjected repeatedly to fractional distillation. In column 31 a bottom fraction is produced comprising predominantly hydrocarbons having five carbon atoms, which is taken through line 33, and a lighter fraction substantially free from C_5 components. The latter is taken overhead through line 35 to fractionator 37, where a bottom fraction comprising predominantly hydrocarbons having mostly four carbon atoms is produced and withdrawn through line 39. Remaining gases substantially free from C_4 and heavier components are withdrawn overhead through line 41.

Thus, separate C_3 and C_4 fractions are taken through lines 33 and 39, respectively.

The C_4 fraction which contains butadiene is led through line 39 to column 43, wherein it is subjected to extractive distillation with a suitable solvent having a relatively high boiling range and greater solvent power for butadiene than for butylenes and butanes. This liquid is supplied to the top of extractor 43 through line 45 and is contacted with the ascending C_4 vapors so as to produce a "fat" solvent charged with substantially pure butadiene. This fat solvent is eliminated from the bottom of the column 43 through line 47. This "fat" liquid is separated by fractional distillation in fractionator 49 into the "lean" solvent and butadiene. The butadiene so produced is withdrawn through overhead line 51 while the "lean" solvent is drawn off at the bottom through line 45 and is returned to extractor 43. The butylenes and butanes separated from the butadiene in column 43 are withdrawn through line 53. The large proportion of olefines in this fraction makes it valuable for the manufacture of polymer or alkylate gasoline.

The C_5 fraction, rich in pentadiene, is given a treatment similar to that of the C_4 fraction. Line 33 leads it to column 55, wherein it is extracted in

the vapor phase by a lean solvent supplied through line 57. The fat solvent is drawn off through line 52, and the residual pentanes and amylenes are withdrawn through line 61. The fat solvent is fractionally distilled in fractionator 13 to isolate pentadienes which are withdrawn through line 65, while the lean solvent is recirculated through line 57.

Suitable solvents for the vapor phase extraction of dienes include, for example, alcohols such as butyl alcohols, amyl alcohols, cyclohexanol, etc.; aldehydes such as furfural, acrolein, crotonaldehyde, etc.; ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, acetophenone, cyclohexanone; ethers such as di-isopropyl ether, dichlorethyl ether, dioxane; organic nitrogen bases such as aniline, toluidine, phenylhydrazine, ethylene diamine, ethanol diamine, phenols such as phenol, cresol, xylenols; esters such as ethylene chlorhydrin, dimethyl phthalate, diethyl tartrate, ethylene dichloride, lactic acid nitrile, acetonitrile, di-isopropyl or allyl sulfate, ethyl borate or ethyl orthosilicate; other organic derivatives of mineral acids such as nitrobenzene, nitromethane, nitroethane, and many other polar compounds.

The recovered pentadienes usually comprise a mixture of isoprene (2-methyl butadiene), piperylene (n-pentadiene) and cyclopentadiene. This mixture may be either withdrawn through line 67 or, if desired, may be further fractionated to separate the several C_5 dienes from one another by leading it through line 69 to zone 71, where the cyclopentadiene is dimerized by subjecting the mixture to moderate heat in the liquid phase. The resulting product is fractionally distilled, the dimer forming the distillation residue which is withdrawn through line 73 to be withdrawn through line 75, or to be regenerated by exposure to high temperature and vacuum in a depolymerizing zone 79, to which line 77 leads. The vapors of the a-cyclic pentadienes are removed from the dimerization zone 71 through line 81, and may be further separated in fractionator 83 to produce isoprene which is taken overhead through line 85 and piperylene, which is obtained at the bottom, through line 87.

The process as illustrated in Fig. 1 can also be carried out in a different manner if desired. The cracking in coil 7 may be intensified, for example, by reducing the space velocity to about 20 under the same conditions of pressure and temperature so as to obtain a gasification of about 65%. The naphtha fraction produced under these circumstances and taken through line 21 from fractionator 19 contains aromatic hydrocarbons.

These valuable hydrocarbons may be separated and the recycle stock recovered by convenient methods, such as fractional and extractive distillation, or liquid-liquid extraction, or both. For example, the liquid withdrawn through line 21 is led through line 89, and preferably through zone 27 where it is freed of polyolefines, to fractionator 91 wherein it is split into a narrow C_6 overhead fraction taken through line 93 and a bottom fraction of C_7 and heavier components withdrawn through line 95. This line leads to fractionator 97, wherein another narrow C_7 overhead fraction is separated and taken through line 99, and a bottom fraction substantially free from C_7 hydrocarbons which is withdrawn through line 101, either to be discarded or further treated, as will be described.

