Jan. 31, 1967 R. W. KING ETAL 3,301,915

RECOVERY OF ISOPRENE FROM HYDROCARBON FRACTIONS

Filed Nov. 5, 1965 3 Sheets-Sheet 1

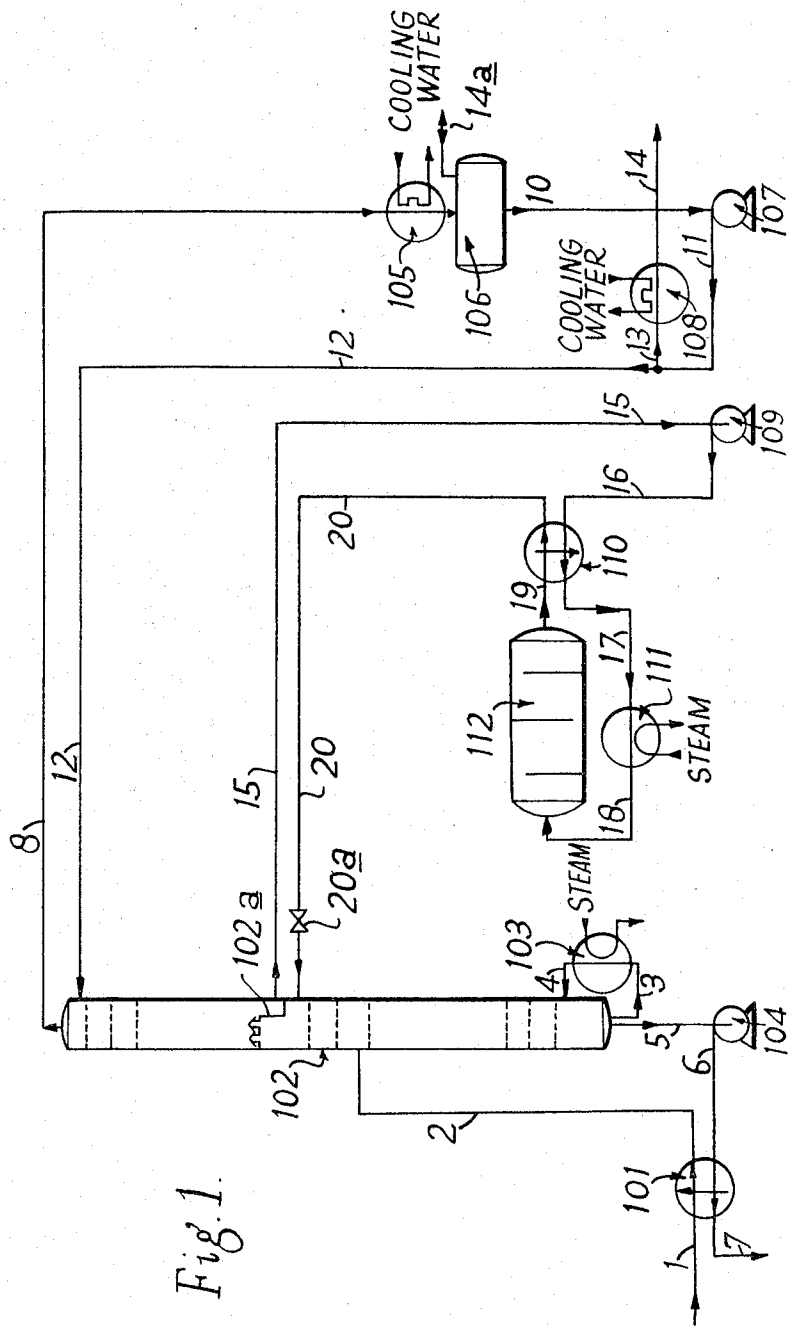


Fig. 1.

