

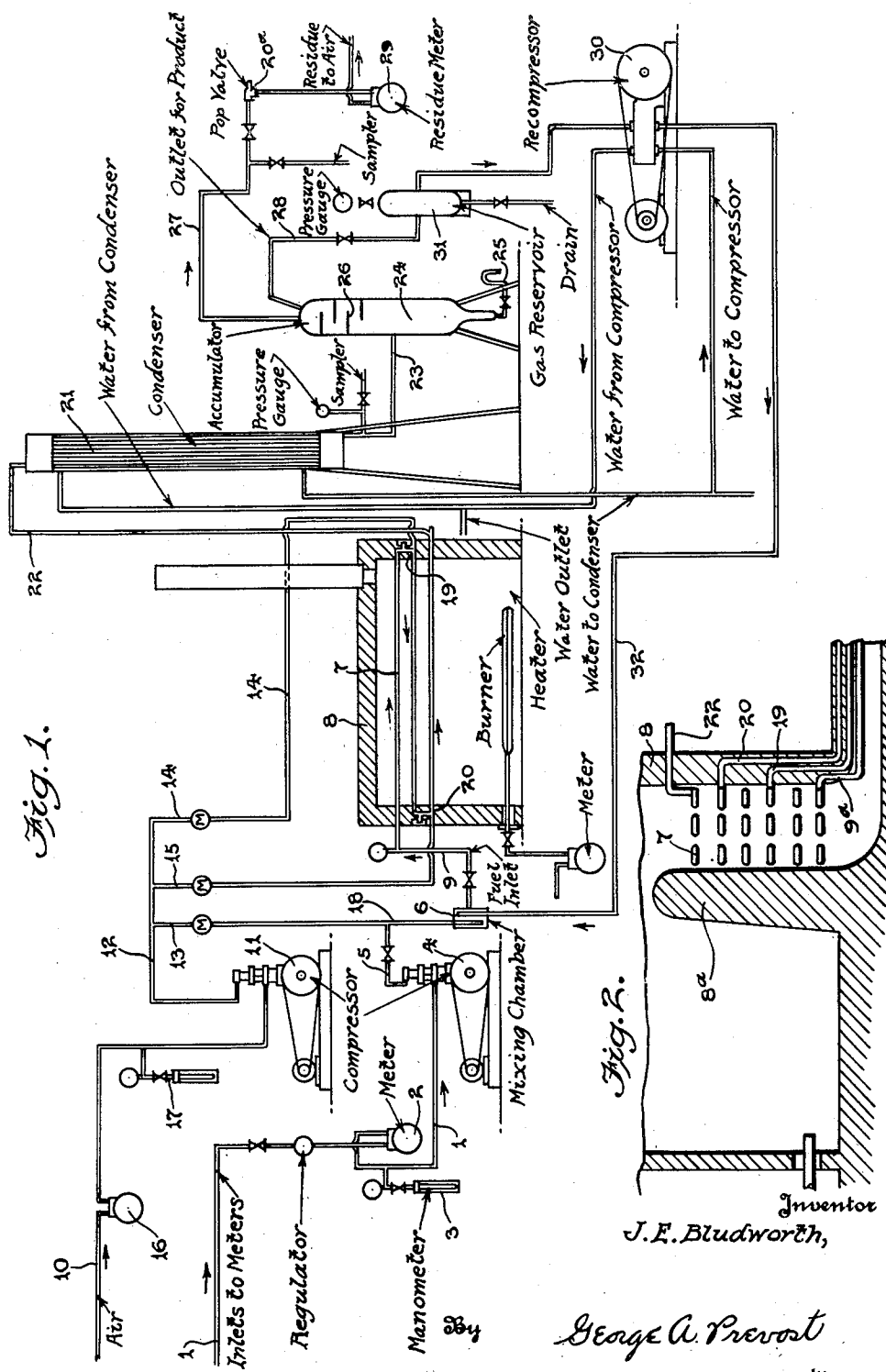
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PROCESS FOR OXIDIZING GASEOUS HYDROCARBONS

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PROCESS FOR OXIDIZING GASEOUS
HYDROCARBONSJoseph E. Bludworth, Eastland, Tex., assignor to
Hanlon-Buchanan, Inc., Tulsa, Okla.Application December 24, 1930
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4 Claims. (Cl. 260—156)

This invention consists in new and useful improvements in a process of oxidizing gaseous hydrocarbons to produce a mixture containing methanol, acetone, acetaldehyde, and similar chemicals and constitutes an improvement on the process described and claimed in my co-pending application filed of even date herewith.

