PROCESS STEAM TO PLANT

STEAM-GAS EXHAUST TO ATMOSPHERE

EXHAUST TURBINE

274.4°F
45 PSIA
864# STEAM/MIN.

310°F
291 PSIA
299# STEAM/MIN.
1060# WATER/MIN.
364# CO₂/MIN.
985# N₂/MIN.

296°F
291 PSIA
299# STEAM/MIN.
264# CO₂/MIN.
985# N₂/MIN.

PROCESS STEAM TO PLANT

274.4°F
45 PSIA
371# STEAM/MIN.

274.4°F
45 PSIA
40#/MIN.

274.4°F
45 PSIA
980# WATER/MIN.

HOT WATER TO PLANT

200°F
471 GPM
3940#/MIN.

SEPARATOR #2

THROTTLE VALVE

SEPARATOR #3

HOT WATER MIXER

HEAT EXCHANGER

CONDENSATE RETURN FROM PLANT

250°F
864#WATER/MIN.

372°F
310 PSIA
1160# STEAM/MIN.
160# WATER/MIN.
364# CO₂/MIN.
985# N₂/MIN.

TOPPING TURBINE

STEAM GAS

274.4°F
45 PSIA
332# STEAM/MIN.

SOLID REFUSE TO RECLAIMING PLANT
66.1# SOLID/MIN.
66.1# WATER/MIN.

274.4°F
45 PSIA
760# WATER/MIN.

518°F
1404 PSIA
1320# STEAM/MIN.
364# CO₂/MIN.
985# N₂/MIN.

SEPARATOR #1

518°F
1404 PSIA
1153# WATER/MIN.
66.1# SOLIDS/MIN.

THROTTLE VALVE

SEPARATOR #4

FILTER

274.4°F
45 PSIA
824# WATER/MIN.
66.1# SOLIDS/MIN.

REACTORS

190°F
1444 PSIA

400°F
1444 PSIA

COMPRESSOR

80°F

INTERCOOLERS

COLD WATER FROM PLANT MAINS
35°F
2200#/MIN.

139°F
2200#/MIN.

PUMP

SULPHITE WASTE LIQUOR FROM PLANT
300 GPM
190°F
14.7 PSIA

AIR INTAKE
1280#/MIN.
60°F
14.5 PSIA

COMPRESSOR

460°F

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## METHOD FOR THE CONTINUOUS SELF-SUSTAINING FLAMELESS OXIDATION OF COMBUSTIBLE MATERIALS

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Application December 14, 1953, Serial No. 397,959

7 Claims. (Cl. 210—63)

The present invention relates to a method for continuously oxidizing combustible materials with an oxygenating gas in an aqueous dispersion under conditions such that the oxidation process is self sustaining and generates heat energy in excess of that required to maintain the flameless oxidation. More particularly, the present invention is characterized by feeding a combustible material dispersed in liquid water into a reaction zone which contains a large quantity of combustible material and liquid water and inducing a flameless oxidation while maintaining the quantity and concentration of the combustible material in the reaction zone substantially constant and oxidizing only at the rate at which fresh oxidizable material dispersed in water is fed to the zone.

The invention also relates to the continuous transformation of mass energy latent in combustible material, by oxidation while in aqueous dispersion, into useable energy form in water vaporized from the liquid phase in such manner that the non-condensible gases present, such as formed during oxidation and in the oxygenating gas, become a carrying medium for the water vapor in which the utilizable energy is stored.

In my copending application Serial 152,264, filed March 27, 1950, for "Waste Disposal," now Patent 2,665,249, issued January 5, 1954, which is in turn a continuation-in-part of my prior-filed application Serial 118,834, filed September 30, 1949, now abandoned, which was a continuation-in-part of my earlier-filed application Serial 618,065, filed September 22, 1945, now abandoned, I described the operation of a method for the oxidation of wastes in which temperatures and pressures were adjusted so as to provide a continuous flameless oxidation of organic materials dispersed in water and in the presence of oxygen-containing gases. It has now been discovered that, substantially independently of any adjustment of pressure and temperature, the concentration of combustible materials in water in the reaction zone may be adjusted to deliver desired degrees of oxidation. This discovery permitted an entirely new conception of the non-criticality of pressure and temperature in permitting continuous substantially complete oxidation of the oxidizable material in a self-sustaining system.

Accordingly, it is a purpose of this invention to provide a process for continuously oxidizing combustible materials dispersed in liquid water which includes the steps of continuously passing a combustible material dispersed in liquid water and an oxygen-containing gas into a reaction zone while maintaining in said zone the concentration of combustible material dispersed in the liquid water sufficiently high to oxidize all the combustible material at the rate at which it is fed into the reaction zone. The upper limit of the concentration of combustible material in water is that at which the amount of energy liberated by the oxidation is insufficient to vaporize all of the water in the reaction zone.

In this connection it is therefore an object of this invention to provide a continuous self-sustaining flameless process for oxidizing substantially any type of combustible materials dispersed in liquid water by the maintenance of a desired concentration of combustible material in a reaction zone.

It is also an object of this invention to utilize the presence of non-condensible gases, either reaction products, or non-condensible gases injected into the system, in a ratio of non-condensible gases to the entire aqueous system above at least that ratio necessary to ensure the carrying off of the energy loaded water vapor by the non-condensible gases present or supplied, and recovering therefrom substantially completely oxidized material and an energy enriched mixture of condensible and non-condensible gases. It will be seen that heat exchange including transformation of energy is thus accomplished without the use of a conventional solid barrier. The intimate contact of water at the energy liberation area and the action of the gases, both condensible (water vapor) and non-condensible, i. e., carbon dioxide, oxygen, nitrogen, in direct contact with each other eliminate the conventional solid interface and make available exchanger efficiencies hitherto unattained.

