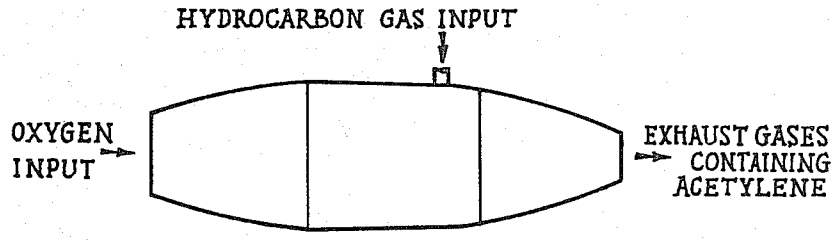
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METHOD FOR CONTROLLING REACTIONS IN HOT GASEOUS REACTION MIXTURES

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METHOD FOR CONTROLLING REACTIONS IN HOT GASEOUS REACTION MIXTURES

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This invention is for improvements in or relating to a method for controlling reactions in hot gaseous reaction mixtures and has for an object to provide a method whereby reactions taking place in hot gaseous mixtures may be controlled so as to stabilise a reaction or certain reaction products existing in said hot gaseous mixture.

An example of a hot gaseous reaction mixture for control by the method of the present invention is the mixture of gases produced by the partial oxidation, pyrolysis or cracking of saturated hydrocarbons such as ethane and methane in the presence of limited amounts of oxygen or atmospheric oxygen for the production of unsaturated hydrocarbons such as ethylene and acetylene, and also relates to the partial oxidation and/or pyrolysis or cracking of organic substances and has for a further object to provide an improved process for the conversion of organic substances such, for example, as the production of acetylene, ethylene and other unsaturated hydrocarbons from saturated gaseous or liquid hydrocarbons such as methane and ethane.

It is well known that by subjecting ethane and methane to high temperatures, such as 1300° C. to 1500° C. a partial cracking takes place with the production of carbon, acetylene and/or other hydrocarbons. However, acetylene is itself unstable at such high temperatures and acetylene produced at high temperature is rapidly converted, for example to carbon black, unless the temperature of the gaseous mixture containing the acetylene is very rapidly reduced.

This problem has been recognised in the past and processes for the production of acetylene from saturated hydrocarbons have involved, what is termed, "shock cooling," i. e. the temperature of the hot gases is abruptly reduced. A variety of methods have been adopted for securing the shock cooling, amongst which may be mentioned the passing of the gases under the body of a cooling liquid or the introduction of cooling sprays into the stream of hot gas.

According to the present invention, there is provided a method for controlling reactions in hot gaseous reaction mixtures which comprises introducing a stream of hot reaction gases into a turbine and controlling the reactions taking place in the gaseous phase by very rapidly reducing the temperature and/or pressure of said hot gases in said turbine to such a value or values as will stabilise the reaction at a predetermined stage. Preferably, the control of the reactions is effected substantially entirely by controlling the adiabatic expansion of the gases within the turbine, for example, by abstracting useful work as a result of the expansion of the gases within the turbine.

A feature of the invention consists in that the control of the reactions may be further effected by cooling those turbine parts in contact with the stream of hot gases at a selected position or positions in the turbine.

This leads to the second object of the invention namely the process for converting organic substances, by partial

oxidation, pyrolysis or cracking, to valuable decomposition products.

Known processes of producing acetylene from hydrocarbons such as methane, ethane and ethylene are based on the dehydrogenation of hydrocarbons by:

(1) Arc processes,
(2) Cracking processes, and
(3) Partial combustion processes.

In all three processes the fundamental consideration is the heating of the hydrocarbon to a sufficiently high temperature (methane, for example, requires 1500° C., ethane 1300° C.) coupled with the fact that the time at which this high temperature should be maintained must be as short as possible to avoid the decomposition or further reaction of the acetylene thus produced to carbon black and hydrogen or other intermediate products. The partial pressure of the acetylene should also be kept as low as possible in relation to the initial pressure whilst the gas, after its formation, should be cooled as rapidly as possible. Water which may be formed during the reaction introduces further side reactions at the high temperatures employed and further tends to decrease the amount of unsaturated hydrocarbon produced.

