

UNITED STATES PATENT OFFICE

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PROCESS FOR THE PREPARATION OF SUBSTANTIALLY PURE TERTIARY OLEFINS

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The invention relates to the production of substantially pure tertiary olefins (hydrocarbons capable of forming tertiary alcohols upon hydration) such as gamma butylene, tertiary amylene and the like, from the corresponding tertiary alcohols in general, and in particular from hydrocarbon fluids containing tertiary olefins, such as derived by the pyrogenetic treatment of peat, coal, tars, oil shales, petroleum oils and products, natural gas and like carbonaceous materials whether the treatment comprises distillation and/or cracking. The hydrocarbon fluid may be obtained from the products which are formed by the destructive hydrogenation of carbonaceous materials such as coal, brown coal, coal tar, petroleum and petroleum products, and other carbonaceous materials which are suitable for treatment by destructive distillation.

For illustrative purposes only, reference will be had to the production of substantially pure gamma butylene although it is to be understood that corresponding members of the class or higher homologues of the tertiary olefins may be obtained in a similar fashion with slight modifications obvious to one skilled in the art, since it is well-known that the sensitivity of tertiary compounds of any series towards a reagent or under fixed conditions of pressure, temperature and/or catalyst, increases with the number of carbon atoms in the molecule.

We have found that under regulated conditions gamma butylene, which is exemplary only, can be produced directly from tertiary butyl alcohol by its thermal decomposition in the presence of water and an acid catalyst, preferably a mineral acid such as H_2SO_4 , H_3PO_4 or the sulfonic acids of benzene and its homologues or acid salts of polybasic acids such as the alkali-metal salts of sulfuric acid, phosphoric acid, etc., or the corresponding acid alkyl salts of polybasic acids may be utilized as RHSO_4 , RH_2PO_4 , R_2HPO_4 , etc., wherein R represents an alkyl grouping and that a very good yield of substantially pure gamma butylene is obtainable.

To carry out the process we may either start with tertiary butyl alcohol and sulfuric acid diluted with water to the proper strength or else we may form the tertiary butyl alcohol necessary for the preparation of the gas in another part of the process as hereinafter described. When using tertiary butyl alcohol either in the anhydrous state or as its mixture with water, we add this alcohol to aqueous sulfuric acid in such proportion that the acidity of the resulting mixture is not more than about 50% free H_2SO_4 . We

prefer to dilute the mixture to a free acidity of from about 10% to 30% H_2SO_4 . When the mixture is maintained at a temperature of from about 70° to 85° C., gamma butylene is evolved. If the concentration of acid is carried substantially beyond 50% H_2SO_4 in the mixture, upon adding heat to this, a large proportion of the hydrocarbons is lost through the formation of polymers of gamma butylene such as di- and triisobutylene.

The process may be also carried out in continuous, intermittent or batch fashion. In the former two cases, alcohol may be fed into the mixture, heat being supplied so as to maintain the evolution of gas, at about the same rate at which gamma butylene is evolved. If the operation is carried out under such conditions that the water formed by the dehydration of the alcohol and that contained in the alcohol feed is also evaporated at the same rate at which it is formed or fed into the system, the process is truly continuous and may be operated until the slight side reactions occurring cause the sulfuric acid to become contaminated to an extent impairing its usefulness. If the operation is conducted under conditions such that more water is formed or fed into the system than is evaporated during evolution of the gas, the sulfuric acid becomes more and more diluted. It may be reconcentrated and returned to the main reaction system. Undecomposed alcohol whose vapor accompanies the gamma butylene and water vapor in every case, may be recovered and returned to the system.

In general, as the acid concentration becomes lower, the temperature of the mixture may be raised without danger of excessive polymerization.