Further, noxious odors from wastes are not emitted to the atmosphere in the closed system of this invention. The process may be carried on in metropolitan areas without endangering the health and well-being of the community while returning to useable form substantially all of the water required by industrial processes without hampering the quantities of the water for sustaining aquatic life. Heat losses characteristic in hitherto known waste disposal processes can be simply controlled. Plantwise economies can be realized by utilizing the excess of energy, from the exothermic character of oxidation, above that required to render the system self sustaining, since the chemical combinations occurring in the union of oxygen with the combustible elements and compounds of fuels provides the source of heat as for power generation. The steam boilers presently in use absorb heat efficiently and not much improvement can be expected in such apparatus. Any marked increase in the efficient generation of steam therefore resolves into the problem of increasing the efficiency of combustion and avoiding the use of metallic barriers as between the conventional boiler furnace and water of the boiler. It is the physical introduction of oxygen (a non-condensible gas) into the presence of combustible substances in liquid water in such manner as to assure complete oxidation, while at the same time insuring the utilization of all or of the maximum proportion so supplied, that is the most important and difficult problem in the burning of fuels.

The general requirements for proper combustion include the admission of an air supply such as will assure sufficient oxygen for complete combustion without permitting the dilution of the product of combustion with excess air; the air must come into intimate contact with the combustible substances, including any combustible gases distilled from solid combustible particles; the combustible substances must be maintained at a temperature above their ignition temperature until combustion is complete; and provision must be made for the expansion of gases during the period of their combustion.

This process for the generation of heat energy permits complete combustion of the fuel; eliminates conventional metallic thermal exchange barriers; permits the use of dilute aqueous combustible substances, such as carbonaceous wastes, as fuel; eliminates the problem of expansion of gases during combustion; and, permits maintaining combustibles in liquid phase above their ignition temperatures whereby their flameless oxidation is accomplished.

The invention is particularly characterized by the fact that it is unnecessary to reduce the volume of the raw effluents containing the combustible materials as by procedures such as dehydration, evaporation, or precipitation. In general, a flameless combination of oxygen with combustible matter takes place in the presence of the liquid

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water of the effluent with the accompanying liberation of heat energy. The application of this heat energy results in a power cycle. The cycle contemplates the oxidation of the dilute aqueous oxidizable substances in their natural or dilute liquid state for the purpose of converting them to heat and mechanical energy. My process is limited to the self-sustaining oxidation of the oxidizable materials in aqueous dispersion carried out at flameless combustion while the oxidizable materials are dispersed in liquid water, which water is maintained at least partially in the liquid phase in the reactor. It is clearly distinguishable from oxidation or combustion of oxidizable materials in the dry state such as in a furnace in which the temperature of self-sustaining oxidation is several hundred degrees above the range of the present process and little or no liquid water is present.

The efficiency in the power cycle inherent in my process is partially derived from the elimination of much of the conventional energy-consuming and wasting equipment employed by heretofore existing processes for conversion of aqueous dispersions of carbonaceous substances to heat and mechanical energy. Whereas the prior processes developed in this field have provided more or less complicated steps directed at the concentration of these carbonaceous substances, because of what has always been regarded as their undesirable water content, my process employs this liquid water content as an essential element in the conversion of the carbonaceous substances to useable energy.

The invention also makes it not only possible but desirable in instances to generate steam energy from low grade powered fuels by first mixing such fuel in a relatively large quantity of water. Such a process for the conversion of the potential heat energy in the fuel to useable steam energy has several important advantages. Among these advantages are the elimination of the troublesome fly ash problem, water pre-treatment plants, and the elimination of the conventional boiler and the energy losses resulting from their efficiency limitations. The kernel of the problem is the fact that heretofore no process has ever been developed by which the waste effluents could be utilized as a fuel without at least partial concentration of the liquor containing the carbonaceous substances before converting the carbonaceous substances to heat energy. Thus, the usual way of obtaining energy from a dilute aqueous waste involves evaporation of water. For this evaporated water the latent heat of vaporization must be supplied and is lost in the process. The quantity of heat absorbed in vaporizing the water is so great that the over-all process of utilizing the fuel in these waste liquors or effluents is not efficient. This factor alone makes these processes generally consumers of heat energy rather than sources of heat energy. All of the existing processes, having as their objective the obtaining of heat energy from these aqueous materials, have employed high temperature combustion of the carbonaceous substances in their dry or substantially dry state. None of them has attempted to obtain the heat energy from the carbonaceous materials by low temperature flameless oxidation in their raw condition as dilute aqueous dispersions.

There are other factors rendering these processes economically impractical. The standard practice of obtaining heat energy from these waste effluents involves the following steps: (1) concentrating the waste by some means, such as multiple effect evaporators, and, (2) burning the concentrated waste in a boiler. Such a process has a low over-all efficiency.

This invention eliminates, for the first time, these heat energy wasting steps. Instead of attempting to refine the steps of these standard processes, to render them more efficient this invention eliminates a major portion of the energy wasting steps, whereby the energy producing step is permitted to predominate, rendering the over-all process highly efficient. My invention not only makes

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the process self sustaining but changes the balance between energy generation and consumption to such an extent that the process is capable of producing substantial quantities of energy in excess of that required to sustain the oxidation reactions.