RECOVERY OF ISOPRENE FROM HYDROCARBON FRACTIONS

Filed Nov. 5, 1965 3 Sheets-Sheet 2

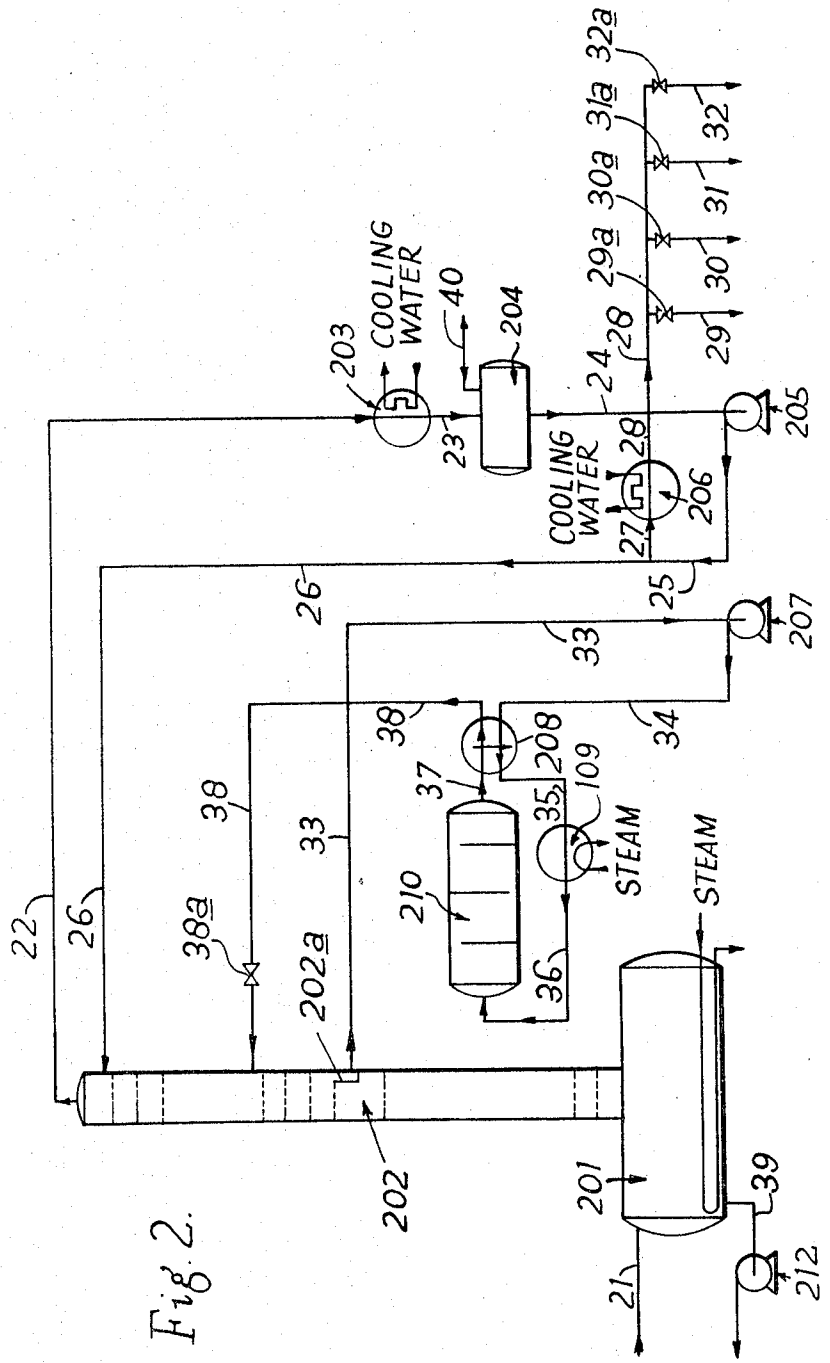


Fig. 2.