The rate of decomposition to gamma butylene of the alcohol-acid mixture is dependent on the concentration of tertiary butyl alcohol in the decomposing kettle charge. The higher the concentration of tertiary butyl alcohol, the faster the rate of evolution of gamma butylene. It is therefore advantageous to maintain the concentration of tertiary butyl alcohol in the gamma butylene regeneration unit by addition of crude tertiary alcohol as fast as it is decomposed so as to maintain a desired high alcohol-acid ratio in the regeneration unit.

If we add to a mixture of one part of phosphoric acid (H_3PO_4) and one part of water, 1.8 parts of tertiary amyl alcohol and heat the mixture, tertiary amylenes (unsymmetrical methylethylethylene and trimethylethylene) are evolved rapidly and in good yield.

Instead of employing tertiary butyl alcohol as raw material for the preparation of gamma butylene, we may also prepare a solution of this alcohol in aqueous sulfuric acid by absorbing in the latter gamma butylene from hydrocarbon gases or liquids containing it. For this purpose we prefer to use a mixture of narrow boiling range containing substantially no hydrocarbons other than butanes and butylenes. It is known that while acid of 65-70% H_2SO_4 concentration readily absorbs gamma butylene, it has no action whatever on saturated hydrocarbons and absorbs alpha and beta butylenes at a very much lower rate. We have found that the gamma butylene, when absorbed in aqueous sulfuric acid, is converted to a large extent into tertiary butyl alcohol. We take advantage of this by conducting the absorption in such a manner that gamma butylene may enter the acid mixture in amounts up to molal equivalency of the water present. This may be accomplished by adjusting the strength of the acid we employ so as to provide a sufficient quantity of water for the hydration of the butylene to alcohol. In this way, starting with a mixture containing 35% by weight H_2SO_4 , we have prepared a solution containing 7.2 mols. of alcohol per mol. of acid. With 60% acid, we can absorb up to 3.6 mols. of gamma butylene for each mol. of H_2SO_4 . With 50% acid, we can absorb 5.4 mols. of gamma butylene. As the aqueous content of the acid employed increases the number of mols. of gamma butylene capable of reacting increases but a higher temperature and longer reaction period is required. The mixtures so prepared may be used in the process described above for the preparation of gamma butylene. During the absorption step, the heat of reaction should be removed to a sufficient extent to avoid increase in temperature sufficient to cause polymerization or the loss of tertiary alcohol. When the mixture is diluted and heated, some of the alpha and beta butylene which has been absorbed from the hydrocarbon mixture is converted into secondary butyl alcohol and may be removed from the gas by condensation. That portion of alpha and gamma butylene which has been physically absorbed together with butane and has not been converted to alcohol, may be removed from the acid liquor by any conventional degassing process before heating. We may prefer to arrange the operation in a continuous cycle by reconcentrating the sulfuric acid to the strength required for the absorption of gamma butylene and returning it to the absorption system. Various combinations of the continuous cycles disclosed are possible and will be evident to those skilled in the art.

While the process for the production of gamma butylene here disclosed may be operated with advantage as described, the rate of evolution of the gas from the acid solution may be increased and the tendency to polymer formation reduced by the addition of certain catalysts. We have found that sulfates of bivalent elements, such as those of zinc, magnesium, cadmium or lead, are especially well suited for this purpose when added to the alcohol-acid mixture in such proportions that their concentration in solution or in suspension is from about 0.02 to 0.5 molal per mol. H_2SO_4 . It is not necessary that the catalyst employed be completely soluble. Lead sulfate, for example, which is only slightly soluble, operates efficiently as a catalyst. Alternatively, the metals themselves or their oxides or hydroxides may be advantageously employed as they form the salt

of the acid catalyst present during the execution of the process and at the same time contribute to the lowering of the acidity to that desirable for the evolution of tertiary olefines. The catalyst does not interfere with the absorption process; it may therefore be added at any stage of the process. Spent acid from the regeneration process may thus be utilized in the absorption process permitting economy of acid.