The quantity of the oxygen-containing gas required is preferably that theoretically required to convert all of the combustible matter in the aqueous dispersion to its end products, such as carbon dioxide, water, nitrogen, sulfates, nitrates, carbonates, phosphates, et cetera, or slightly in excess of such amount, which is readily determinable by standard methods from the analysis of the combustible material and its oxygen demand.

It has been found that rates of oxidation vary for differing types of combustible materials and are somewhat dependent upon particle size and that, as the ratio of combustible material in water is increased, the rate of oxidation is thereby increased in any given unit of time at any given temperature and pressure. The pressure is selected to maintain the water in the reaction zone at least partially in the liquid phase.

For any concentration of combustible material in water, therefore, in a given unit of time and assuming static conditions of pressure and temperature some oxidation may occur. If the products of the reaction are not rapidly removed from the reaction zone, this results in a lowering of the concentration of unoxidized material in the water in the zone. If the reaction products are withdrawn along with vaporized water the concentration of the combustible material in the liquid water in the reaction zone can be increased. Thus, by withdrawing products of the reaction and vaporized water from the reaction zone at a rate such that the original concentration in the reaction zone is maintained, a continuous process is made available whereby substantially all of the combustible material is oxidized from a relatively dilute raw effluent. In effect, the same amount of combustible materials, water, and oxygen is inserted into the reaction zone to balance stoichiometrically products removed from the reaction zone. Results indicate that this process is adaptable to any combustible material dispersed, i. e., dissolved, emulsified, or, suspended, in liquid water.

These and other objects and purposes of my invention will be apparent to those acquainted with the art of oxidation of aqueous combustible materials upon reading the following specification and the accompanying drawings.

In the drawings:

The single figure is a schematic flow diagram illustrating one way of practicing my invention as a power generating procedure, utilizing waste sulphite pulp mill liquor.

Although my process is equally suitable whether the primary objective is power generation or the removal of undesirable combustible materials from industrial wastes, in the following description of my process it will be described as applied to pulp mill wastes. The fact that my process may be applied for the purpose of waste disposal does not detract from its value as a heat generating procedure. The selection of pulp mill wastes as the dilute aqueous combustible material to be employed as fuel is for illustrative purposes only and is not to be considered limiting.

Referring now to the drawings:

The flow sheet details the process as applied to a supply of 300 gallons per minute of ordinary waste sulphate liquor. The said liquor is pumped under a pressure of 1400 to 1500 pounds per square inch gauge into a reactor vessel which may be a vertical tower, constructed to withstand pressures up to, for example, 200 atmospheres. Air or any suitable mixture of gases containing oxygen is compressed and passed through inter-coolers in heat exchange relation with cold water, if a large supply of hot water is desired for related plant purposes. The

air is then further compressed to the same pressure as the sulphite liquor and admitted to the said reactor.

The pressure in the reactor is sufficient to maintain substantially all of the water in the liquid phase. The temperature in the reactor, which may, in starting up, require heating to the ignition temperature of any particular fuel under the pressure employed, maintains itself generally in a range above 500 degrees Fahrenheit and the critical temperature of water, depending upon the proportions of oxygen to combustible substance in the feed. In the instance of sulphite liquor a temperature of 260 degrees centigrade to 315 degrees centigrade is readily maintained.

An offtake is provided from the reactor to a first separator from which fixed gases including nitrogen and carbon dioxide, and steam in desired amount are flashed through a topping turbine for power generation purposes. The exhaust from the said turbine may be passed through a heat exchanger to supply progress steam for a related plant operation and thence to a second separator. From said second separator additional steam is flashed, at a temperature of about 300 degrees Fahrenheit, accompanied by the fixed gases, through an exhaust turbine to generate further power. From said second separator the water not flashed is led through a throttling valve to a third separator and process steam flashed off for related plant use. The liquid water remaining, having a temperature of about 275 degrees Fahrenheit, may be used as hot water in related plants.

Returning now to the liquid discharged from said first separator, this is led into a fourth separator from which process steam is flashed at a temperature of about 275 degrees Fahrenheit for related plant use. The discharge from said fourth separator is filtered to remove any suspended inorganic solids and the hot water from the filter is available for related plant use.

The flow diagram sets forth the quantities, temperatures and pressures of the various materials in a manner which will instruct those skilled in the art to enable an understanding of the invention herein claimed.

The first step toward initiating the process is charging the reactor, at least partially with liquor. This charge of liquor is then heated by a suitable means such as an oil ring as to a temperature of 500 to 550 degrees Fahrenheit. The heating of the liquor in the reactor is stopped and compressed air supplied to the reactor. The admission of the compressed air to the reactor initiates the oxidation of the combustible substances, and thereafter, the reaction is self sustaining, requiring no further external heat. In certain instances, reactor design and availability of fuels may warrant the application of external heat or the injection of fuel values into the aqueous oxidizable materials being processed.

The air may be admitted through a single port at the bottom of the reactor but preferably it is admitted through a dispersion head to effect intimate dispersion of the air through the liquor. The air may even be admitted at additional points along the reactor, if such is desired. The primary object is to get a thorough dispersion or diffusion of the air throughout the liquor to assure oxidation of each of the carbon-containing molecules or other combustible substance in the liquor. A plurality of interconnected reactor zones may be employed if desired. The oxidation of the carbon compounds results in the degradation of the complex carbon-containing molecules to the end products of water and carbon dioxide.