RECOVERY OF ISOPRENE FROM HYDROCARBON FRACTIONS

Filed Nov. 5, 1965 3 Sheets-Sheet 3

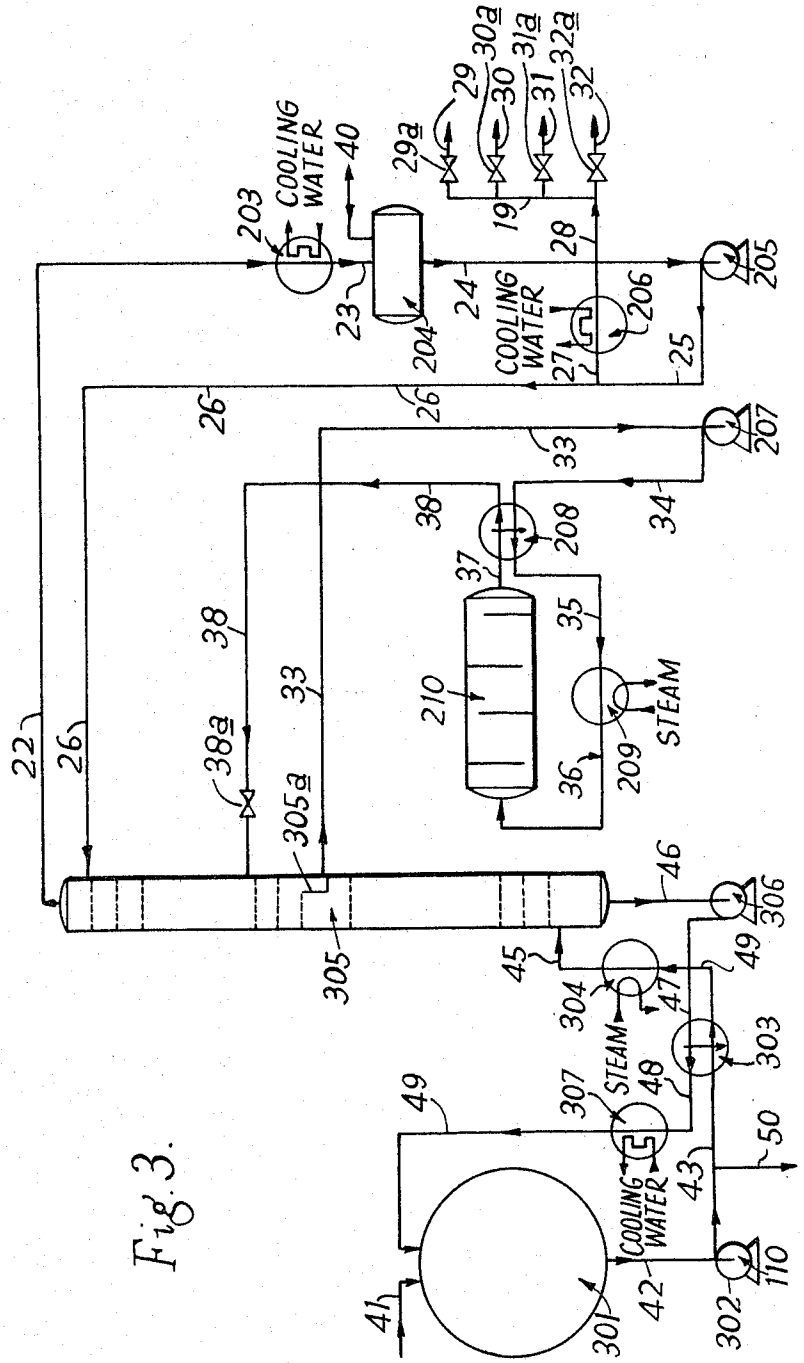


Fig. 3.

United States Patent Office 3,301,915 Patented Jan. 31, 1967

3,301,915

RECOVERY OF ISOPRENE FROM HYDROCARBON FRACTIONS

Ralph William King, London, and Barry Owen Shorthouse, Southampton, England, assignors to The International Synthetic Rubber Company Limited, Southampton, England

Filed Nov. 5, 1965, Ser. No. 513,632
Claims priority, application Great Britain, Nov. 6, 1964, 45,358/64
11 Claims. (Cl. 260—681.5)

This invention relates to the recovery of isoprene from hydrocarbon streams consisting wholly or predominantly of C_5 hydrocarbons and particularly from such streams which contain in addition to isoprene appreciable amounts of cyclopentadiene and usually also of piperylenes.

Isoprene-containing hydrocarbon streams are available which are obtained (i) by the chemical or catalytic dehydrogenation of C_5 olefin and/or paraffin hydrocarbons, (ii) by thermal demethenation of specific C_6 hydrocarbons such as 2 methyl pentene 2, and (iii) as a by-product stream of the thermal cracking of naptha and other hydrocarbon feedstocks for the production of ethylene. This by-product stream forms a particularly suitable feedstock for the process of the invention. In the last mentioned process other valuable unsaturated gaseous hydrocarbons (propylene, butadiene) are produced simultaneously and usually separated and recovered.

The liquid product from the cracking operations referred to above is normally separated into two or more fractions of different or overlapping boiling range, the main fraction consisting of raw gasoline with a boiling range of approximately 20 to 150° C. This main fraction contains appreciable amounts of C_5 hydrocarbons, both cyclic and acyclic paraffins, mono and di-olefins including cyclopentadiene, piperylenes and isoprene, and smaller amounts of acyclic acetylenes and acetylenic olefins.

When it is desired to recover isoprene, cyclopentadiene or other C_5 hydrocarbons from the main liquid fraction, it is normally first separated by fractional distillation into a stream consisting mainly of C_5 hydrocarbons having an approximate boiling range of 25 to 50° C., and a heavier hydrocarbon stream which may be employed after suitable treatment in motor gasoline.

The C_5 hydrocarbon stream so obtained may vary considerably in composition since this is dependent on the cracking conditions employed, the composition of the cracking feedstock, and the subsequent processing of the cracked product. The concentration of the main components in the mixture generally lie within the following ranges:

Components:	Weight, percent
Isoprene	8 to 16.
Piperylenes	6 to 14.
Cyclopentadiene	4 to 25.
Isopentane	9 to 20.
N-pentane	25 to 45.
Cyclopentane	2 to 12.
Pentenes	12 to 30.
Isopropenyl acetylene	0.02 to 0.2.
Other acetylenes	less than 0.1.

The composition of a C_5 stream from an ethylene producing plant employing a standard hydrocarbon charge stock may show far less variation than has been indicated above.

Many methods have been suggested for the concentration or separation of isoprene and other valuable C_5 hydrocarbons from such cracked C_5 hydrocarbon streams.

The following initial operations are a common feature of many of the methods suggested:

(1) The liquid is treated under pressure at a temperature in the range 100 to 140° C., for several hours. The treatment is carried out in a soaking chamber under sufficient pressure to prevent vapourisation. The object of the treatment is to convert the greater part of the cyclopentadiene present in the original mixture to the less volatile compound dicyclopentadiene, which is readily separated from isoprene during subsequent distillation.

(2) The product after heat treatment is fractionally distilled in one or more columns of high efficiency at a high reflux ratio. The main object of this distillation is to separate the mixture into an isoprene rich fraction having a very low piperylene content, and a heavier fraction of low isoprene content and higher piperylene content.

Such treatment is capable of giving an isoprene rich fraction containing 25 to 40% by weight of isoprene, and 0.1% by weight or less of piperylenes.

