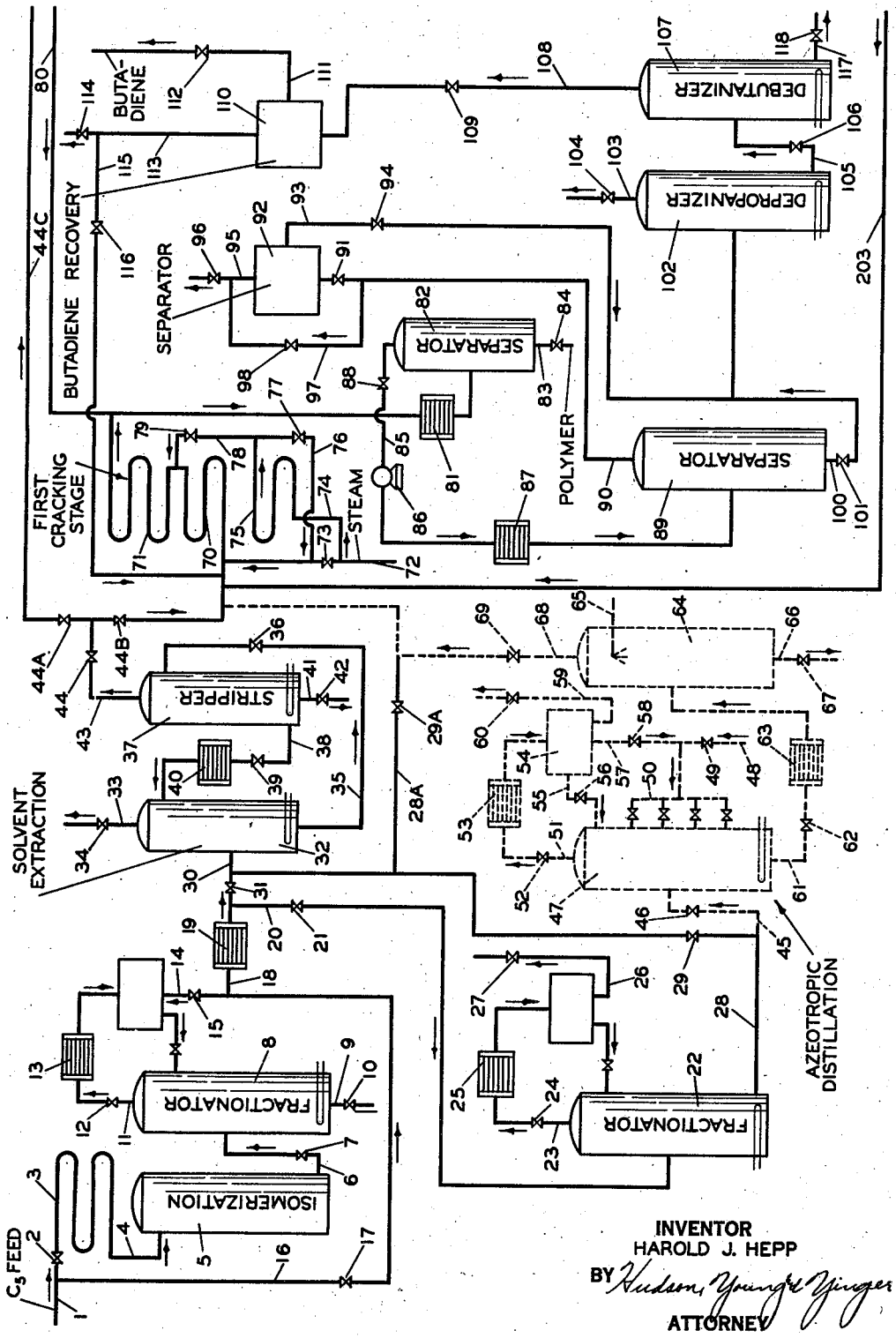
Dec. 18, 1945. H. J. HEPP 2,391,158

MANUFACTURE OF DIOLEFINS

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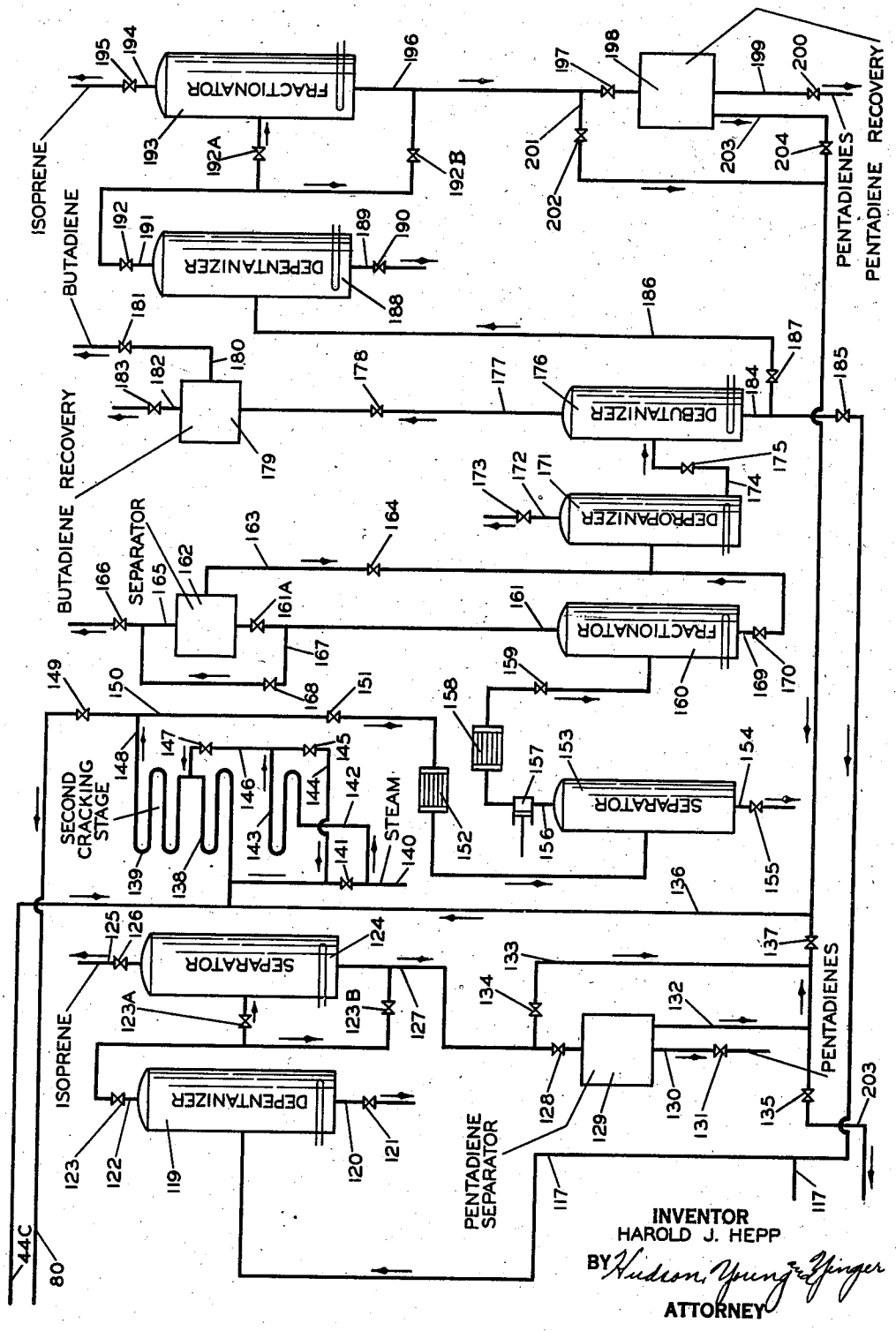


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MANUFACTURE OF DIOLEFINS

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UNITED STATES PATENT OFFICE

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MANUFACTURE OF DIOLEFINS

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2 Claims. (Cl. 260—680)

This invention relates to the production of conjugated diolefins, and more specifically, to the utilization of amylenes as a source of diolefins.

Butadiene and related diolefins have been found in numerous instances among the products of low-pressure pyrolysis of various simple hydrocarbons, including both paraffins and olefins. In general, the diolefin yields reported in the literature are low. However, I have found, as the result of numerous experiments, that enhanced yields of diolefins are obtained when the pyrolysis is conducted at a high temperature, with the time of heating limited to periods small enough so that a part of the hydrocarbon being pyrolyzed survives the heating unchanged. The yield of diolefins is further improved in some cases if the pyrolysis is conducted at low pressure or in the presence of diluents such as steam, flue gas, methane, and the like.

I have found that under suitable conditions of low pressure, high temperature and very short heating time, good yields of diolefins containing four and five carbon atoms per molecule can be obtained from certain of the amylenes; namely, pentene-2 and trimethylethylene, while the yields from other pentenes occurring in cracked gasoline in appreciable amounts; i. e., 3-methylbutene-1 and pentene-1, are not as high.

I have found that the yield of diolefins is materially improved when the pyrolysis is conducted at temperatures above 700° C., and the degree of pyrolysis limited by controlling the time of heating so that not more than about 10 per cent of polymers boiling above about 50° C. is present in the products from the conversion zone. The yield of diolefins may be further improved, or the amount of pentene reacted per passage through the heating zone increased, with consequent reduction of pentene-recycle, without encountering excessive loss to polymers by conducting the pyrolysis at subatmospheric pressure or by reducing the partial pressures of the pentenes by the use of diluents such as steam, flue-gas, methane, and the like.

Under the conditions outlined above, the cracking behaviors of pentene-2 and of trimethylethylene are radically different.