The initial heat supplied to the starting charge of raw waste liquor is essential because the oxidation process will not start unless the liquor is heated to or above the autogenetic oxidation temperature of the carbonaceous or other combustible materials. Provided the liquor is maintained under a pressure sufficient to keep the water substantially in the liquid phase, this ignition temperature has been found to be a minimum of approximately 160 degrees centigrade. Preferably temperatures above 191

degrees centigrade are used and the optimum range is from 232 degrees centigrade to 329 degrees centigrade. The three essentials for initiating the process are subjecting the aqueous dispersion to pressure sufficient to maintain a substantial part of the water in the liquid state, heating it to a temperature at which autogenetic oxidation of the combustible substances will occur at a rapid rate, i. e., in a few seconds or a fraction of a second, and, providing an adequate supply of gaseous oxidizing agent such as air or otherwise desirably diluted oxygen, preferably that amount theoretically necessary to convert all of the carbon in the combustible substance to carbon dioxide.

When the liquor leaves the reactor, it enters the first of a series of separators or flash chambers. In each flash chamber the pressure is lowered a predetermined amount, thus, the flash chambers are in effect a series of pressure reduction steps. In the first chamber the pressure is reduced sufficiently to release as an elastic fluid the fixed gases such as nitrogen and carbon dioxide, together with a desired quantity of high-pressure water vapor. Subsequently, steam is released at varying pressures as desired. The precise procedure by which the process steam is made available is immaterial to the principle of my invention, so long as the steam is flashed after the oxidation reaction has been completed.

The heat generated by the oxidation of the combustible materials is in excess of that necessary to heat the liquor entering the reactor to a temperature at which the autogenetic oxidation of the raw liquor will occur. Because of this autogenetic heat, once the reaction has been established as a source of heat energy, the liquor may even be introduced into the reactor at room temperature, that is, about 70 degrees Fahrenheit. The heat generated by the oxidation reaction already taking place in the reactor is sufficient to raise the temperature of the incoming liquor to the combustion temperature of the carbonaceous or other combustible material therein present, such as sulphur.

In order to render the process more efficient as a heat energy generator, the incoming liquors may be preheated by means of a heat exchanger utilizing the effluent discharged from the last flash chamber after the release of the fixed gases and process steam. The effluent discharged from the last flash chamber is at an elevated temperature of about 200 degrees Fahrenheit. Although liquors are normally discharged from the pulping process at approximately 190 degrees Fahrenheit and may be supplied to the reactor at this temperature, my process will operate efficiently when supplied with liquor cooled to normal room temperature, that is, approximately 70 degrees Fahrenheit. If it is desired to preheat the colder liquors, the effluent discharged from the flash chamber may be utilized as a source of heat by means of a heat exchanger for heating these incoming liquors. In this manner, less of the heat generated in the reactor needs to be utilized to raise the fresh liquor to the temperature at which autogenetic oxidation will occur. This heat energy may be conserved to develop greater quantities of process steam. Heat may also be conserved by insulating the reactors and piping. These structural refinements in the equipment for carrying out my process are improvements directed at increasing the efficiency of my process and do not affect the fundamental principle of the process whereby an oxidation of dilute aqueous combustible substances may be successfully accomplished.

It will be seen that the oxidation of the combustible material is accomplished by flameless autogenetic oxidation utilizing the waste liquor directly as it is discharged from the pulping process. No concentration of raw liquor is needed. I have found that my process is capable of exothermally oxidizing aqueous combustible dispersions having a B. t. u. value greater than the specific heat requirement of water at the temperature at which the oxidation becomes self sustaining. During the actual

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process of oxidizing the combustible materials, the liquor is heated by the energy given off in the oxidation reaction. The quantity of liquor vaporized in the reactor zone is determined by the pressure maintained therein. The energy absorbed by this vaporization produces useful process steam and, as such, the energy is productive of a valuable end-product of the process rather than absorbed by an essential operating requirement of the process itself. Since the specific heat of water, in its liquid state is relatively small, many times less than the latent heat of water in its gaseous form as steam, the operating energy requirements of my oxidation process are less than that of any process requiring the vaporization even of small quantities of water.

Within the reactor a heat exchange occurs. The aqueous system is preserved therein and upon the liberation of heat energy from the reaction the heat is transferred to the water, converting the water to vapor and the energy laden vapor is carried off from the reactor in the non-condensible gases present because of the low specific heat of the non-condensibles. No solid barrier exists between the contact of water in the area of reaction and heat transfer and transmittal is accomplished with an actual increase in available energy over conventional energy transformation procedures where there is no ultimate water contact and no non-condensible carriers. The absence of such a barrier made possible by this heat exchanger concept, eliminating a thermal metallic heat exchange barrier, avoids hitherto difficult sealing and corrosion problems inherent in conventional heat exchangers. The utilization of this transferring and transmitting conception where non-condensible gases are present with water is also the basis for preheat advantage. The following explanatory data will illustrate the role of admixing non-condensible gases and water to enhance the heat transfer characteristics of the admixture of water and non-condensible gases prior to admission of the same into the reactor. This materially reduces the energy required within the reactor necessary for maintaining required heat of ignition and thus contributes to the overall efficiency of the energy-producing system.

### PREHEAT EXPLANATORY DATA

Ten pounds of water was heated to 500 degrees Fahrenheit at 1000 p. s. i. a. pressure and absorbed 4878 British thermal units. It could not absorb more British thermal units because that is the limit of the specific heat of water at that temperature.

Ten pounds of air was heated to 500 degrees Fahrenheit at 1000 p. s. i. a. pressure and abstracted from the heat medium maintained at 500 degrees Fahrenheit 1160 British thermal units.

