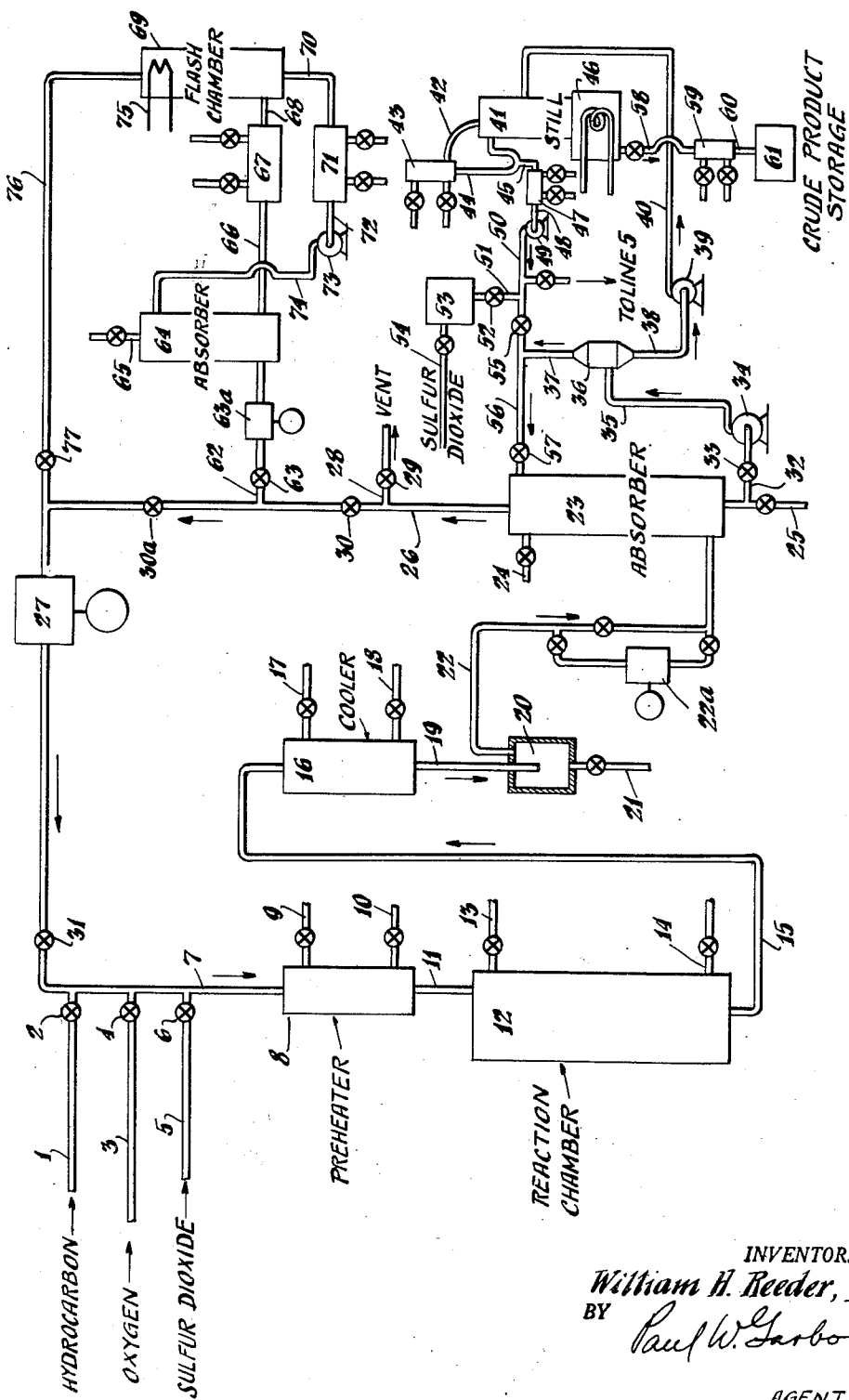


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PARTIAL OXIDATION OF HYDROCARBONS
IN THE PRESENCE OF SULFUR DIOXIDE
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AGENT

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PARTIAL OXIDATION OF HYDROCARBONS IN THE PRESENCE OF SULFUR DIOXIDE

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Continuation of abandoned application Serial No. 676,469, June 13, 1946. This application March 25, 1952, Serial No. 278,423

12 Claims. (Cl. 260—604)

The present invention relates to the limited oxidation of hydrocarbons, and more particularly of the normally gaseous saturated aliphatic hydrocarbons, for the formation of partially oxygenated compounds and particularly of aldehydes and ketones. It is also applicable to the limited oxidation of other hydrocarbons, such as benzene and petroleum fractions. This application is a continuation of copending application Serial No. 676,469, filed June 13, 1946, now abandoned.

An object of this invention is to prepare partially oxygenated compounds by the oxidation of hydrocarbons in such a manner that the nature of the products may be controlled and limited in the main, preferably to carbonyl compounds such as aldehydic and ketonic compounds, hereinafter generically termed "aldehydic compounds" or "products." A further object of this invention is to provide a process for the oxidation of hydrocarbons wherein the yields of such partially oxygenated compounds are high and the number of such compounds formed is relatively small, and whereby such compounds may be easily separated in relatively pure form from the products of reaction. Other objects of this invention will appear from the following detailed description.

In the principal commercial direct oxidation processes for the production of partially oxygenated compounds, the partial oxidation of the normally gaseous aliphatic hydrocarbons is accomplished by contacting the hydrocarbon with oxygen or free oxygen containing gas such as air, as the primary oxidizing agent. In such processes, in some cases, it has been suggested that minor proportions of nitrogen oxides or sulfur oxides be added as catalysts, but not as the direct oxidizing agents. The number of oxygenated products formed in such processes is large and extends through the whole range of oxidation to the carbon oxides. Thus, from each hydrocarbon being oxidized, there is formed a series of products which includes, in greater or lesser amounts, the corresponding alcohols, aldehydes or ketones and carboxylic acids, and the oxides of carbon. Such mixtures of products are generally very difficult to separate into commercially pure components. Moreover, in such processes, because the intermediate products are generally more easily oxidized than the parent hydrocarbons, it is difficult to prevent the formation of considerable quantities of the oxides of carbon, with the result that the amount of hydrocarbon converted to intermediate, partial oxidation products is relatively small, and the consumption of the oxygen oxidant is high. Only moderate improvements with regard to yields and number of products formed have been obtained in these processes by the use of catalysts, gaseous diluents, short times of contact or by the application of special methods of contacting or cooling.