My present invention is particularly directed to a means for more accurately controlling the rate and degree of reaction, thereby making it possible to appreciably increase the percentage of methanol, acetone, acetaldehyde and other chemicals formed by the reaction of oxygen upon the hydrocarbons, and more completely eliminating the formation of undesired materials such as acids, carbon and formaldehyde. It is obvious that water is always formed as a by-product of the oxygen reaction in processes of this character.

As stated in my co-pending application, it is a well-known law of physical chemistry that reactions between materials are progressively selective and that if the proper conditions of temperature and pressure are applied, then the character and quantity of the end product or products can be controlled. It is through a proper application of this knowledge to the field of producing methanol, acetone and acetaldehyde from hydrocarbons such for example as propane and butane, that serves as the fundamental of this invention as well as the invention described in my co-pending application just referred to.

I accomplish this accurate control of the reaction, by causing a plurality of injections of air or other oxidizing gas at successive points in the reaction zone, as contrasted with the total introduction of air or other oxidizing gas at the outset of the process as called for in my co-pending application.

With the above and other objects in view which will appear as the description proceeds, my 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 accompanying drawing, in which numerals of like character designate similar parts throughout both views,

Fig. 1 is a schematic layout of one form of apparatus by which my process may be practiced, and

Fig. 2 is a modification showing one form of heating element or reaction zone for facilitating

the multiple injection of oxidizing gas according to my invention.

In the drawing, referring to Fig. 1, 1 represents a pipe line for conducting the gaseous hydrocarbon, such for example as propane or butane or mixtures of the same into the system, and is provided with a meter 2 and a manometer 3 for indicating the volume and pressure respectively of the hydrocarbon entering the system. The line 1 terminates at the inlet of a compressor 4, the discharge side of which is connected to a pipe line 5 which leads to the interior of a mixing chamber 6, which is in communication with the coils 7 in the furnace 8 through the medium of the pipe line 9.

10 represents an air or oxidizing gas line which leads from any suitable source to a second compressor 11, the discharge outlet of which is connected to a pipe line 12, the latter leading to three branch pipe lines 13, 14 and 15, each of which is equipped with a suitable meter for indicating the volume of oxidizing gas passing therethrough. As in the case of the pipe line 1, the pipe line 10 is equipped with a suitable meter 16 and manometer 17 at points anterior to the compressor 11.

The pipe line 13 is connected as at 18 to the pipe line 5 which leads to the mixing chamber 6, for injecting an initial quantity of oxidizing gas into the mixing chamber. The pipe line 14 leads to a point in the heating or reaction coil 7 designated by the numeral 19, said point in the reaction zone being determined by the temperature at that particular point. The pipe line 15 leads to a second point 20 in the reaction coil 7, which point as in the case of the connection at 19, is determined by temperature and in addition, the time of passage through the reaction zone.

It will be understood that while I have shown one initial injection of oxidizing gas and two additional injections in the reaction zone, I may employ a lesser or greater number of injections, according to the character of the apparatus used and the end products desired.

21 represents a suitable cooler or condenser into which the mixture of hydrocarbon and oxidizing gas passes through line 22, after leaving the reaction coil 7, discharging from the condenser through line 23 into a separator 24, the lower extremity of said separator forming a liquid accumulator which terminates in a liquid draw-off 25. The upper end of the separator 24, as in my co-pending application, may be provided with a series of baffles 26, and opens

into two pipe lines 27 and 28, the former leading through a residue meter 29 and from thence to vent. The line 28 leads to a compressor 30 and may have interposed at a suitable point therein, a gas reservoir 31, which serves as a source of supply for the compressor 30.