The total amount of British thermal units abstracted from the heating medium maintained at 500 degrees Fahrenheit is 6038 British thermal units. This is all the energy that can be extracted from a heat exchanger medium that will heat the two materials up to 500 degrees Fahrenheit.

By mixing the air and water before passing it through the heat exchanger the air is heated and requires about 1160 British thermal units. The water available is being volatilized and abstracts 12,174 British thermal units from the heating amount and gives steam which is slightly superheated.

Thus 13,334 British thermal units are extracted by mixing the two components before entering the heat exchanger. Without admixing the gas with the water only 6038 British thermal units can be extracted.

By maintaining a back pressure of 1000 pounds per square inch ten pounds of water were heated to 500 degrees Fahrenheit abstracting 4878 British thermal units. Five pounds of similarly heated air abstracted 580 British thermal units for a total of 5458 British thermal units when heated separately.

By combining the air and gas before the heat exchange

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the five pounds of air contains 580 British thermal units. 7.95 pounds of steam resulted containing 9550 British thermal units and 2.05 pounds of water with 1020 B. t. u. for a total of 11,150 British thermal units.

Examples at other pressures and temperature and varying ratios of water to air showed corresponding results.

It will thus be observed that exchange efficiencies are enhanced by mixing non-condensible gases with water prior to admitting the admixture to the reactor and in the preheater. This illustration serves as well to illustrate the enhanced heat exchange principle within the reactor continuously accompanying the oxidation process.

The following example illustrates the use of my process:

The apparatus used consisted of a pump for the aqueous carbonaceous dispersion; an air compressor; an oil-jacketed tower reactor, provided with means to remove periodically any precipitate therein; and, a flash chamber to receive the reaction product from the reactor.

In starting up the apparatus, air under a pressure of about 1500 pounds per square inch gauge was admitted to the reaction system. The oil bath around the reactor was heated to about 536 degrees Fahrenheit and the reactor filled about two-thirds full of waste sulfite liquor.

Lime sufficient to convert the sulfur in the waste sulfite liquor to calcium sulphate had been added. The liquor had the following analysis:

| | Pounds/Gallon |
|---|---|
| Solids content | [1]0.75 |
| Carbon | 0.268 |
| Sulphur | 0.040 |
| Calcium oxide | 0.80 |
| Ash | 0.190 |
| Oxygen demand (iodate value) | 0.865 |

(pH—9.4; Specific gravity—1.042.)

[1] 8,000 B. T. U. per pound.

When the liquor in the reactor reached a temperature of about 518 degrees Fahrenheit, sufficient liquor was pumped into the reaction system to fill the same with liquid. The heating of the oil was discontinued and air was continuously supplied to the reactor at a pressure of about 1500 pounds per square inch gauge and a temperature of about 186 degrees Fahrenheit. The rate of air supply was 300 pounds per hour, providing 69.5 pounds of oxygen per hour. Waste liquor at a temperature of about 65 degrees Fahrenheit was pumped into the reactor under a pressure of about 1500 pounds per square inch gauge at a rate of about 78 gallons per hour.

The precipitated calcium sulphate was periodically removed from the reactor. The liquor leaving the reactor was passed into the flash chamber. From this chamber the fixed gases, i. e., nitrogen, carbon dioxide, and any excess air, were bled off with steam at about 1500 pounds per square inch gauge. The liquid effluent from the flash chamber and the condensate steam with the fixed gases had an oxygen demand less than two percent of the oxygen demand of the raw waste sulfite liquor.

The effluent from the flash chamber amounted to 5.8 pounds per gallon of liquor fed to the reactor and was at a temperature of 540 degrees Fahrenheit. The flash contained 2.2 pounds of water per gallon of liquor fed, under a pressure of 1500 pounds per square inch gauge. The heat balance on a run of 171 gallons shows:

| Input: | B. T. U. |
|---|---|
| 171 gallons × 0.75 pounds solids per gallon × 8,000 B. T. U. | 1,026,000 |
| Recovered: | |
| 375 pounds of steam (540° F.) × 1160 B. T. U. and the heat increment in noncondensibles | 504,000 |
| 992 pounds effluent (540° F.) × 504 B. T. U. | 500,000 |
| | 1,004,000 |

The figures were checked by the rise in the temperature of the cooling water through which the effluent and flash condensate were passed. This shows an actual recovery of 93.4 percent of theory of the fuel value of the combustible material in the form of useable heat energy, which figure while well above the figure possible by other processes of combusting such materials, is even higher in large scale equipment due to a decrease in radiation loss particularly.

In a manner similar to that just described for sulphite waste liquor, I have operated my process utilizing "Masonite" wood waste liquor, whey from cheese plants, "Kraft" liquor, number three fuel oil at a concentration of 0.556 pound per gallon of water, and aqueous coal dispersions. While the minimum starting or ignition temperatures varied somewhat, the process operated smoothly and at efficiencies of 95 percent or better of theory in each instance at temperatures of 500 to 550 degrees Fahrenheit.

