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PROCESS OF PRODUCING ISOPRENE

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This invention relates to a process of producing isoprene from terpene hydrocarbons. More particularly, it relates to an improved process of producing isoprene whereby higher yields and greater efficiency may be realized from the materials employed.

It is known that when terpene hydrocarbons are brought into contact with an incandescent element, isoprene is formed to a greater or less extent. It is further known that when isoprene is brought into contact with an incandescent element, it decomposes into other hydrocarbons and hydrogen at a relatively high velocity. This accounts for the fact that, at best, the yields of isoprene are not high when thermally decomposing terpene hydrocarbons by a heated element, in a manner such as is disclosed by Gottlob U. S. Patent 1,065,522. A disadvantage of the Gottlob process is that some of the isoprene is continually returned to the reaction zone with the refluxing oil and, therefore, repeatedly subjected to decomposition, at least in part. This becomes more apparent when it is realized that any given area heated to the efficient temperature for isoprene generation will distill about 40 lbs. of terpene hydrocarbons for every pound of isoprene it produces at the start of the processing, and the ratio of terpenes distilled to the isoprene formed increases, until near the end of the operation, 400 lbs. or more of terpene hydrocarbons may be distilling and refluxing for every pound of isoprene produced. Thus a fraction of 1% of isoprene in the reflux returning to the reaction zone is a serious matter as regards yield.

I have found that when a fractionating tower is interposed between the isoprene generating vessel and the reflux condenser so that the vapors can travel up the column, partially condense, and the reflux flow back down the column so as to cause efficient fractionation, the yield is instantly improved; the isoprene finally escaping from the tower and condensed is of improved quality, i. e., contains a lower percentage of higher boiling oils, and there is less residue left in the generator at the end of the processing. Furthermore, if an electrically heated incandescent element is used, the yield of isoprene per kilowatt hour of current consumed in heating the element is increased, and a greater output of isoprene is realized per day.

A comparison of two runs was made, in one of which runs a fractionating tower with a reflux condenser on top of it was used, and in the other of which the reflux condenser was positioned directly on the generator vessel without a fractionating tower. Otherwise, the runs were the same as to conditions of operation and raw material. The run with the fractionating column gave a yield of 64% by volume of crude isoprene, whereas the run without a column yielded only 44% by volume of crude isoprene of the same quality.

The lower yield, when using only a reflux condenser as in Gottlob is believed to be due largely to the ineffectiveness with which the isoprene can be separated from the reflux returning to the generator. It is also believed to be due in part to the incapability, when using a reflux alone, of effecting the return to the generator of certain low boiling by-product hydrocarbons that are formed by the thermal decomposition of the terpene and that are themselves convertible into isoprene by the incandescent element. With a reflux condenser used as the only means of separation, the bulk of such hydrocarbons follows the isoprene, whereas by incorporating adequate fractional distillation, substantial proportions of such hydrocarbons can be returned to the generator for conversion into isoprene, but without returning any substantial proportion of isoprene, which, if returned, would be largely destroyed.

From a consideration of partial vapor pressures of isoprene and dipentene at various temperatures, applying Raoult's law, I have determined that more than twice as much isoprene can be held in solution in dipentene at 165.5° C. as at 172° C.

If this determination from theoretical considerations is correct, it should be possible to find confirming experimental evidence by examination of conditions in the generator when operating with and without the column. The temperature of the charge undergoing decomposition must be higher when a column is used, if the latter reduces the concentration of isoprene in the generator. To prove this a generator was set up with a reflux condenser on top so that the products of distillation and decomposition could enter it. The isoprene was allowed to pass the reflux condenser while the higher boiling oils, principally dipentene, were condensed and returned to the generator. Water was circulated through reflux condenser at 37 to 40° C. A charge of dipentene was brought to boiling without sufficiently high temperature of the heating element to cause decomposition, and a uniform reflux established. The temperature of the boiling dipentene registered 178° C. The dipentene was then refluxed with an incandescent element at the same rate. Isoprene was formed. The temperature of the charge dropped to 165.5° C. while the reflux or boiling was maintained without interruption and continued at this temperature. When the incandescent element was shut off and the plain heating element again used, the temperature rose to 178° C.

A fractionating column was then interposed between the same generator and the same reflux condenser, and otherwise the same conditions

repeated as before. The temperature of the charge dropped only from 178 to 172° C. or amounting to only 6° C. for the column as compared to 12.5° C. for the reflux condenser only. On a large scale with a large efficient column the maximum drop was found to be 3.5° C. When the incandescent element was shut off and plain heating again used, the temperature rose to 178° C. as it did with the plain reflux condenser.

Another serious drawback of the Gottlob process using only a reflux condenser is the limitation imposed upon the composition of the condensate in the reflux condenser. If it is desired to operate such a process so that the isoprene distillate collecting beyond the reflux condenser is relatively rich in isoprene, then the condensate in the reflux condenser must also be rich in isoprene, so that the excess isoprene and fixed gases sweeping past the reflux condenser will be composed largely of isoprene. Under these conditions the reflux runs high in isoprene, and therefore much returns to the generator to be decomposed into useless products. If an attempt is made to avoid this by purging the reflux condenser of isoprene and so distilling the terpenes largely into the reflux condenser, these oils condense at high temperature, permitting the isoprene and fixed gas and by-product hydrocarbons to sweep out the terpenes and related oils, resulting in an impure distillate running low in isoprene.

