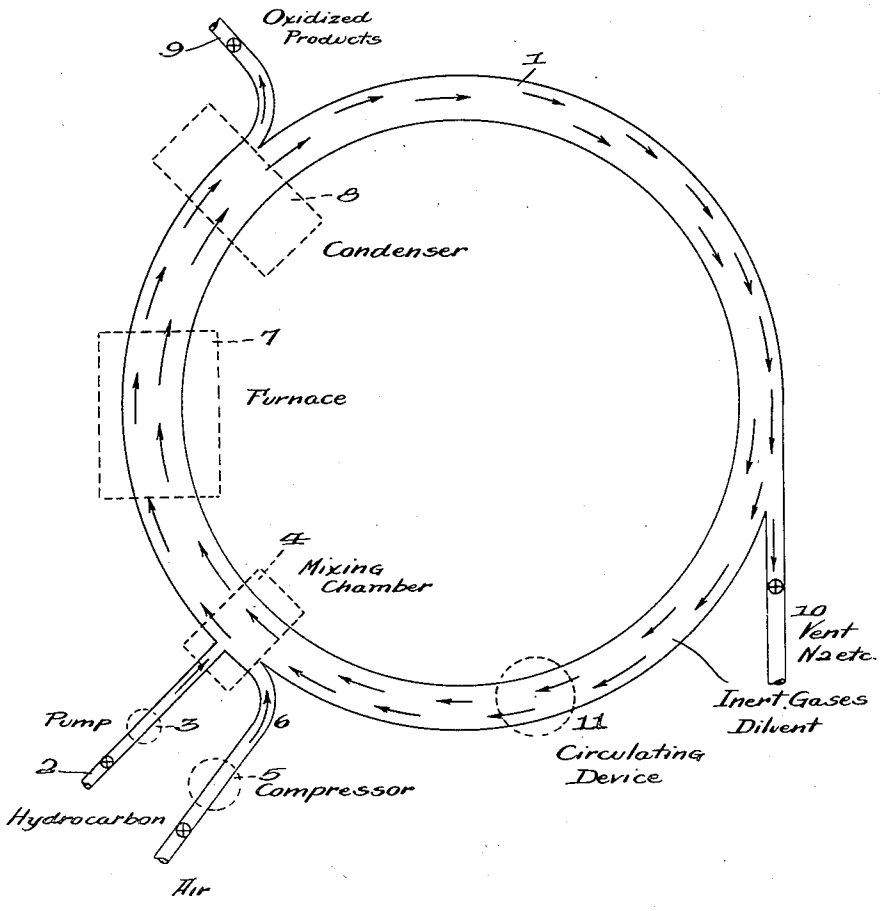
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PROCESS FOR PARTIAL OXIDATION OF GASEOUS HYDROCARBONS

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PROCESS FOR PARTIAL OXIDATION OF GASEOUS HYDROCARBONS

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Our invention consists in new and useful improvements in a process for the manufacture of a mixture containing methanol, acetone, acetaldehyde and other products which result from the partial oxidation of hydrocarbons, using as a starting material a substance consisting mainly of a low boiling hydrocarbon or mixtures of various low boiling hydrocarbons.

We are familiar with a considerable amount of research which has been carried out in the utilization of the by-products and waste materials resulting from the petroleum industry, such for example, as methane, ethane, propane and butane. Some of this research has resulted in processes which rely upon the use of catalysts to effect the desired reactions, and others depend upon first cracking the stable saturated hydrocarbons to the unstable unsaturated hydrocarbons after which combination is effected with air or oxygen.

To the best of our knowledge however, none of these processes have been successful in a commercial way because of the low yields of product, expensive equipment, poisoning of the catalyst, excessive carbon and tar deposits in the apparatus, formation of excessive amounts of carbon dioxide and water at the expense of the hydrocarbon, and for numerous other reasons.

