UNITED STATES PATENT OFFICE

2,516,849

METHOD OF PRODUCING BUTADIENE FROM ALCOHOLS

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No Drawing. Application October 9, 1945, Serial No. 621,368

17 Claims. (Cl. 204—154)

My present invention relates to methods of producing butadiene and is disclosed in my prior U. S. patent applications Serial No. 442,136, filed May 7, 1942, which has become abandoned, for Method of Manufacturing Synthetic Rubber and Devices Therefor; Serial No. 442,137, filed May 7, 1942, which has become Patent Number 2,429,217, for Devices for Treatment of Matters with High Speed Electrons; Serial No. 442,138, filed May 7, 1942, which has become abandoned, for Method for Treatment of Matter; Serial No. 450,923, filed July 14, 1942, which has become abandoned, for Method and Means for Treatment of Perishable Substances and Products so Obtained; Serial No. 451,370, filed July 17, 1942, which has become abandoned, for Method and Means for Treatment of Vegetative Substances and Products so Obtained; Serial No. 487,179, filed May 15, 1943, which has become abandoned, for Process for Cracking Hydrocarbons by Means of Ultra High Speed Electrons; and Serial No. 488,278, filed May 24, 1943, which has become abandoned, for Preparation and Cracking of Hydrocarbons and Other Chemical Compounds by Means of Ultra High Speed Electrons to Obtain Rubber Starting Materials. Accordingly, this application is a continuation in part of the above applications.

It is an object of my present invention to produce butadiene from alcohols in a simple inexpensive way.

It is a further object of my present invention to produce butadiene from alcohols by methods by which a great proportion of the alcohols used as initial materials is transformed into butadiene.

Still another object of my present invention consists in methods of obtaining butadiene without use of very high temperatures and/or pressure as commonly employed in the known processes of this type and without use of the rather expensive active catalysts used up to now for these purposes.

With the above objects in view, my present invention mainly consists in producing butadiene from alcohols comprising the steps of dehydrogenating and dehydrating the alcohol serving as initial material by treating, i. e. bombarding it with high speed electrons whereby the alcohol is decomposed and butadiene is formed.

The term "high speed electrons," as used above and in the following description and claims, is intended to define electrons of a velocity equivalent to more than one million volts. Preferably, however, high speed electrons of a velocity equivalent to more than two million volts are employed for the processes of producing butadiene in accordance with my present invention.

In accordance with a preferred embodiment of my present invention, I treat, i. e. bombard the alcohol repeatedly during consecutive periods with high speed electrons in such a manner that each of these repeated treatment periods lasts less than 10^{-4}, preferably about 10^{-6}, of a second. I have found that by using such short treatment periods it is possible to avoid almost entirely the formation of undesired by-products which constitute a basic disadvantage of all known processes.

I wish also to stress that it is advisable to use high speed electrons of a velocity equivalent to more than one, preferably two million volts; such high speed electrons have such a high energy that they are able to cause the desired decomposition of the electron bombarded alcohol within the extremely short periods mentioned above.

I have found that treatment of an alcohol in the way proposed by me results in decomposition of the electron bombarded alcohol into mono-olefines from which in turn di-olefines, mainly butadiene, are formed.

More particularly, if ethyl alcohol is used as initial material, the same is dehydrogenated to ethylene; from this ethylene by subsequent conjuncture of the molecules butadiene is formed.

The electron bombardment of the alcohols as proposed by me can be carried out at room or slightly raised temperature by which all unwanted side reactions are avoided which are due in commonly used processes to the fact that the same have always to be carried out at temperatures above 800° C.

For example, in accordance with the present invention, it is possible to dehydrate and dehydrogenate ethyl alcohol by bombarding the same with high speed electrons as proposed above at a temperature between 130 and 160° C., thus substantially reducing the amounts of by-products obtained during usual dehydration and dehydrogenation processes. The main reaction products obtained by such electron bombardment consist of butadiene and other valuable by-products formed by the interaction of di-olefines and/or olefines, more particularly of aromatic compounds such as toluene, xylene, phenol, and others. Contrary thereto, in processes used at the present time on a commercial scale, more than twenty other by-products are formed during production of the butadiene, most of them containing oxygen and being practically valueless.

