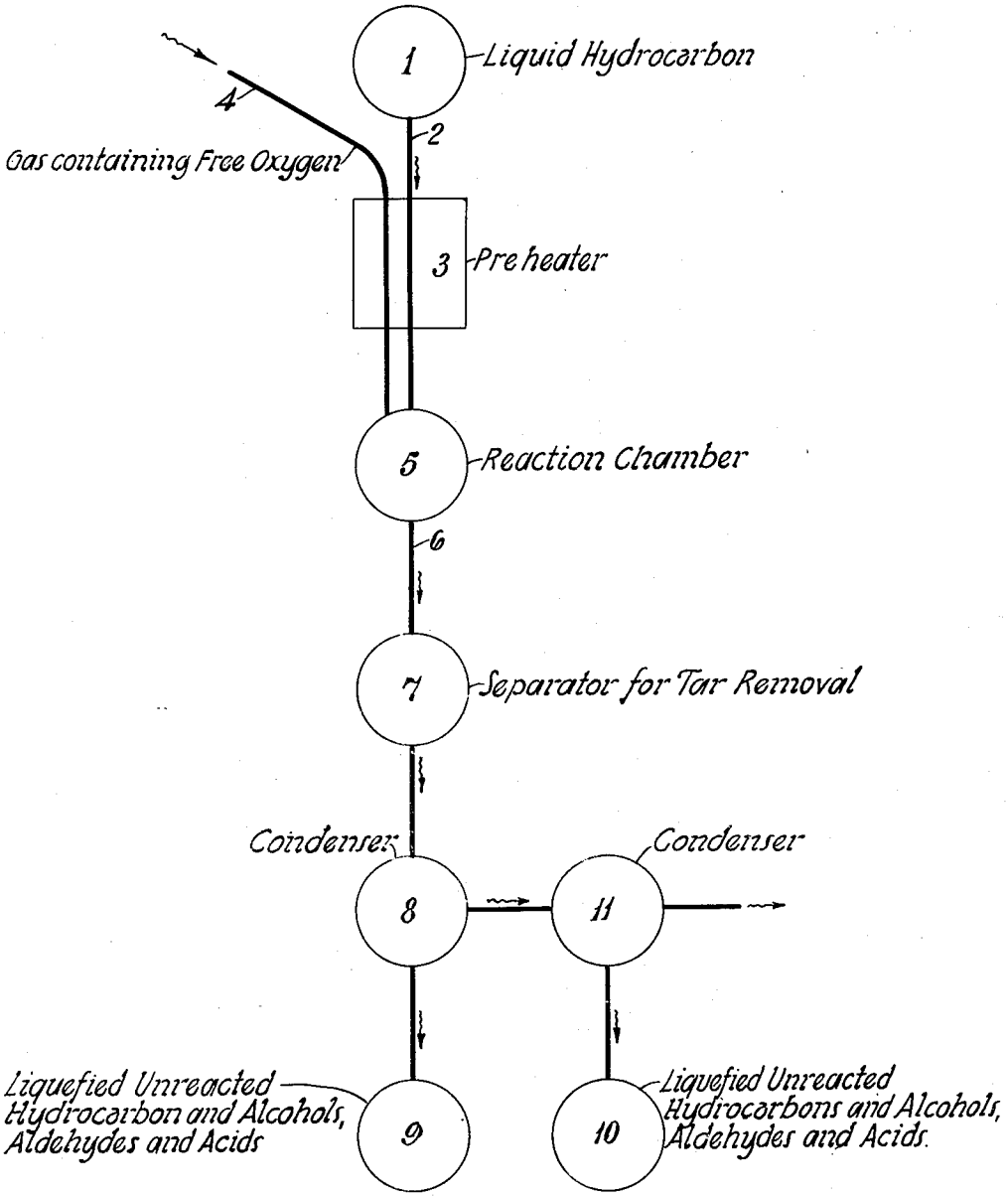
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OXIDATION OF HYDROCARBONS

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OXIDATION OF HYDROCARBONS

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1 Claim. (Cl. 260—451)

This invention relates to a new and improved process for the preparation of chemical compounds by the oxidation of aliphatic hydrocarbons in the presence of a catalyst, and more particularly to such a process wherein the reaction products comprise aliphatic alcohols, aldehydes and acids.

This application is a continuation-in-part of our copending application Serial No. 108,478, filed October 30, 1936, now Patent No. 2,190,453, and is a division of our copending application Serial No. 199,636, filed April 2, 1938.

The higher aldehydes of the aliphatic series have considerable value as chemical compounds and a number of them have found use in industry as perfumes. The difficulties in the way of preparing such compounds, however, have kept their costs so high as to limit their field of usefulness. An improved and simpler method of obtaining such aldehydes would make more accessible a very desirable class of products. The same condition holds in the case of a number of the higher aliphatic alcohols and acids also, for example those containing in the neighborhood of 8 to 12 carbon atoms.