When an efficient column is interposed between the generator and the reflux condenser whereby the reflux is allowed to flow down the column, the condensate may be very rich in isoprene at the reflux condenser, but the reflux entering the generator will have the very lowest amount, or none at all of isoprene in it, thus saving the isoprene from destruction on the hot element. Thus, by substituting fractional distillation involving a multiplicity of redistillations for a single fractional condensation, a greatly improved result is obtained.

While a fractionating column is the preferred agency for carrying out this invention, other means may be used, although probably not so efficiently or economically. Since the invention resides in returning to the generator, reflux or equivalent unreacted oil freed of isoprene, all of the vapors from the generator may be condensed as a distillate to give a solution of isoprene in terpene oils and this solution may then be fractionated in a separate fractionating still where the isoprene is collected as a distillate and from which the terpene oils freed of their isoprene are fed back to the reaction zone of the generator for further thermal decomposition.

By the process of my invention the lowest concentration of isoprene can be maintained in the reaction zone, resulting in the advantages heretofore mentioned.

It is therefore an important object of this invention to provide an improved process of making isoprene from terpene hydrocarbons by the use of an immersed heating element, in accordance with which the terpene hydrocarbons distilled off along with isoprene from the reaction mass are freed from the isoprene before being returned to the reaction zone for conversion there into further quantities of isoprene.

It is a further important object of this invention, in a process for making isoprene from terpene hydrocarbons by means of an incandescent element, to provide for a more efficient utilization of the excess heat of such element, whereby the heat, in excess of that used in effecting the thermal decomposition of the terpene hydrocarbons to isoprene, is effectively used to carry out a multiplicity of redistillations of isoprene from the reflux before the latter is permitted to return to the generator, thereby preventing the destruction of isoprene that would otherwise return to the zone of reaction and increasing the yield of isoprene from the by-product hydrocarbons that are returned to the reaction zone with the isoprene freed reflux.

Other and further important objects of this invention will become apparent from the following description and appended claims.

The following will serve as an example of a preferred embodiment of my invention, it being understood the process and apparatus described are merely for purposes of illustration and that the invention is not to be considered as limited to the details given in the example.

Example

The apparatus used consisted of a steel vessel of 127 gal. total capacity, provided with a fractionating column 21 inches in diameter and 12 feet long. The column was filled for 11 feet of its length with ½ inch clay saddles and contained four pancake coils with tap water connections at the top. A distillate condenser was connected to the top of the column above the pancake coils and ice water was circulated through the condenser. The discharge pipe from the condenser passed through another condenser, which was cooled by solid carbon dioxide. A vent to a gas meter and thence to the atmosphere was taken off near the bottom of this coil condenser, while the liquid isoprene outlet of the coil condenser was connected to a receiving tank.

The steel vessel was fitted with a heating element which consisted of 68 inches of No. 5 nichrome wire connected across two heavy copper leads, which were sufficiently long to permit the heating element, in coil form, to be held near the bottom of the vessel, while the upper ends of the copper leads projected out through the top of the vessel and were there held by insulating collars. The leads were connected to a controlled source of electrical current of from 30 to 40 volts and from 250 to 300 amperes. The object of the gas meter was to measure the rate of flow of fixed gas coming from the process as a by-product.

Fifty-four gallons of a commercial dipentene, containing also terpinenes, terpinolene and small amounts of other similar hydrocarbons, were charged into the vessel. 31 volts were then applied to the heating element, water turned on the pancake coils, ice water circulated through the condenser, and solid carbon dioxide packed around the last condenser coil. As soon as the charge was boiling, 37 volts were applied to the heating element, causing a current of 275 amperes to flow through the element and thus elevate the temperature of the nichrome wire to above 475° C. The log of the run was as follows:

Time	Temp. of charge	Volts	Amps.	Vol. gas	Volume in gal. isoprene condensate
	Degrees			*Cu. ft.*	
11:05 A. M.	178	31	250	14	.01
4:05 P. M.	177	37	280	71	5.60
12:00	178	38	285	187	15.00
9:00 P. M.	180	38	295	363	25.60
6:00 A. M.	186	39	300	561	33.60

The volume of residual product in the reaction vessel was 17 gallons.

In another run, using 54 gallons of dipentene of greater, chemical dipentene purity, 46 gallons of isoprene condensate were obtained with a residue of only 9.5 gallons left behind in the reaction vessel.

The isoprene distillate, so obtained, may not be pure enough for some purposes. It is easily purified by fractional distillation, giving as an illustration:

	Percent
Fraction of heads, boiling up to 34° C., probably containing isopentane and also some isoprene	10
Pure isoprene	70
Still residue, containing xylene and other aromatic hydrocarbons	20

While, in the foregoing example, the heating medium has been described as an electrical resistance element formed of nichrome wire, other metals, such as iron, platinum, nickel, tungsten, tantalum and various alloys, may be employed in place of nichrome. In other words, metals are used primarily because they are conductors of electricity and not because of any special chemical effect that they may have. The heating element may be surfaced with glass or carbon, for example, and function equally as well.