The C_6 and C_7 fractions thus separated are rich in benzene and toluene, respectively.

The C_6 fraction is conducted through line 93 to column 103 wherein it is subjected to extractive distillation with a lean selective solvent for aromatics introduced through pipe 105. The fat solvent rich in benzene leaves through line 107 and the residual C_6 hydrocarbons are withdrawn overhead through line 109 or may be returned to the cracking coil 7 through lines 25 and 8. The fat solvent is fractionally distilled in fractionator 111 so that the lean solvent is recovered as the bottom fraction and returned through line 105 to extractor 103, and the benzene is obtained overhead through line 113.

The gaseous C_7 fraction is conducted through line 99 to column 115 wherein it is extracted with a lean solvent for aromatics introduced through line 117. The fat solvent rich in toluene leaves through line 119, and the residual C_7 hydrocarbons are withdrawn overhead through line 121 and may be returned to the cracking coil 7 through lines 25 and 8. The fat solvent is fractionated in fractionator 123, so that the lean solvent is recovered as the bottom fraction and is returned through line 117 to extractor 115. The toluene is obtained overhead through line 125.

Suitable solvents for the recovery of aromatics by extractive distillation are, for example, phenol, cresylic acids, alkyl phenol mixtures, aniline, alkyl anilines, diphenyl amine, ditolyl amines, carbitols (diethylene glycol mono-ethers) such as methyl, ethyl and propyl carbitols, chlorinated dialkyl ethers such as beta-beta-dichlorethyl ether, nitrobenzene, nitrotoluene, nitroxylenes, naphthols, alkyl naphthols, benzo phenone, phenyl tolyl ketone, diphenyl ketone, alkyl phthalates such as dimethyl phthalate, alkyl salicylates such as methyl salicylate, benzyl alcohol, benz chlorides, i. e., benzyl, benzal, and benzo chlorides, benzonitrile, diphenyl oxide, ditolyl oxide, hydroxy pyridine, nitropyridine, chlorinated pyridines, quinoline, isoquinoline, chlorinated quinoline, hydroxy quinolines, 5-nitro quinoline, tetrahydrofurfuryl alcohol, furfural alcohol, furfural, the mono glycerol ethers, such as 1-methoxy glycerol, 2-methoxy glycerol, 1-ethoxy glycerol, 2-ethoxy glycerol, 1-propoxy glycerol, 2-propoxy glycerol, 1-isopropoxy glycerol, 2-isopropoxy glycerol; the glycerol di-ethers such as 1,2-dimethoxy glycerol, 1,3-di-methoxy glycerol, 1,2-di-ethoxy glycerol, 1,3-di-ethoxy glycerol, 1,2-dipropoxy glycerol, 1,3-di-propoxy glycerol, 1,2-di-isopropoxy glycerol, and 1,3-di-isopropoxy glycerol; the mixed di-glycerol ether esters such as 1-ethoxy, 2-methoxy glycerol, 1-methoxy, 3-propoxy glycerol, and 1-ethoxy, 2-isopropoxy glycerol.

The heavier than C_7 bottom fraction from fractionator 97 obtained through line 101 contains aromatics. The latter are preferably separated by liquid-liquid extraction with a liquid having greater solvent power for aromatics than for olefinic hydrocarbons, for example, liquid SO_2. For this purpose, the hydrocarbon liquid is delivered through line 101 to extractor 126 wherein it is extracted with liquid SO_2 entering through conduit 128. The raffinate passes through line 130 to a stripper 132 wherein it is stripped of dissolved SO_2 and thence is preferably returned to the cracking coil 7 through lines 134 and 8. The extract containing aromatics is conveyed from extractor 126 through line 136 into separator 138 wherein a bottom fraction comprising mainly SO_2-free aromatics and an overhead fraction of SO_2 are produced. The aromatics are obtained through conduit 140 while the SO_2 is taken overhead through line 142 to be liquefied in cooler

144 together with the SO_2 taken from stripper 132 through line 146. The liquefied SO_2 is then re-introduced through conduit 128 into extractor 126.

Other solvents suitable for the liquid-liquid extraction are, for example, nitrobenzene, methyl acetate, phenyl acetate, methyl or ethyl cellosolve, furfural, acetone, aniline, phenol, cresylic acids, dichlorethyl ether, antimony trichloride, SO_2 benzene mixtures, or combinations of solvents and anti-solvents such as phenol or cresol with propane, etc.