Pentene-2 cracks to butadiene as the major diolefin, accompanied by smaller amounts of pentadienes. Trimethylethylene, on the other hand, yields isoprene as the major diolefin, accompanied by minor amounts of butadiene. In the pyrolysis of trimethylethylene, isomerization to 2-methylbutene-1 occurs to only a minor extent, if at all, and this simplifies the problem of recovering isoprene of good purity since efficient fractionation only is required.

The cracking rate of petene-2 is very fast compared to trimethylethylene. At temperatures in the region of 780° C., pentene-2 cracks at about 7 times the rate of trimethylethylene. As brought out later, it is relatively easy to recover from the C_5 fraction of pressure still gasoline a concentrate composed largely of a mixture of pentene-2 and trimethylethylenes, but it is quite difficult to separate pentene-2 and trimethylethylene by distillation or by extraction procedures. Consequently, if it is desired to convert olefin concentrates obtained from sources containing both pentene-2 and trimethylethylene, it will frequently be desirable to treat the olefin mixture rather than to separate the individual olefins and treat them separately. The wide difference in the cracking rates of the two olefins leads to the rather undesirable situation that, if they are converted to diolefins by a single step pyrolytic method, when conditions of time and temperature are maintained to give optimum conversion of pentene-2, only a small percentage of trimethylethylene reacts, and, consequently, the recycle volume of pentenes is large. On the other hand, when conditions are maintained to effect substantial conversion of trimethylethylene, then the pentene-2 reacts too far to yield maximum amounts of butadiene.

One aspect of my invention is to provide a two step pyrolytic process for converting such mixtures to diolefins. In the first pyrolysis step, con-

ditions of time and temperature are maintained in the region where best yields of butadiene are obtained from pentene-2, and the unconverted pentenes from this step, now considerably enriched in the refractory trimethylethylene, are cracked in a second step under more drastic conditions of time and temperature to yield isoprene.

While the above discussion has disclosed the conversion of mixtures of pentene-2 and trimethylethylene, my invention is not limited to the pyrolytic conversion of such mixtures to diolefins. Trimethylethylene from any source, whether associated with pentene-2 or not, may be efficiently converted to isoprene when pyrolyzed under the conditions outlined above.

The objects of my invention are:

1. To effect the pyrolytic conversion, by a recycle process, of trimethylethylene into useful and substantial yields of isoprene.

2. To utilize a hydrocarbon fraction containing five carbon atoms per molecule and containing a considerable proportion of amylenes, such as the C_5 fraction from typical cracking still gasoline.

3. To produce a conversion feed stock rich in the preferred olefins and differing in olefin composition from such a C_5 fraction by an economical separating means, and to convert this feed stock by a pyrolytic process to butadiene and pentadienes.

4. To convert isopentane to isoprene by an advantageous combination of catalytic dehydrogenation and pyrolytic conversion means.

5. The production of diolefins and other by-products.

Other objects of my invention will be apparent from the following detailed description.

Briefly, my invention comprises the conversion of mixtures of trimethylethylene and n-pentenes, to diolefins by a pyrolytic method.

The economical preparation of aliphatic conjugated dolefins from hydrocarbons of petroleum origin, and particularly the preparation of butadiene, isoprene, and piperylene, which are especially suitable for the manufacture of synthetic rubber, has been a very serious problem in the art and has not to my knowledge been entirely satisfactorily solved. The present invention aims to provide a solution of this problem in a simple and economical manner by enabling the production of these diolefins from certain of the amylenes.

In accordance with my invention in a broad aspect, a mixture comprising preponderantly or consisting essentially of pentene-2 and trimethylethylene, prepared by any method, is first cracked under such conditions as to selectively destroy the pentene-2 content forming butadiene, i. e. so that a major portion of the pentene-2 is destroyed or converted to butadiene while the trimethylethylene content is substantially unaffected.

The uncracked C_5 content of the effluent from the first stage is then passed to a second cracking step where such conditions are maintained as to destroy the major portion or substantially all of the trimethylethylene content, forming isoprene.

The selection of the mild and drastic cracking conditions for the first and second cracking stages respectively to attain the desired results will be obvious to those skilled in the art in the light of this disclosure. In general however the first cracking step may be conducted at above 700° up to about 900° C. and preferably from about 750 to about 850° C., at pressures from about 0.1 to about 2 atmospheres and preferably substantially atmospheric, and using throughput rates such that from about 20 to about 70%, and preferably 30–70%, of the pentene-2 content of the feed is decomposed per pass.

The conditions for the second cracking step may involve the same pressure and temperature ranges as given for the first stage. The time-temperature relationship should be significantly greater. This may be attained by using higher temperature in the ranges given and/or using longer contact times. The conditions should be adjusted so that from about 15 to about 80% and preferably from about 15 to about 50% conversion of the trimethylethylene content of the feed per pass is obtained. The contact time may range from about 0.01 to about 5 seconds.

Other features of my invention involve recycling of butenes from the first stage effluent to the first stage feed, optional use of a common diolefin recovery means for both stages, and extraction of butadiene from the first stage effluent and isoprene from the second stage effluent.