Although some of these processes appeared to be quite promising on a laboratory scale, they proved inoperative on a larger commercial basis.

It is well known that any process which has as one of its steps a "cracking operation" is almost sure to give excessive tar and carbon deposits, and when subsequently used in conjunction with a catalyst, the carbon deposits will quickly foul and poison the catalyst.

Another objectionable feature in processes heretofore known for the manufacture of products of partial oxidation by combining hydrocarbon gases and oxygen, has been the danger of operating within the explosive limits. It is a well known fact that when oxygen and a combustible gas are mixed in certain proportions and then a spark, flame or source of temperature above the kindling point is applied to the mixture, said mixture will or will not explode, depending upon the relative proportions of the two gases.

If, for example, a mixture of 5.3% of methane and 94.7% of air which contains oxygen should be sparked it will not explode. However, if the methane be increased above this proportion, an explosion will take place. Likewise a mixture of 14.0% of methane and 86.0% of air will not explode, but any increase in the air will cause an explosion. A mixture of the first mentioned proportions is known as the lower explosion limit and a mixture of the second mentioned proportions, the upper explosion limit. Any mixtures between these two proportions or between the upper and lower explosion limits will cause a violent explosion if sparked or heated to the kindling point.

It is the object of our invention to overcome these difficulties and at the same time to use an oxidizing medium-hydrocarbon ratio which will produce high yields of product at low cost, and to this end we have devised a process which does not employ a catalyst nor include a pre-cracking of the gases, and in which only relatively small amounts of carbon dioxide and water are formed.

While in our process we operate within the explosion limits, so far as the mixture of hydrocarbon, air or oxygen is concerned, we avoid the possibility of explosion by diluting the mixture with an inert gas prior to the point where heat is applied to the mixture to effect a reaction. In other words, our process consists essentially in cycling a quantity of inert gases in a closed ring and injecting into this cycling diluent the desired amounts of air or other oxidizing medium and hydrocarbon gas, after which the mixture is conducted through a reaction zone and thence to a condenser where the oxidized products are removed by condensation, the inert gases, having been denuded of practically all of the hydrocarbon content, continuing to cycle through the ring. At a predetermined point in the ring, we permit a certain quantity of nitrogen and other inert gases to be vented from the system in order to maintain said system in the proper equilibrium.

With the above and other objects in view which will appear as the description proceeds, our invention consists in the novel features herein set forth, illustrated in the accompanying drawing and more particularly pointed out in the appended claims.

Referring to the drawing which for convenience diagrammatically illustrates our invention, 1 represents a pipe line which is connected essentially in a circle or ring. 2 represents a pipe line which is connected to a source of hydrocarbon gas and by means of a pump 3 injects the hydrocarbon gas into the mixing chamber 4. 5 represents a compressor which injects air through the pipe 6 into the mixing chamber 4. Here the two gases are thoroughly mixed with the recycled inert gas to be described later and since the

quantity of this recycling gas is under our control, any ratio of hydrocarbon and air may be used and the explosion limit at no time be exceeded.

Although we prefer to introduce the hydrocarbon and air separately into the mixing chamber 4 because of the fact that in so doing the mixture is never permitted to reach the lower explosion limit and is therefore always safe, it is obvious that if desired, we may first mix the air and hydrocarbon and then inject said mixture into the mixing chamber, since the dilution would be effected by the inert gases before the hydrocarbon and air reached the furnace or reaction zone.

We inject the hydrocarbon gas into the mixing chamber 4 by means of the pump 3 and we inject the air into the mixing chamber 4 by means of the compressor 5, so regulating the pump and the compressor that the ratio of air to hydrocarbon will be that which we desire. Likewise we so operate the compressor and the pump that the pressure in the mixing chamber 4 will be above atmospheric, preferably about 350 pounds per square inch. In the mixing chamber the hydrocarbon and the air are met by the stream of inert gas which is being continuously cycled through it by means of the circulating device 11. In the mixing chamber the inert gas, the oxidizing material and the hydrocarbon are all thoroughly commingled.