The compressor 30 is connected with the interior of the mixing chamber 6 through the medium of a pipe line 32, whereby the compressed vapors are circulated through the system as will be hereinafter set forth.

Referring to Fig. 2 of the drawing, the furnace 8 is of the indirect heating type, being provided with a masonry baffle wall 8a between the burner and the series of coils 7. With this structure, the mixture of hydrocarbon and the initial charge of oxidizing gas enters at 9a, the additional injections of oxidizing gas, as with the apparatus heretofore described, being made at the points 19 and 20.

Having thus described the layout of one form of apparatus by which my process may be practiced, its operation is as follows:—

A saturated gaseous hydrocarbon is introduced into the system through the pipe line 1, the charge being compressed by the compressor 4 and passing through line 5 into the mixing chamber 6. Simultaneously, air or other oxidizing gas from line 10 is compressed by the compressor 11 and discharged into line 12, from whence, through the medium of line 13, it is injected in the line 5 at the point 18, thus entering the mixing chamber 6 along with the charge of gaseous hydrocarbon. It will be understood that all gas volumes are corrected to standard conditions of temperature and pressure before entering the apparatus. The compressors 4 and 11 compress the hydrocarbon gas and oxidizing gas respectively under the desired pressure, preferably above 200 pounds per square inch.

The mixture entering the mixing chamber 6 is then mixed with a quantity of recycled gas from line 32 as will be hereinafter referred to, and from thence conducted to the reaction coil 7 in the furnace 8, the temperature of which is preferably maintained between 450° and 900° F.

During the passage of the mixture through the reaction zone, additional oxidizing gas is injected at points 19 and 20 and it will be understood that the quantity of oxidizing gas introduced into the mixture at any one point in the apparatus is only sufficient to cause a series of successive controlled reactions. In other words, a sufficient quantity of oxidizing gas is introduced at 18 to cause an oxidizing reaction upon those compounds which oxidize at temperatures below 400° F., for example, which is partially the result of the heat of compression from the compressors 4 and 11. By the time the mixture has reached the point 19 in the reaction zone, the oxygen content thereof has been completely utilized by the hydrocarbon, and the saturated hydrocarbons, due to the elements of temperature, time and pressure, are in a state to be acted upon by additional oxidizing gas when it is injected at the point 19.

During the passage of the mixture of gaseous hydrocarbon and newly injected oxidizing gas from the point 19 to the point 20 in the reaction zone, further reaction takes place due to the elements of time and temperature. While the temperature between these two points is not materially raised above that of the point of the injection at 19, the time of passage between

these points is largely responsible for the complete utilization of the charge of oxidizing gas introduced at 19, and those compounds which oxidize at temperatures below 900° F., for example, are caused to undergo an oxidizing reaction.

After the point 20 in the reaction zone, there may remain in the mixture a number of saturated hydrocarbons which are in a state to be further acted upon by additional oxidizing gas, and the injection of such additional oxidizing gas at the point 20 causes a further reaction upon those hydrocarbons, due to the element of time of passage through the remainder of the reaction zone.

From the reaction zone, as in the case of my co-pending application, the mixture is conducted through pipe 22 to the condenser 21 where a portion of the mixture is condensed, both the condensed and uncondensed portions being then transferred to the separator 24 where the condensate accumulates in the lower end, said condensate forming the desired mixture which includes methanol, acetone, acetaldehyde and other chemicals as before stated, which chemicals may be removed or separated from the mixture by fractionating or other known means, which form no part of this invention.

At the upper extremity of the separator 24, the uncondensed vapors are separated into two streams, one leading through pipe 27 to vent, the major portion of the uncondensed vapors being led through pipe 28 to the reservoir 31, which serves as a source of supply for the compressor 30. The gas from the reservoir 31 is compressed by the compressor 30 and returned to the system by means of the pipe line 32 and the mixing chamber 6 where it is completely mixed with the charge of fresh hydrocarbon gas and oxidizing gas introduced through pipe 5. The mixture of fresh hydrocarbon gas, oxidizing gas, and recycled gas is then led through the reaction zone and condenser repeating the cycle just described.