If it is attempted to crack a mixture of pentene-2 and trimethylethylene in a single cracking step under conditions such as to destroy a major portion of each, the yields of desirable butadiene and isoprene from each is excessively low. The reason for this is that the ideal conditions for conversion of pentene-2 are quite different from those for trimethylethylene. I have discovered that if the mixture is first cracked under conditions ideal for pentene-2, butadiene recovered from the effluent, and the uncracked C_5 in the effluent (low in pentene-2) cracked separately under conditions ideal for conversion of trimethylethylene, the yield of desirable diolefins is unexpectedly very much greater and recovery thereof is easier. I have further discovered that the normally undesirable effect of the presence of the other amylene in the cracking of one amylene is unexpectedly minimized by proceeding in the way outlined.

Thus by cracking pentene-2 under mild conditions without appreciably affecting the trimethylethylene, the latter does not interfere, and by destroying most of the pentene-2 in the first cracking, it does not interfere with efficient production of isoprene from trimethylethylene in the second cracking stage.

The trimethylethylene may be from any source; for example, from the catalytic dehydrogenation of isopentane. A large amount of trimethylethylene associated with other amylenes is present in the hydrocarbon fraction containing five carbon atoms per molecule obtained from cracking still gasoline. The composition of a typical C_5 fraction of cracking still gasoline is roughly as follows: 3-methylbutene-1, 5%; pentene-1, 9%; pentene-2, 17%; trimethylethylene, 9%; and the remainder predominantly pentanes. The low boiling olefins, 3-methylbutene-1 and pentene-1, may be separated from such a mixture, along with isopentane, by fractional distillation, or they may be partly isomerized to pentene-2 and trimethylethylene by passing over a suitable catalyst. In this manner, a concentrate of pentene-2, trimethylethylene, and n-pentane may be obtained, from which the n-pentane may be separated either by fractional distillation with an entrainer such as acetaldehyde, propionaldehyde, propylene oxide, and the like,

or by solvent extraction with furfural, furfural alcohol, levulinic acid, and the like.

However, the separation of the trimethylethylene and the pentene-2 isomers by distillation or extraction procedures is difficult. As shown in the examples below, the cracking velocity of pentene-2 differs widely from that of trimethylethylene. At a given temperature, pentene-2 cracks about 7 times as fast as trimethylethylene. Accordingly, I prefer to pyrolyze mixtures of pentene-2 and trimethylethylene in two steps. In the first step, much of the pentene-2 is cracked to yield butadiene and relatively small amounts of pentadienes, while only a small proportion of trimethylethylene is cracked. The pentenes surviving the first step, which are rich in trimethylethylene compared with the starting material, form the feed to the second step. Isoprene, accompanied by relatively small amounts of butadiene and other pentadienes, are produced in the second step.

In the accompanying drawings is shown a flow diagram illustrating a process for preparing a pentene-2, trimethylethylene concentrate from a C_5 fraction containing these olefins, and converting this concentrate to diolefins by a two step pyrolytic process. The drawings also embrace a process wherein a concentrate of trimethylethylene prepared in any manner is pyrolyzed by a single-step process to yield isoprene.

The feed-stock, which may be a C_5 fraction such as may be separated from cracking-still gasoline and which contains pentene-2 and trimethylethylene, is introduced into the system through pipe 1. The feed-stock may be passed by means of valve 2, through heating arrangement 3, wherein the stream is heated to a temperature in the range of 150 to 350° C., and pipe 4 to isomerization step 5. In the isomerization step, the stream is contacted with phosphoric acid, aluminum sulfate, or similar catalyst for a period of time, in the range of 2 seconds to 3 minutes, sufficient to effect substantial isomerization of pentene-1 to pentene-2; there will be some conversion of unsymmetrical amylene to trimethylethylene.

A typical refinery C_5-fraction, such as that being charged to the isomerization step, would have about the following composition: pentene-1, 9%; pentene-2, 17%; trimethylethylene, 9%; unsymmetrical amylene, 5%; and the remainder predominantly pentanes. Isomerization would effect such conversion that the ratio of pentene-1 to pentene-2 would be about 1 to 10.

The products from the isomerization step are passed through pipe 6, controlled by valve 7, to a fractionating step 8. The C_5-hydrocarbons and heavier products are separated as kettle product and withdrawn from the system through pipe 9, controlled by valve 10. Pentane-pentenes and any lighter hydrocarbons present are passed overhead through pipe 11, controlled by valve 12, to cooler 13, which supplies a liquid condensate for reflux to column 8, pipe 14, valve 15, pipe 18, and heat exchanger 19 to pipe 30, to be subjected to further separation steps.

