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TREATMENT OF HYDROCARBONS

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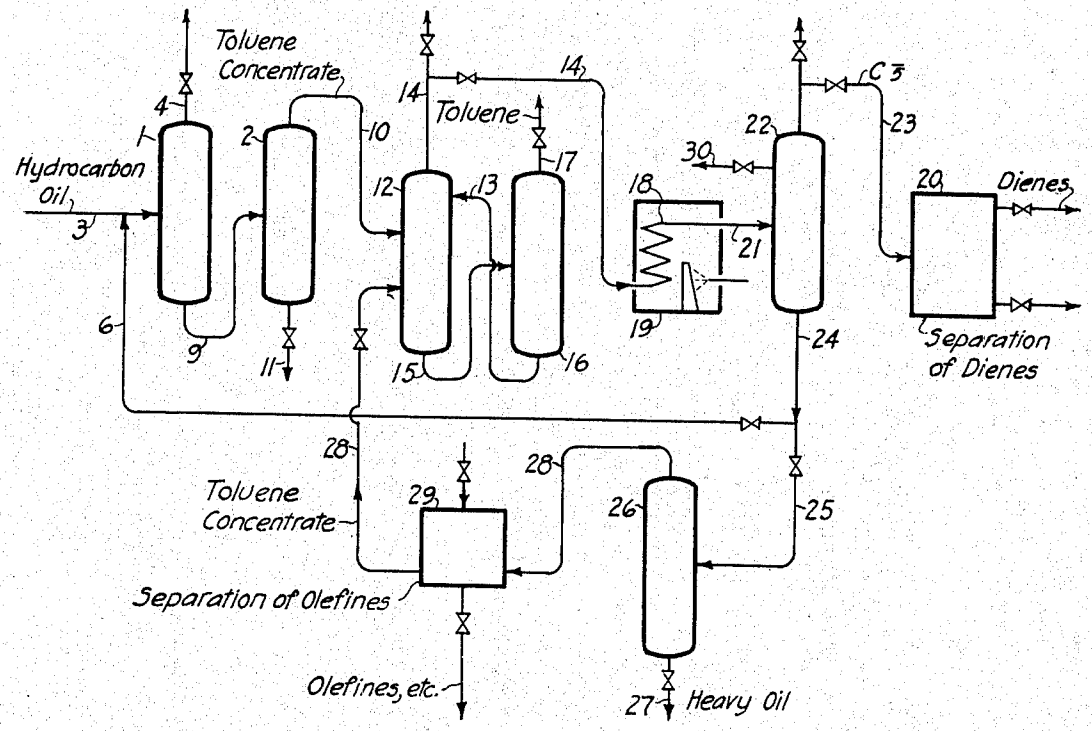