Similarly, instead of connecting the heating element to a source of direct or alternating current, a type of heating element may be employed that can be heated by induction. Gas or oil fired tubes might likewise be used in place of an electrically heated element, although not nearly so conveniently or efficiently.

The temperature range for the heating element is broad. The reaction is in progress at the first visible red heat, and has been found to be proceeding when a platinum element was melted. For the purposes of this specification and claims, the temperature range is defined as that range which causes the element to have a visible glow, viz., is incandescent in the broadest sense.

The terpene hydrocarbon charge to the isoprene generator may be mixed with hydrocarbons which do not form isoprene, as, for example, the residue from a previous run, so that the isoprene will be formed in the presence of a higher proportion of oils and their vapors. Although this results in better chemical yields of isoprene, it is generally done at some sacrifice of time and current, or other source of heat energy.

The process can easily be made continuous by using several interconnected generators in series, flowing the terpene hydrocarbons into the first and continuously removing the residual product from the last, while the distilled oil freed of isoprene is returned to the vessels continuously.

While the process of the example was carried out at atmospheric pressure, it may nevertheless be operated at pressures either above or below normal atmospheric, with good results in either case.

The quality of the hydrocarbons affects the yield, some terpene hydrocarbons giving much better yields of isoprene than others. Since pure limonene or dipentene is extremely difficult to prepare, it is preferred to use the less pure commercial products. Myrcene besides limonene or dipentene gives good yields, while pinene or turpentine gives poor yields. Therefore, for the purpose of this specification and the claims, the term "terpene hydrocarbon" is meant to include all of those hydrocarbons belonging to the terpene class, whether they are monocyclic, bicyclic or acyclic, provided that they can be pyrolyzed to isoprene at all by the process of my invention.

Instead of submerging the heating element or medium in a body of the liquid terpene hydrocarbon, the latter might be passed in the form of a spray against the heating element or medium. It is essential for the proper carrying out of my process that a liquid terpene hydrocarbon be at all times in close association with the heating element, and that distillation of the hydrocarbon occur jointly with the generation of isoprene; and that the isoprene be fractionated completely or substantially completely from the oils that distill with it before returning said oils to the reaction zone.

It will, of course, be understood that various details of the process may be varied through a wide range without departing from the principles of this invention and it is, therefore, not the purpose to limit the patent granted hereon otherwise than necessitated by the scope of the appended claims.

I claim as my invention:

1. In the process of making isoprene by jointly distilling and thermally decomposing terpene hydrocarbons on an incandescent element in a reaction zone, the improvement comprising substantially completely freeing the hydrocarbons so distilled of isoprene before returning said distilled hydrocarbons to said reaction zone.

2. In the process of making isoprene by jointly distilling and thermally decomposing terpene hydrocarbons on an incandescent element immersed in a body of such hydrocarbons, the improvement comprising fractionating the isoprene substantially completely from the hydrocarbons and isoprene so distilled and returning the hydrocarbons to said body of hydrocarbons.

3. In a process of making isoprene by the conjoint distillation and thermal decomposition of terpene hydrocarbons by means of an incandescent element in contact with such terpene hydrocarbons in liquid phase, the improvement comprising fractionating the isoprene from the distilled hydrocarbons and isoprene to recover said isoprene, and returning to the zone of said incandescent element the hydrocarbons so distilled and substantially completely freed from isoprene.

4. In a process of making isoprene by the conjoint distillation and thermal decomposition of dipentene by means of an incandescent element in contact with such dipentene in liquid phase, the improvement comprising fractionating the isoprene from the distilled dipentene and isoprene to recover said isoprene, and returning to the zone of said incandescent element the dipentene so distilled and substantially completely freed from isoprene.

5. In a process of making isoprene in which an incandescent element submerged in a body of terpene hydrocarbons in liquid phase effects the conjoint distillation and thermal decomposition of such terpene hydrocarbons into isoprene and other by-product hydrocarbons capable themselves of being thermally decomposed into isoprene, the improvement comprising fractionating the isoprene from the distilled terpene hydrocarbons and by-product hydrocarbons to recover said isoprene, utilizing the excess heat of said element to effect a multiplicity of redistillations in the reflux resulting from said fractionating step to free said reflux from isoprene and returning the

reflux freed from isoprene but containing terpene hydrocarbons and said by-product hydrocarbons to said liquid body of terpene hydrocarbons.

6. In a process of making isoprene in which an incandescent element submerged in a body of liquid terpene hydrocarbons effects the conjoint distillation of said terpene hydrocarbons and the thermal decomposition of such terpene hydrocarbons into isoprene, the improvement comprising repeatedly fractionally condensing the distilled vapors so produced to form a reflux and to recover isoprene separate therefrom, and repeatedly redistilling portions of the reflux so formed to substantially completely free said reflux from isoprene, and returning the reflux substantially completely freed from isoprene to said body of liquid terpene hydrocarbons.

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