If desired, the charge in line 89 may by-pass the fractionators 91 and 97 through a by-pass not shown and all the aromatics separated by liquid-liquid extraction in extractor 126, as described; or alternatively, if desired, the liquid-liquid extraction step may be replaced by further fractional and extractive distillation of the several fractions.

The separation of buta- and pentadienes may be conducted as described above by extractive distillation or other vapor phase extraction with similar solvents; or by azeotropical distillation in the presence of anhydrous ammonia, methylamine, CO_2, lower alcohols, etc.; or by liquid-liquid extraction with acetone, furfural, aniline, phenol, etc.; or through formation of complex compounds with copper or silver salts, SO_2, etc.; or by polymerization under the influence of heat, pressure, light, or catalysts such as Na, K, H_2SO_4, H_3PO_3, P_2O_3, $AlCl_3$, etc.; or a combination thereof.

It may sometimes be preferred to separate the dienes or the aromatics, or both, without prefractionation or following a degree of fractionation less thorough than described. Alternatively, it may also sometimes be desirable to produce a sharper fractionation before further recovery or to use directly fractions rich in dienes or aromatics, or both, produced by very sharp fractionation.

The following examples further illustrate our invention:

A cracked gasoline distillate obtained by liquid phase cracking of a California crude and having a boiling range of 98° to 205° C., an ASTM octane number of 65, a bromine number of 57 and an aromatic content of 15% was cracked in a bronze tube filled with quartz chips at 750° C. with a liquid space velocity of 182. Gasification was 40%. The gaseous products had the following composition:

	Per cent
H_2	0.7
CH_4	13.0
C_2H_4	21.1
C_2H_6	5.5
C_3H_6	19.8
C_3H_8	1.5
C_4H_6 butadiene	6.8
C_4H_8	13.8
C_4H_{10}	0.3
C_5H_8 pentadiene	7.5
C_5H_{10}	9.0
C_5H_{12}	0.8

From the ungasified portion, a gasoline was recovered amounting to 51.8% of the charge and having an ASTM octane number of 75.

A cracked gasoline distillate (ASTM boiling range 42°–115° C.) produced by liquid phase cracking in a Dubbs cracking unit of California gas oil was recracked in a phosphor-bronze tube at a temperature of 750° C. and space velocity of 128. Gasification was 64%. Analysis of the recovered gas was as follows:

	Per cent
C_3 and lighter components	39.3
C_4H_6 butadiene	5.3
NC_4H_8	8.4
Iso-C_4H_8	4.5
C_4H_{10}	.4
C_5H_8 pentadienes	8.3
C_5H_{10}	16.4
C_5H_{12}	17.4

We claim as our invention:

1. In the process of producing diolefins the steps comprising cracking a straight run hydrocarbon oil selected from the group consisting of naphtha, kerosene and gas oil at a temperature below 540° C., fractionating the resulting cracked products to produce a cracked distillate consisting of C_5 and higher hydrocarbons boiling below about 120° C., having a bromine number above 60 and an aromatic content below 15%, treating said distillate to remove gum forming components, pyrolyzing said cracked distillate and a recycle oil produced in said process in the absence of metals containing predominating amounts of iron at a temperature between 650° C. and 850° C. under conditions to gasify 15–85% thereof, whereby diolefins are formed and separating from the resulting cracked products at least the following fractions: a diolefin fraction, said recycle oil which is substantially free of tarry and normally gaseous hydrocarbons and contains less than 30% aromatics, and a tarry fraction.

2. The process of claim 1 wherein said recycle oil is substantially free of polyolefins.

3. In the process of producing diolefins the steps comprising cracking a straight run hydrocarbon oil selected from the group consisting of naphtha, kerosene and gas oil at a temperature below 600° C., fractionating the resulting cracked products to produce a cracked distillate consisting of C_5 and higher hydrocarbons boiling below about 120° C., having a bromine number above 40 and an aromatic content below 30%, treating said cracked distillate to remove gum forming components, recracking said cracked distillate at a temperature between 650° C. and 850° C. under conditions to gasify 15% to 85% thereof, whereby diolefins are formed and separating said diolefins and aromatics from each other and the other resulting cracked products.

4. The process of claim 3 wherein said cracked distillate has a bromine number above 60.

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