At a point posterior to the mixing chamber 4 we provide a furnace or other suitable heating means 7 for heating a portion of the closed ring 1. 8 represents a condenser or the like which is connected at a suitable point in the ring 1, said condenser having a discharge pipe 9 through which the condensed products of oxidation are withdrawn from the system. At a point posterior to the condenser 8 we provide a vent 10 which is equipped with a suitable relief valve for permitting the escape of a portion of the inert gases hereinafter referred to. 11 represents a circulating device which may be in the form of a compressor or fan which is located posterior to the vent 10.

In the operation of our process we use a quantity of air or other oxidizing medium with a quantity of the desired hydrocarbon gas, preferably using about one part of hydrocarbon to ten or eleven parts of air, assuming that the latter is the oxidizing medium employed. In other words, comparing the amount of hydrocarbon to that of oxygen, air consisting of approximately 0.2 oxygen, we use one part of hydrocarbon to two parts of oxygen, or a ratio of 33.33 parts of hydrocarbon to 66.66 parts of oxygen.

From the mixing chamber 4 the mixture of hydrocarbon, oxidizing medium and inert diluent passes directly to the heating zone 7. The temperature of the reaction zone is maintained below 900° F., preferably about 800° F., at which temperature the reaction between the oxygen and hydrocarbon takes place and the products are oxidized directly or through several intermediate steps to the finished products without undergoing to any appreciable extent, any pyrolysis or cracking. As long as our mixture includes the proper amount of inert diluent to avoid coming within the explosion limits, and the temperature is maintained below 900° F., we have discovered that we can operate the process indefinitely without the deposition of carbon or tar within the apparatus and at the same time with large yields of the desired products of oxidation.

From the heating zone the reacted mixture passes to the condenser 8 where the oxidized products are condensed and drawn off from the system at 9, said products consisting of a mixture containing methanol, acetone, acetaldehyde, and other products of commercial value. It will be noted that in the condenser, practically all of the hydrocarbon content of the mixture is extracted and that the uncondensed gases which leave the condenser and continue on in the ring 1 are essentially inert gases such as nitrogen and the like.

In order to maintain the system in equilibrium, the vent 10 containing a relief valve is provided intermediate the condenser 8 and the circulating device 11, whereby sufficient nitrogen and other gases are vented to atmosphere, to compensate for the volume of fresh nitrogen in the air fed into the system through compressor 5 and other non-condensible gases formed in the reaction. As before stated, the injection into the cycling system of the fresh hydrocarbon gas and air maintains the pressure of the gas in the system and to prevent an increase in pressure, the relief valve at 10 is set to permit the escape of sufficient inert gas so that the pressure in the system will be maintained at the value to which the relief valve is set.

It will thus be seen that the inert gases continue to cycle through the ring 1 with a continuous injection of fresh hydrocarbon gas and air and the continuous withdrawal of oxidized product and a continuous bleeding off of a definite amount of inert gas, and consequently the process can be continued indefinitely without shutting down.

In practice we have found that we secure better results and less undesirable products if the ratio of air to hydrocarbon is such that there will always be a slight excess of hydrocarbon over the amount actually necessary to combine with the oxygen in the air or other oxidizing medium being used. In operation therefore, we manipulate in such a manner that the vent gases or circulating gases never show oxygen on analysis and usually give a test for only small amounts of hydrocarbons.

The following is an illustration of our process showing the quantities at different steps, although it will be understood that they may be varied without departing from the spirit of our invention.