All these processes suffer from the disadvantage that power and/or energy consumption is extremely high. The arc process, for example, requires on an average about 4½ kilowatt hours per lb. of acetylene produced, a power consumption of the same order as that required for acetylene production from carbide.

Cracking processes require considerable heat energy which is generally obtained by the combustion of the by-product gases, whilst the high temperatures required for acetylene production introduce serious refractory problems, particularly when methane is used.

The third process of partial combustion requires the use of oxygen in order to obtain the necessary high flame temperature and needs very accurate control. Approximately 5 tons of oxygen are usually required by this process for the production of 1 ton of acetylene which, of course, adds considerably to the cost of operation. The by-product gases from the combustion process. however, consist largely of carbon monoxide and hydrogen which can be produced in such proportions as to allow of their use for the manufacture of the methyl alcohol.

Accordingly, therefore, the present invention also provides a process for the partial oxidation and/or pyrolysis or cracking of organic substances which comprises continuously feeding an organic substance in gaseous or finely divided form together with molecular oxygen (which may be air or oxygen or air enriched with oxygen) into the combustion chamber of an internal combustion gas turbine system igniting the mixture in said combustion chamber to create the necessary temperature to effect the desired conversion of said organic substance and passing the combusted, partially combusted or combusting mixture through the turbine wherein the said mixture is cooled to a temperature such as to prevent or minimise further or undesired conversion of the products, the rates of gas flow and/or the pressures in the combustion chamber and in the ducts leading to the turbine and the ratio of the feed of the organic substance to the feed of molecular oxygen being controlled so as to produce the temperature and pressure conditions necessary to the desired conversion of the organic substance and the rates of gas flow, temperatures and/or pressures in the stages of the turbine being so controlled as to produce the desired degree of cooling of the hot gaseous reaction mixture within the turbine itself. An inert gas may, if desired, be introduced into the system at any desired point; a still further feature of the invention con-

sists in that the control of the reaction is effected by an inert gas being introduced as a diluent into the gas stream at a selected position or positions in the turbine. For example, nitrogen or carbon dioxide may be introduced into the gas stream; the introduction of the inert gas may have the dual function of, on the one hand, reducing the temperature by heat exchange as between the hot gas stream and the inert gas and, on the other hand, of reducing the partial pressure of the reacting gases in the hot gaseous mixture, the inert gas may be mixed with the feed of oxygen or of organic substances prior to mixing and combustion or it may be introduced into the system at any point during or after combustion. It will be understood that the temperature and pressure conditions for the conversion of the organic substance are preferably maintained at their controlled values for the optimum time to secure the maximum yields.

One advantage of the process of this invention is that useful work may be obtained from the turbine whereas, in prior processes, the energy available in the hot reaction gases has been generally dissipated to waste.

It will be understood that in the operation of internal combustion gas turbines, the temperature conditions in the combustion chamber are susceptible of control in a variety of ways as a result of which the temperature of the combusting gases can be accurately controlled.

It will further be understood that, by appropriate design of the stages of the gas turbine, the temperature of the gases flowing through the turbine can be readily and accurately controlled so that in the process of the present invention, it is easily possible to produce the high temperatures necessary for the partial oxidation, pyrolysis or cracking of the organic substances in the combustion chamber of the turbine and to effect the necessary rapid temperature drop in the various stages of the turbine so as to bring the temperature of the reacting gases below the temperature at which further or undesired conversion of the reaction products takes place, this very rapid temperature drop occurring substantially entirely within the turbine itself. The design and operation of the gas turbine can, therefore, be so arranged that the gases issuing from the last stage of the turbine are under conditions of temperature (and, if desired, pressure) which will render the composition of the mixture substantially stable and the issuing gases may, if desired, be further cooled for convenience of handling by means of a quenching spray of water or a selective solvent, e. g. acetone, in the case of acetylene.

A further feature of the invention consists in that modifying agents (i. e. substances which influence the rate and extent and, in certain cases, nature of the chemical reactions taking place) are introduced into the gases flowing through the turbine system to control and/or modify the reactions in the hot gaseous mixture; these modifying agents may be introduced into the system at any desired point. Ethylene dibromide, which can arrest active combustion of a methane-air mixture, is an example of a modifying agent.