Fig. I

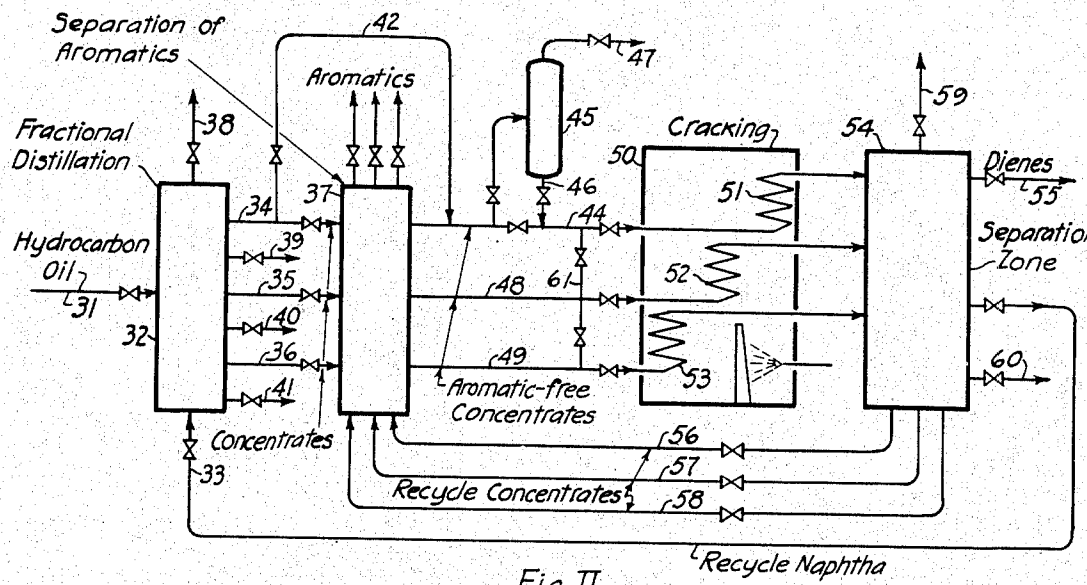



Fig. II

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2,366,570

## TREATMENT OF HYDROCARBONS

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Application May 26, 1942, Serial No. 444,607

3 Claims. (Cl. 260—680)

This invention relates to a process for the preparation of unsaturated hydrocarbons from petroleum distillates and, more particularly, of aromatics such as toluene and diolefines, such as butadiene, isoprene, and other homologous diolefines, and is a continuation-in-part of the invention described in our co-pending application Serial No. 406,274, filed August 11, 1941.

It has heretofore been proposed to separate aromatics, e. g. toluene, from natural or cracked petroleum distillates by concentrating the toluene through distillation to obtain a concentrate containing upwards of 5% toluene, and by extracting the resulting concentrate within the vapor phase with a suitable selective solvent to obtain pure or substantally pure toluene. It has, further, been proposed to produce butadiene and similar diolefines by pyrolysis of various hydrocarbons, either with or without catalysts, followed by the concentration and separation of the diolefines from the conversion products by means of solvents or by chemical treatment.

According to the present invention it was found that the yield of aromatics can be considerably improved, and that an excellent conversion to diolefines can be effected by subjecting certain hydrocarbon fractions which are associated with aromatics and are in general contained in aromatic concentrates and from which the aromatics may be removed by treatment with solvents, to pyrolysis under conditions favoring the formation of unsaturated hydrocarbons having conjugated double bonds, and then separating these valuable hydrocarbons. During this last-named separation it is preferred to concentrate the aromatics contained in the cracked products in narrow boiling fractions and recycle the resulting concentrates to the solvent separation steps.

A hydrocarbon fraction to be suitable for the purpose of this invention is one in which has been concentrated the major amount and preferably substantially the entire amount of a single aromatic hydrocarbon or a single group of metameric aromatic hydrocarbons, e. g., benzene, or toluene, or xylenes and ethyl benzene, etc., which amount was originally contained in the hydrocarbon distillate under treatment. This fraction or concentrate should have a boiling range as narrow as possible consistent with the requirement of containing the major portion of the aromatic, and it should be substantially free of components boiling above or below the boiling range over which the aromatic boils when the fraction is subjected to a close fractional distillation.

In producing these suitable concentrate fractions, highly efficient fractional distillation equivalent at least to 20 theoretical plates at a reflux ratio of 2:1 should be employed. Such narrow fractions are preferably produced by continuous fractionation and if so produced will, in general, upon being subjected to analytical distillation, show at least 95% boiling within the following ranges:

| Concentrate containing | Maximum range | Preferred range |
|---|---|---|
| | °F. | °F. |
| Benzene | 156–185 | 164–178 |
| Toluene | 195–245 | 206–231 |
| Xylenes and ethyl benzene | 260–300 | 267–290 |

Analytical distillation as herein defined is a laboratory batch distillation operated over 30 equilibrium plates and at a reflux ratio of at least 20:1.

For the purpose of our invention the composition of the concentrates may be said to consist of 3 component parts: (1) an aromatic or a group of metameric aromatic hydrocarbons, (2) non-aromatic desirable hydrocarbons which form upon cracking large amounts of dienes, and (3) non-aromatic less desirable hydrocarbons which do not give such high yields of dienes. These three components cannot be separated from each other by simple fractional distillation, i. e., distillation conducted in the absence of added separating agents, and in order to effect a separation it is necessary to distill the concentrates in the presence of a selective solvent for one of the components of the aromatic hydrocarbons. However, after separation of aromatics or if aromatics are present in but a small proportion, simple fractional distillation is capable of separating the desirable non-aromatic hydrocarbons which boil higher from the less desirable non-aromatics which boil lower.