Using substantially the same apparatus as in example one, but utilizing a jacketed preheater, a run was made with semi-chemical waste liquor to illustrate operation where the temperature in the reactor was maintained at about 320 degrees Fahrenheit and the back pressure maintained at about 200 pounds per square inch. In this run, steam and reaction products were drawn off from the reactor and a separator used to extract the liquid water and unoxidized material from the material withdrawn and these were returned to the reactor. The noncondensible gaseous products, carbon dioxide and nitrogen, and water vapor were then cycled through the preheat exchanger and then into a separator from which the non-condensibles were recovered. Energy beyond the requirements of the preheater was available for work. The flow of feed liquor was adjusted so that the reactor was maintained about three-fourths full of liquid. The amount of combustible material maintained in the reactor during the run was approximately forty times the amount of combustible material in the liquor fed into the reactor each hour. Air containing sufficient oxygen to oxidize completely all of the combustible material in the feed liquor was introduced simultaneously with the liquor. The oxidized products removed from the reaction zone balanced stoichiometrically the combustible materials in the feed liquor. Over the course of several hours various runs demonstrated results as to reduction of oxygen demand of the feed liquor compared to the effluent comparable to that obtained in example one.

It will be understood that the particular results secured depend upon the nature of the dispersion of combustible material or liquid waste effluent undergoing treatment and particularly the amount, i. e., concentration of oxidizable organic or combustible matter which is present. This must be sufficient at least to supply enough heat energy upon oxidation to maintain the temperature in the reactor zone above the ignition temperature of the particular material being treated and is readily calculable from the B. t. u. value of the solids in the aqueous dispersion. The precise temperature and pressure required to initiate and sustain a self-sustaining oxidation reaction depend, in part, upon the chemical characteristics of the particular combustible material selected. While I have referred above to the use of compressed air as my oxidizing agent it is to be understood that compressed diluted oxygen or any other compressed gaseous oxidizing agent containing free oxygen or elemental oxygen-furnishing material may be utilized. These and other changes in my process and each of the modifications are to be considered as included within the scope of the hereinafter appended claims except as said claims by their language expressly provide otherwise.

The following explanatory data will illustrate further the general import of the minimum concentration aspects of the invention.

## EXPLANATORY DATA

(A) Ten grams of relatively finely ground charcoal, selected because it illustrates a substantially pure chemical which oxidizes almost completely to gaseous end products, was put into one liter of water and placed in an autoclave with the amount of oxygen theoretically required to convert all of the carbon in the charcoal to carbon dioxide. The temperature was established at 250 degrees centigrade and 800 pounds per square inch pressure. The degree of oxidation after thirty minutes was 56 percent.

(B) Two hundred grams of relatively finely ground lignin charcoal was put into one liter of water in the same autoclave used in A (above) and under identical conditions of temperature and pressure, i. e., 250 degrees centigrade and a pressure of 800 pounds per square inch with the amount of oxygen theoretically required to convert ten grams of the charcoal to carbon dioxide. After thirty minutes, the autoclave was chilled to room temperature and the content analyzed. Approximately ten grams of the charcoal (carbon) had been converted to carbon dioxide, using all of the available oxygen.

(C) A suitable reactor was devised for translating the results of the static experiments A and B (above) into a dynamic continuous process. Two hundred grams of relatively fine ground lignin charcoal was placed in the reactor with one liter of water. The reactor was maintained at 250 degrees centigrade and 800 pounds per square inch pressure. The liquid level was observed through a sight glass and maintained constant by the regulation of suitable heating and cooling devices. Ten grams of charcoal suspended in water was fed continuously at a uniform rate into the reactor each thirty minutes, together with air containing the required quantity of oxygen theoretically necessary to convert ten grams of charcoal (carbon) to carbon dioxide every half-hour. Analysis showed ten grams of the charcoal was oxidized to carbon dioxide each thirty minutes.

The run was continued as above for one hour and almost exactly 20 grams of charcoal was completely oxidized and vented from the reactor as carbon dioxide, as evidenced by analysis of the exit gases and residue from the reactor.

It will be seen from the above data that, from the point of view of the oxidation occurring in the reactor, oxidation is therein incomplete. But, from the point of view of the amount of combustible materials continuously introduced to the reactor, the oxidation is complete, since the products withdrawn are stoichiometrically equal to the amount of material fed into the reactor.

The explanatory data also shows that, by increasing the amount of combustible material within the reaction zone, the rate of oxygen consumption is increased independently of temperature and pressure. The permissible concentration of the oxidizable material in relation to the water in the reaction zone is governed by the physical properties of this concentration especially as regards viscosity. The viscosity must always be low enough to permit easy passage of gases and a smooth absorption of oxygen as well as a smooth segregation of the ash as it forms.

The above explanatory data alone does not illustrate the type of material which places the invention to the test of demonstrating its effectiveness when the effluent treated is not oxidizable completely to gaseous form and where the effluent might contain some non-combustible material. Such residual non-combustible matter, which may be soluble or insoluble in water is called "ash." The following example will illustrate the treatment of a material in liquid water which contains combustible and non-combustible substances.

(D) One gallon of semi-chemical liquor was used, weighing 8.90 pounds. It contained 1.11 pounds of solids (decomposition products of a wood cook, such as sodium lignin sulfonate, sodium acetate, carbohydrates, sodium

sulfite, et cetera) and 7.79 pounds of water. It was placed in an autoclave in the presence of 3.55 pounds of air. The temperature was established at 250 degrees centigrade and a pressure of 800 pounds per square inch was maintained. No noticeable oxidation was observed in one minute and only a slight oxidation occurred in twenty minutes.

(E) The concentration of semi-chemical waste liquor was increased four times, so that a liquor which contained 4.44 pounds of solids to the gallon of solution was obtained by removal of water from raw liquor. One gallon of this concentrate was placed in the autoclave used in D (above) and under identical conditions of temperature and pressure, i. e., 250 degrees centigrade and 800 pounds per square inch pressure, with air containing the oxygen theoretically required to oxidize completely the combustible material in one gallon of liquor prior to concentration. After twenty minutes, analysis showed the oxygen demand of the material had decreased by one-quarter.