A suitable continuous method for carrying out our invention may be executed as follows:

The alcoholic acid mixture is fed into a decomposition unit which may be partially heated by steam coils or other heating means and partially heated by the vapors (alcohol and water) entering it from a stripping column into which is fed the overflow from the decomposition unit. The stripping column may be operated with live steam. The column and condenser which are in communication with the decomposition unit rectify and cool the tertiary olefine leaving the decomposition unit and reflux alcohol back into it. The decomposition unit is thus, by the combination of rectification and stripping, maintained at the desired composition with respect to alcohol and acid most favorable for decomposition in good yield to tertiary olefine. The number and design of the structural parts will depend upon economical factors and operating details.

This case is a continuation-in-part of our application 632,792, filed September 12, 1932.

While we have in the foregoing described in some detail the preferred embodiment of our invention and some variants thereof, it will be understood that this is only for the purpose of making the invention more clear and that the invention is not to be regarded as limited to the details of operation described, nor is it dependent upon the soundness or accuracy of the theories which we have advanced as to the reasons for the advantageous results attained. On the other hand, the invention is to be regarded as limited only by the terms of the accompanying claims, in which it is our intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

We claim as our invention:

1. A process for the preparation of substantially pure tertiary olefine, comprising: heating an aliphatic tertiary alcohol with an aqueous acidic compound in a molal ratio greater than 1:1 at an elevated temperature whereby substantially pure tertiary olefine is evolved while maintaining the alcohol concentration by feeding alcohol at a rate at which tertiary olefine is formed.

2. A process for the preparation of substantially pure tertiary olefine, comprising: heating an aliphatic tertiary alcohol with aqueous sulfuric acid in a molal ratio greater than 1:1 to an elevated temperature whereby substantially pure tertiary olefine is evolved while maintaining the alcohol concentration.

3. A process for the preparation of substantially pure gamma butylene, comprising: heating tertiary butyl alcohol with an aqueous acidic compound in a molal ratio greater than 1:1 to an elevated temperature whereby substantially pure gamma butylene is evolved while maintaining the alcohol concentration.

4. A process for the preparation of substantially pure tertiary olefine, comprising: heating an aliphatic tertiary alcohol with an aqueous acidic compound to an elevated temperature in the presence of an inorganic salt of a bivalent

metal which permits the evolution of olefine in sulfuric acid whereby substantially pure tertiary olefine is evolved, while substantially maintaining the alcohol concentration.

5. A process for the preparation of substantially pure gamma butylene comprising: heating an excess of tertiary butyl alcohol with aqueous sulfuric acid in the presence of a sulfate of a bivalent metal which permits the evolution of olefine in sulfuric acid.

6. A process for the preparation of substantially pure gamma butylene comprising: heating tertiary butyl alcohol with aqueous sulfuric acid in the presence of a sulfate of a bivalent metal which permits the evolution of olefine in sulfuric acid in about 0.02 to 0.5 molal concentration with respect to sulfuric acid.

7. A process for the preparation of substantially pure gamma butylene, comprising: heating a mixture containing tertiary butyl alcohol, water and sulfuric acid and having a free H_2SO_4 content of not more than about 50% to a temperature not greater than about 85° C. while substantially maintaining the alcohol concentration in a molal ratio greater than 1:1 compared with the sulfuric acid.

8. A process for the preparation of substantially pure gamma butylene, comprising: heating a mixture containing tertiary butyl alcohol, water and sulfuric acid and having a free H_2SO_4 content of not more than about 50% to a temperature between about 70° C. to 85° C. at an absolute pressure of substantially one atmosphere while substantially maintaining the alcohol concentration in a molal excess above that of the sulfuric acid.

9. A process for the preparation of substantially pure gamma butylene, comprising: heating a mixture containing tertiary butyl alcohol, water and sulfuric acid and having a free H_2SO_4 content of not more than about 50% to a temperature not greater than about 85° C. in the presence of a sulfate of a bivalent metal which permits the evolution of olefine.