A further feature of the invention consists in that further quantities of organic substance and/or molecular oxygen are fed into the turbine system at a point along the direction of gas flow subsequent to the initial feed point. By operating in this manner, the gas flowing through the turbine system may be suddenly enriched at a point where the combustion conditions are stable and where the temperature and pressure conditions are at about the optimum values for the production of optimum quantities of the desired conversion products, e. g. acetylene or other unsaturated hydrocarbons.

A still further feature of the invention consists in that a combustion promoter is introduced into the system at a selected point or points. A combustion promoter may be defined as being a substance which, either by itself or by its decomposition products, facilitates ignition or reduces the time lag of ignition (thus shortening the length of the reaction zone in the combustion chamber) or promotes combustion of mixtures which normally are too rich to burn stably (thus stabilising combustion when enrichment takes place as above mentioned and extending the range of mixture strengths which can support combustion). Ethyl nitrate and ethyl nitrite are examples of combustion promoters in current use in compression ignition engines. The combustion promoters can be introduced at various points in the system, for example, they may be introduced in the compressors feeding the oxygen or organic substance into the combustion chamber, into the ducts leading to the combustion chamber from the compressors or into the combustion chamber itself; they may also, or alternatively, be introduced into the gas stream at any point between the combustion chamber and the exhaust outlet from the turbine, for example, they may be introduced together with the additional amounts of oxygen or organic substance mentioned above or together with the feed of inert gas, i. e. utilising these feeds as carriers for the combustion promoters. Thus, it will be appreciated that the combustion promoters may be introduced into the system in concentrated form or in dilute form with a liquid or gaseous carrier.

In a modification, it is a feature of the invention that the initial charge for combustion consists of an easily combustible fuel, other than said organic substance, and molecular oxygen, said organic substance and, if desired, additional molecular oxygen being fed into the combusted or partially combusted initial charge. By operating in this way, the combustion in the early stages of the turbine is maintained by the use of an "extraneous" fuel, i. e. a fuel not participating in the desired reactions and the organic substance to be converted is then fed into the hot gaseous mixture flowing through the turbine.

In order to assist in the reduction of temperature of the reacting gases for the purpose of preventing undesired or further conversion, it is a still further feature of the invention that a coolant fluid is introduced into the gases flowing through any stage in the turbine; the coolant fluid may be a volatile liquid or any other cooling fluid. The use of the volatile liquid is advantageous since the volatile liquid will absorb considerable quantities of heat, as a result of taking up latent heat of evaporation. An inert gas may also, or alternatively, be introduced into the gas stream flowing through the turbine, preferably after combustion has taken place. The inert gas may be used to fulfil either or both of the functions of the coolant fluid or as a diluent for the purpose of reducing the partial pressures of the reacting gases.

Yet a further feature of the invention consists in the use of a combustion process based on the principle of a diffusion flame, in which a stream of hydrocarbon and a stream of molecular oxygen, with or without a diluent, flow parallel to each other and in the same direction at substantially equal velocities, the reactants meeting only at the interface between the two gas streams where combustion occurs and is supported by molecular diffusion only, in this manner creating a narrow zone of intense heat, part of which heat is transferred, mainly by conduction and convection to the hydrocarbon, raising it to the necessary temperature for dehydrogenation. Combustion could be stopped at any desired subsequent stage with a porous metallic or ceramic flame trap, having its internal surfaces coated, if necessary, with a combustion arrester, such as potassium chloride. It will be understood that the above-mentioned features of the invention relating to the use of modifying agents, combustion promoters and to the introduction of further quantities of organic substances and hydrocarbons can also be applied to this particular combustion process.

It will be appreciated that, due to the design of the turbine, cooling of the gas stream flowing through the turbine will take place substantially entirely owing to the controlled, substantially adiabatic, expansion of the gases, but it may be an advantage to assist this cooling effect

by applying cooling to the internal surfaces of the turbine system. Such cooling may be effected by circulation of cooling fluid through jackets or hollow passages within the component parts of the turbine, but a preferred method of cooling the turbine parts is by means of "sweat cooling" in the manner indicated in prior British specification No. 619,634.