(F) From the experimental results of D and E (above) it will be observed that the rate of oxidation of the combustible materials is markedly increased by an increase in the concentration of the same in liquid water.

A suitable reactor was then devised for translating the results of the static experiment into a dynamic continuous process. A gallon of the concentrated semi-chemical liquor which contained 4.44 pounds of solids was placed in the reactor. The reactor was maintained at 250 degrees centigrade and 800 pounds per square inch pressure. The liquid level was observed through a sight glass and the level of the liquid was kept constant by the regulation of suitable heating and cooling devices. Raw semi-chemical waste liquor was continuously introduced into the reactor with air containing the oxygen theoretically required to oxidize completely all of the combustible materials in the feed, so as to maintain within the reactor an amount of combustible material having substantially the same oxygen demand as the original reactor charge after equilibrium conditions are established. The reaction products were vented from the reactor and sufficient energy was generated by the oxidation reaction to sustain the reaction temperature in the reactor, provide preheat energy, and an excess of energy in utilizable form. The reaction products were nitrogen, water vapor, carbon dioxide, and sodium sulfate, the latter removable as ash, or rendered soluble at other stages and removed as a solution. The following chart illustrates material balance on a per gallon feed basis for a prolonged run under the conditions above-described:

### Input—Pounds

| | |
|---|---|
| Liquor | 8.90 |
| Solids—1.11 | |
| Water—7.79 | |
| Air | 3.55 |
| | 12.45 |

### Output—Pounds

| | |
|---|---|
| $N_2$ | 2.73 |
| $CO_2$ | 1.04 |
| $O_2$ | 0.07 |
| Steam ($H_2O$ vapor) | 6.16 |
| Ash | 0.45 |
| Water | 2.00 |
| | 12.45 |

As a consequence of static experimentation it was discovered that every combustible material has a minimum practical oxidation temperature; i. e., that temperature below which substantially no oxidation will occur irrespective of concentration. An extreme example of this is seen when it is understood that at temperatures as low as 150 degrees centigrade the bulk of the materials in waste liquor can be oxidized at a rate dependent upon the concentration of the substance in water, i. e., the amount

of the material in the reaction zone. The rate of complete oxidation can be changed within wide limits using the same reactor, temperature and pressure, by varying the amount of combustible material originally placed into the reaction zone.

Referring now to the actual continuous oxidation within a reaction zone a balance of water and non-condensible gases must be maintained to accomplish efficient exchange. As the latent energy in the combustible material is liberated by oxidation under static conditions of temperature and pressure the water must be available for intimate contact with the reaction and for transferring the energy liberated into useable form, i. e., enhanced partial pressure of steam. The role of the non-condensible gases present (nitrogen, oxygen, carbon dioxide, et cetera) is to carry off the energy-laden water vapor as it is formed so as to accomplish efficient exchange with substantially no heat loss. The low specific heat of the non-condensible gases makes the non-condensible gases peculiarly well adapted to act as vehicles for carrying off the energy liberated by the reaction and act as an elastic medium for shock conditions of energy liberation occurring within the reactor. The non-condensible gases present way be reaction-produced gases or they may be, as in the case of nitrogen where air is used as an oxidizing agent, unused gaseous fractions of materials fed into the reactor. Expressed in terms of water, the ratio of liquid water to combustible material must be maintained at least above that necessary to absorb the energy available from the reaction by continuous vaporization of water from the aqueous system. Expressed in terms of the ratio of non-condensible gases to the entire water available in the aqueous system, the ratio of non-condensible gases to the aqueous system in the reaction zone under static conditions of temperature and pressure must be at least that ratio necessary to insure absorption of the exothermally liberated energy by the water vapor transferred to enhanced partial pressure and carried off by the non-condensible gases. The explanatory data with respect to the preheating of an admixture of air and water illustrates adequately the enhanced efficiency of a thermal heat transfer where a non-condensible gas is admixed with water. This phenomena, carried into the reactor, creates a heat exchanger of extremely high efficiency. Thus, by maintaining the ratio of non-condensible gases to the aqueous system in a reaction zone under static conditions of temperature and pressure above at least that ratio necessary to insure absorption of the carbonaceous exothermal liberation of energy by water vapor transmission to the partial pressures of the non-condensible gases and water vapor, energy from an oxidation reaction is made utilizable and a heat exchanger has been devised eliminating the need for a solid thermal metallic barrier in the preheater and in the reactor.

While the description has proceeded with particular reference to waste sulfite liquors the process herein disclosed is equally applicable to all wastes containing combustible materials in aqueous dispersions. The invention can be utilized whenever the nature of the waste effluent is such that it contains combustible matter susceptible of being complete or substantially completely oxidized to innocuous end-products under relatively moderate temperature and pressure conditions. While it is not practicable to give an exhaustive summation of the various liquid waste effluents to which the present invention can be applied, the uses are many and include waste sulphite and Kraft liquors resulting from paper and pulp mill operations, the waste resulting from sewage disposal systems, the waste effluent resulting from slaughterhouse operations, the waste produced by plants manufacturing synthetic or other chemicals or products such as plastics, rubber, dyes, pharmaceuticals, et cetera, and the liquid waste materials resulting from the production of various products from milk and milk solids. The construction of any commercially feasible plant requires only the adjustment

and maintenance of the initial reactor charge in order to adapt itself to any volume program. Where products difficult to oxidize are present the minimum temperatures of oxidation of the various components are simply determined by static tests as outlined and an operable concentration selected for the reactor stages wherein the unoxidized fraction is treated independently of the whole of the liquor.

