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PRODUCTION OF MALEIC ACID FROM
BRANCHED-CHAIN DIENES

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This invention relates broadly to oxidation of hydrocarbons to organic acids and anhydrides and more specifically to the vapor phase catalytic oxidation of certain steam cracked petroleum fractions containing C_6 diolefins to give dibasic acids with substantial amounts of maleic acid.

It is to be understood that the term "maleic acid" as used throughout this specification and claims includes also the anhydride. It is also to be noted that the term "crude maleic acid" is used to include both maleic acid and small amounts of other dibasic acids which are also obtained to a lesser extent in oxidation of the mixtures.

It has been discovered that certain petroleum fractions of definite boiling ranges which contain substantial quantities of C_6 diolefin compounds such as the methyl pentadienes can be oxidized in high yields to crude maleic acid by a vapor phase catalytic process.

Further, it has been found that feeds consisting solely of these C_6 diolefins, for example, branched-chain hexadienes or methyl-pentadienes, give good yields of crude maleic acid even though no aromatics are present.

This ready oxidation of branched chain pentadienes is in itself surprising and unusual since in order to convert a compound of this type to maleic acid, a carbon to carbon bond must be broken. In terms of over-all reaction, an alkyl group must be oxidized away and replaced by a hydrogen atom. This type of chemical conversion is a very unusual and little known one and it is particularly surprising that it occurs under relatively vigorous oxidizing conditions.

Petroleum fractions containing unsaturated hydrocarbons of the diolefin type may be obtained by steam cracking volatile petroleum stocks, such as naphtha cuts and gasolines. Temperatures of the order of 1000° to 1600° F and pressures of 1 to 10 atmospheres are most favorable. The charging stock is preferably diluted with a relatively large amount of steam in the cracking zone. This tends to restrict carbonization.

The hot cracked products issuing from the cracking zone are quenched. In processing these quenched cracked petroleum products, the aromatic naphtha, together with the lower boiling hydrocarbons and steam, are removed overhead as volatiles to separate them from the higher boiling cracked products which are quenched to a liquid state. These higher boiling products are subjected to controlled fractional distillation treatment from which suitable cuts may be selected for subsequent oxidation to crude maleic acid.

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A crude fraction boiling in the range of 60-120° C. contains substantial amounts of conjugated dienes of the C_6 series, benzene, toluene, and smaller amounts of other hydrocarbons. A closer boiling fraction of the range 75-85° C. contains larger amounts of conjugated dienes, mostly of the methyl pentadiene type, together with benzene and smaller amounts of other hydrocarbons. For maximum operating efficiency in the oxidation of such fractions to maleic acid, a fraction of intermediate boiling range such as 80-100° C. has been found particularly valuable. These cuts may be subjected to oxidation directly following the fractionations or they may be clay treated or otherwise further purified before conversion to acids.

The oxidation may be carried out by any convenient procedure for vapor phase catalytic oxidations. Special kinds of construction materials are not required since corrosion troubles are negligible. Iron or steel reactors have been found quite satisfactory. The catalyst may be employed in a fixed bed or it may be of the moving bed or fluid flow type such as have been found especially advantageous in other catalytic operations.

A transfer line reactor may offer special advantages. In this type of reactor the finely divided, fluidized oxidation catalyst is introduced into the bottom of the reaction zone by means of a stream of inert gaseous carrying medium. The catalyst is carried upward through the reaction zone into which the hydrocarbon feed is also introduced. Oxygen or air may also be introduced into the reaction zone either with the catalyst or separately. The oxidized products are removed as the outlet stream from the upper portion of the reactor. After passing through the reaction zone the catalyst particles are exposed to a stripping treatment, for example, by steam to remove products and unreacted feed. The stripped catalyst is passed continuously through a standpipe to the lower portion of the reactor and thence recycled through the reaction zone. This arrangement gives a valuable advantage in carrying out exothermic oxidations as heat can be removed from the catalyst while it is outside the heat generating reaction zone.

As catalysts for this reaction there may be used any of those commonly employed for catalytic oxidations. Among the best-known are the vanadium-containing catalysts. These may be vanadium oxide alone or they may be mixtures of vanadium and other oxides, as for example, molybdenum oxide. Suitable promoters such as sod-

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ium or potassium sulfate may be added to these catalysts.

These catalysts may be of the supported type, using as supporting agent some material which is inert to the reaction conditions. The catalytic material may be employed without support, thus simplifying separation steps. The catalyst may be of the formed type, such as the fluidized catalysts. An especially valuable form for use in such apparatus as the transfer-line reactor is a catalyst having the shape of micro-spheres. These spheres may be produced by heating the catalyst material to fusion followed by treatment to give the catalytic material the form of micro-spheres. These microspheres can be used satisfactorily for longer periods of time since they are not subject to the attrition and grinding difficulties inherent in the use of other forms of catalyst particles. Problems created by dust formation are also reduced to a minimum.

The oxidation can be carried out either with or without the presence of an oxidizing gas in the reaction zone.

The oxidizing gas which is used may be any oxygen-containing gas. Pure oxygen may be used with or without a diluent such as steam. Air is a very convenient and useful oxidizing mixture. Synthetic mixtures can also be used in which oxygen is admixed with an inert gas such as nitrogen.

It is also possible to carry out the oxidation in the absence of an oxidizing gas. Certain catalysts, in particular those of vanadium oxides, may be employed as oxygen carriers which can be enriched with oxygen in a zone completely separated from that in which reaction occurs. This type of reaction can be carried out in a number of ways. It is particularly well adapted for use in a modified transfer line type reactor.