A disadvantage of the treatment described above lies in the relatively high cyclopentadiene content of the isoprene rich fraction, which under the best conditions is usually in the range 0.5 to 1.0% by weight or 2.0 to 4% by weight based on isoprene in the product. Cyclopentadiene is a particularly injurious impurity when the product is required to be used without further purification or concentration as feed to catalytic polymerisation processes for the production of polyisoprene, e.g., using lithium butyl as catalyst. Though it may prove possible to reduce the cyclopentadiene content of the isoprene rich fraction to 0.3 wt. percent, it is not practical to reduce it further.

Examination of the subsequent fractional distillation step for the recovery of isoprene in the heat treated feed as an isoprene concentrate of low piperylene content, shows that unconverted cyclopentadiene monomer in the feed is not effectively separated from isoprene in the overhead fraction unless a large proportion of the isoprene is allowed to be lost in the bottoms product. Under conditions of high isoprene recovery in the overhead concentrate, the cyclopentadiene content of the overhead fraction is generally higher than the cyclopentadiene content either of the feed to the column or of the bottoms product.

This behaviour of cyclopentadiene in the fractionating column, which is anomalous when considered in relation to the boiling points of isoprene, cyclopentadiene and cis- and trans-piperylene, appears to result from the non-ideal behaviour of the hydrocarbons of different types (cyclic-di-olefin, branched and straight chain di-olefins, olefins, paraffins, etc.). In scientific terms, the activity coefficient of cyclopentadiene in the liquid is significantly higher than the activity coefficient either of isoprene or of piperylene, these being nearly identical in any particular mixture.

It has now been found that in the fractionation of an isoprene and cyclopentadiene containing C_5 fraction such as is referred to above, either before or after the heat treatment, the cyclopentadiene content of the liquid during the fractionation is at a maximum value at an intermediate point in the fractionation column. This maximum cyclopentadiene content may be many times (between five and twenty) the cyclopentadiene content of the isoprene concentrate which is removed as overhead product, and the peak concentration is generally found near and most commonly slightly above the mid-point in the fractionating column.

It has further been found that by withdrawing liquid from the column in the area of high cyclopentadiene concentration, dimerizing the major part of the cyclopentadiene in the withdrawn liquid and recycling the liquid product mixture to an appropriate point in the column, an isoprene concentrate can be obtained as overhead which contains a high proportion (i.e. 80 to 96% by weight) of the isoprene in the feed material, but only

traces (less than 0.1% by weight and, if necessary, considerably less) of cyclopentadiene and piperylenes.

The invention thus consists in a process for recovering an isoprene-enriched fraction with a relatively low cyclopentadiene content from a hydrocarbon stream containing isoprene and cyclopentadiene and consisting predominantly of C_5 hydrocarbons, which process comprises fractionally distilling the hydrocarbon stream to obtain an isoprene-enriched overhead fraction and during the course of the distillation withdrawing liquid from an intermediate point in the fractionation system at which a relatively high cyclopentadiene concentration exists, subjecting the withdrawn liquid to dimerisation conditions for the dimerisation of cyclopentadiene, and returning the resulting liquid product to an intermediate point in the fractionation system, which will normally be close to the point from which liquid is withdrawn.

The feed material will usually contain piperylenes (cis- and trans-) as well as cyclopentadiene and the piperylenes will be separated in the bottoms fraction.

In the dimerisation treatment during which higher polymers of cyclopentadiene may also be formed, suitable conditions are a temperature of 100 to 160° C., preferably 120 to 140° C., a pressure of from 10 to 30 atm., preferably 15 to 25 atm., at least sufficient to maintain the cyclopentadiene in the liquid phase and a contact time of from 10 minutes to 6 hours, preferably 20 minutes to 3 hours.

By dimerising a liquid containing an increased amount of cyclopentadiene as compared with the starting material, the rate of dimerisation is increased and the size of the dimerisation reactor can be reduced. Also the possibility of reaction between the cyclopentadiene and isoprene is much reduced, thereby largely avoiding an appreciable loss of isoprene.

The process of the invention may be carried out as a continuous, batch or semi-continuous operation in suitably designed equipment.

The feed material to which the process of the invention may be applied is a hydrocarbon stream containing the hydrocarbons isoprene, cyclopentadiene, and usually cis- and trans-piperylenes. Preferably the feed material is a fraction of relatively narrow boiling range (25 to 50° C.) and consisting predominantly of C_5 hydrocarbons.

If the cyclopentadiene content of the feed material is high or if a product with a very low cyclopentadiene content is required, the feed material may first be subjected to a heat treatment for several hours in the liquid phase at an elevated temperature preferably in the range 100 to 140° C., and under pressure as in the known method previously described. Suitable conditions are a contact time of 3 to 6 hours, a temperature of 125° C., and a pressure of at least 10 atmospheres absolute, preferably in the range 15 to 30 atmospheres, to prevent vapourisation of the material during heat treatment. This pretreatment is desirable when the feed has more than 10% of cyclopentadiene, and may advantageously be employed when the cyclopentadiene content is over 5%.