Using as our raw materials commercial butane and air,

Quantity of butane entering mixing chamber	999.7 cu. ft.
Quantity of air entering mixing chamber	10,200.0 cu. ft.
Ratio of butane to air	1 to 10.2
Circulating gases	142,367.0 cu. ft.
Ratio of butane to circulating gases	1 to 142
Circulation rate	45.6 cu. ft. per minute
Vent gas	9,563.8 cu. ft.
Temperature (max. in reaction zone)	835° F.
Exit temperature of treated gases	750° F.
System pressure (maximum)	350 lbs. gage.
Condensed finished products	18.9 gal. or 156.7 lbs.

Composition of materials charged

		Percent
Air:	Nitrogen	79.2
	Oxygen	20.8

Butane and air entering mixing chamber

	Percent
Butane	8.93
Nitrogen	72.13
Oxygen	18.94

Butane, air and circulating gases after mixing in chamber

	Percent
Butane	0.65
CO_2	4.17
O_2	1.39
CO	5.93
Illuminants	0.28
*Residual	87.58

*Largely nitrogen, but containing non-condensed finished product, excess hydrocarbon, etc.

**Condensed product*

	Percent
Acids (as acetic)	2.05
Esters (as methyl acetate)	7.95
Alcohols (as methyl)	3.57
Formaldehyde	23.90
Higher aldehydes (as acetaldehyde)	28.80
Ketones (as acetone)	16.80
Water and undetermined	16.93

*This analysis is only approximate as some of the constituents were undetermined and some calculated as pure when in reality they were mixtures.

Vent and circulating gases

	Percent
CO_2	4.5
O_2	0.0
CO	6.4
Illuminants	0.3
*Residual gas	88.8

*Largely nitrogen, but containing non-condensed finished product, excess hydrocarbon, etc.

It will be noted that on the run tabulated above, only trivial "cracking" or pyrolysis occurred and the mixtures of gases in the heating zone were through the medium of the cycling diluent, maintained below the explosion limits.

It is to be understood that while we may use in our process a pressure of from 100 to 350 pounds, this pressure is used not because it has any desirable effect on the reaction taking place in the heating zone, but rather because by carrying this pressure we secure more complete condensation of the reaction products, this because the partial pressure of the condensed liquids is practically the same at higher pressure as at the lower pressures, and consequently the less total uncondensed reaction products escaping from the vent. Also by working at these pressures, the total cost of apparatus is lowered.

One important feature of our process is that while we use large quantities of circulating inert diluent gases, as for example, 142,000 cubic feet per 1000 cubic feet of butane, it is not necessary to expend any considerable amount of energy to compress this circulating gas. Once having compressed it in the system, it is circulated with a small expenditure of energy and it is only necessary to compress the fresh air, which in the example given is 10,200 cubic feet.

In our process, a feature is that the cycling gases are cooled in passing through the condenser to a temperature almost equal to the cooling water. On coming back and mixing continuously with the input air and hydrocarbon and afterwards passing onto the heating zone, because of the high specific heat of these gases, the temperature rise in the heating zone is never abrupt. The reaction takes place therefore smoothly and gradually and this is an additional reason for the high yield of desirable products we obtain and there is also less likelihood of "cracking".

Products resulting from our operation consist of oxygenated hydrocarbon products, the list that can be made includes formaldehyde, acetaldehyde and higher aldehydes, acetone and other ketones, methyl, ethyl and butyl alcohol, and formic, acetic and higher fatty acids. Since these products react with each other, it is obvious that various amounts of secondary reaction products will form depending on the length of time the condensate is allowed to stand. As an example, esters of the various acids will usually be found in the condensate. It is possible to vary the quantities of these various constituents, thus for example, a high oxygen percent and a low cycling rate tend to increase the amount of fatty acids. A low oxygen percent and a high cycling rate tends to increase the alcohols. Intermediate values increase the aldehydes. Higher temperatures also increase the amounts of acids. By varying the conditions within our control, we have been able to make a reaction product containing practically no alcohols.

It is possible to so operate that the percentage of alcohol in the condensate is below 8% and the acids below 2% thus producing a product predominating in aldehydes with a small percentage of ketones. Just what products are desired will be determined by market conditions prevailing at any time.