The above-defined concentrates, particularly if containing only minor amounts of aromatics, may when separated from a straight run-distillate give higher yields of dienes upon vapor phase cracking than higher or lower boiling fractions or than the petroleum distillate from which the concentrates are separated. The mixture of non-aromatic hydrocarbons including both the desirable ones and the less desirable ones, which is obtained by separating the aromatic hydrocarbons from the remainder of the concentrate, gives higher yields of dienes than the concentrate itself. The particularly desirable non-aromatic hydrocarbon obtained from this mixture by fractional distillation produces by cracking still higher yields of dienes.

It will be apparent that narrower fractions than the above-described may be used with advantage and that inclusion of small amounts of higher or lower boiling hydrocarbons will give inferior results, the extent of depreciation depending upon the amount of these hydrocarbons

included. Such variations may be produced, for example, by less efficient fractionation of the petroleum distillate when producing the narrow boiling fractions.

Fractions boiling in the above range, particularly the preferred range, allow also the separation of pure aromatics practically free of other hydrocarbons and boiling within 1° F.

The nature of the invention will be better understood from the following detailed description, taken together with the drawing forming a part of this specification which illustrates certain preferred embodiments thereof, in which:

Figure I is a flow diagram illustrating a particularly preferred form of the improved process; and

Figure II is a flow diagram illustrating the general steps of the process.

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

Referring to Figure I, which illustrates the process of this invention as applied to the toluene concentrate, 1 and 2 are fractional distillation columns provided with conventional reboilers, condensers, etc. and equipped with bubble trays or other contact means, not shown. The hydrocarbon feed mixture containing toluene is introduced through line 3 from a source not shown. It may be of any provenience, either cracked or straight-run, although straight-run gasoline which contains appreciable quantities of toluene are preferred. Toluene-rich naphthas produced in the process, as hereinafter described, may be added thereto through line 6. As large a portion of the hydrocarbon as is practical for the retention of most of the toluene in the bottom product is taken off overhead at 4. For example, it was found convenient to remove overhead material boiling below 206° F. The distillation residue is taken off at 9 and fed into the column 2, wherein as small a proportion of hydrocarbons as is practical for the recovery of most of the toluene in the overhead is taken off as a distillate at 10. For example, the distillate may include materials boiling below 231° F. The bottom product from column 2 is withdrawn at 11.

The narrow fraction so obtained, boiling between about 195° F. and 245° F., and preferably between about 206° F. and 231° F., will contain all or most of the toluene (boiling point, 231.4° F.) in the feed. The columns 1 and 2 may, however, be operated to other temperature limits so as to include in the distillate a somewhat wider boiling range or a slightly narrower boiling range, for example, 203° F. to 239° F. It is usually desirable to produce a distillate containing at least 5% and preferably 8% or more of toluene. Thus, it was found that when using an East Texas straight-run gasoline, a concentrate containing from 8% to over 10% of toluene, and in the case of a West Texas straight-run gasoline a concentrate containing from 10% to over 15% of toluene, could be produced.

The narrow fraction taken overhead at 10, and hereafter designated as the toluene concentrate, is fed into the solvent treater 12. A suitable solvent for separating the toluene from the other constituents of the concentrate is fed at 13; separated toluene, either with or without solvent, is withdrawn at 15, and the substantially toluene-free remainder of the toluene concentrate is taken off at 14.

The solvent treater may be of any type suitable for the separation of toluene, such as a liquid-liquid solvent extraction apparatus, wherein a liquid solution of toluene in a solvent having selective solvent power for aromatic hydrocarbons is separated from a liquid hydrocarbon phase freed from all or most of the toluene; or an azeotropical distillation column, wherein toluene is obtained as the distillation residue, either pure or together with some solvent (depending upon the amount of solvent added) and other hydrocarbons, together with solvent are separated as a distillate having a low boiling point. It is preferred, however, to employ a vapor phase extraction or extractive distillation apparatus, i. e. a column in which the toluene concentrate is distilled in the presence of a liquid solvent selective for aromatic hydrocarbons such as phenol, which retains the toluene in the bottom product while permitting the other constituents of the concentrate to pass off as overhead vapors. Solvents other than phenol which are suitable for use in the solvent treater 12, and particularly in the extractive distillation step, include 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, tetra hydro furfuryl 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 and 2-isopropxy glycerol, the glycerol, di-ethers such as 1,2-di-methoxy glycerol, 1,3-di-methoxy glycerol, 1,2-di-ethoxy glycerol, 1,3-di-ethoxy glycerol, 1,2-di-propoxy glycerol, 1,3-di-propoxy glycerol, 1,2-di-isopropxy glycerol, and 1,3-di-isopropoxy glycerol, the mixed di-glycerol ether esters such as 1-ethoxy, 2-methoxy glycerol, 1-methoxy, 3-propoxy glyerol and 1-ethoxy, 2-isopropoxy glycerol.