In cases where the feed material has an excessively high cyclopentadiene content, it is preferably subjected additionally to a simple distillation step before the further treatment described below, to separate the major part of the C_5 hydrocarbons in the feed from cyclopentadiene polymers formed by the heat treatment, and so lessen the degree and incidence of fouling in the subsequent processing equipment. When such a simple distillation step is carried out, the maximum temperature during distillation should not exceed 140° C., and should preferably be below 100° C., to reduce or prevent thermal depolymerisation of the cyclopentadiene dimers separated from the bulk of the C_5 hydrocarbons during the distillation.

In carrying out the process of the invention, the feed material, with or without the pretreatments described above, may be fractionated in an efficient fractional distillation plant or column containing the equivalent of between 60 and 200 theoretical plates—preferably between 100 and 150 theoretical plates. The column is provided with a means of withdrawing part or all of the liquid reflux passing down the column from an intermediate point in the column which is preferably situated slightly above the mid tray of the column. The column is also provided with a point for returning the liquid removed for processing to an intermediate point in the column, which may be above or below the point from which liquid is removed. In a plant designed for continuous operation, the point of liquid return is preferably located on the plate immediately below the point from which liquid is removed. In a plant designed for batch operation, the point of liquid return is preferably several plates above the point from which liquid is removed. The material is usually returned to a point at which the isoprene/piperylenes ratio substantially corresponds to that of the returned material.

By subjecting the withdrawn liquid to dimerisation conditions for the dimerisation of cyclopentadiene, e.g. in a soaking vessel, and returning the liquid product to the column, the maximum cyclopentadiene content of the liquid in the column may be reduced to 1 wt. percent or less.

A number of embodiments of the invention are described below, by way of example, with reference to the accompanying drawings in which:

FIGURE 1 is a flow diagram illustrating the continuous treatment of a C_5 fraction containing 5 wt. percent or less cyclopentadiene,

FIGURE 2 is a flow diagram illustrating a batch operation according to this invention, and

FIGURE 3 is a flow diagram illustrating a modified form of batch operation.

It should be understood that feed streams having a cyclopentadiene content higher than 5 weight percent are best subjected to the pretreatment steps of heat treatment and in certain cases simple distillation as described previously to reduce the cyclopentadiene content of the feed before being treated by the processes described below.

The feed material may also be subjected to a further pretreatment before entering the continuous version of the process shown in FIGURE 1. This pretreatment consists of a "topping distillation" in a high efficiency fractionating column, e.g. equivalent to 40 to 100 theoretical plates. The object of this topping operation is to remove C_4 hydrocarbons and other light ends, and particularly isopropenyl acetylene which is an active catalyst poison in many polymerisation processes employing isoprene. At the same time, some of the other low boiling C_5 hydrocarbons in the feed, e.g., isopentane, may be partially removed without significant loss of isoprene. This results in a higher concentration of isoprene in the end product from the process.

Referring to FIGURE 1, the isoprene and cyclopentadiene containing feed stream, subjected if necessary or if desired to one or more of the treatments described above, passes as liquid in line **1** to the heat exchanger **101** where it is preheated to a suitable temperature (30 to 90° C. depending on the column pressure) before entering the fractionating column **102** at an intermediate point via line **2**. The preheater **101** is not essential and may be dispensed with. The fractionating column **102** is a high efficiency liquid vapour counter-current contacting device fitted with a number of trays or filled with a suitable type of packing, in known fashion. The column efficiency is preferably not less than 60 theoretical plates, and desirably not less than 100 theoretical plates.

Part of the liquid passing down to the base of the column leaves by line **3** to the reboiler **103** where it is partially vapourised by indirect heat exchange with steam or other convenient heating medium, and returns to the column by line **4**. The rest of the column base product,

substantially free of isoprene, passes via line **5** to pump **104** and thence via line **6** to heat exchanger **101** in which it is cooled, and then by line **7** to storage or further treatment before utilisation, e.g. in the production of motor gasoline.

Overhead vapour from the column passes via line **8** to the condenser **105**, from which condensed hydrocarbon liquid passes via line **9** to the reflux drum **106**. The pressure in the column, reflux drum and other processing equipment is controlled by admitting or withdrawing gas or vapour to or from the reflux drum via line **14***a*. The pressure in the reflux drum may be controlled at any suitable pressure from atmospheric to 20 atmospheres, but a pressure of 2 to 3 atmospheres absolute is generally found most convenient.

Liquid passes from the reflux drum **106** via line **10** to the pump **107**, from which it is discharged by line **11**. Part of the pump discharge is returned as reflux to the top of the column via line **12**.

The remainder passes via line **13** to the cooler **108** where it is further cooled, and thence via line **14** to product storage. This is the isoprene rich concentrate containing only traces of cyclopentadiene and piperylene which is the final product from the process.

A special liquid draw-off tray **102***a* is provided in the column, usually a few trays above the feed tray. Part and preferably all of the liquid descending on to this tray is removed via line **15** and passes to pump **109**, which raises its pressure by at least 10 atmospheres and preferably 15 to 30 atmospheres. Liquid passes from the pump via line **16** to the heat exchanger **110** where it is preheated to a temperature in the range 70 to 120° C. The liquid leaves the heat exchanger via line **17**, passing to the additional heater **111**, where it is heated by indirect heat exchange with steam or other suitable medium to a temperature in the range 100 to 150° C.