I have found that by dehydrating and dehydrogenating alcohols as set forth above, it is possible to obtain a yield of butadiene amounting to substantially more than 40% of the theoretically determined maximal yield. In addition thereto, up to 50% of the exit gases consist of olefines, mainly ethylene, which can be recycled and subjected to repeated electron bombardment so as to transform part of the same also into butadiene. Thus, it is possible to obtain by electron bombardment of the alcohol serving as initial material and of the recycled ethylene, a yield of butadiene amounting up to 60% of the theoretically determined maximal yield.

It should also be stressed that the butadiene obtained by the methods proposed by me above is, due to its comparatively low content of by-products, of very high purity.

The above mentioned high yield of butadiene obtainable by electron bombardment of alcohol as proposed above is mainly due to the fact that it is possible to apply and control the high speed electronic energy used for decomposition, i. e. dehydration and dehydrogenation of the alcohol in such a manner as to carry out the decomposition selectively, namely to obtain only or mainly the desired compounds without undesired by-products.

The very low proportion of undesired oxygen-containing by-products obtained by the present process can be explained by the fact that the actual impact of high speed electrons in the formation of butadiene from alcohols is reduced to a minimal fraction of the time as compared with standard pyrolytic processes. The chance of interaction of the unsaturated compounds with the oxygen present is consequently reduced to a minimum. Thus, unsaturated aldehydes, alcohols, ketones, etc. as well as their saturated analogs are practically absent. Furthermore, the methane and ethane content of the exit gases is markedly reduced; since both these compounds are not utilizable for the preparation of any useful intermediates, this constitutes an appreciable improvement.

The reaction mixture obtained by electron bombarding the alcohols as explained above is then freed by well-known procedures of butadiene and of the desired aromatic by-products. The remaining reaction mixture can then be recycled and yields another 20 to 25% of butadiene and valuable by-products. It might be advisable to add to the recycled part of the reaction mixture before recycling fresh alcohol, thus increasing the effect of electron bombardment upon the recycled mixture.

In my above described processes, the alcohols are electron bombarded in absence of catalytic substances. Since catalytic substances of the type used at present for processes of producing butadiene from alcohols are highly expensive, the possibility to avoid such catalysts is of great advantage and importance.

However, I have found that it is of great importance to be able to regulate the length of the reactions caused by the electron bombardment, particularly in case of consecutive short electron bombardments lasting each only a fraction of a second. It is evident that no particular advantages would be attained by bombarding the alcohols with electrons during separate extremely short periods if between these short periods the once started reactions would automatically continue.

In order to be able to regulate the length of the single reactions periods, I have found it advisable to add, e. g. to admix to the alcohols to be electron bombarded a small percentage of agents which are adapted to prevent or at least to retard continuation of the reactions caused by electron bombardment after discontinuation and termination of the same. I have found that such materials called by me "contact materials" have a double effect, namely they not only retard continuation of the reactions after termination of the electron bombardment, but they also facilitate and expedite the reaction during such electron bombardment, without being themselves catalytically active.

I have found that for the purposes of my present invention I may very well use as contact materials various metal oxides which are not only inexpensive but also available in large amounts. Particularly adapted as contact materials for the processes proposed by me are oxides of the metals of the second, third and fourth groups of the periodic system, as magnesium, zinc, aluminum, silicon, and others.

A very material disadvantage of the use of catalysts in known processes lies in the inavoidable secondary reactions as incurred under the conditions of the standard pyrolytic processes that lead to the formation of oily polymerization products. These soon lower the activity of the catalysts so markedly that a reactivation is necessary, the oily polymers poisoning the entire active surface of the catalyst. Additional poisoning is caused by the formation of pyrolytic decomposition products due to the necessary high temperatures in standard cracking processes. Whereas the first inactivation is reversible, the second one is irreversible, thus completely destroying the activity of that part of the catalysts.