The toluene obtained through line 15 is freed of the solvent, preferably by fractional distillation, in column 16. The solvent-free toluene is obtained overhead through line 17 while the toluene-free solvent forms the bottom product and is returned to solvent treater 12 through conduit 13.

The toluene-free overhead product in line 14 is led into cracking coil 18 in furnace 19, wherein it is heated rapidly to a peak temperature of 1100° F. to 1450° F., and preferably 1300° F. to 1400° F., in order to crack it, whereby unsaturated hydrocarbons such as olefines, dienes, and aromatics are formed. The time of cracking at these high temperatures is governed so as to gasify about 30% to 70%, and preferably 45% to 55%, of the feed per pass, gasification being defined as conversion of the liquid feed to molecules having 5 or less carbon atoms.

The heating of the hydrocarbons to the cracking temperature may be achieved by contact with a heated solid surface, for example, in an ex-

ternally heated coil as has been described, or may be realized by admixture of hot substantially inert gases such as flue gases, carbon dioxide, hydrocarbon gases, steam, etc., or by a combination of both methods.

In order to prevent excessive coke formation it is desirable to avoid the contact of ferrous metals with the hydrocarbon at cracking temperatures. Copper-containing alloys such as alumium or phosphor-bronze, or refractory ceramic materials do not cause rapid coking when used in the construction of surfaces exposed to hydrocarbons at cracking temperature.

Cracking according to this invention is preferably purely thermal, i. e. non-catalytic, and is conducted in the absence of catalyst, be it added catalysts such as gaseous halogenated compounds, solid catalytic metals or oxides, or catalysts preformed in situ, e. g. lustrous carbon or pyrophoric metals.

The cracking should be conducted at pressures about atmospheric or below and preferably not substantially above 100 to 150 lbs. p. s. i. Preferably, pressures not in excess of those required to overcome the resistance of the cracking unit are employed. The use of an inert diluent such as steam is advantageous.

The actual time for which the vapors are subjected to cracking conditions should be below about 0.1 second to avoid decomposition of the butadiene formed. This time is, however, very difficult to estimate correctly because of volume variations during cracking. The liquid space velocity is, on the contrary, easy to estimate and, for given temperatures, pressures and admixtures, determines the actual vapor space velocity and cracking time. Liquid space velocity is the volume of liquid delivered per hour to the cracking zone, per volume unit of said zone. The cracking zone is defined as the space occupied by gases in which the temperature is within 40° F. of the peak temperature. The cracked vapors are rapidly cooled or quenched after passing through the cracking zone.

The liquid space velocity which is chosen depends on the temperature and pressure in the cracking coil. At 1380° F. and atmospheric pressure a liquid space velocity of about 35 results in gasification of about 50% and the formation per pass of about 8% of toluene and about 14% $C_4$ and $C_5$ dienes, of which about half are butadienes. Mono-olefines and other aromatics such as benzene are also formed. This conversion to diolefines and aromatics, particularly toluene, is unusually high, much higher than is obtainable with conventional cracking stocks of different boiling ranges. This is particularly the case with a fraction boiling between 206° F. and 231° F. The presence of hydrocarbons boiling immediately below and above these limits tends to lower the yields of valuable unsaturated hydrocarbons containing conjugated double bonds.

The cracked products emerging from coil **18** are led through line **21** into column **22** wherein they are fractionally distilled to separate a $C_5$ and lighter fraction. This fraction, which comprises olefines and up to 25% to 30% dienes, passes through overhead line **23** and a naphtha substantially free of lighter hydrocarbons is withdrawn through line **24**. This naphtha contains normally about 16% of toluene and may be recycled through lines **24**, **6** and **3** to column **1** to be further treated as part of the above-described feed.