The heated liquid passes via line **18** into the soaking vessel **112**, which is preferably provided with internal baffles to reduce back mixing and short circuiting within the vessel. The vessel is freed of gas or air before start up. The volume of the vessel **112** is so arranged as to produce a liquid residence time in the vessel in the range 10 minutes to 6 hours, preferably between 20 minutes and 3 hours, depending on the temperature in the vessel and the degree of cyclopentadiene removal required. Liquid leaving the soaking vessel **112** via line **19** is cooled by heat exchange with incoming liquid in **110** and returned to the column, preferably to the tray below the liquid draw-off, by line **20**. When all liquid is withdrawn from tray **102***a*, the returning liquid should desirably enter the tray below the tray **102***a*. Line **20** is provided with a throttling or back-pressure control valve **20***a*, preferably of the automatic type, to prevent loss of pressure and vapourisation in the soaking vessel **112**.

Preheater **111** may be by-passed or dispensed with when the amount of cyclopentadiene in the feed is high, since the dimerisation of cyclopentadiene occurring in **112** raises the temperature of the liquid and so causes an adequate temperature difference across the heat transfer surface of the heat exchanger **110**.

FIGURE 2 shows a flow diagram of the process in which the invention is applied in a batch manner. This has advantages over continuous processing where the scale of operation is relatively small, particularly in so far as it reduces or eliminates the need for the pretreatment required in many cases with the continuous process. It also enables a distilled heavy C_5 fraction of low cyclopentadiene and dicyclopentadiene content to be produced (e.g. for motor gasoline manufacture) without the need for further processing equipment.

Referring to FIGURE 2, a charge of isoprene- and cyclopentadiene-containing feed liquid is introduced into the kettle **201** via line **21** at the start of a batch. The kettle **201** is provided with a steam coil or other suitable means of heating.

The batch charge in the kettle **201** is heated and vapourised in the normal manner, vapour passing through the high efficiency fractionating column **202**, leaving via line **22** and passing to the condenser **203**. Condensed liquid passes from the condenser via line **23** to the reflux drum **204**, which is preferably designed to have a very low liquid capacity in relation to the capacity of the kettle **201**. The pressure in the equipment described is controlled by admitting or withdrawing gas or vapour to or from the reflux drum via line **40**.

Condensed liquid passes from the reflux drum **204** via line **24** to the reflux/product pump **205**, from which it is discharged via line **25**. The major part of this stream returns as reflux to the top of the column **202** via line **26**, whilst the smaller part passes as product via line **27** to the cooler **206**, which it leaves via line **28**.

In the batch process, several other overhead fractions may be separated from the charge in addition to the isoprene rich concentrate, thus eliminating the need for additional equipment generally required in conjunction with the continuous process. Product line **28** is connected to branch lines **29**, **30**, **31** and **32** for removal of the various overhead fractions.

Line **29** is used for removal of the first fore-running fraction which consists of C_4 hydrocarbons, isopropenyl acetylene, isopentane and other low boiling C_5 hydrocarbons, but is substantially free of isoprene. This fraction may be employed in the manufacture of motor gasolene. Line **30** is used for removal of the isoprene rich concentrate, substantially free from cyclopentadiene, piperylenes and isopropenyl acetylene. This is the main product from the process. Line **31** may be used for removing an intermediate fraction containing both isoprene and piperylenes after the main product has been removed.

This intermediate fraction may advantageously be added to the charge of a subsequent batch and so be reprocessed.

Line **32** is used for withdrawing a heavy C_5 distillate fraction containing piperylenes, pentenes, normal and cyclopentane and higher boiling hydrocarbons. This fraction, which is substantially free of cyclopentadiene and dicyclopentadiene, may be used in the manufacture of motor gasoline with the minimum of further treatment.

Part of the liquid descending the fractionating column **202** is withdrawn from a specially provided draw-off tray **202***a* via line **33** to pump **207**, which raises its pressure to at least 10 atmospheres and preferably to 15 to 30 atmospheres. The liquid passes via line **34** to the heat exchanger **208** where it is heated to a temperature in the range 70 to 120° C. and thence via line **35** to auxiliary heater **209** which raises the temperature of the liquid further to 100 to 150° C. before entering the soaking vessel **210**, via line **36**, provided with internal baffles as in the continuous process and designed to give a liquid residence time which is preferably within the range of 30 minutes to 3 hours. Liquid leaving the soaking vessel via line **37** is cooled by heat exchange with incoming liquid in heat exchanger **208** and returned to the column via line **38**. This line is provided with a throttling valve **38***a*, preferably of the automatic type, to prevent loss of pressure and liquid vapourisation in the soaking vessel **210**.

The point at which the liquid is returned to the column is in the case of the batch process preferably several plates higher in the column than the point of liquid offtake. The reason for this is that the composition of the liquid at any point in the column is continuously changing during batch distillation, so that by the time the liquid leaving the take-off tray has passed through the time tank, the concentrations of isoprene and piperylenes in the liquid correspond to those of a point in the column higher than the point from which the liquid has been removed from treatment.