If desired or convenient, the feed-stock may be products obtained from dehydrogenation of isopentane in which case it will be desirable to omit the isomerization step. The feed-stock would be passed from pipe 1 through pipe 16, controlled by valve 17, pipe 18 and heat exchanger 19, pipe 20, controlled by valve 21, to fractionating step 22. Separation is effected, the cut point being in the range of 30° to 34° C., and isopentane containing some low-boiling olefins is passed overhead through pipe 23, controlled by valve 24, to cooler 25, which supplies a liquid condensate for reflux to column 22, to pipe 26 and, controlled by valve 27, is recycled to the dehydrogenation system. The high-boiling fraction is recovered as kettle product and passed through pipe 28, controlled by valve 29, to pipe 30, or it may be passed through pipe 28a and valve 29a to pipe 68 and to the cracking coil 70. Alternately, the products from the dehydrogenation of isopentane may be passed directly to the solvent extraction step 32 via pipe 16, valve 17, heat exchanger 19, valve 31 and pipe 30.

The stream from pipe 30, whether from cracking-still or from dehydrogenation products, may be subjected to further separation, such as extraction with furfural, levulinic acid, dimethyl formamide, furfuryl alcohol, phenolwater, and the like. Extraction separation is effected in column 32, under suitable conditions of temperature and pressure, and a fraction, composed predominantly of pentanes, pentene-1, 2-methylbutene-1, and 3-methylbutene-1 or such of these hydrocarbons as were introduced to the step, is recovered overhead and withdrawn from the system through pipe 33, controlled by valve 34. Pentene-2 and trimethylethylene, along with solvent, are recovered as kettle product and passed through 35, controlled by valve 36, to stripping tower 37. The stripped solvent is recovered as kettle product and may be recycled, by pipe 38, valve 39, and cooler 40, to the extraction step or any portion may be withdrawn from the system through pipe 41, controlled by valve 42. Pentene-2, trimethylethylene and other hydrocarbons present are recovered overhead and passed through pipe 43, controlled by valve 44, to a cracking step.

If desired, the separation may be effected by means of azeotropic distillation rather than by solvent extraction. The stream is passed, by proper control of valve 29, from pipe 28 through pipe 45, and valve 46 to tower 47. Entrainer, such as acetaldehyde, propionaldehyde, propylene oxide, and the like, is introduced through pipe 48, controlled by valve 49, and manifold 50. The overhead product, which is composed largely of pentane and entrainer is passed through pipe 51, controlled by valve 52, to condenser 53 and accumulator 54. In some cases, a portion of the entrainer will separate out as a separate phase in 54; when this occurs, the proper amount of each phase is returned to tower 47 through pipe 55 and valve 56. Likewise, when phase separation occurs, excess entrainer phase may be returned to 47 by means of pipe 57, valve 58, and pipe 48. A fraction, which is composed of n-pentane and low-boiling amylenes such as pentene-1, etc., and which is free of entrainer, is passed through pipe 59, controlled by valve 60 and withdrawn from the system. Entrainer, enriched with pentene-2 and trimethylethylene, is recovered as kettle product and passed through pipe 61, controlled by valve 62, and cooler 63 to tower 64. The entrainer is scrubbed out, with water or other suitable solvent introduced through pipe 65, is recovered as kettle product and withdrawn through pipe 66, controlled by valve 67. The desired olefins are recovered overhead and passed through pipe 68, controlled by valve 69, to pipe 43, and

a cracking step. Other methods of separating entrainer, such as cooling and decantation may be employed.

The pentene-2-trimethylethylene concentrate, prepared as disclosed above, or by other means, from pipe 43 is passed to a heating system which is herein represented by a convection coil, 70, and a radiation coil, 71. Steam or other stable, volatile diluent may be added to the charge-stock; from pipe 72 steam, etc., may pass, by means of valve 73 and pipe 43, directly to the convection coil of the furnace or it may pass from pipe 72 through pipe 74 to a separate heating coil, 75, and thence through pipe 76, by means of valve 77, to the convection coil of the furnace or through pipe 78, controlled by valve 79, to a radiation coil of the furnace.

Charging stocks rich in trimethylethylene as, for example, from the dehydrogenation of isopentane may be passed from pipe 43 via valves 44a and 44b and pipe 44c directly to the second cracking step as described later.

The charge stock is cracked in the furnace at temperatures above 700° up to 900° C., and preferably in the range of 750 to 850° C. The heating time varies inversely with the temperature, decreasing as the temperature is increased, and is adjusted to effect 30 to 70% conversion of the pentene-2 per pass through the heating zone. The decomposition should be maintained in the lower part of the conversion range when no diluent is used, or when the partial pressure of the pentene-2 is near or slightly above atmospheric pressure. The higher conversions may be effected when the pyrolysis is conducted at pressures below atmospheric, or when diluents such as steam are employed. The total pressure will usually be substantially atmospheric but may range from 0.1 atmosphere to 2 atmospheres.