As stated in my co-pending application, valved connections are placed on the various parts of the equipment in order to control pressures and rates of flow, and the pressures are indicated by suitable gauges placed on different parts of the equipment. I have found that the operation can be carried out under a considerable range of pressures, but from experience have determined that they should preferably be as before stated, in excess of 200 pounds per square inch in the reaction zone. I have likewise found that the process can be carried out under a considerable range of temperatures, but in practice have found that this should preferably be in excess of 450° F. in the reaction zone. On the other hand, I have found that temperatures higher than 900° F. are undesirable and do not permit of the definitely controlled character of reaction which constitutes one of the important fundamentals of my process.

Having described a form or type of apparatus in which my invention can be carried out and the operation of the process, I will now proceed to describe some of the features of my process which differentiate it from other processes and which features are directly or indirectly responsible for the improved results I achieve. One of the fundamental weaknesses or faults of all the processes with which I am familiar is that the reaction is not under sufficiently definite control and consequently proceeds to a point

where over-oxidation occurs and as result undesired products in quantity are formed. Instead of attempting to get any considerable percentage of reaction on one passage of the reacting agents through the reaction zone, I have discovered that the reaction can very definitely be controlled with a maximum production of methanol, acetone, acetaldehyde and the like by stopping the reaction per pass through the reaction zone with only a part of 1 per cent of the reaction possible. By way of specific illustration, when an ultimate yield of eight gallons of desired liquid products (methanol, acetone, acetaldehyde) are to be produced from one thousand cubic feet of butane, I would produce not in excess of five ten thousandths (0.0005) gallons per pass based on each cubic foot of raw butane used, and usually only about two or three ten thousandths (0.0002) gallon. To bring about this controlled quantity of reaction, I introduce only sufficient air or oxygen to permit of such a degree of reaction. The specific character of my invention can probably be better understood when I state that at no time in the reaction zone do I permit the oxygen content to materially exceed 1.25% of the mix in the reaction zone or fall below .4%. For example, when using propane as raw material, I found the composition of the material entering the reaction zone to be:

N ₂ -----	67.5
CO-----	5.
CO ₂ -----	6.
Propane-----	16.
Hydrogen-----	2.8
Unsaturates-----	1.8
Oxygen-----	0.9
	<hr/>
	100.00

By recycling the reacting hydrocarbon a sufficient number of times to complete the reaction of all of the hydrocarbons for example fifteen (15) or more times and on each recycle introducing only a small amount of air, the reaction is controlled so that over-oxidation is not affected, which means that I can produce methanol, acetone and acetaldehyde without the formation of quantities of undesirable products such as acids, carbon, etc. By my process, methanol, acetone and acetaldehyde are formed simultaneously or rather are taken from the process simultaneously but I have found that when the reaction is permitted to go to say .0005 gallons of methanol, acetone and acetaldehyde per pass, then a greater percentage of acetaldehyde is formed than when such reaction is permitted to go to only .0003 gallons per pass, based on each cubic foot of raw butane used. By decreasing the quantity of reaction per pass I can very materially decrease the percentage of acetaldehyde formed and correspondingly increase the methanol. In other words, there is a considerable flexibility in the relative percentage of methanol and acetone on the one hand and acetaldehyde on the other, depending on the percentage of reaction permitted per pass. On the other hand, when the percentage of reaction per pass is permitted to materially exceed .0005 gallons per pass, then the beneficial results of my process no longer are available because the reaction promptly gets out of control. In practice, I find that a desirable ratio of recycle mix to fresh mix to be about 96% recycle and about 4% fresh butane or propane, in which case the

reacting agent would pass through the reaction zone more than twenty-four times.

In using butane as raw material this 4% fresh butane would be mixed with three to five parts (by volume) of air and one part of butane, which in turn would mean that the material entering the reaction zone would be three or five parts air to about twenty-five parts of material other than air, i.e., recycle and fresh hydrocarbon. The preferred raw hydrocarbons for my process are propane and butane, although I have found it useful when using other hydrocarbons.