A process in which higher yields based on hydrocarbon consumed, and in which a single aldehydic product or a simple, easily separated mixture of partially oxygenated products is obtained from the limited oxidation of the normally gaseous aliphatic hydrocarbons, is disclosed in U. S. Patent 2,532,930 to Fredlee M. McNall. In this

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process, sulfuric acid, in the absence of oxygen or free oxygen containing gas, is employed as the oxidizing agent. The reaction is conducted, for example, in the presence of liquid sulfuric acid at high temperatures and preferably, but not necessarily, in the presence of a catalyst dissolved in the hot sulfuric acid.

It has been found that in carrying out the reaction as disclosed in the aforesaid McNall patent in which the hot sulfuric acid acts as the oxidizing agent, that, although the amount of hydrocarbon consumed that is converted to the desired oxygenated products is large, there is a high consumption of the sulfuric acid and a correspondingly high production of sulfur dioxide, resulting in a high cost of operation. Furthermore, the process, when conducted under conditions to secure effective yields of formaldehyde from methane in mixtures of hydrocarbons such as occur in natural gas, does not oxidize the higher hydrocarbons with good yields of aldehydic or ketonic products.

A method for the limited oxidation of hydrocarbons whereby a much more effective utilization of oxidizing agent is obtained at no sacrifice in the high yield based on hydrocarbon consumed is disclosed in my copending application Serial No. 675,372, filed June 8, 1946, which eventuated in Patent No. 2,590,124, on March 25, 1952.

As therein described, it has been found that hydrocarbons can be converted in good yields to partially oxygenated compounds by using gaseous sulfur trioxide as the oxidizing agent in the presence of a contact mass or catalyst comprising a suitably prepared or activated, adsorptive catalytic material. Temperatures employed for this vapor-phase process are in the order of 175° to 450° C. By the vapor phase process of my Patent No. 2,590,124 I am enabled to secure a more effective utilization of the oxidizing agent, as well as other advantages in control and operation.

In both of the aforesaid processes, whether sulfuric acid or sulfur trioxide be used as the oxidizing agent, it appears that two molar equivalents of sulfur trioxide or sulfuric acid are converted to sulfur dioxide for each molar equivalent of hydrocarbon partially oxidized to the corresponding aldehyde. For each equivalent of hydrocarbon oxidized to carbon monoxide or carbon dioxide, correspondingly more of the oxidizing agent is converted to sulfur dioxide. For the most economical operation of either process sulfur dioxide is suitably recovered and reconverted in an auxiliary installation into sulfur trioxide or sulfuric acid.

I have now found that in my vapor-phase process for the limited oxidation of hydrocarbons to partially oxygenated compounds, a mixture of sulfur dioxide and oxygen in which the oxygen is present in a minor proportion can be used. As in the case of the vapor-phase process of my Patent No. 2,590,124 employing gaseous sulfur trioxide as the oxidizing agent, the reaction is conducted in the presence of a contact mass comprising a suitably prepared or activated adsorptive catalytic material. I employ temperatures not in excess of about 450° C. or less than about 175° C. Yields of partially oxygenated compounds based on both hydrocarbon and oxygen consumption are high. The number of partially oxygenated compounds formed is relatively small.

The fact that relatively much smaller quantities or none of the oxides of carbon are formed by the limited oxidation of hydrocarbons with sulfur dioxide-oxygen mixtures serves to distinguish this reaction from the one occurring when hydrocarbons are subjected to direct oxidation with oxygen or free oxygen-containing gas, such as air.

The use of sulfur dioxide-oxygen mixtures thus possesses the advantages of high yields and simplicity of products plus the important additional advantage that, by employing recycle operation as hereinafter described, the sulfur dioxide can be used over and over again.

The present process is applicable to the treatment of methane, its homologues, aromatic hydrocarbons, petroleum fractions, and other hydrocarbons which are in the gaseous state at the reaction pressures and temperatures hereinafter described. The principal products resulting from such treatment are the corresponding partially oxygenated compounds, notably, aldehydes, ketones, and phenols.

Adsorptive catalytic materials of widely varying types may be used and it appears that the important characteristic from the standpoint of the desired reaction is their adsorptive character rather than their specific chemical composition, although minor variations in behavior result from the latter. Thus, widely varying adsorptive materials may be employed, such as charcoal, silica gel, fused porous silica, alumina, fuller's earth, bauxite, kieselguhr, aluminum silicates, hydrated aluminum and magnesium silicates, and the like. It will be appreciated that in some cases, particularly of natural minerals, the adsorptive materials may be treated preliminarily with sulfuric acid to improve their adsorptive and catalytic action.

Metallic salts or oxides which promote or catalyze the oxidation of hydrocarbons may be deposited on the adsorptive material to increase the effectiveness of the limited oxidation of hydrocarbons and to aid in reducing the production of oxides of carbon. Suitable for this purpose are the salts and oxides of the elements of the *Ib* periodic group and the transition elements and mixtures thereof. The transition elements include the metals Sc, Ti, V, Cr, Mn, Fe, Co and Ni in the 4th long series, Y, Zr, Nb, Mo, Tc, Ru, Rh and Pd in the 5th long series, La, Ce and the other rare earths, Hf, Ta, W, Re, Os, Ir and Pt in the 6th long series, and Ac, Th, Pa and U in the 7th series. It will be noted that in the long period arrangement of the elements and in the Bohr classification the elements of the *Ib* group, viz., Cu, Ag and Au, follow immediately the transition elements in their respective series and share with them the property of variable valency. See, for example, Ephraim, *Inorganic Chemistry*, 4th ed., revised, New York, 1943, pages 25 and 29.