The effluents from the cracking step are passed from the furnace through pipe 80 to cooler 81; the cooled effluents are passed to separation step 82. Polymers and water from the cracking step are withdrawn from the bottom of the separating column through pipe 83, by means of valve 84. The gases pass overhead, controlled by valve 88, through pipe 85, compressor 86, and cooler 87, to separation step 89. The uncondensed vapors pass overhead through pipe 90, controlled by valve 91, to separator 92 wherein C_4 and C_5 hydrocarbons are recovered, as by oil absorption, refrigeration, or similar means, and recycled through pipe 93, controlled by valve 94, to a depropanizer, and light gases, hydrogen, methane, and C_2 and some C_3 hydrocarbons, are withdrawn as overhead products through pipe 95, controlled by valve 96. If separation of C_4 and heavier hydrocarbons has been effected to a substantial degree in 89, the separator 92 may be by-passed, as through pipe 97, controlled by valve 98.

The condensed products are passed from the bottom of separator 89 through pipe 100, controlled by valve 101, to depropanizer 102. Propane and lighter products are separated overhead and are withdrawn from the system through pipe 103, controlled by valve 104. The kettle product from the depropanizer is passed through pipe 105, controlled by valve 106, to debutanizer 107.

In the debutanizer, the C_4 hydrocarbons are recovered as overhead product and are passed through pipe 108, controlled by valve 109, to a separation step, 110, wherein butadiene is separated from other C_4 hydrocarbons. This separation may be effected by any one of several means: fractional distillation may be employed wherein butene-1 and isobutylene, if present, are separated in a first step following which butadiene is separated from butene-2; the separation may be effected by an azeotropic fractionating step using an entrainer such as ethylene oxide, acetaldehyde, and the like, supplemented by fractional distillation. Solvent extraction, employing furfural or other selective solvents, is an especially efficient method for separating butadiene of high purity. Or butadiene may be separated and recovered by reacting the C_4 hydrocarbons with sulfur dioxide to form butadiene monosulfone. The butadiene monosulfone formed by the latter method may be separated from the unreacted products by decantation and/or distillation, and the diolefin regenerated by heating the monosulfone to temperatures above about 80° C., and preferably above about 120° C. The reaction between diolefins and sulfur dioxide may be suitably conducted in the dense phase at temperatures in the range of 30 to 180° C., and preferably in the range of 100 to 150° C. Inhibitors such as pyrogallol, and/or phenyl-beta-naphthylamine, may be employed in the low temperature range to avoid the formation of insoluble, refractory polysulfones which do not regenerate and diolefin readily, but inhibitors are not necessary at temperatures above about 110° C., as polysulfones are formed only in small amounts, if at all, at these temperatures. The time required for completion of the sulfone reaction varies inversely with the temperature and ranges from several days at 30° C. to about ½ to 2 hours at 150° C. The sulfur dioxide used may be in the range of 2 to 20 moles per mole of diolefin. The reaction is a second-order reaction, and the time required is decreased as the amount of sulfur dioxide and/or diolefin is increased. The butadiene is withdrawn from the system through pipe 111, controlled by valve 112. The separated butenes are passed through pipe 113 and may be vented from the system by means of valve 114 or recycled in any proportion to the cracking step through pipe 115, controlled by valve 116, and pipe 80.

The kettle product from debutanizer 107 is passed through pipe 117, controlled by valve 118, to dependanizer 119 wherein C_6 and heavier hydrocarbons are separated as kettle product and withdrawn from the system through pipe 120, controlled by valve 121. The C_5 hydrocarbons are passed overhead from the dependanizer through pipe 122, controlled by valve 123, to separating step 124 wherein isoprene and low boiling olefins are separated and passed overhead through pipe 125, controlled by valve 126, and discharged from the system or subjected to further separation to recover isoprene, by means not shown, if desired.

The kettle product from 124 may be composed of pentene-2, trimethylethylene, and high boiling pentadienes. If appreciable quantities of pentadienes are present, the kettle product is passed through pipe 127, controlled by valve 128, to separation step 129 wherein pentadienes are separated from unconverted C_5 olefins and withdrawn from the system through pipe 130, controlled by valve 131. The separation step, 129, may be bypassed, as through pipe 133 and valve 134, if appreciable quantities of pentadienes are not present. The unreacted C_5 olefins are recycled through pipe 133 or, if pentadiene separation is

effected, through pipes 132 and 203, by means of valve 135, to pipe 43 and the cracking step 70, and/or is passed in any proportion by means of valve 137, through pipe 136 to a second cracking step.

The unreacted C_5 olefins, which are now rich in trimethylethylene, are passed to a second cracking system which is herein represented by a convection coil, 138, and a radiation coil, 139. Steam or other stable, volatile diluent may be added; from pipe 140 steam, etc., may pass, by means of valve 141, directly to the convection coil of the furnace or it may pass from pipe 140 through pipe 142 to a separate heating coil, 143, and thence through pipe 144, by means of valve 145, to the convection coil of the furnace or through pipe 146, controlled by valve 147, to a radiation coil of the furnace.

