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PARTIAL OXIDATION OF HYDROCARBONS

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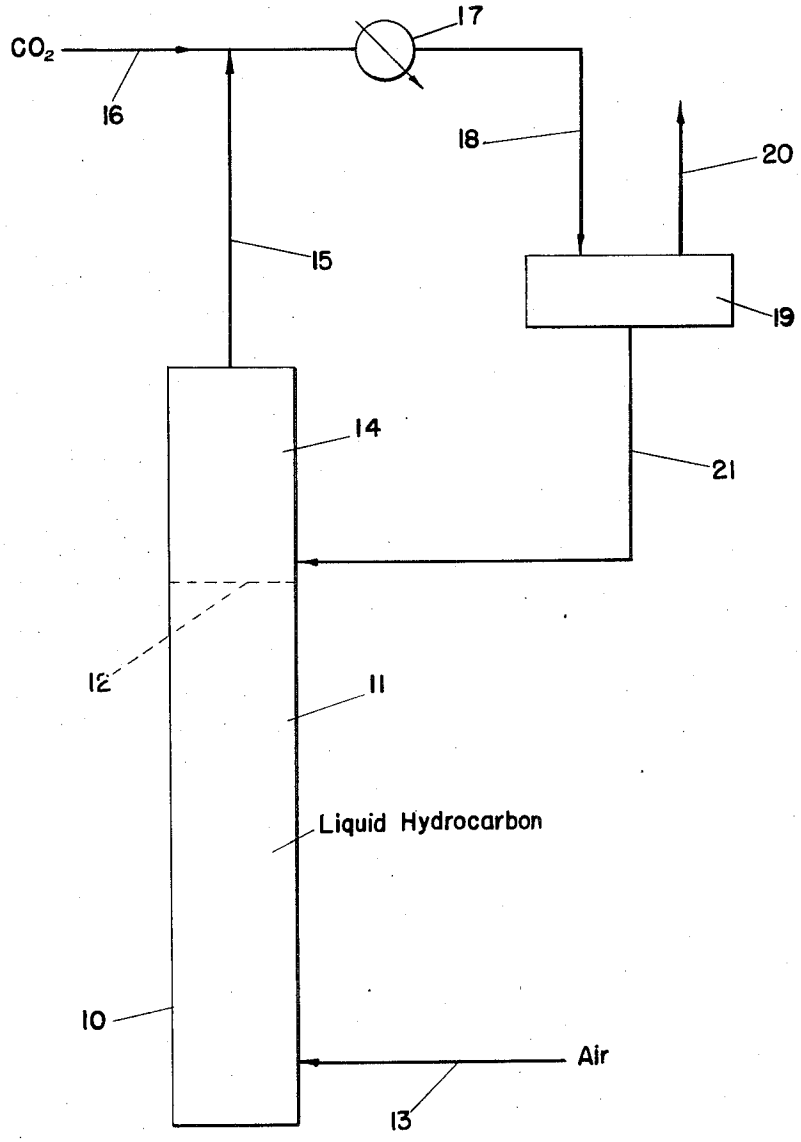

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PARTIAL OXIDATION OF HYDROCARBONS

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This invention relates to the partial oxidation of hydrocarbons, and more particularly to a manner of eliminating explosion hazards in such oxidation.

It is known in the art to partially oxidize hydrocarbon materials to produce various oxygenated products including carboxylic acids, alcohols, ketones, aldehydes, etc. In such processes, it is customary to contact hydrocarbons in vapor or liquid phase with a free-oxygen containing gas under conditions, generally involving elevated temperature and presence of catalyst, resulting in partial oxidation of the hydrocarbons to produce oxygenated compounds. A problem which frequently arises in such processes is the formation of explosive mixtures of oxygen and hydrocarbon vapors or gases. The present invention provides a novel manner of minimizing explosion hazards in oxidation processes.