The liquid charge introduced into the kettle for batch operation should be large in relation to the capacity of the soaking vessel **210**, and the period of the total batch cycle

should be at least 24 hours, preferably 72 hours or more for efficient operation of the process described.

The operation is started at total reflux and sufficient time is given for the concentration gradient to be established in the column before off-take of fore-runnings via line **29** is commenced. The soaking vessel **210** is conveniently left full of liquid from the previous batch, and flow of liquid through the soaking vessel is commenced as soon as reflux liquid is descending the column. The reflux ratio is preferably increased progressively during withdrawal of each fraction, but lowered on commencement of a fresh fraction.

The liquid left in the kettle at the end of the distillation will contain 95% or more of the cyclopentadiene in the feed in the form of dimer and higher polymers and co-polymers. It is not advisable to attempt to remove all heavy C_5 hydrocarbons from the kettle by raising the temperature too far at the end of the batch distillation, since this can cause depolymerisation of di-cyclopentadiene in the kettle. The kettle temperature at the end of the distillation should not exceed 150° C., and should preferably not exceed 100° C.

Liquid remaining in the kettle at the end of the distillation is removed via line **39** by pump **212**, by which it is pumped to separate storage. This liquid may be utilised for the manufacture of cyclopentadiene and its derivatives.

Control valves **29***a*, **30***a*, **31***a* and **32***a* are suitably provided in the lines **29**, **30**, **31** and **32** respectively. Valve **38***a*, a back pressure valve similar to valve **20***a* of FIGURE 1, is provided in line **38**.

As previously stated, a modified batch process which may be referred to as a semi-continuous process, is illustrated in FIGURE 3. In place of the kettle in the batch process, the charge is contained in a tank or suitably constructed vessel **301** which is maintained at a lower temperature than that in the kettle for the batch process. The charge is fed to vessel **301** by line **41** and is circulated at a high rate via line **42** by pump **302**, thence via line **43** through heat exchanger **303**, thence via line **44** through the vapouriser **304** and finally via line **45** into the base of the column **305** above the liquid level in the column. Liquid is removed from the base of the column **305** via line **46** by pump **306**, thence via line **47** to heat exchanger **303**, thence via line **48** to cooler **307**, and back into the charge vessel **301**. The rest of the operation and equipment is as described for the batch process, the same reference numerals being used to designate the rest of the equipment as are used in FIGURE 2, with the exception that the plate from which liquid is withdrawn is designated **305***a*. Liquid left in the charge vessel **301** at the end of the distillation is pumped away via line **50**.

The main advantage of the semi-continuous process is that it enables very large batches of material to be processed over a long batch cycle, (i.e. a week or more) without subjecting the material to prolonged residence times at the kettle temperature, and consequent loss of isoprene and fouling, which would be a disadvantage of the batch process under similar circumstances.

The semi-continuous process further enables isoprene in the feed to be recovered in the product concentrate at yields in excess of 95%, with a cyclopentadiene content of less than 0.05 wt. percent.

The fractionation column is operated at a high reflux ratio. In the case of continuous distillation, the preferred reflux: feed ratio lies within the range 10:1 and 20:1. In the case of batch distillation the reflux ratio is preferably increased continuously as distillation of the isoprene rich concentrate proceeds, e.g., from an initial reflux: product ratio of 5:1 to a final reflux: product ratio of 25:1.

Whilst a single column has been shown in the processes described above, it should be understood that this may consist of two or more columns placed in series with intermediate vapour lines, liquid transfer lines and pumps. Such an arrangement is frequently used where a large number of theoretical plates are required.

The process of the invention and the advantage obtained thereby is illustrated by the following example.

EXAMPLE

A high efficiency continuous pilot plant fractionating column equipped with special gauze packing was set up with ancillaries as shown in FIGURE 1. An internal overflow weir allowed all liquid to flow down the column when the soaking vessel (**112**) was not in use and no liquid was being withdrawn. The efficiency of the column was tested at a total reflux at a top pressure of 15 p.s.i.g. using a mixture of iso- and normal pentanes as test mixture. Analyses of samples taken from the reflux drum and column base showed that the column had an average efficiency of 78 theoretical plates.

The feed point to the column corresponded to 36 theoretical plates above the reboiler. The liquid draw-off tray was located immediately above the feed point, and the liquid from the soaking vessel was returned to the feed point in the column.

The column was fed with 65 pounds per hour of a cracked C_5 hydrocarbon feed at 50° C. from which part of the cyclopentadiene had been removed by heat treatment and distillation.

The composition of the treated feed, analysed by gas-liquid chromatography was as follows:

	Weight percent
Isopentane	13.4
n-Pentane	22.6
2-methyl butene-1	9.4
Pentene-1	8.6
Pentene-2 (cis- and trans-)	7.3
2-methyl butene-2	3.8
Isoprene	10.6
Piperylenes (cis- and trans-)	11.5
Cyclopentane	11.9
Cyclopentadiene	0.7
Unidentified	0.2

The column was operated at a top pressure of 15 p.s.i.g. and a top temperature of 49° C. The liquid boil up rate and reflux return were adjusted to give an internal reflux:feed ratio of 16:1, i.e., an internal reflux rate of 1040 pounds per hour. The soaking vessel **112** had a capacity of 20 cubic feet, corresponding to a liquid residence time of approximately 40 minutes, and was operated at a temperature of 130° C. and a pressure of 290 p.s.i.g.