The cracking operations are carried out in the second step under more drastic conditions than in the first step, i. e., at higher temperatures or for longer times, to effect more efficient and complete conversion of the refractory trimethylethylene. The stream is cracked in the furnace at temperatures of above 700° up to 900° C. and preferably in the range of 750 to 850° C. and for periods of time in the preferred temperature range of 1.5 to 0.01 seconds, sufficient to effect 15 to 80% conversion, preferably 15 to 50%, of the trimethylethylene per pass through the heating zone. The cracking conditions are affected by the amount of pentene-2 present and the amount of diluent added.

The effluents from the second cracking step leave via line 148 and may be recycled through pipe 80, by means of valve 149, to the separation system hereinbefore described. This arrangement effects economies in the separation system but has the disadvantage that the products from both cracking steps are intermingled. This results in a decrease in the trimethylethylene content of the total feed to the second cracking step, and also makes it desirable to remove isobutylene, formed in the cracking of trimethylethylene, from the recycle butenes.

The effluents from the second cracking step may be more desirably treated in a second separation system. The stream is passed from pipe 148 through pipe 150, by means of valve 151, and cooler 152 to separation step 153. Polymers and water from the cracking step are withdrawn from the bottom of the separating column through pipe 154, by means of valve 155. The gases pass overhead, controlled by valve 159, through pipe 156, compressor 157, and cooler 158, to separation step 160. The uncondensed vapors pass overhead through pipe 161, controlled by valve 161A, to separator 162 wherein C_4 and C_5 hydrocarbons are recovered, as by oil absorption, refrigeration, or similar means, and passed through pipe 163, controlled by valve 164, to a depropanizer 171, and light gases are withdrawn overhead and discharged from the system through pipe 165, controlled by valve 166. The separator, 162, may be by-passed as through pipe 167 and valve 168.

The condensed products are passed from the bottom of separator 160 through pipe 169, controlled by valve 170, to depropanizer 171. Propane and lighter products are separated overhead and are withdrawn from the system through pipe 172, controlled by valve 173. The kettle product from the depropanizer is passed through pipe 174, controlled by valve 175, to debutanizer 176.

In the debutanizer, C_4 hydrocarbons are recovered as overhead product and are passed through pipe 177, controlled by valve 178, to a separation step wherein butadiene is separated from other C_4 hydrocarbons. This separation may be effected by solvent extraction, azeotropic distillation or sulfone formation. Butadiene is recovered, as through pipe 180 and valve 181. The separated butenes are withdrawn from the system through pipe 182, controlled by valve 183. In most cases, this stream will be undesirable as a recycle stock because of the high concentration of isobutylene. Removal of isobutylene, as by selective catalytic polymerization or by HCl reaction, or by other means would be necessary to prepare the stream for recycling to heater 10.

The kettle product from the debutanizer may be passed through pipe 184, controlled by valve 185, to pipe 117 and the depentanizer, 119, to be treated as hereinbefore described for recovery of isoprene and other pentadienes. This combination, while diluting the stream to the piperylene-separation step, may be advantageous in some cases.

The kettle product from debutanizer 176 may be passed from pipe 184 through pipe 186, by means of valve 187, to depentanizer 188. C_6 and heavier hydrocarbons are separated as kettle product and are withdrawn from the system through pipe 189, controlled by valve 190. The C_5 hydrocarbons are passed overhead from the depentanizer through pipe 191, controlled by valve 192, and through valve 192A to separating step 193 wherein isoprene and low-boiling olefins are recovered overhead and discharged from the system through pipe 194, controlled by valve 195, or are subjected, if desired, to further separation means not shown to recover isoprene.

The kettle product from 193 is passed through pipe 196, controlled by valve 197, to separation step 198 wherein pentadienes are separated from unconverted C_5 olefins and are withdrawn from the system through pipe 199, controlled by valve 200. The unreacted olefins from the separation step 198 or, if this separation step is by-passed through pipe 201 and valve 202, the unreacted olefins from the separation step 193 are passed through pipe 203, controlled by valve 204, are recycled through pipe 136 to the second cracking step. Alternately, the overhead product from 188 may pass directly to separation step 198 via 191 and valves 192 and 192B, where total pentadienes are recovered.

It is to be understood that all columns are equipped with pumps, heat exchangers, heating coils, overhead condensers and reflux return and, where necessary, points of entry of solvent of entrainer that, though omitted here to simplify the flow-sheet, are known to the art and are used commonly as a part of the equipment for such operation as herein described.

Examples

Pentene-2 and trimethylethylene were cracked by passing through heated tubes of negligible catalytic activity under conditions of time and temperature as shown in the following table. Butadiene yields ranging from 26 to 34 per cent by weight of the pentene reacted, and pentadiene yields of 6.4 to 10.7 per cent were obtained from pentene-2. Unlike pentene-2, trimethylethylene yielded only 4 per cent of butadiene. However, isoprene amounting to 40 per cent by weight of the trimethylethylene reacting were obtained. Detailed data are given in the following table.