When the metallic salts are employed, soluble salts of the selected metal or mixture of metals are dissolved in water and the resulting solution is thoroughly mixed with the adsorptive material, which is then dried and heated as hereinafter described. The oxides or other insoluble compounds of the metal selected may be precipitated in the adsorptive material, if desired. The particular salt or compound which is employed does not appear to affect the reaction. Thus, chlorides, nitrates, sulfates, acetates or formates or other soluble salts of the metals may be employed, providing they are sufficiently soluble to permit of securing the desired proportion of the metallic salt or salts in the adsorptive material. The amount of metallic compound incorporated into the adsorptive material is suitably from about 1 to about 25 percent and preferably from about 2 to about 10 percent, based on the amount of adsorptive material. In general, the inorganic salts are preferred, since they do not leave a carbonaceous residue when the mixture with the adsorptive material is heated to drive off moisture and to activate the mixture, or during reaction.

When the metallic oxides are employed they may be prepared on the inert adsorptive material by appropriate treatment of the salts deposited as above or in any other fashion common to the art.

Irrespective of whether the adsorptive material does or does not contain a metallic salt or oxide, its effectiveness may frequently be increased by a preliminary heat treatment or activation, which may be carried out either before or after the catalyst has been placed in the reaction chamber in which it is to be used. This treatment is effected by heating the adsorptive material, with or without added metal compound, at a high temperature, in the order of 400° to 600° C. or higher. The optimum temperature of activation for each adsorptive material or

catalyst combination may vary within this range and may be selected on the basis of prior experiment or test or in accordance with the known practices in the art for the activation of such contact masses. Good results are secured by heating the adsorptive catalytic material or contact mass while passing through the chamber containing it a stream of air, of sulfur oxides, of the hydrocarbon gas to be oxidized, or of mixtures thereof, providing, of course, that if a hydrocarbon be present, the activation temperature does not exceed the cracking temperature of the hydrocarbon. Only a short period of heat treatment is required, say ½ to 1 hour, longer treatment doing no apparent harm and in some cases being advantageous, as with alumina. The heat treatment may suitably be effected at the beginning of an operation, while passing hydrocarbons alone, air or inert gas through the reaction chamber and before beginning the introduction of sulfur dioxide. In reactivating catalyst which has become spent or partially spent in use, a similar heat treatment is applied, in which air should be used.

In carrying out the reaction, the hydrocarbon gases, gaseous sulfur dioxide, and oxygen in the proper proportions may be simultaneously introduced into the reaction zone, which is maintained under the desired reaction conditions, or they may be mixed in the desired proportions prior to entering the reaction chamber. Thus hydrocarbon gas, either before or after its admixture with the desired amount of oxygen, may be passed through water or other suitable fluid in which such an amount of sulfur dioxide is dissolved that, under the conditions of temperature and pressure used, the effluent gaseous mixture contains the desired proportions of sulfur dioxide. (The water vapor carried into the reaction chamber in this way has no apparent deleterious effect and may be helpful in controlling the reaction.) Instead of passing the hydrocarbon gas, either before or after admixture with oxygen, through a suitable solvent containing dissolved sulfur dioxide, the gas may be passed through liquid sulfur dioxide maintained at a temperature and pressure such that the effluent gas mixture contains the desired proportion of sulfur dioxide. If desired, gaseous sulfur dioxide may be directly mixed with hydrocarbon gas and oxygen before entering the reaction chamber. The amount of sulfur dioxide introduced is controlled so that its concentration in the gas entering the reaction zone does not exceed 50 to 60 percent by volume and preferably is not greater than 20 percent.

The reaction is preferably conducted under superatmospheric pressures, say in the order of 20 to 600 pounds per square inch or higher, although the process may be carried out effectively at atmospheric pressure or at sub-atmospheric pressures. Reaction pressures preferred for the limited oxidation of different individual hydrocarbons or hydrocarbon mixtures are those lying in the range prescribed, resulting in the most economic operation with regard to effective utilization of hydrocarbon and oxidant and to ease of recovery of partially oxygenated products.

The gases leaving the reaction chamber, which contain partially oxygenated compounds, water vapor, sulfur dioxide, and oxides of carbon, are passed through a cooler and any resulting condensate is collected and removed from the reaction system. The cooled vapors are then passed through an absorber in which the remaining partially oxygenated products are removed from the vapors and gases by contacting with water or other suitable fluid. The resulting solution, also containing sulfur dioxide, is passed through a product recovery system, suitably a product still, and aldehydes, other oxygenated products, and sulfur dioxide are recovered. Products are similarly recovered from the condensate.

The unreacted hydrocarbon gases containing sulfur dioxide in the desired proportion are recycled; that is, they are returned to the reaction chamber, make-up hydrocarbon gas and oxygen being added to compensate for hydrocarbon and oxygen consumed. Sulfur dioxide re-

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covered from the product recovery operation may similarly be recharged to the reaction system.

Apparatus suitable for carrying out the invention is illustrated diagrammatically in the accompanying drawing.

Referring to the drawing, the numeral 1 designates a line for introducing hydrocarbon gas into the system, suitably into recycling line 7. The rate of hydrocarbon introduction is controlled by valve 2. Oxygen is admitted through line 3, controlled by valve 4, and sulfur dioxide is admitted through line 5, controlled by valve 6. The newly admitted gases mix with the recycle gases in line 7 and the resulting mixed gases are then passed into the jacketed preheater or heat exchanger 8, in which the temperature of the combined gases is raised to the desired level. A suitable heating fluid may be circulated through the jacket by means of lines 9 and 10.

The preheated gas passes through line 11 into the reaction chamber 12, into which is charged the suitably prepared or activated adsorptive catalytic material or contact mass used to catalyze the reaction. The reaction chamber may be constructed in any of the numerous styles common to the art of contacting heated gases in the presence of solid catalysts. Thus, fixed bed catalyst cases may be used, or moving bed systems, or the adsorptive catalytic material may be finely powdered and maintained in fluidized state in the reaction chamber. Suitable means are provided for applying heat to or removing heat from the reaction chamber 12; for example, if a fixed bed case, it may be jacketed or provided with internal tubes or both, and a suitable heat transfer agent, such as diphenyl or diphenyl oxide, fused fluid salt mixtures or the like may be circulated through the jacket or around the tubes by means of lines 13 and 14. Thus it may be necessary to apply heat to initiate the reaction; but since the reaction is exothermic, the amount of heat developed, particularly when operating under pressure, may be more than sufficient to maintain the desired temperature level and cooling may be required.