This process can be operated and products obtained with pressure ranges from atmospheric up to any suitable value. For reasons given above however, we prefer to operate at a pressure of from 100 to 350 pounds.

Generally speaking, the reaction rate is very slow below 600° F., and excess amounts of undesirable products are produced above 900° F. We prefer to operate within these temperatures and have found a temperature of approximately 800° F. to be very satisfactory, especially if aldehydes are the desired product.

The proportion of mixtures entering the system can of course be varied greatly, but there is a theoretical proportion at which all of the hydrocarbon and all the oxygen combine. Under a given set of conditions, this theoretical proportion is known to have been reached, when the analysis of the vent gases shows neither the presence of free oxygen nor of hydrocarbon gases. We prefer to operate with the vent gases showing a small percent of hydrocarbon and no oxygen. Such conditions are generally reached when the ratio of the incoming reaction gases are one volume of butane to approximately eleven volumes of air. For hydrocarbons other than butane, other ratios will be used. It should be pointed out however, that this mixture never goes into the reaction zone, but is diluted below the explosion limits before entering the reaction or heating zone by the cycling inert gases.

Our reason for preferring butane and propane are that those materials occur in larger amounts as a waste or by-product in the manufacture of petroleum products and being normally gaseous must be transported in liquefied form usually in sturdy containers at great cost and hazard, or

as is frequently the case, are allowed to waste into the air. While these low boiling materials are preferred in our process, it is obvious that we do not limit ourselves to them, as our improved method may be successfully applied to a large number of hydrocarbons made available by the petroleum industry.

By low boiling hydrocarbons is meant those hydrocarbons which evaporate rapidly on exposure to atmospheric pressure and a temperature of 60° F.

Under any given sets of pressure and temperature, the quantity of cycling gas in the system is always the same, but by increasing the rate of the cycling of gas through the system we decrease the concentration of the oxygen and hydrocarbon in proportion. Also, because of the high specific heat of the cycling gases, we absorb much more heat in the heating or reacting zone. For this reason, the rate of cycling is of great importance. We have found that if 142,000 cubic feet of inert gas be cycled for each 1000 cubic feet of butane introduced into the system, we get highly satisfactory results. However for certain desired products we vary this rate, usually decreasing. Under no conditions do we ever reduce the rate of cycling inert gases to such a point that the oxygen and hydrocarbon become an explosive mixture.

It will be noted that the varying of the proportion of air to hydrocarbon to increase or decrease the yield of aldehydes or alcohols as hereinbefore pointed out, does not affect the recycling ratio or any conditions in the system. The recycling ratio is based upon the amount of butane or other hydrocarbon charged. If an increased amount of air is charged the amount of nitrogen vented off will be correspondingly increased. Since the apparatus is set to vent at a given pressure, equilibrium will be quickly established in the system and everything will vent down to the pressure at which the system is set, in the specific example given, 350 pounds. In other words, the recycling, pressure and temperature conditions will remain the same regardless of the proportion of air and hydrocarbon charged to the system.

Of course we can, if we so desire, change any of these conditions. That is, we can burn more gas in the furnace and increase the temperature or we can set the pop-off valve on the vent so that the pressure will be greater or less, but when it is merely a matter of increasing or decreasing the air-hydrocarbon ratio, the system will automatically vent off such quantities of inert gas as to maintain the pressure the same, and since we regulate the temperature to a predetermined point, for example 750° F., none of these conditions will change.

It will thus be seen that we have produced an improved process which consists in injecting hydrocarbon gas and a suitable source of oxygen gas such as air, in a novel manner into a stream of cycling inert gas, the resulting mixture having such proportions as to enable us to control the reaction to bring about a maximum yield of desirable products and at the same time avoid dangerous conditions in the practice of the process when said mixture is subsequently heated.