Products of pyrolysis of pentenes

	Example No.			
	1	2	3	4
H. C. charged	Pentene-2	Pentene-2	2-Me-butene-2	2-Me-butene-2.
Average temperature	1400° F. (760° C.)	1431° F. (778° C.)	1432° F. (779° C.)	1495° F. (813° C.).
Total pressure—millimeters	745	745	745	745.
Time (sec.)	0.1	0.015	0.018	0.03.
Steam/H. C. ratio		1.7	1.8	1.5.
Percent reacted	73.22	36.23	3.1	20.6.
Reaction velocity constants (k)	13.1	29.35	1.84	7.7.
Yield C_4H_8 based on C_5H_{10} reacted	25.6	34.1	4.3	4.2.
Yield C_5H_8 based on C_5H_{10} reacted	10.7	6.35	16.3	40.0.
Composition of products (weight percent):				
H_2	0.22	0.11	0.03	0.15
CH_4	10.33	4.32	0.38	2.21
C_2H_2	0.19	0.09		0.50
C_2H_4	4.71	2.26	0.03	0.05
C_2H_6	2.38	1.06		0.65
C_3H_6	6.88	2.66		0.02
C_3H_8	0.39	0.31		0.88
C_4H_8	18.70	12.33	0.13	5.39
i-C_4H_8	0.0	5.26	0.92	1.21
n-C_4H_8	10.2		0.44	0.0
C_4H_{10}	0.0	0.0	0.08	
C_5 (4–24° C.)		2.06	0.64	8.23
Pentadiene	7.58	2.30	0.52	79.39
Pentenes	26.78	63.77	96.83	
C_5H_{12}	0.27	0.0		1.30
Heavier	11.16	3.41		0.0
Carbon	0.0	0.0	0.0	
Total [1]	99.86	99.94	100.00	99.98

[1] Difference in total and 100.0 is the CO and CO_2 found in the effluent gas.

The cracking conditions used may be governed by the following considerations.

For the feed to the cracking unit in the first stage, the time-temperature relationship to obtain from 20 to 70% cracking of pentene-2 per pass is determined by the following Equation 1

$$(1) \qquad \log t = \frac{13{,}900}{T} - (14.85 \pm 0.37)$$

where t is reaction time in seconds and T is cracking temperature in degrees Kelvin.

For the feed to the cracking unit in the second stage the most useful range is 15 to 50% by weight of trimethylethylene cracked per pass. The following Equation 2 covers the time-temperature relationship for this region:

$$(2) \qquad \log t = \frac{13{,}350}{T} - (13.65 \pm 0.31)$$

The exact amount of decomposition selected depends upon the presence or absence of diluents. With diluents, a higher decomposition per pass may usually be employed without loss of efficiency. The amount of decomposition also depends upon the temperature used. Thus, in the lower temperature ranges, the extent of decomposition per pass will usually be maintained in the lower portion of the range of per cent cracked.

I claim:

1. The process for the production of diolefins from a mixture of pentenes comprising pentene-2 and trimethylethylene which comprises subjecting said mixture to pyrolysis in a first zone at substantially atmospheric pressure and at a temperature within the range of 700° C. to 900° C. for a period of time sufficient to convert from 30 to 70 per cent of the pentene-2 content of said mixture to other materials with optimum yield of butadiene; separating the butadiene so formed from the effluent of said first zone; and subjecting the mixture of unreacted pentene-2 and trimethylethylene contained in the effluent of said first zone to pyrolysis in a second zone at substantially atmospheric pressure and at a temperature within the range of 700 to 900° C. for a period of time materially greater than that employed in the first zone and sufficient to convert from 20 to 80 per cent of the unreacted trimethylethylene content of said mixture of unreacted pentene-2 and trimethylethylene to other materials with an optimum yield of isoprene.

2. The process for the production of diolefins from a mixture of pentenes comprising pentene-2 and trimethylethylene which comprises subjecting said mixture to pyrolysis in a first zone at substantially atmospheric pressure and at a temperature within the range of 700° C. to 900° C. for a period of time within the limits defined by the following Equation 1:

$$(1) \qquad \log t = \frac{13{,}900}{T} - (14.85 \pm 0.37)$$

where t is the reaction time in seconds and T is the temperature in degrees Kelvin, such that from 30 to 70 per cent of the pentene-2 content of said mixture is converted to other materials with optimum yield of butadiene; separating the butadiene so formed from the effluent of said first zone; and subjecting the mixture of unreacted pentene-2 and trimethylethylene contained in the effluent of said first zone to pyrolysis in a second zone at substantiallly atmospheric pressure and at a temperature within the range of 700° C. to 900° C. for a period of time in excess of that employed in the first zone and within the limits defined by the following Equation 2:

$$(2) \qquad \log t = \frac{13{,}350}{T} - (13.65 \pm 0.31)$$

where t is the reaction time in seconds and T is the temperature in degrees Kelvin, under conditions such that from 20 to 80 per cent of the trimethylethylene content of said mixture of unreacted pentene-2 and trimethylethylene is converted to other materials with optimum yield of isoprene.

HAROLD J. HEPP.