The reacted gases containing partially oxygenated compounds pass out of the reaction chamber 12, through line 15, and into a suitable jacketed cooler 16. Heat transfer fluid is circulated through the jacket of the cooler 16 by use of lines 17 and 18. The cooled gases, with any condensate formed therefrom, pass out of cooler 16 through line 19 into receiver 20. Any liquid collected in receiver 20 may be withdrawn through valve controlled line 21, and, if found to contain appreciable quantities of partially oxygenated compounds, may be suitably treated or distilled for the recovery thereof.

Uncondensed vapors and gases, which contain the balance of the partially oxygenated products formed, pass out of the receiver 20 through line 22 into the absorber 23, in which they are contacted with water or other suitable absorption fluid, and substantially all of the partially oxygenated compounds are removed from them. Water or other suitable fluid may be supplied to the absorber 23 through line 24. The absorber 23 may be of any suitable type, for example, a packed tower or a bubble plate tower. The absorption fluid, in passing through the absorber 23, removes, in addition to the partially oxygenated compounds, part of the sulfur dioxide and oxides of carbon contained in the gases and vapors. The enriched absorption fluid leaves the absorber 23 through the line 25 and may pass to a suitable product recovery system (not shown) where partially oxygenated compounds are separated from the absorption fluid, sulfur dioxide and other products of reaction.

The vapors and gases leaving the absorber 23, and which contain sulfur dioxide, and water vapor (if any), in addition to unreacted hydrocarbons, oxygen, and inert gaseous materials, are conducted through the recycling line 26 to the recycle compressor or blower 27, by which they are forced into line 7 and returned to the preheater 8, along with the make-up of hydrocarbon, oxygen, and sul-

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fur dioxide admitted into the reaction system through lines 1, 3 and 5 respectively, as hereinbefore described.

In the event of the excessive accumulation of non-reactive gases or of unwanted hydrocarbons, that is, of hydrocarbons whose partial oxidation products differ from those preferably being produced by the operation, a vent line 28, controlled by valve 29, is provided to permit partial or complete venting of the system.

The system as above described is adapted for recycling operation. In case it is desired to use it for once-through or single pass operation, the recycling compressor 27 may be cut out of the system by closing valves 30 and 31, fresh hydrocarbon gas being then supplied continuously through line 1 and the effluent gases from the absorber 23 being discharged continuously through the line 26 and the vent line 28.

When formaldehyde is produced by the limited oxidation of methane or hydrocarbon gases of high methane content, the absorption fluid passed in a countercurrent direction to the gas stream through the absorber 23 may suitably be liquid sulfur dioxide, the temperature and pressure of the absorption operation being such that the sulfur dioxide remains in the liquid state. Since about 1 mol of water is formed for each mol of formaldehyde, a concentrated aqueous formaldehyde solution is formed, which solution is only moderately soluble in liquid sulfur dioxide. When such a product mixture in the vaporous state is contacted with liquid sulfur dioxide two different fluid phases are formed. At room temperature and at pressures high enough to assure the sulfur dioxide remaining in the fluid state, say at pressures of about 45 pounds per square inch and higher, the lighter of the two fluid phases is composed of liquid sulfur dioxide containing only a small proportion of formaldehyde. The heavier fluid phase is composed of concentrated aqueous solution of formaldehyde containing substantial quantities of dissolved sulfur dioxide.

In the drawing means are shown whereby the formation of two fluid phases in the absorber 23 when using liquid sulfur dioxide as an absorbent is advantageously utilized as the basis of an effective product recovery system. If it is desired to operate the absorber at a higher pressure than is used in the reaction chamber, a compressor or blower 22a may be provided for introduction of the product vapors into the absorber 23. With the valves in lines 24 and 25 closed and valves 33 and 57 in lines 32 and 56 open, the mixture of the two fluid phases is withdrawn through line 32, by the pump 34 and is forced through line 35 into a separator 36, which may be a vessel of any suitable construction in which the heterogeneous liquid mixture is allowed to separate into two homogeneous layers. The absorber and separator may suitably be operated at pressures of about 45 to about 600 pounds per square inch or higher and temperatures of about 20° to about 60° C. or higher, respectively, the temperature and pressure being preferably controlled so that the formaldehyde, in aqueous solution, is the bottom layer. The bottom layer or crude product is withdrawn from the bottom of separator 36 through line 38 and is forced by the pump 39 through line 40 into the continuously operated product still 41.

The top layer or liquid sulfur dioxide passes from the top of separator 36 into line 37 and thence into line 56 and is returned to the top of the absorber 23.

The still 41 may be connected in any suitable manner with a vapor take-off line 42, a cooled dephlegmator or condenser 43, a reflux line 44, a product take-off line 45 and a suitably heated reboiler 46. In the still or flash column 41, sulfur dioxide is flashed off the liquid mixture of sulfur dioxide and aqueous formaldehyde, withdrawn as a gas through vapor-take-off line 42, and condensed in dephlegmator 43. A portion of the condensate (sulfur dioxide) is returned to the still 41 as reflux through reflux line 44 to control the operation of the still. The remainder is removed through line 45, suit-

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ably cooled in a cooler 47, and forced by pump 49 either through the lines 50 and 51 to the liquid sulfur dioxide storage tank 53, or through lines 50 and 56 to the top of the absorber 23. The initial charge and the make-up of sulfur dioxide are introduced into the sulfur dioxide storage tank 53 through line 54.

The crude product (formaldehyde) is removed from the still reboiler 46 through line 58 and is suitably cooled in cooler 59. It then passes through line 60 to the crude product storage tank 61.

When the hydrocarbon to be partially oxidized is of such a nature that it can be separated from its mixtures with nitrogen by its selective absorption in an oil or other suitable absorption fluid, air can be charged to the oxidation system instead of oxygen. In the drawing there is shown a system wherein, by means of suitable absorption and subsequent flashing, the unreacted hydrocarbon gases leaving the absorber 23 can be separated from their mixtures with nitrogen and thus can be recirculated in the oxidation system. When this system is used, it is to be understood that air is introduced into the oxidation system through line 3 rather than oxygen of high purity, and further, that, when necessary for the economical operation of the process, sulfur dioxide is relatively completely removed from the gases leaving the absorber 23, and is then suitably recovered from the liquid absorber effluent and reintroduced into recycle gas through line 5.