An object of our invention is an improved method for the production of alcohols, aldehydes, and acids by the incomplete oxidation of aliphatic hydrocarbons. A further object is such a process in which carefully controlled conditions allow a high degree of efficiency in the preparation of the desired products. A still further object is a process in which the several products obtained may be separated in relatively pure form. Additional object will be disclosed as the process is further described hereinafter.

We have found that the foregoing objects may be accomplished by the process of our invention which comprises introducing a normally liquid hydrocarbon in the vapor phase into a heated chamber, together with an oxidizing agent comprising a gas containing free oxygen. The oxidation step is carried out in the presence of benzoyl peroxide as a catalyst. Within the reaction chamber the mixed gases and vapors are subjected to a temperature between 250 and 500° C. While the oxidation of the hydrocabons constitutes an exothermic reaction, the heat evolved will not be sufficient to maintain the desired temperature and external heating will be necessary. It is essential that the reaction period be kept at a relatively short time interval, and we have found 15 seconds to be the maximum allowable time. Preferably we employ a reaction period not greater than 12 seconds, in order that the oxidation may not proceed too far. The reacting materials and reaction products are removed from the heated chamber while still in the vapor phase and are condensed by any desired method and apparatus under such conditions and in such an atmosphere that further reaction cannot take place. The amount of hydrocarbon will be above the explosive limit in all cases. We have found it desirable to use an amount of hydrocarbon of at least 10% by volume of the gaseous reaction mixture, and preferably between 20 and 40%.

It will be a desirable step in our process also to utilize the unreacted hydrocarbon resulting from the process and to recycle it to an additional similar oxidation step, whereby the advantages of the presence of an excess of hydrocarbon are obtained with no loss in non-reacting material.

The accompanying drawing shows diagrammatically a flow sheet of one method of carrying out our process. From a reservoir 1, the normally liquid hydrocarbon is forced through conduit 2 into the preheater 3. The gas containing free oxygen is passed through conduit 4 through the preheater 3, en route to the reaction chamber 5. Both the vaporized hydrocarbon and the oxygen containing gas pass into the reaction chamber 5 where they become intimately mixed and where a temperature of 250 to 500° C. is maintained, said catalyst, promoting partial oxidation, being present, whereby partial oxidation of the hydrocarbons is brought about. The vapors pass out the conduit 6 into separator 7, where any tar formed in the process is separated out. The mixed vapors and gases then pass through condenser 8, where the products capable of condensation become liquefied. The liquid condensate flows into reservoir 9, while a second vessel 10 receives any further condensed product not caught in chamber 9, but condensed in 11. The reservoirs 9 and 10 contain the liquefied unreacted hydrocarbon that has passed through the process, and also condensed water and the alcohols, aldehydes and acids resulting from the oxidation process. Such alcohols, aldehydes and acids will commonly be found in the water-insoluble layer.

Specific operating conditions suitable for our process for the production of alcohols, aldehydes, and acids are shown in the following example. This is to be considered as merely illustrative, however, and not limiting in its application.

Example

One gram of benzoyl peroxide was dissolved in

200 cc. of naphtha. This mixture was vaporized in the usual manner and mixed with air at a temperature of 387° C. The time of reaction was 5.2 seconds and the percentage of hydrocarbon in the reaction mixture was 18.7. The yield was approximately 16.84% aldehydes and 14.15% acids.

The method of operation according to the present invention produces alcohols, aldehydes and acids. However, it is especially favorable to the production of alcohols.

The alcohols, aldehydes and acids resulting from the oxidation of hydrocarbons according to the process of our invention, are products of considerable economic value and of desirable properties, and the process described offers a novel and advantageous method of obtaining such products. Our process is characterized by higher yields and greater efficiency than any process in the art.

The alcohols, aldehydes and acids may be separated from the hydrocarbon condensate and from one another by the use of suitable solvents. In the case of aldehydes, for example, a saturated solution of sodium bisulfite was found desirable for extraction, the bisulfite subsequently being made alkaline and being subjected to steam distillation. The acids were desirably extracted by means of sodium hydroxide solution. The alcohols are preferably extracted by means of phosphoric acid.

While our process has been described in detail in the foregoing, it will be understood that many variations in procedure may be employed without departing from the scope of our invention. In the example cited, a hydrocarbon fraction of a specific distillation range was used, but it would be a highly desirable procedure also to start with a single aliphatic hydrocarbon, for example octane, or a mixture of octanes.

We wish to be limited, therefore, only by the following patent claim:

We claim:

The process for producing partially oxidized products of normally liquid aliphatic hydrocarbons which comprises introducing said hydrocarbons in vapor phase, together with an oxidizing agent comprising a gas containing free oxygen, into a reaction chamber at a temperature between 250° C. and 500 C., maintaining the amount of hydrocarbon in the hydrocarbon-oxygen ratio above the explosive limit, and reacting said materials for a period not exceeding 15 seconds in the presence of benzoyl peroxide.

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