Having thus described a process for the continuous oxidation of organic waste material in an aqueous dispersion, I claim:

1. In a process for continuously oxidizing combustible materials dispersed in liquid water, the steps for capacity regulating which include: charging into a reaction zone a concentrated aqueous dispersion of combustible matter; introducing into said reaction zone a continuous feed of combustible materials dispersed in liquid water having a heat value concentration less than said reaction zone charge; introducing simultaneously into said reaction zone with said feed a continuous feed of an oxygen-containing gas in a stoichiometric amount to oxidize substantially completely all of said combustible materials in the feed; pressurizing said reaction zone to maintain at the temperature of the reaction at least some of the water therein in the liquid phase; varying the fuel value concentration of the charge in the reaction zone inversely proportional to the ratio of combustibles to water in the feed; regulating the introduction of feed and gas to said reaction zone at the rate of production of reaction products in the reaction zone to maintain the ratio of combustibles to water in the reaction zone; and, withdrawing reaction products, fixed gases and water vapor from said reaction zone equivalent to the rate of introduction of reactants in the feed to the reaction zone.

2. In a process for continuously oxidizing combustible materials dispersed in liquid water, the steps for regulating which include: providing in a reaction zone a charge of combustible materials dispersed in liquid water wherein the combustible materials are sufficient in amount to supply at least the heat energy, upon substantially complete oxidation thereof, to maintain the temperature in the reaction zone above the autogenetic oxidation temperature at the rate at which a lower heat valve concentration dispersion is fed to the reaction zone; introducing into said zone an aqueous dispersion of combustible material having a heat value concentration less than said charge; introducing simultaneously a continuous feed of an oxygen-containing gas in amount stoichiometrically required to oxidize substantially completely all of said combustible materials in the feed; initiating in said reaction zone a flameless reaction proceeding at the rate at which said dispersion and gas are being fed to said zone; pressurizing the said zone to maintain at least some of the water therein always remains in the liquid phase; withdrawing from said reaction zone water vapor, fixed gasses and the reaction products at a rate which balances stoichiometrically the rate at which the dispersion and the oxygen-containing gas are fed to the reaction zone and varying continuously the ratio of combustible material to water in the reaction zone in response to variations of the ratio of combustibles to water in the feed material.

3. In a process for continuously oxidizing combustible materials dispersed in liquid water as set forth in claim 1 wherein heat from an external heat source is applied to said reaction zone to establish a flameless reaction in said reaction zone applying said heat until the reaction proceeds at the rate at which said dispersion and gas are being fed to said zone.

4. The process for regulating the capacity of a continuous flameless autogenetic oxidation process for combustible materials dispersed in water in a reaction zone which includes: charging a reaction zone with a concen-

tration of combustible material to water at least above the concentration of the feed; continuously passing a feed of combustible material dispersed in liquid water and an oxygen-containing gas into said reaction zone under superatmospheric pressure; withdrawing combustion products and water vapor at a rate which balances stoichiometrically the rate at which the combustible material and oxygen-containing gas are fed to said reaction zone to maintain the concentration of the charge of the reaction substantially constant in a ratio proportionally above the heat value concentration of the feed.

5. In a process for capacity regulation of an aqueous phase autogeneous oxidation of combustible material dispersed in water, the steps comprising: introducing into a reaction zone an aqueous dispersion of organic matter, having a heat content concentration substantially greater than that of an aqueous dispersion which is to be fed to the reaction zone, to establish a reaction mixture which will promote aqueous phase autogenous oxidation; introducing in a continuous manner into said reaction zone an aqueous feed having a heat content concentration substantially less than that first introduced into said reaction zone and in an amount equal to the rate of production of reaction products while simultaneously introducing with said feed an oxygen containing gas in an amount at least stoichiometrically sufficient to oxidize all of said combustible matter in said feed; pressurizing the reaction zone to maintain at least a part of said aqueous dispersion in the liquid phase at the autogenous oxidation temperature; and withdrawing reaction products, fixed gases and water vapor in an amount substantially equal in weight and heat content to that of the feed.

6. In a process for capacity regulation of an aqueous phase autogenous oxidation of combustible materials dispersed in water as set forth in claim 5 wherein said reaction zone dispersion heat value concentration is varied substantially inversely proportional to the heat value concentration of said feed and substantially directly proportional to the volume of said feed.

7. In a process for continuously oxidizing combustible materials dispersed in liquid water, the steps for regulating capacity which include: charging into a reaction zone a concentrated aqueous dispersion of combustible matter; introducing into said reaction zone a continuous feed of combustible materials dispersed in liquid water having a heat value concentration less than said reaction zone with said feed charge; introducing simultaneously into said reaction zone a continuous feed of an oxygen containing gas in a stoichiometric amount to oxidize substantially all of said combustible materials in the feed; pressurizing said reaction zone to maintain at the temperature of the reaction at least some of the water therein in the liquid phase; varying the fuel value concentration of the charge in the reaction zone inversely proportional to the ratio of combustibles to water in the feed; regulating the introduction of feed and gas to said reaction zone at the rate of production of reaction products in the reaction zone to maintain the ratio of combustibles to water in the reaction zone; withdrawing reaction products, fixed gases and water vapor from said reaction zone equivalent to the rate of introduction of reactants in the feed to the reaction zone; and converting at least a part of the heat energy in the gases withdrawn from the reaction zone to mechanical energy; and, recycling at least a portion of said heat energy to preheat the incoming dispersion of feed to the reaction zone.

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