With valve 30a in line 26 closed, and valves 63 and 77 in lines 62 and 76 open, the unreacted hydrocarbon gases in mixture with nitrogen and other inert gases are passed from the top of the absorber 23 through line 26 into line 62 and are forced by compressor or blower 63a into absorber 64. There they contact with oil or other suitable absorption fluid which is continuously admitted into the top of absorber 64 through line 74. The major portion of the hydrocarbon gas is absorbed by the oil and the nitrogen and other inert gases are discharged from the top of the absorber 64 through vent line 65. The effluent absorption liquid, rich in hydrocarbon gas content, is passed through line 66 and heater 67 into flash chamber 69. In the heater 67 the temperature of the liquid is raised sufficiently to cause the dissolved hydrocarbon gases to vaporize when the fluid enters flash chamber 69. The vaporized hydrocarbon gases pass from the top of flash chamber 69 through line 76 to the recycling compressor or blower 27. A cooling coil 75 prevents carry-over of absorption liquid or oil. The hot lean oil passes from the bottom of flash chamber 69 through line 70 into cooler 71, where its temperature is lowered sufficiently to ensure effective hydrocarbon absorption. The cooled absorption fluid passes from the cooler 71 through line 72 to the pump 73 and is returned through line 74 into the top of absorber 64.

As hereinafter described, in carrying out the limited oxidation of an hydrocarbon or hydrocarbon mixture by the process of the present invention, high yields of particular partially oxygenated products, based on both hydrocarbon and oxidant consumption, are obtained when process variables are carefully controlled within the limits hereinbefore specified. Those hydrocarbons, catalysts, temperatures and pressures of reaction and reactant concentrations are used which favor high conversion of hydrocarbon to desired product and at the same time suppress the occurrence of side reactions or the more complete oxidation of hydrocarbons to the oxides of carbon.

In carrying out the process, the hydrocarbon gas employed is one consisting largely of the hydrocarbon or hydrocarbons which it is desired to oxidize into aldehydic products. For the production of formaldehyde, for example, the gas should be one composed largely or entirely of methane. Thus natural gas may be employed, or substantially pure methane gas, or mixtures of methane and hydrogen derived from natural gas. It has also been found that gas prepared for illuminating and heating pur-

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poses and consisting largely of methane may be used, even though such gas contains varying proportions of other constituents derived from coal gas, water gas or the like. In general, for the most effective production of formaldehyde, it is preferred that the methane content of the gas used be in the order of 75 percent or higher.

Similarly, for the most effective production of a higher aldehyde or aldehydes or ketones, the hydrocarbon gas to be oxidized should be one composed largely of the corresponding higher homologue of methane which on partial oxidation, yields the desired product. For example, if the desired product be acetaldehyde, the hydrocarbon gas to be oxidized should be composed largely of ethane. However, it is to be noted that by suitable selection of catalyst, temperature, pressure and contact time employed in the reaction zone, higher hydrocarbons can be effectively partially oxidized to aldehydes or mixtures of aldehydes having fewer carbon atoms per molecule than the parent hydrocarbon. For example, ethane may be partially oxidized to yield substantial amounts of formaldehyde. Similarly, mixtures of formaldehyde and acetaldehyde may be obtained from the oxidation of propane.

The higher aliphatic hydrocarbons such as butane, isobutane, pentane and the like and also the cyclic and aromatic hydrocarbons and petroleum fractions which are in the gaseous state at the temperatures and pressures at which the process is carried out, may be partially oxidized to the partially oxygenated compounds or mixtures thereof by the process of the present invention. When a hydrocarbon which is a liquid at ordinary temperatures and pressures is to be partially oxidized in accordance with the present invention, it is suitably vaporized either by heating to its vaporization temperature or by passing recycle gas through the liquid hydrocarbon maintained at such a temperature as to give the desired concentration of hydrocarbon in the recycle gas.

If desired, particularly when normally liquid hydrocarbons are being subjected to the process of this invention, the recycle gas stream may be composed either wholly or in part of an inert gaseous diluent such as nitrogen, carbon dioxide, or the like. In such case methane or hydrocarbon mixtures of high methane content, such as natural gas, may also be used as a diluent for operations in which the temperature of reaction is not sufficiently high to effect in any substantial amount, the limited oxidation of methane.

As hereinbefore set forth, a wide range of adsorptive catalytic materials may be used in the contact mass and specific ones have been referred to which are of various types; for example, carbonaceous, siliceous and aluminiferous. For purposes of illustration, examples of operation with certain of these will be given, but it has been found that the others may be employed, the principal requisites being that the material employed shall be adsorptive and shall be inert at the temperatures employed to the hydrocarbons and the sulfur dioxide present in the sense that it does not enter directly into reaction with them. In the case of activated carbon or other carbonaceous material there may be some slight reaction with oxygen, which is one constituent of the reaction mixture, but this reactivity does not appear to have a harmful effect on the reaction, although it may result in some wastage of oxygen and of the contact mass.

The effectiveness of these adsorptive materials appears to result primarily from their adsorptive characteristics and apparently any sufficiently inert highly adsorptive material may be employed. However, there are certain differences in the behavior of individual adsorptive materials. All of them are effective in the range of temperatures hereinbefore set forth, but their optimum activity may appear in different parts of the range. Thus, with activated carbon or other carbonaceous adsorptive material, a relatively high rate of reaction to produce partially oxygenated compounds is secured at somewhat

lower temperatures within the range set forth than is secured with alumina or similar alumina-containing material. With a siliceous material such as silica gel, the optimum reaction conditions are secured with temperatures intermediate between those for carbon and for alumina but the efficiency of the activated silica gel is somewhat less than that of the other adsorptive materials containing carbon and alumina. With fused porous silica, as contrasted with silica gel, optimum reaction rates with high yields of partially oxygenated products are secured at relatively higher temperatures than those used with alumina.