In cases where an oxidizing gas is used, it should be present in a substantial excess in the feed mixture over the hydrocarbons being oxidized. Usage of this kind of excess tends to decrease formation of tarry by-products by over-oxidation and decomposition. A preferred method for operation at maximum efficiency employs a feed having hydrocarbon concentrations of 0.50 to 2.00 mole per cent. The optimum concentration will depend to a certain extent on the particular components which are present in the feed and on the control of variables during the reaction.

The temperature employed in carrying out the oxidation reaction is not unduly critical. It may be somewhere in the range of 300° C. to 700° C. The temperature within the catalytic zone, that is to say, the catalyst temperature, should be high enough to effect the desired conversion of the feed to dibasic acids but not so high as to give excessive combustion resulting in loss of product, contamination of the catalyst, and impurities which give expensive and unnecessary separation difficulties. An optimum temperature has been found to be 500–600° C. This optimum depends somewhat on type of apparatus and catalyst composition of feed, catalyst contact time, and other variables of the process.

The mixture of oxidizing gas and hydrocarbon feed should be contacted with the catalyst at such a rate as to be practical for commercial operation, allowing sufficient time for such conversion to the crude diacid product as is most desirable. It has been found preferable to operate the process at a catalyst contact time of about 0.1 to 1.0 second. Any feed stock which is un-

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oxidized may be recovered from the exit gases and recycled to the reaction zone.

While, in general, the preferred fractions are of boiling ranges that necessarily contain aromatics such as benzene and toluene, the total yield of dibasic acid cannot be accounted for by the aromatics in the feed mixtures.

It is of particular advantage that these mixtures of hydrocarbons containing aromatics and diolefins can be utilized without purification or separation of the components. Thus a considerable saving is effected both in time and expense by operating with crude mixtures. Herefore it was believed necessary to separate these diolefin impurities from the benzene and toluene cut before attempting to oxidize the aromatics to maleic acid. Now by employing this new discovery, such separation steps are completely eliminated. Furthermore, the relatively worthless by-products in the crude fraction are converted into valuable products, no further separation difficulties are created and a substantially higher yield is obtained than that to be expected from the aromatics.

Examples

Example 1.—A mixture of methyl pentadienes containing mainly 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene and air was contacted with a catalyst of the approximate composition of 12% V_2O_5 and 4–5% MoO_3 suspended on corundum and promoted with a small amount of sodium sulfate. The catalyst temperature was maintained at 450–500° C. The concentration of hydrocarbon feed was about 1.0 moles per 100 moles of air and an over-all feed rate of 4200 volumes of air per volume of catalyst per hour corresponding to a contact time of about 0.3 second. The exit gases from the reaction zone were condensed and the crude maleic acid recovered. A good yield of maleic acid was obtained. The acid was easily identified by its neutral equivalent and by its conversion to fumaric acid through isomerization.

Example 2.—A mixture of 3-methyl-1,3-pentadiene and air was contacted with an oxidation catalyst composed of approximately 12% V_2O_5 and 4–5% MoO_3 , suspended on a corundum support and promoted with a small amount of sodium sulfate. A catalyst temperature of 550–600° C. was used. About 1.0 mole of feed was used per each 100 moles of air and the rate of contact was 4200 volumes of air per volume of catalyst per hour. A contact time of about 0.3 second was used. The exit gases were condensed and the crude maleic acid recovered. After suitable purification, a good yield of maleic acid was obtained.

Example 3.—A gaseous mixture of air and a steam-cracked petroleum fraction boiling at 80–100° C. and containing substantial amounts of C_6 diolefins was contacted with an oxidation catalyst at temperatures ranging from 500 to 600° C. The catalyst was a mixture of three parts by weight of vanadium pentoxide and one part by weight of molybdenum oxide fused into 8–12 mesh size. The feed to air mole ratio was about 1.0. The rate of feed was 3340 volume per volume of catalyst per hour. A contact time of about 0.4 second was used. The exit gases were condensed and the crude acids absorbed in water. There was obtained a good yield of maleic acid which may be further purified in any manner desired.

Example 4.—A gaseous mixture of air and a steam-cracked petroleum fraction of boiling

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range 65-80° C. containing methyl pentadienes was contacted with an oxidation catalyst. The catalyst was composed of V_2O_5 and MoO_3 supported on corundum. A temperature in the range of 500-600° C. was used. The mole per cent ratio of hydrocarbon feed to air varied from 0.75 to 1.00. The rate of material contacted was about 4200 volume of air per volume of catalyst per hour. The catalyst contact time was about 0.3 second. The exit gases were water-scrubbed and a good yield of maleic acid recovered.

In the above example there may also be used a catalyst composed of a fused mixture of V_2O_5 and MoO_3 which has been shaped into microspheres. This type of catalyst is especially advantageous for use in the transfer line type fluid reactor and, under certain conditions, may give somewhat higher yields of the dibasic acids.

What is claimed is:

1. A process for the preparation of maleic acid which comprises contacting a gaseous mixture of 0.5 to 2.0 mole per cent of 2-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, and air with a vanadium oxide catalyst at a temperature of 500-600° C. and a catalyst contact time of 0.1 to 1.0 second.

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2. A process for the preparation of maleic acid which comprises contacting a gaseous mixture of 0.5 to 2.0 mole per cent of 3-methyl-1,3-pentadiene and air with a vanadium oxide catalyst at a temperature of 500-600° C., and a catalyst contact time of 0.1 to 1.0 second.

3. A process for the preparation of maleic acid which comprises selectively oxidizing a gaseous mixture of C_6 diolefins of boiling range 65-80° C., and consisting essentially of methyl pentadienes, with air in the presence of a vanadium oxide catalyst at a temperature of 500-600° C.

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