In mixtures of oxygen with hydrocarbon vapors or gases, in the absence of inert, nonflammable gases, there is generally a range of hydrocarbon content within which explosion may occur. This range of concentrations is known as the explosive range, or the explosive limits. For example, in mixtures of oxygen and a xylene, the explosive range at atmospheric pressure and room temperature is within the approximate range from 1 to 30 volume percent of xylene. Thus, if the concentration of xylene is below about 1% or above about 30%, an explosive mixture is not present, and there is no danger of explosion.

In instances where inert gases such as nitrogen are also present, the explosive range is generally narrower than in the case where inert gases are not present. Thus for example in the case of mixtures of air and xylene, the explosive range at atmospheric pressure and room temperature is about 1 to 5 volume percent of xylene.

In cases where the concentration of oxygen, based on nonhydrocarbon constituents, is below a certain limit, there is no explosive range at all, since there is no concentration of hydrocarbon which will produce an explosive mixture. The concentration of oxygen based on nonhydrocarbon constituents at this limit will be hereinafter referred to as the threshold concentration. This concentration is readily determined for any mixture. In the case of xylene and a typical diluent, for example, the threshold concentration at atmospheric pressure and room temperature is about 10 volume percent. Thus, addition of xylene to a mixture of oxygen and a typical inert gas containing, say, 8% of oxygen will not produce an explosive mixture at any concentration of xylene, since the oxygen concentration based on nonhydrocarbon materials is below the threshold concentration.

According to the invention, an oxidation process is carried out wherein hydrocarbon materials are contacted with free-oxygen containing gas in proportions such that the oxygen concentration in the vapor phase material in the oxidation zone is above the threshold concentration, and the hydrocarbon content of the vapor phase material is above the upper explosive limit. The mixture is maintained above the upper explosive limit by suitable

regulation of the relative amounts of hydrocarbon and nonhydrocarbon materials which are contacted with each other in vapor phase.

Prior to condensation of unoxidized hydrocarbon constituents of the reaction mixture, an inert nonflammable gas is introduced into the mixture in order to reduce the oxygen concentration to a level below the threshold concentration. This is done in order to prevent the hydrocarbon concentration of the vapor phase material from being, during a portion of the condensation, within the explosive range. If this were not done, liquefaction of a certain amount of the hydrocarbons in the vapor phase materials by condensation would result in a reduction in the hydrocarbon concentration in the vapor phase material to a level within the explosive range. This is avoided according to the invention by, prior to condensation, reducing the oxygen concentration to a level below the threshold concentration, so that reduction of hydrocarbon concentration to any level is incapable of producing an explosive mixture.

The partial oxidation according to the invention is carried out in such manner that the oxygen concentration of the vapor phase material is, in an early stage, above the threshold concentration. Such operation is desirable in many oxidations in order to provide optimum oxidation rate and/or product distribution. The process according to the invention provides these benefits in an appropriate oxidation while eliminating explosion hazards in the condensation stage.

The invention is applicable generally to known oxidations of hydrycarbon materials by free-oxygen containing gas, wherein oxygen concentrations above the threshold concentration are involved. In the oxidation of aliphatic and naphthenic hydrocarbons in petroleum fractions such as petroleum naphtha, such conditions are frequently involved, and also in oxidation of aromatic or alkyl aromatic hydrocarbons, e.g. xylenes.

The invention is applicable generally to the use as oxidizing agent of substantially pure oxygen or mixtures of oxygen with other gases, as known as in the art for such use. Any of the known diluents for oxygen can be employed, e.g. nitrogen, carbon dioxide, flue gas, etc. The inert gas added at a later stage in the process according to the invention can be the same as, or different from, the diluent gas, if any, employed in the earlier stage. The inert gas thus added is one which is not condensed together with the hydrocarbon to an extent such that the oxygen content rises above the threshold concentration during the condensation.