The several adsorptive materials also exhibit differences with regard to the temperature at which the formation of carbon oxides becomes excessive. For example, with charcoal there is a tendency to the formation of the oxides of carbon in the reaction at lower temperatures than with non-carbonaceous adsorptives such as alumina and silica gel. Consequently when charcoal is employed, the differential between the temperatures for optimum formation of the desired partial oxidation products and those for the formation of carbon oxides is less and a more careful control of temperature of operation is required. With alumina, for example, this differential is somewhat greater.

The adsorptive materials also differ somewhat in their behavior in respect of side reactions. Thus, with activated carbon, the temperature at which excessive reduction of the sulfur dioxide to sulfur and hydrogen sulfide takes place is likewise lower than in the case of alumina and the spread between the temperatures for optimum aldehyde or other oxygenated compound formation and for excessive reduction of sulfur dioxide is less in the case of carbon than in the case of alumina, silica gel standing between the two in these respects. Consequently although specific temperatures for optimum results within the range indicated may be somewhat lower with carbon than with alumina, when the former is used a somewhat more careful control of the operation is required. Under conditions of temperature which promote side reactions, silica gel appears to favor the more extensive reduction of the sulfur dioxide to free sulfur, as compared with other adsorptive materials.

In general, the efficiency of the reaction may be improved by incorporating in the adsorptive material compounds such as the salts or oxides of the metals of the Ib periodic group of the transition elements or mixtures thereof. For example, silver, copper, molybdenum, cerium, iron, cobalt, nickel and platinum salts as well as salts of other such metals have been employed as well as mixtures of them, such as mixtures of cobalt and silver salts, cobalt and copper salts, cobalt and molybdenum salts, and the like. These metal salts modify the reaction in various ways; in some cases by lowering the temperature at which most efficient reaction takes place and in other cases by reducing the losses through excessive oxidation of the hydrocarbons present or excessive reduction of the sulfur dioxide to sulfur and hydrogen sulfide.

Furthermore, the metallic salts or oxides which have been referred to hereinbefore vary somewhat in their effects when incorporated into different adsorptive catalytic materials, all of them being found to have a beneficial effect either in the direction of promoting the formation of partially oxygenated compounds or of minimizing side reactions. Thus, the addition of cerium salts to activated carbon does not apparently increase the product formation at a given temperature, but does appear to decrease the reduction of the sulfur dioxide to sulfur and hydrogen sulfide. With both silica and alumina similar amounts of cerium appear to increase the rate of product formation at a given temperature or to permit the use of somewhat lower temperatures for equivalent rates of product formation. Similar variations

have been found in the effects of the other metallic promoters.

The reaction chamber, which contains the adsorptive material either with or without added metals, salts, or oxides, is maintained at a temperature of from 175° to 450° C. There is however, an optimum reaction temperature range for each different hydrocarbon. For example, in the treatment of methane, effective oxidation of the hydrocarbon gas is secured with good yields of formaldehyde relative to the hydrocarbon consumed at temperatures of 325° to 425° C. By the process of the present invention, ethane is oxidized in good yield to acetaldehyde preferably at temperatures of 270° to 350° C. Optimum reaction temperatures for the partial oxidation of the higher homologues of methane and ethane are correspondingly lower; for example, with propane and the butanes suitable temperatures would be in the order of 175° to 300° C. Benzene may be effectively oxidized to yield phenol in substantially the same temperature range preferred for the partial oxidation of methane.

As hereinbefore set forth, a wide range of reaction pressures may be employed. Within the range from atmospheric pressure to pressures of about 600 pounds per square inch, it has been found that higher rates of conversion of hydrocarbon to the desired partially oxygenated compounds are obtained at the higher pressures. With a particular catalyst or contact mass, the rate of conversion of hydrocarbon is approximately doubled when the pressure under which the reaction is conducted is doubled. It has also been found that at the higher pressures, the tendency toward the excessive formation of carbon oxides is substantially less than at lower pressures. For example, when methane, ethane, or propane are partially oxidized in accordance with the present invention, at temperatures such as are previously specified and at pressure above 100 pounds per square inch, the formation of carbon oxides is negligible.

With the higher concentrations of sulfur dioxide in the reacting gases, say from 20% to 60%, there is a greater tendency for the formation of free sulfur and hydrogen sulfide than when concentrations of sulfur dioxide of 2 to 20% are maintained. When a high sulfur dioxide concentration obtains, the formation of excessive amounts of free sulfur and hydrogen sulfide may be avoided or reduced by the use of lower temperatures at which the rates of hydrocarbon conversion to partially oxygenated compounds are lower.

Likewise, although highly effective results from the standpoint of hydrocarbon conversion are secured with oxygen content in the gas fed to the reactor of from 0.2% up to about 20%, it is preferred that it should not exceed about 2% to about 5% in operation at atmospheric pressures, in order to minimize the production of carbon oxides. At higher pressures the tendency to form oxides of carbon is diminished and the higher proportions of oxygen may be used. It will be apparent that, when economic considerations are such that losses of sulfur dioxide through excessive reduction, or of hydrocarbon through excessive oxidation can be disregarded, proportions of sulfur dioxide and oxygen in the higher range may be used.

The operation may be conducted as a once-through operation. However, it has been found that the best over-all yields of partially oxygenated compounds on the basis of the hydrocarbon consumed can be secured by operating with relatively low yields per pass, generally below about 10% and suitably from 0.1 to 2% at atmospheric pressure. At higher pressures of operation, the higher yields per pass may be used without material reduction in over-all yields.

The following examples are illustrative of operations conducted in accordance with the present invention. In these examples the term "space velocity" has been used to designate the volume of gas (at standard conditions of temperature and pressure, i. e., 760 mm. Hg pressure

and 0° C.) circulated per hour per unit volume of catalyst. The "apparent contact time" is the reciprocal of the hourly "space velocity" converted to a time base of seconds, or $1/\text{space velocity} \times 3600$.

Example 1

In an operation carried out at atmospheric pressure and using activated carbon in which the adsorptive material or contact mass in the reaction chamber was maintained at a temperature of 350° C., the gas fed to the reactor contained about 2% SO₃, 30% SO₂ and 0.8% oxygen, with about 67% of methane and inert gases. The space velocity per hour was 286 with an apparent contact time of about 12.6 seconds. The molar yield of formaldehyde based on hydrocarbon consumed in this operation was in excess of 95%. Considered on a single pass basis, the ratio of volume yield of formaldehyde (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 1.3.