Starting with butane, I have recovered as high as eight gallons of methanol, acetone and acetaldehyde, of which six gallons was methanol with one gallon each of acetone and acetaldehyde. These results were obtained when the reacting material was passed through the reaction zone about thirty (30) times and on each pass exposed to reaction temperatures for not more than 30 seconds.

Using commercial propane as raw material I have produced up to six gallons of methanol, acetone, acetaldehyde from 1000 cubic feet of raw material, with the relative percentage of the three desired end products substantially the same as when using butane as raw material. As previously stated the relative percentage of acetaldehyde can be increased by permitting a greater percentage of reaction per pass with fewer total passes. For example with from fifteen to twenty passes (15 to 20) there was formed about two gallons of acetaldehyde from 1000 cubic feet of raw butane.

In the run where I formed the eight gallons of methanol, acetone, acetaldehyde liquid, exclusive of the water by-product which always is formed, I used a temperature in the reaction zone of about 700° F. and a pressure of about 300 pounds. The quantity of residual gas discharged from the system through pipe 20 obviously is a function of the number of passes and the quantity of fresh hydrocarbon-air mix introduced into the system, as well as the operating pressure. The quantity of this residual gas released can be automatically controlled by means of a pressure release valve which is set at any desired operating pressure. It will be noted that the B. t. u. content and quantity of this residual gas can be varied at will.

The essence of the present invention lies in the multiple introduction of oxygen or air into successive parts of the reaction zone, as contrasted with the total introduction at one place in my co-pending application. It is possible that by injecting the full proportion of air at one point of the process might under certain conditions so heavily impregnate the gas mixture with oxygen that the reaction would proceed to a point that would be detrimental to the quantity and quality of the products produced, because of the uncontrolled degree of reaction at the point just beyond such introduction into the reaction zone. Since the mixture entering the reaction zone is composed chiefly of materials which have previously and repeatedly passed through the reaction zone there have been formed and are present in the mix entering the reaction zone appreciable percentages of unsaturated hydrocarbon materials which unsaturated materials are particularly sensitive toward reaction with oxygen under elevated temperatures prevailing. This condition can be largely controlled according to my present invention, by introducing the

oxygen or air at successive points or stages in the heating coil or reaction zone. By way of example, I have found that the reaction can very definitely be controlled by introducing one-half of the total weight of oxygen used prior to the initial point of inlet to the reaction zone making this entry in company with the recycle material and the new or fresh butane or propane; one-fourth of the oxygen or air to be introduced at a point one-third of the length of the heating coil or reaction zone; and the remaining one-fourth, two-thirds the length of the heating coil or reaction zone. Actual increase of production of methanol, acetone and acetaldehyde from propane or butane of from 10 to 20% have been achieved. During this multiple stage introduction of air I have observed the following temperature conditions in the reaction zone or coil. At the initial point of entry the temperature was about 350° F., at the second point of air injection the temperature was 750° F., and at the third point of air injection the temperature was 750° F., while at the exit of the coil or reaction zone the temperature was about 700° F. From these temperatures observed it is to be noted that the temperature throughout the reaction zone does not exceed a desired temperature, in this case 750° F., whereas if total injection of air or oxygen were made at the initial inlet the temperature attained during the first part of the reaction zone might not be controlled and excessive oxidation might occur in the formation of undesired carbon monoxide, carbon dioxide, formaldehyde and acids. If total injection of the oxygen is made at the inlet of the reaction coil as in my co-pending application I have found the composition of the incoming material using propane as raw material to be about as follows: 67.5% nitrogen, 0.9% oxygen, 5% CO, 6% CO₂, 1.8% ethylene, 2.8% of hydrogen and 16% propane. From experience I have determined that this 0.9% oxygen, while apparently very small, is still too high to best control the reaction. By introducing only half of the oxygen at this inlet the above percentage of 0.9% would obviously be reduced to 0.45%, with which percentage I find that I can far better control the oxidation to bring about the desired end product and reduce to a minimum the undesired end products. In broad terms the object of my invention is to maintain substantially uniform throughout most of the reaction zone, the percentage of available free oxygen, and at all times said percentage being between 0.4 and 1.25 per cent.