The diene-rich gases in line **23** are advantageously treated in zone **20** so as to separate the valuable dienes. This separation may be effected by fractional distillation, or by extractive or azeotropical distillation, or by solvent extraction by means of a polar solvent having greater solvent power for dienes than for mono-olefines and saturated hydrocarbons, or by selective polymerization, or by complex formation, or by a combination of these methods, etc.

If the feed introduced through line **3** from the outside is relatively poor in toluene, it may be advantageous, instead of commingling it with the cracked recycling naphtha, to prepare from the latter a separate toluene concentrate having a toluene content different from that of the concentrate in line **10** and introduce the former into the extractor **12** at the same or different level from that at which the latter enters.

For this purpose the column **22** may be operated so as to yield a bottom fraction substantially free of components boiling below 195° F. and preferably 206° F. by taking in addition to the gas fraction in line **23** an appropriate side stream through line **30**. If desired, two columns may be used to produce the three fractions. The bottom fraction is led through lines **24** and **25** to fractional distillation column **26** wherein it is refractionated to yield a light fraction boiling below 245° F. and preferably 231° F., which is removed overhead through line **28**. This fraction boiling substantially between 195° F. and 245° F. is a cracked toluene concentrate which comprises most of the toluene produced in the cracking. This concentrate is led through line **28** to column **12**. A heavy liquid boiling above 231° F. is withdrawn from column **26** through line **27**.

This cracked toluene concentrate may contain substantial amounts of olefines, and particularly polyolefines, produced in the cracking. Olefines have solubilities in polar solvents, such as those usel for extractive distillation in column **12**, which are intermediate between those of paraffinic hydrocarbons and of toluene. This makes it more difficult to separate olefines, and especially polyolefines, than to separate paraffins from toluene by extractive distillation. Thus, it is often advantageous to free the concentrate in line **28** from olefines. This can be done in olefine separation zone **29** by one of the methods which eliminates or transforms preferentially polyolefines or poly- and mono-olefines without substantially affecting aromatics and paraffins. Such methods are, for example, absorption in dilute acids such as sulfuric acids or complex-forming reagents, e. g. $CuCl_2$, AgCl, $SO_2$, etc.; hydrogenation in the presence of a suitable catalyst such as nickel, copper, etc.; or polymerization followed by fractionation, especially catalytic polymerization, in the presence of suitable catalysts such as solid phosphoric acid or one of those listed in National Petroleum News of November 20, 1935, page 45 and following, or in U. S. Patent 2,171,207; partial oxidation in the presence of a catalyst such as silver, etc., followed by fractional distillation, etc.; or a combination thereof.

Referring now to Figure II, which illustrates an application of this process in which one concentrate, e. g. the benzene or the toluene or the xylene concentrate, or any two concentrates, or the three concentrates simultaneously, are being treated. It will not be described in regard to the last-mentioned case, it being understood that by proper variation of the flow scheme any other case may be realized.

A hydrocarbon distillate containing aromatics

is admitted from storage not shown through line 31 to fractional distillation zone 32. A suitable distillate produced in the process may be admitted thereto through line 33. In this fractionation zone 32 the admitted distillates are fractionated to produce the desired narrow boiling concentrates and separate them from the remainder of the distillate. The concentrates may be conducted through lines 34, 35 and 36 to aromatic separation zone 37. The remainder may be withdrawn through lines 38, 39, 40 and 41. If an aromatic is present in too small quantities in the concentrate to make its recovery worthwhile (e. g., less than 4%) it may by-pass the aromatic separation zone 37. In this case it is often preferable to conduct the fractional distillation in zone 32 so as to produce a narrower boiling fraction containing only the more desirable non-aromatics. Thus, for example, if benzene is present in but very small amounts a fraction boiling from 170° F. to 185° F. is advantageously obtained from zone 32 through line 34 and conducted through line 42 to line 44 which leads to cracking zone 50.