Similar operations were conducted at various temperatures throughout the range with effective conversion of the methane content of the gas to formaldehyde. In these, the proportions of sulfur trioxide in the gas fed to the reactor varied from 1.9 to 2.4%; those of sulfur dioxide from 14 to 50%; those of oxygen from 0.4 to 1% and those of hydrocarbon and inert gases from 47 to 84%. The molar yields of formaldehyde based on hydrocarbon consumed varied from 43% to over 95% and the ratio of volume yield of formaldehyde per hour to unit volume of catalyst varied from .2 to about 1.4. There was evidence of reduction of sulfur oxides to sulfur, greater at the upper range of temperatures above 350° C., say at 375° to 400° C. and higher and at a given temperature, greater with the higher ranges of sulfur dioxide concentration in the feed gas to the reactor, above 20%.

Using activated carbon containing salts of the various metallic promoters hereinbefore named in proportions from 1% to 5%, the overall production of formaldehyde relative to hydrocarbon consumed was not appreciably increased. However, throughout the entire range of temperatures, formation of sulfur by excessive reduction of sulfur oxides was reduced or eliminated and in the lower temperature range of 300° to 320° C. the yield per pass as indicated by the ratio of volume of product per hour to volume of catalyst was somewhat increased, apparently due to reduced formation of carbon oxides.

Example 2

In an operation carried out at atmospheric pressure, using activated silica gel at the temperature of 385° and with a feed gas containing 92% methane and inerts, 1.8% SO₃, 4.3% SO₂ and .63% oxygen, the overall ratio of formaldehyde produced to hydrocarbon consumed on a molar basis was 40%, the volume yield of product (as gas at standard pressure and temperature) per hour per unit volume of catalyst being about .2. In this operation the space velocity was 670 and the apparent contact time was about 5.4 seconds.

Similar operations were conducted using activated silica gel alone as the catalyst at various temperatures through the entire range. In general, the activity at a given temperature with respect to formaldehyde production was less than at corresponding temperatures with the activated carbon. At higher temperatures there was an increased yield of formaldehyde per unit volume of catalyst, but this was apparently at the expense of efficiency since there was also greater formation of carbon oxides and a lower ratio of yield of formaldehyde to hydrocarbon consumed. In this series of experiments, the proportion of hydrocarbon and inert gases in the reactor feed gas ranged from about 89% to about 95%; of sulfur trioxide from about 1% to about 3%; of sulfur dioxide from about 2.4% to about 5.5% and of oxygen from about .2% to 1%.

The addition of the metallic promoters to the silica gel in general effected some reduction in the formation of carbon oxides and increased the overall production of formaldehyde relative to hydrocarbon consumed but did not increase the rate of production of formaldehyde at a given temperature.

Example 3

An operation using activated alumina as the adsorptive material was carried out at atmospheric pressure and a temperature of 380° C. The feed gas to the reactor contained 89% methane and inert gases; about 1.5% SO₃; about 9% SO₂ and about .2% oxygen. The operation was conducted with a space velocity of 789 and an apparent contact time of 4.56 seconds. In this operation the molar ratio of formaldehyde produced to hydrocarbon consumed was in excess of 95%. The volume yield of formaldehyde per hour per unit volume of catalyst was about 0.2. There was no evidence of formation of sulfur by excessive reduction of sulfur oxides. However, there was some evidence of the formation of carbon oxides from the hydrocarbon.

Similar experiments were conducted using activated alumina at various temperatures throughout the entire range hereinbefore set forth. In general, substantially higher temperatures were required than with the activated carbon to secure similar rates of conversion. On the other hand, with the activated alumina, there was no evidence of excessive reduction of sulfur oxides to sulfur or hydrogen sulfide until temperatures of 400° and higher were reached. In this series of experiments the content of hydrocarbon and inert gases in the gas feed to the reaction chamber varied from about 89% to 96%; that of SO₃ from about 1% to about 1.5%; and that of oxygen was in the neighborhood of .2% throughout.

Example 4

In an operation carried out at atmospheric pressure using activated charcoal containing 5% CeSO₄, 5% CoSO₄·7H₂O, and 0.5% AgNO₃ in which the adsorptive material in the reaction chamber was maintained at a temperature of 285° C., the gas fed to the reactor contained about 8% SO₂ and 1% oxygen, with about 69% of ethane and inert gases. The space velocity per hour was 734 with an apparent contact time of 4.9 seconds. The molar yield of aldehyde on hydrocarbon consumed in this operation was in excess of 82%. Considered on a single pass basis, the ratio of volume yield of aldehyde (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 0.71.

Example 5

In an operation at atmospheric pressure, using activated alumina containing 5% CoSO₄·7H₂O and 0.5% AgNO₃ in which the adsorptive material in the reaction chamber was maintained at a temperature of 250° C., the gas fed to the reactor contained about 10% SO₂ and 0.3 to 1.7% oxygen, with about 89% of propane and inert gases. The space velocity per hour was 720 with a contact time of 5.0 seconds. The molar yield of carbonyl compounds, principally propionaldehyde, on hydrocarbon consumed in this operation was in excess of 86%. Considered on a single pass basis, the ratio of volume yield of aldehyde (as a gas at standard temperature and pressure) per hour per unit volume of catalyst was 0.803.

Example 6

In an atmospheric pressure operation using activated alumina containing 10% (NH₄)₂MoO₄ and 14.3% CoSO₄·7H₂O in which the adsorptive material in the reaction chamber was maintained at a temperature of 265° C., the gas fed to the reactor contained about 15% SO₂ and 2% oxygen, with about 76% of iso-butane and inert gases. The space velocity was 692 with an apparent contact time of 5.2 seconds. The molar yield of aldehydic products, mainly isobutyraldehyde, on hydrocarbon con-

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sumed was in excess of 61%. Considered on a single pass basis, the ratio of volume yield of aldehydic products (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 0.17.