Any suitable conditions for partial oxidation of hydrocarbons, as known in the art, can be employed. In liquid phase oxidation of alkyl aromatic or nonaromatic hydrocarbons, suitable temperatures generally include those within the approximate range from 200° F. to 400° F. The oxidation can be performed at atmospheric pressure, or at elevated pressure if desired, preferably not exceeding 500 p.s.i.g. Known oxidation catalysts such as cobalt or manganese salts of carboxylic acids such as naphthenic acids or fatty acids can be employed. In vapor phase oxidation of aromatics, alkyl aromatics, etc., generally higher temperatures are employed, e.g. up to 800° F. or 900° F. Any of the known catalysts for vapor phase oxidation can be employed, e.g. vanadium pentoxide, etc.

The invention will be further described with reference to the attached drawing, which is a schematic illustration of one embodiment of the invention.

Referring to the drawing, oxidation vessel **10** is charged with liquid hydrocarbon, such as xylene, to form a body of liquid **11** having an upper surface **12**. The body of liquid is heated to suitable oxidation temperature, e.g. 300° F., by means not shown such as heating coils in the bottom of vessel **10**. The pressure in vessel **10** is

maintained at about 100 p.s.i.g. Air is introduced through line **13** by means of suitable distributing means not shown into a lower portion of the body of liquid **11**. Air bubbles rise through the heated xylene, and cause partial oxidation thereof to form carboxylic acid products such as phthalic acids. The xylene contains a small amount of an oxidation catalyst, such as cobalt naphthenates, to promote the oxidation.

The air, now having depleted oxygen content as a result of reaction of oxygen with xylene, is separated from the body of liquid and enters the vapor space **14** thereabove in vessel **10**. Also present in vapor space **14** is vaporized xylene evolved from the body of liquid as a result of heating provided by the heating coils, and also by the heat of reaction. Low boiling products of oxidation are also present in vapor space **14**.

The concentration of oxygen in vapor space **14** is above the threshold concentration. However, an explosive mixture is not present, since the xylene content of the material in vapor space **14** is above the upper explosive limit. This amount of xylene is maintained in the vapor space **14** by suitable regulation of the temperature and the rate of passage of air through the body of liquid. In the light of the present specification, a person skilled in the art can select proper operating conditions to produce this result.

Vapor phase material is withdrawn from vapor space **14** through line **15** and introduced into condenser **17**. Prior to such introduction, the vapor phase material is admixed with inert nonflammable gas such as carbon dioxide introduced through line **16**. The oxygen content is thereby reduced below the threshold concentration, so that during condensation of xylenes in condenser **17**, there is never an explosive mixture in the vapor phase material.

The uncondensed material and the liquid xylenes are introduced through line **18** into separator **19**, the uncondensed material being withdrawn through line **20** for suitable further processing as known in the art, and the liquid xylene being recycled to oxidation vessel **10** through line **21**.

By operating under conditions such that the oxygen content in vapor space **14** is above the threshold concentration, highly satisfactory oxidation is obtained in vessel **10**. By reducing the oxygen content of vapor phase material to below the threshold concentration prior to condensation in zone **17**, the formation of an explosive mixture at any stage of the process is prevented.

The following examples illustrate the invention:

Example I

Meta-xylene is introduced into a vessel such as that illustrated in the drawing and heated to a temperature of about 300° F. under a pressure of about 100 p.s.i.g. The xylene contains cobalt naphthenates in amount to provide about 0.05 weight percent of cobalt based on xylene. Air is bubbled through the liquid xylene. The gas in the space above the liquid contains about 12 volume percent oxygen and 20 volume percent xylene. The xylene concentration is above the upper explosive limit, and there is no danger of explosion.

Prior to condensation of xylene, carbon dioxide is introduced into the gaseous material in amount to produce a mixture containing 50 volume percent carbon dioxide, 6 volume percent oxygen, and 10 volume percent xylene. The oxygen content on the xylene-free basis is now about 6.7 volume percent, which is below the threshold concentration, so that an explosive mixture is not formed at any stage of the condensation.