The other aromatic-free concentrates may be obtained through lines 48 and 49 which lead, as well as line 44, to cracking zone 50. Prior to cracking, these aromatic-free concentrates may be again separated by fractional distillation, each into two fractions, both of substantial proportions, and only the higher boiling cracked. Thus, the benzene-free benzene concentrate may be advantageously separated in fractional distillation column 45 into a bottom portion boiling above 170° F., which is obtained through line 46 and conducted to line 44, and overhead fraction withdrawn through line 47. Other concentrates may be treated similarly, e. g., the toluene-free toluene concentrate may be fractionated in a distilling column not shown to separate constituents boiling below 210° F., which are withdrawn while the remainder is conducted to cracking zone 50. Here the three concentrates are cracked under conditions similar to those previously described for the toluene concentrate in cracking coils 51, 52 and 53. It is preferred to crack the concentrates under independently controlled conditions of time and temperature, as their thermal stability is different, the lower boiling ones being less stable and requiring greater liquid space velocities for the same gasification. If desired, the several concentrates may be combined by means of line 61 and cracked together in one coil.

The cracked products after rapid quenching are treated in separation zone 54 to separate therefrom dienes which may be withdrawn through line 55, an aromatic-rich naphtha having a broad boiling range taken through line 33 to zone 32, or one or more cracked concentrates taken through lines 56, 57 and 58 to zone 37; and other hydrocarbons may be withdrawn at 59 or 60.

Olefines which may interfere with the separation of aromatics or cracking may be separated in separation zone 29 as described above.

The following example may further illustrate this invention:

*Example*

A West Texas straight-run gasoline boiling from about 86° F. to 305° F. was cracked at 1382° F. at a liquid space velocity of 32. The gaseous portion of the cracked products (i. e., gases having less than 6 carbon atoms in the molecule) contained 8.25% of dienes.

A toluene concentrate boiling from 206.6° F. to 230° F., and from which the toluene was removed by extractive distillation, gave upon cracking under the same conditions a yield of diene equal to 14.0% of the vapor phase.

A xylene concentrate prepared from this gasoline and from which the xylenes were removed by extractive distillation, boiled from 257° F. to 268° F. and gave upon cracking under the same conditions 12.8% of dienes in the gaseous products.

We claim as our invention:

1. In the process of manufacturing unsaturated hydrocarbons having conjugated double bonds from a petroleum oil boiling over a relatively wide range, the steps comprising separating from said petroleum oil at least two of three narrower fractions, one boiling substantially between 156° F. and 185° F., a second between 195° F. and 245° F. and a third between 260° F. and 300° F.; treating one of said fractions to separate the aromatic hydrocarbons contained therein, combining the remainder of said fraction with one other of said three narrower fractions, subjecting the combined products to cracking in the vapor phase between 1100° F. and 1450° F. for a time to gasify 30% to 70% thereof whereby substantial amounts of unsaturated hydrocarbons having conjugated double bonds are produced and separating said unsaturated hydrocarbons from the resulting cracked products.

2. In the process of manufacturing unsaturated hydrocarbons having conjugated double bonds from a petroleum oil boiling over a relatively wide range the steps comprising separating from said oil a fraction boiling substantially between 170° F. and 185° F. and one of two other fractions, the first boiling between 195° F. and 245° F. and a second boiling between 260° F. and 300° F., treating one of said last-named fractions to separate the aromatic hydrocarbons contained therein, combining the remainder thus obtained with said fraction boiling between 170° F. and 185° F., subjecting the combined products to cracking in the vapor phase between 1100° F. and 1450° F. for a time to gasify 30% to 70% thereof whereby substantial amounts of unsaturated hydrocarbons having conjugated double bonds are produced and separating said unsaturated hydrocarbons from the resulting cracked products.

3. In the process of manufacturing unsaturated compounds having conjugated double bonds from a petroleum oil boiling over a relatively wide range below and above the boiling temperature of toluene, the steps comprising separating two fractions, one boiling between 195° F. and 245° F. and containing most of the toluene comprised in said oil, and the other boiling between 170° F. and 185° F., separating the toluene contained in the former fraction, subjecting the remainder of said former fraction and the latter fraction to cracking conditions in the vapor phase between 1100° F. and 1450° F. for a time to gasify 30% to 70% thereof, whereby substantial amounts of valuable unsaturated hydrocarbons having conjugated double bonds are produced, and separating said valuable hydrocarbons from the resulting cracked products.

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