10. A process for the preparation of substantially pure tertiary olefine from its mixture with other hydrocarbons, comprising: the steps of: contacting said hydrocarbons with aqueous sulfuric acid and subsequently liberating said tertiary olefine from said acid by the application of heat while maintaining the alcohol concentration in a molal ratio greater than 1:1 compared with the sulfuric acid.

11. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid and subsequently liberating said gamma butylene from said acid by the application of heat while maintaining the alcohol concentration in a molal excess above that of the sulfuric acid.

12. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid and subsequently liberating said gamma butylene from said acid by heating to a temperature below 90° C. while maintaining the alcohol concentration in a molal ratio greater than 1:1 compared with the sulfuric acid.

13. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid of not more than about 70% H_2SO_4

concentration, and subsequently liberating said gamma butylene from said acid by the application of heat while maintaining the alcohol concentration in a molal ratio greater than 1:1 compared with the sulfuric acid.

14. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid of not more than about 70% H_2SO_4 concentration, removing said acid from contact with said hydrocarbons, diluting it to not more than about 50% H_2SO_4 concentration and subsequently liberating gamma butylene from said acid by the application of heat while maintaining the alcohol concentration in a molal ratio greater than 1:1 compared with the sulfuric acid.

15. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid of not more than about 70% H_2SO_4 concentration, removing said acid from contact with said hydrocarbons, diluting it to not more than about 50% H_2SO_4 concentration and subsequently liberating gamma butylene from said acid by heating to a temperature between about 70° C. and 85° C. while maintaining the alcohol concentration in a molal excess above that of the sulfuric acid.

16. A process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons comprising the steps of: contacting said hydrocarbons with aqueous sulfuric acid of not more than about 70% H_2SO_4 concentration, removing said acid from contact with said hydrocarbons, diluting it to not more than about 50% H_2SO_4 concentration and subsequently liberating gamma butylene from said acid by heating to a temperature between about 70° C. and 85° C. in the presence of a sulfate of a bivalent metal which permits the evolution of olefine in sulfuric acid.

17. A process for the preparation of substantially pure gamma butylene comprising the steps of: heating tertiary butyl alcohol with aqueous sulfuric acid and continuously supplying tertiary butyl alcohol to the reaction chamber to replace that decomposed at a rate at which tertiary butylene is formed so as to keep the alcohol concentration within the reaction chamber at a substantially constant value and in a molal ratio greater than 1:1 compared with the sulfuric acid.

18. In a process for the preparation of substantially pure gamma butylene from its mixture with other hydrocarbons, the steps of: absorbing gamma butylene in aqueous sulfuric acid of a strength less than 60% by weight until an excess of three mols butylene for each mol H_2SO_4 is present in the aqueous acid.

19. In a process for preparing a mixture of sulfuric acid and tertiary butyl alcohol, the steps of absorbing gamma butylene in aqueous H_2SO_4 of a strength not greater than 60% by weight until more than 3 mols of butylene react with the water present for each mol H_2SO_4 present in the aqueous acid.

20. In the process of heating a mixture of H_2SO_4 , H_2O and tertiary alcohol whereby substantially pure tertiary olefine is evolved, the steps of: commencing the operation with not less than two molecules of alcohol per molecule of acid in the acid mixture and supplying tertiary alcohol to the reaction chamber at a rate at which tertiary olefine is formed.

21. In the process of heating a mixture of H_2SO_4 , H_2O and tertiary alcohol whereby substantially pure tertiary olefine is evolved, the steps of: commencing the operation with not less than two molecules of alcohol per molecule of acid in the acid mixture and maintaining the alcohol concentration in the acid mixture above this minimum.

22. A process for the preparation of substantially pure tertiary olefine from its mixture with

other hydrocarbons, comprising the steps of: contacting said hydrocarbons with aqueous H_2SO_4 in the presence of a sulfate of a bivalent metal which permits the evolution of olefine in sulfuric acid and subsequently liberating said tertiary olefine from said acid by the application of heat.

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