The column was first operated with the soaking vessel out of commission, valves on line **15** and **20** being closed, and all liquid on the take-off tray overflowing down the column.

After careful adjustment of the temperature and flow rates, there were obtained 26 pounds/hour of overhead product from line **14** containing 25.5% isoprene, 0.2% piperylenes and 1.1% cyclopentadiene.

The bottoms product from line **7** contained 0.5% isoprene, 18.7% piperylenes and 0.4% cyclopentadiene as monomer.

The column continued to operate on the same feed and at the same feed rate as before: the valves on lines **15** and **20** were opened, and the pump, heat exchangers and soaking vessel were brought gradually into commission. A period of 28 hours was allowed to reach steady conditions from the time the soaking vessel was full of liquid.

25 pounds per hour of overhead product were withdrawn from line **14**, containing 26.4% isoprene, 0.15% piperylenes and 0.08% cyclopentadiene.

The bottoms product from line **7** contained 0.4% isoprene, 18.2% piperylenes and 0.05% of cyclopentadiene as monomer.

These runs showed that operation in accordance with the invention as compared with a normal fractional distillation resulted in a 14-fold reduction in the cyclopentadiene content of the overhead product without loss of isoprene.

All percentages referred to in the example are percentages by weight.

We claim:

1. A process for the recovery of an isoprene fraction with a very low cyclopentadiene content as an overhead fraction by fractional distillation from a hydrocarbon stream containing isoprene and cyclopentadiene and consisting predominantly of C_5 hydrocarbons, in which process liquid is withdrawn during the course of the fractional distillation from an intermediate point in the fractional distillation system in an area of relatively high cyclopentadiene concentration, the withdrawn liquid is subjected to dimerisation conditions for the dimerisation of cyclopentadiene and the resulting liquid product is returned to an intermediate point in the fractional distillation system.

2. A process as claimed in claim 1, in which the hydrocarbon stream contains piperylenes and in which an isoprene-enriched fraction is recovered as overheads and a piperylene-enriched fraction is also recovered, the isoprene-enriched fraction having a considerably reduced cyclopentadiene and piperylenes content.

3. A process according to claim 2 in which the said resulting liquid product is returned to a point in the fractional distillation system at which the isoprene/piperylene ratio corresponds approximately with that of the said resulting liquid product.

4. A process as claimed in claim 1, in which the hydrocarbon stream contains more than 10% by weight of cyclopentadiene and is subjected to a preliminary treatment for the dimerisation of cyclopentadiene to reduce the cyclopentadiene content below 5% by weight.

5. A process as claimed in claim 4, in which the hydrocarbon stream contains more than 5% by weight of cyclopentadiene and is subjected to the said preliminary treatment.

6. A process as claimed in claim 4, in which the hydrocarbon stream after said preliminary treatment is distilled to separate the polymers formed and then fractionally distilled to recover the overhead isoprene fraction.

7. A process as claimed in claim 1, in which the hydrocarbon stream is subjected to a preliminary distillation to obtain a stream of increased isoprene content, which is subjected to said fractional distillation.

8. A process as claimed in claim 1, in which the withdrawn liquid is heated to a temperature of from 100 to 160° C., under a pressure of 10 to 30 atmospheres sufficient to maintain the cyclopentadiene in the liquid phase and for a period of from 10 minutes to 6 hours.

9. A process as claimed in claim 8, in which the withdrawn liquid is heated to a temperature of from 120 to 140° C., under a pressure of from 15 to 25 atmospheres and for a period of from 20 minutes to 3 hours.

10. A process for the recovery of an isoprene fraction with a considerably reduced cyclopentadiene and piperylenes content from a hydrocarbon stream containing isoprene, piperylenes and more than 5% by weight of cyclopentadiene and consisting substantially completely of C_5 hydrocarbons, which process comprises subjecting the hydrocarbon stream to a preliminary treatment for dimerisation of cyclopentadiene to reduce the cyclopentadiene content below 5% by weight, distilling the hydrocarbon stream to separate the polymers formed therefrom, fractionally distilling the hydrocarbon stream from which the polymers have been separated, withdrawing during the course of the fractional distillation liquid from an intermediate point in the fractional distillation system in an area of relatively high cyclopentadiene concentration, subjecting the withdrawn liquid to dimerisation conditions for the dimerisation of cyclopentadiene, returning the resulting liquid product to an intermediate point in the fractional distillation system, and recovering an isoprene-enriched fraction as overheads product and a piperylenes-enriched fraction as bottoms product.

11. A process as claimed in claim 10, in which the withdrawn liquid is heated to a temperature of from 120 to 140° C., under a pressure of from 15 to 25 atmospheres and for a period of from 20 minutes to 3 hours.

References Cited by the Examiner

UNITED STATES PATENTS

2,704,778	3/1955	Maisel	260—681.5
2,768,224	10/1956	Page et al.	260—681.5

DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*