It will be noted that, as in the case of my co-pending application, my present invention does not contemplate the use of catalysts in any form.

From the foregoing it is believed that the objects, advantages, and operation of my improved process 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 of structure of the apparatus as well as the process, without departing from the spirit of my invention as set forth in the following claims. For example, while I have mentioned the use of butane and propane as raw materials, it is to be understood that these are merely illustrative, and I may use other raw materials, preferably however, those consisting mainly of a saturated normally gaseous hydrocarbon or mixtures of various saturated gaseous hydrocarbons.

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

1. A process for the manufacture of a mixture containing methanol, acetone and acetaldehyde which comprises combining a saturated hydrocarbon gas with a suitable oxidizing gas having the oxidizing characteristics of air, compressing said mixture and passing the same through an elongated passageway of restricted cross section, heating the mixture as it flows through the passageway to between 450° and 900° F. to cause partial oxidation of the hydrocarbon gas, introducing into the mixture as it flows through said passageway and before it has been heated to the maximum degree, an oxidizing gas having the oxidizing characteristics of air, then cooling the mixture to effect condensation of a portion thereof, collecting the condensate, and cycling continuously a portion of the uncondensed gases and vapors for admixture with the combined fresh saturated hydrocarbon gas and an oxidizing gas.

2. A process for the manufacture of a mixture containing methanol, acetone and acetaldehyde which comprises mixing a saturated hydrocarbon gas with an oxidizing gas having the oxidizing characteristics of air, compressing said mixture and then heating the same to a temperature of about 400° F. to cause an oxidizing reaction upon those compounds which oxidize at temperatures below 400° F., then raising the temperature of the mixture to between 450° F. and 900° F., injecting a quantity of oxidizing gas having the oxidizing characteristics of air into the mixture at a point during said increased heat step to cause an oxidizing reaction upon those compounds which oxidize at temperatures between 450° F. and 900° F., then cooling the mixture to effect condensation of a portion thereof, and collecting the condensate.

3. A process for the manufacture of a mixture containing methanol, acetone and acetaldehyde which comprises mixing a saturated hydrocarbon gas with an oxidizing gas having the oxidizing characteristics of air, compressing said mixture and then heating the same to a temperature of about 400° F. to cause an oxidizing reaction upon those compounds which oxidize at temperatures below 400° F., then raising the temperature of the mixture to between 450° F. and 900° F., injecting a quantity of oxidizing gas having the oxidizing characteristics of air into the mixture at a point during said increased heat step to cause an oxidizing reaction upon those compounds which oxidize at temperatures between 450° F. and 900° F., then injecting into the mixture at a second point during the increased heating step, an additional amount of an oxidizing gas having the oxidizing characteristics of air, to cause an oxidizing reaction upon those compounds which oxidize at a temperature between 450° F. and 900° F. but over a longer reaction period, then cooling the mixture to effect condensation of a portion thereof, and collecting the condensate.

4. A process for the manufacture of a mixture containing methanol, acetone and acetaldehyde which comprises mixing a saturated hydrocarbon gas with an oxidizing gas having the oxidizing characteristics of air, compressing said mixture and then heating the same to a temperature of about 400° F. to cause an oxidizing reaction upon those compounds which oxidize at temperatures below 400° F., then rais-

ing the temperature of the mixture to between 450° F. and 900° F., injecting a quantity of oxidizing gas having the oxidizing characteristics of air into the mixture at a point during said increased heat step to cause an oxidizing reaction upon those compounds which oxidize at temperatures between 450° F. and 900° F., then injecting into the mixture at a second point during the increased heating step, an additional amount of an oxidizing gas having the oxidizing characteristics of air, to cause an oxidizing reaction upon those compounds which oxidize at a temperature between 450° F. and 900° F. but over a longer reaction period, then cooling the mixture to effect condensation of a portion thereof, collecting the condensate, and cycling continuously a portion of the uncondensed gases and vapors for admixture with the combined fresh saturated hydrocarbon gas and an oxidizing gas.

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25	100
30	105
35	110
40	115
45	120
50	125
55	130
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65	140
70	145
75	150