It is, therefore, an important feature of the invention that the cooling of the turbine is effected, at least in part, by "sweat cooling" e. g. by the introduction into the interior of the turbine parts of a coolant fluid, the turbine parts being formed of porous material or with a porous material through which the coolant fluid is passed in a direction towards the gas stream flowing over the turbine parts; it will be appreciated that in effecting the sweat cooling of the turbine, a fluid is caused to pass through porous parts of the turbine blade and/or nozzle ring and this fluid, which may be either liquid or gas, fulfils the dual purpose of cooling the parts of the turbine whilst at the same time forming a protective layer of gas over the surfaces of the turbine parts, thus minimising deposition of solid particles, e. g. carbon, on the turbine parts.

This method of sweat cooling has a number of very great advantages already referred to in prior British specification No. 619,634 above-mentioned and these advantages may be summarised by stating that the sweat cooling of the internal surfaces of the turbine makes it possible to maintain mechanical strength of the parts, reduce surface deposition of materials, particularly of free carbon, upon the turbine parts and, further, by providing a gaseous or vaporous layer over the surfaces of the turbine parts, prevent diffusion of molecules in the hot gas stream towards the metallic surfaces of the turbine and may, in certain circumstances, thereby prevent undesirable surface reactions from taking place or may minimise such surface reactions.

The fluid utilised for sweat cooling may, of course, be the further quantities of organic substance to be converted and earlier referred to as being introduced into the turbine at a later stage.

In some circumstances, it may be desirable to carry out the reactions in the turbine at relatively low pressures, in which case it may be desirable to connect an exhauster to the exhaust from the last stage of the turbine so as to effect a general reduction in pressure throughout the stages of the turbine. The exhauster drive may be coupled to the turbine thereby making use of the energy produced in the turbine by the combustion of the organic substance.

An alternative method of attaining the low pressures would be to provide specially designed ducts communicating between the combustion chamber and the entry to the turbine so as to produce conditions of supersonic flow in the ducts. Supersonic flow involves a considerable drop in the gas pressure from the upstream side of the ducting in which the supersonic flow rates are attained to the section in which supersonic flow is occurring. The problem of designing ducting so as to achieve supersonic flow has been the subject of considerable study and the design of such ducting is the subject of contributions to the art by R. Harrap (Proceedings of the 7th International Congress of Applied Mechanics, London, September 1948) by G. J. Kestin and A. K. Oppenheim (Proceedings of the Institute of Mechanical Engineering 1948) and by J. H. Keenan and E. D. Neumann (Journal of Applied Mechanics, June 1946) to which

reference can be made for assistance in the design of such ducting.

It will be appreciated that variations in the proportions of organic substance and molecular oxygen fed into the combustion chamber of the turbine system and variation of any subsequent amounts introduced in the various stages of the turbine can be used to effect a high degree of control over the partial oxidation, pyrolysis and cracking reactions taking place in the gas stream flowing through the turbine.

The accompanying diagrammatic drawing illustrates schematically how the process may be carried into effect in a gas turbine engine.

We claim:

1. In a process for the pyrolysis of saturated hydrocarbons to unsaturated hydrocarbons by continuously feeding a gaseous charge comprising the saturated hydrocarbon and molecular oxygen into the combustion chamber of an internal combustion gas turbine, the amount of oxygen in said charge being sufficient to effect combustion of a part only of the hydrocarbon to raise the temperature thereof to a sufficiently high level to initiate the conversion of the remainder of said hydrocarbon into gaseous unsaturated hydrocarbons, that improvement comprising directly subjecting the gaseous reaction mixture resulting from said partial combustion and conversion to adiabatic expansion in an expansion stage of said internal combustion gas turbine, said adiabatic expansion causing rapid cooling preventing further undesired conversion of the gaseous unsaturated hydrocarbons produced.

2. A process as claimed in claim 1 wherein the combustion is effected on the principle of a diffusion flame, in which a stream of hydrocarbon and a stream of molecular oxygen flow parallel to each other and in the same direction at substantially equal velocities.

3. A process as claimed in claim 1 wherein the combustion chamber is connected to the expansion stage of the turbine through ducts so designed as to produce conditions of supersonic flow therein.

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