Example 7

In a super-atmospheric pressure operation using silica gel containing 10% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.06% AgNO_3 as the contact mass, in which the reaction chamber containing the contact mass was maintained at a temperature of 317°C ., and a pressure of 200 pounds per square inch gauge, the gas fed to the reactor contained about 13% SO_2 and 0.4 to 1.0% oxygen, with about 86% of methane and inert gases. The space velocity per hour was 26,550 with an apparent contact time of 0.14 second. (It must be noted that the space velocity and apparent contact time are by definition based upon the volume of the gas at standard temperatures and pressures, and not upon its volume at the pressure and temperature obtaining in the reaction chamber). The molar yield of formaldehyde on hydrocarbon consumed in the operation was in excess of 90%. Considered on a single pass basis, the ratio of volume yield of formaldehyde (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 5.8.

Example 8

In an operation using activated alumina containing 10% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.06% AgNO_3 as the contact mass, in which the reaction chamber containing the contact mass was maintained at a temperature of 325°C ., and a pressure of 100 pounds per square inch gauge, the gas fed to the reactor contained about 11% SO_2 and 9% oxygen, with about 79% of ethane and inert gases. The space velocity per hour was 6270 with an apparent contact time of 0.57 second. The molar yield of aldehydic products based on hydrocarbon consumed in this operation was in excess of 90%. The principal product was acetaldehyde with lesser amounts of formaldehyde being formed. Considered on a single pass basis, the ratio of volume yield of aldehydic products (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 18.6.

Example 9

In an operation using activated alumina containing 10% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.06% AgNO_3 as the contact mass, in which the reaction chamber containing the contact mass was maintained at a temperature of 285°C ., and 100 pounds per square inch gauge, the gas fed to the reactor contained about 9% SO_2 and 5% oxygen, with about 79% of propane and inert gases. The space velocity per hour was 8950 with an apparent contact time of 0.4 second. The molar yield of aldehydic or carbonyl compounds on hydrocarbon consumed in this operation was in excess of 90%. The principal aldehydic or carbonyl compounds (by which term I mean aldehydes and ketones) were propionaldehyde, acetaldehyde, and acetone with lesser amounts of formaldehyde being formed. Considered on a single pass basis, the ratio of volume yield of aldehydic products (as gas at standard temperature and pressure) per hour per unit volume of catalyst was 2.35.

Operations under varying conditions have been hereinbefore described. To determine optimum conditions for the production of the desired partially oxygenated compounds, it has been found most convenient, suitably in pilot equipment, to gradually increase the temperature of reaction within the ranges above set forth until either sulfur formation, resulting from reduction of sulfur dioxide, or carbon oxide formation, resulting from excessive oxidation of hydrocarbons, becomes apparent. The reaction temperature is then reduced until the formation of sulfur or carbon oxides just disappears. The temperature may then be held constant until some change is required as a result of changes in composition of gas treated,

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or in the proportions of the reacting materials within the ranges above set forth.

What is claimed is:

1. The method of effecting limited oxidation of hydrocarbons with formation of oxygenated hydrocarbons which comprises reacting in vapor phase a hydrocarbon with oxygen in contact with a solid adsorptive material and in the presence of a volume of sulfur dioxide at least equal to the volume of said oxygen, while maintaining the reaction temperature in the range of about 175° to 450°C .

2. The method of claim 1 wherein the solid adsorptive material comprises as catalyst promoter a compound of a metal of the class consisting of the transition elements and the elements of the Ib group of the periodic table.

3. The method of producing an oxygenated hydrocarbon by the oxidation of a hydrocarbon which comprises passing in contact with a solid adsorptive material in a reaction zone maintained at a temperature in the range of about 175° to 450°C . a gasiform reactant mixture comprising said hydrocarbon, oxygen and sulfur dioxide, the concentration of oxygen in said mixture being within the range of about 0.2% to 20% by volume and the concentration of sulfur dioxide being at least as great as that of oxygen, and withdrawing from said reaction zone gasiform reaction effluent containing oxygenated hydrocarbon thus produced.

4. The method of claim 3 wherein the solid adsorptive material comprises as catalyst promoter a compound of a metal of the class consisting of the transition elements and the elements of the Ib group of the periodic table.

5. The method of producing an aldehydic compound by the oxidation of a saturated aliphatic hydrocarbon of not more than four carbon atoms per molecule which comprises passing in contact with a solid adsorptive material in a reaction zone maintained at a temperature in the range of about 175° to 450°C . a gasiform reactant mixture comprising said hydrocarbon, oxygen and sulfur dioxide, the concentration of oxygen in said mixture being within the range of about 0.2% to 20% by volume and the concentration of sulfur dioxide being greater than that of oxygen, and withdrawing from said reaction zone gasiform reaction effluent containing aldehydic compound thus produced.

6. The method of claim 5 wherein the solid adsorptive material is silica gel comprising as catalyst promoter a compound of a metal of the class consisting of the transition elements and the elements of the Ib group of the periodic table.

7. The method of claim 5 wherein the solid adsorptive material is activated charcoal comprising as catalyst promoter a compound of a metal of the class consisting of the transition elements and the elements of the Ib group of the periodic table.

8. The method of claim 5 wherein the solid adsorptive material is activated alumina comprising as catalyst promoter a cobalt compound supplemented by a silver compound.

9. The method of producing formaldehyde by the oxidation of methane which comprises passing in contact with a solid adsorptive material in a reaction zone maintained at a temperature in the range of about 325° to 425°C . a gasiform reactant mixture comprising said methane, oxygen and sulfur dioxide, the concentration of oxygen in said mixture being within the range of about 0.2% to 20% by volume and the concentration of sulfur dioxide being at least as great as that of oxygen, and withdrawing from said reaction zone gasiform reaction effluent containing formaldehyde thus produced.

10. The method of claim 9 wherein the solid adsorptive material comprises as catalyst promoter a compound of a metal of the class consisting of the transition elements and the elements of the Ib group of the periodic table.

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11. The method of claim 9 wherein the solid adsorptive material is activated alumina comprising as catalyst promoter a cobalt compound.

12. In the method of producing an oxygenated hydrocarbon by the reaction of a hydrocarbon with oxygen, the improvement of minimizing undesired side reactions which comprises conducting in contact with a solid adsorptive material the desired reaction of said hydrocarbon with oxygen in a gasiform mixture comprising said hydrocarbon, oxygen and sulfur dioxide, the volume of sulfur dioxide in said gasiform mixture being at least equal to the volume of oxygen in said gasiform mixture.

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