By way of contrast, in condensation of xylene from the gaseous material without addition of carbon dioxide, when the xylene content of the gaseous material has been reduced to an intermediate level, an explosive mixture is present. It is only when the oxygen content has been reduced to below the threshold concentration that the xylene content can be reduced to any given level without forming an explosive mixture.

Example II

Operation similar to that described in Example I is carried out, the oxidizing agent being substantially pure oxygen, however, and the charge stock petroleum naphtha. The vapor phase material in vapor space **14** has oxygen content above the threshold concentration and naphtha content above the upper explosive limit. Prior to condensation, carbon dioxide is added to change the composition and produce a mixture wherein the oxygen content is below the threshold concentration, so that no explosive mixture is formed during the condensation of naphtha.

Generally similar results to those obtained in Examples I and II are obtained in vapor phase oxidations wherein the composition of the entire reaction mixture corresponds to that of the vapor phase material in those examples, in that the oxygen concentration is above the threshold concentration and the hydrocarbon concentration above the upper explosive limit, and in that the composition is changed, prior to condensation of hydrocarbon, to reduce the oxygen concentration to below the threshold concentration.

The process according to the present invention can be carried out by batch or continuous methods. In a continuous method, for example, a portion of the body of liquid **11** can be withdrawn continuously, filtered to remove solid phthalic acid, and the filtrate returned to the oxidation vessel **10**. Processes for continuous partial oxidation of hydrocarbons are well known in the art, and any suitable known procedure can be employed in the process according to the invention.

The present invention involves, in one part of the process, maintaining hydrocarbon concentration in the vapor phase material above the upper explosive limit, and in another part maintaining the oxygen content of the vapor phase material below the threshold concentration. The numerical values of upper explosive limit and threshold concentration vary according to the nature of the hydrocarbon material and of the diluent if any, and also according to the temperature and pressure employed. However, it is within the ability of a person skilled in the art to determine for a given system, in the light of the present specification, the upper explosive limit and threshold concentration.

The invention claimed is:

1. Process for partially oxidizing hydrocarbons which comprises: contacting at elevated oxidation temperature partially oxidizable hydrocarbons having an upper explosive limit and a threshold concentration, with a gaseous oxidizing agent containing free oxygen in amount above the threshold concentration, thereby to partially oxidize the hydrocarbons; introducing said hydrocarbons and said treating agent into the oxidation zone at a rate sufficient, under the prevailing oxidation conditions, to produce partial oxidation products and to provide and maintain in the oxidation zone a vapor phase material having oxygen content above the threshold concentration and an unoxidized hydrocarbon content above the upper explosive limit; removing said vapor phase material from the oxidation zone; adding to the removed material a nonflammable gas in amount sufficient to reduce the oxygen content to below the threshold concentration; and thereafter condensing hydrocarbons from the vapor phase material; said threshold concentration being the lowest concentration of oxygen, based on nonhydrocarbon materials, at which an explosive mixture of hydrocarbons and said nonhydrocarbon materials can be formed.

2. Process according to claim 1 wherein said hydrocarbons are introduced into the oxidation zone in liquid phase, and the hydrocarbon in said vapor phase material comprises hydrocarbon vaporized in the oxidation zone.

3. Process according to claim 2 wherein said vapor phase material is substantially continuously removed from the oxidation zone, and said nonflammable gas is substantially continuously added to the removed vapor phase material.

4. Process according to claim 1 wherein said hydrocarbons are introduced into the oxidation zone in liquid phase, said contacting is at a temperature in the range 200 to 400° F., the hydrocarbon is xylene, the treating agent is air, the vapor phase material separated from the treated hydrocarbon contains more than 5 volume percent hydrocarbon, and the oxygen content of the vapor phase material after addition of said nonflammable gas is less than 10 volume percent.

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