From the foregoing it is believed that our invention may be readily understood by those skilled in the art without further description, it being borne in mind that numerous changes may be made in the details disclosed without departing from the spirit of the invention as set out in the following claims.

What we claim and desire to secure by Letters Patent is:—

1. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle relatively small portions of a hydrocarbon gas and a gas consisting essentially of oxygen and nirtogen, the relative proportion of said oxygen containing gas being greater than said hydrocarbon gas, conducting said vehicle and gases commingled through a heated reaction zone to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said gaseous vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said gaseous vehicle to maintain constant the pressure in the system.

2. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle an oxidizing gas consisting essentially of oxygen and nitrogen, and a hydrocarbon gas in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a heated reaction zone to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said gaseous vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said gaseous vehicle to maintain constant the pressure in the system.

3. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle an oxidizing gas consisting essentially of oxygen and nitrogen, and a hydrocarbon gas in the proportions of approximately one part of hydrocarbon gas to ten parts of said oxidizing gas, conducting said vehicle and gases commingled through a heated reaction zone to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said gaseous vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said gaseous vehicle to maintain constant the pressure in the system.

4. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle a hydrocarbon gas and air in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a heated reaction zone under a pressure of between 100 and 350 pounds per square inch, to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said vehicle to maintain constant the pressure in the system.

5. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle a hydrocarbon gas and air in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a heated reaction zone at a temperature of between 600° F. and 900° F. and under a pressure of between 100 and 350 pounds per square inch, to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said vehicle to maintain constant the pressure in the system.

6. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle a hydrocarbon gas and air in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a heated reaction zone at a temperature of between 600° F. and 900° F. and under superatmospheric pressure, to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, continuing the circulation of said vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said vehicle to maintain constant the pressure in the system.

7. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, continuously heating a portion of the ring to a temperature of between 600° F. and 900° F., compressing and continuously introducing into said ring anterior to the heating portion, a hydrocarbon gas and air in the proportions of approximately one part of hydrocarbon gas to ten parts of air, cooling the reacted products posterior to the heating portion, removing the condensate, continuing the circulation of said vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said vehicle to maintain constant the pressure in the system.

8. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises continuously flowing a relatively large volume of an inert gaseous vehicle through a passageway, continuously injecting into said flowing vehicle an oxidizing gas consisting essentially of oxygen and nitrogen, and a hydrocarbon gas in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a heated reaction zone to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, and venting at least a portion of the gaseous vehicle substantially free of hydrocarbon and oxygen.

9. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises continuously flowing a relatively large volume of an inert gaseous vehicle through a passageway, continuously injecting into said flowing vehicle air and a hydrocarbon gas in substantially stoichiometric proportions, conducting said vehicle and gases commingled through a reaction zone heated to a temperature of between 600° F. and 900° F., under a pressure of between 100 and 350 pounds per square inch, to cause a substantially complete oxidation of said hydrocarbon gas, cooling the reacted products, removing the condensate, and venting at least a portion of said gaseous vehicle substantially free of oxygen and hydrocarbon.

10. The process of producing partial oxidation products from normally gaseous saturated hydrocarbons which comprises circulating a relatively large portion of an inert gaseous vehicle through a closed ring, injecting into said circulating vehicle an oxidizing gas consisting essentially of oxygen and nitrogen, and a hydrocarbon gas in substantially stoichiometric proportions which undiluted would normally lie within the explosive range, conducting said vehicle and gases commingled through a heated reaction zone to cause a substantially complete oxidation of said hydrocarbon gas, said vehicle serving to dilute the mixture of oxidizing gas and hydrocarbon to avoid explosions and at the same time controlling the reaction to avoid the production of undesirable products, cooling the reacted products, removing the condensate, continuing the circulation of said gaseous vehicle substantially free of hydrocarbon and oxygen, and venting sufficient of said gaseous vehicle to maintain constant the pressure in the system.

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