It should also be stressed that in accordance with my present invention it is necessary to use only a very small percentage of contact material. Contrary thereto, in all known processes of producing butadiene from alcohols, reactions can be obtained only by use of great amounts of rather expensive catalysts. Compared with such known processes, the percentage of contact materials used during electron bombardment is extremely small, practically not more than a few percent of the amount of the rather expensive catalysts needed for the known methods. In addition thereto, it should be stressed that since the contact materials used by me do not participate in the dehydrogenation and dehydration reactions occurring during electron bombardment, their life is much longer than that of the catalytically active catalysts used today in the known processes.

Although I mentioned above as initial materials only alcohols, particularly ethyl alcohol, also other initial substances can be dehydrogenated and dehydrated so as to obtain butadiene. Thus, for instance, in accordance with my present invention, it is possible to use as initial materials not only ethyl alcohol but also other aliphatic alcohols which, when treated as proposed above, form mono-olefines and di-olefines, particularly butadiene, as well as per se highly valuable aromatic by-products which in turn can also be electron bombarded again so as to be transformed also into butadiene. Of course, also other materials, such as propanol, iso-propanol, butanols, fusel oils, various glycols and the like may be used as initial materials and treated as described above.

I have found that the electronic intensity of the discharge necessary for the production of butadiene from various alcohols varies and is dependent on the different chemical characteristics of the different initial substances; however, I have found that the average intensity of electron bombardment employed is preferably chosen so that each molecule of the initial material is hit during bombardment by electrons having a total intensity of at least 10^{-20} of a watt.

As mentioned above, it is possible to use not only ethyl alcohol but also other aliphatic alcohols and to subject the same to electron bombardment causing dehydrogenation and dehydration and formation of butadiene. Thus, for instance, dehydrogenation of 1,3-butylene glycol to butadiene can be obtained by treatment with high speed electrons in presence of contact material as described above. By this process, a particularly pure butadiene is obtained which can be used directly for polymerization purposes. This particular process will be of great importance wherever large amounts of acetylene, e. g. from natural gas, are available.

I wish to stress that it is also possible to use 2,3-butylene glycol as initial material. Bombarding such glycol with high speed electrons in the presence of contact materials of the above described type, it is possible to dehydrate the same to butadiene at room temperature in one step with one recycling of unreacted glycol and to obtain yields of butadiene amounting to up to 85% of the theoretically maximum butadiene yield. Also in this case, the obtained butadiene is particularly easy to purify and can be obtained in better than 99% purity by one azeotropic distillation. A detailed description of this process of obtaining butadiene from glycol seems unnecessary since its details are the same as those of the process of transforming ethyl alcohol into butadiene as described above.

It will be understood that each of the elements described above, or two or more together, may also find a useful application in other types of processes of producing butadiene differing from the types described above.

While I have described the invention as embodied in processes of producing butadiene from various alcohols, I do not intend to be limited to the details shown, since various modifications and changes may be made without departing in any way from the spirit of my invention.

Without further analysis, the foregoing will so fully reveal the gist of my invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehendsd within the meaning and range of equivalence of the following claims.

What I claim as new and desire to secure by Letters Patent is:

1. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by repeatedly bombarding it during a series of consecutive very short periods with high speed electrons of a velocity equivalent to more than one million volts, thereby decomposing said alcohol and forming butadiene.

2. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by repeatedly bombarding it during consecutive periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, thereby decomposing said alcohol and forming butadiene.

3. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by subjecting it to repeated bombardments with high speed electrons of a velocity equivalent to more than 2 million volts, each of said electron bombardments lasting less than 10^{-6} of a second, thus decomposing said alcohol and forming butadiene.

4. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by repeatedly bombarding it with high speed electrons, each of said electron bombardments lasting less than 10^{-6} of a second, thereby decomposing said alcohol and forming butadiene.

5. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by bombarding it during a series of very short irradiation periods with high speed electrons in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued.

6. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by repeatedly bombarding it during a series of consecutive very short periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued, thereby decomposing said alcohol and forming butadiene.

7. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by subjecting it to repeated bombardments with high speed electrons of a velocity equivalent to more than 2 million volts, each of said electron bombardments lasting less than 10^{-4} of a second in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and preventing continuation of said chemical reaction after said electron bombardment has been terminated, thereby decomposing said alcohol and forming butadiene.

8. Method of producing butadiene from aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by bombarding it during a series of very short irradiation periods with high speed electrons in such a manner that on the average each molecule of said alcohol is hit by electrons having a total intensity of at least 10^{-20} of a watt.

9. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by bombarding it during a series of very short irradiation periods with high speed electrons at a temperature of about 130° C., whereby said alcohol is in the gaseous phase during said electron bombardment.

10. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by bombarding it during a series of very short irradiation periods with high speed electrons in the presence of a contact material selected from the group consisting of oxide of metals of the second, third and fourth groups of the periodic system of elements, said contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued.

11. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by bombarding it during a series of very short irradiation periods with high speed electrons in the presence of a contact material selected from the group of metals consisting of zinc, magnesium, aluminum, boron, calcium, strontium and silicon, said contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued.

12. Method of producing butadiene from ethyl alcohol comprising repeatedly bombarding said ethyl alcohol with high speed electrons during a series of very short irradiation periods thus dehydrogenating said ethyl alcohol to ethylene, and then repeatedly bombarding the thus formed ethylene again with high speed electrons during a series of very short irradiation periods, thus transforming said ethylene and forming butadiene.

13. Method of producing butadiene from aliphatic alcohols comprising dehydrogenating and dehydrating said aliphatic alcohols by repeatedly bombarding them during consecutive periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued, thereby decomposing said aliphatic alcohols and forming butadiene.

14. Method of producing butadiene from ethyl alcohol comprising dehydrating and dehydrogenating said ethyl alcohol by bombarding the same during a series of very short irradiation periods with high speed electrons at a temperature of between 130 and 160° C., thus forming a mixture comprising butadiene and aromatic compounds, and thereafter bombarding said aromatic compounds again repeatedly with high speed electrons, thus transforming the same also into butadiene.

15. Method of producing butadiene from an aliphatic alcohol comprising dehydrogenating and dehydrating said alcohol by repeatedly bombarding it during consecutive periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and retarding continuation of said chemical reaction after said electron bombardment has been discontinued, thereby forming a reaction mixture comprising butadiene, removing said thus formed butadiene, and repeatedly bombarding the remaining reaction mixture during consecutive periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, thus decomposing said remaining reaction mixture and transforming the same also nearly entirely into butadiene.

16. Method of producing butadiene from 1,3 butylene glycol comprising dehydrogenating and dehydrating said 1.3 butylene glycol by subjecting it to repeated bombardments with high speed electrons of a velocity equivalent to more than 2 million volts, each of said electron bombardments lasting less than 10^{-4} of a second in the presence of a contact material not participating in the chemical reaction caused by said electron bombardment but facilitating said chemical reaction during said electron bombardment and preventing continuation of said chemical reaction after said electron bombardment has been terminated, thereby decomposing said 1.3 butylene glycol and forming butadiene.

17. Method of producing butadiene from 2,3 butylene glycol comprising dehydrating said 2.3 butylene glycol by repeatedly bombarding it during consecutive periods with high speed electrons of a velocity equivalent to more than one million volts, each of said consecutive periods lasting less than 10^{-4} of a second, in the presence of a contact material not participating in the reaction caused by said electron bombardment but facilitating said reaction during said electron bombardment and retarding continuation of said reaction after said electron bombardment has been discontinued, thereby decomposing said 2.3 butylene glycol and forming butadiene.

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