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Process for ozonating and converting organic materials into useful products

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(54) **PROCESS FOR OZONATING AND CONVERTING ORGANIC MATERIALS INTO USEFUL PRODUCTS**

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(58) **Field of Search** 435/167, 42

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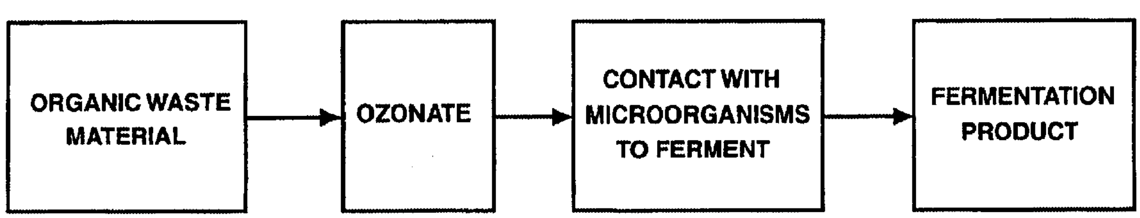
(57) **ABSTRACT**

A process for converting organic waste materials into useable products and products thereof is disclosed. According to the process, organic waste materials are contacted with ozone thereby converting said waste material to a substrate or medium. The substrate is a product of the process and it may be further contacted with organisms for bioconversion to further products. The organisms can include bacteria, yeast, fungi, plant cells, animal cells and genetically engineered organisms which are selected for their ability to bioconvert the substrate and produce a selected product.

15 Claims, 3 Drawing Sheets



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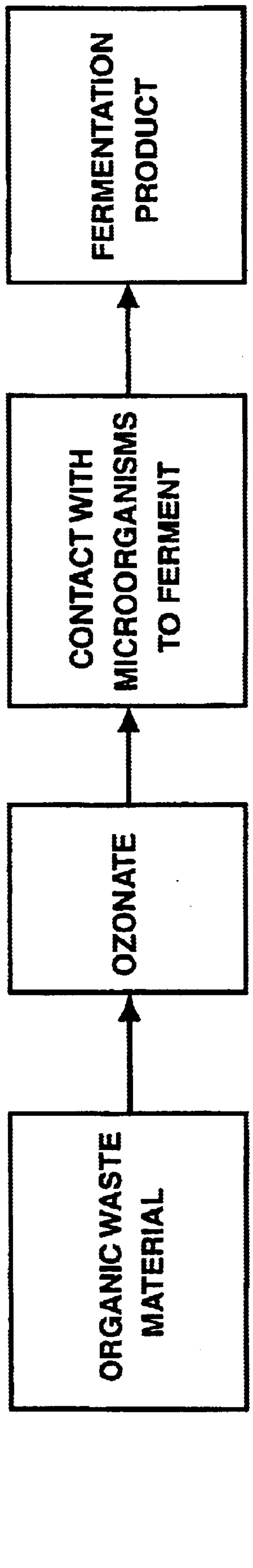
ORGANIC WASTE
MATERIAL
OZONATE
CONTACT WITH
MICROORGANISMS
TO FERMENT
FERMENTATION
PRODUCT

FIG. 1

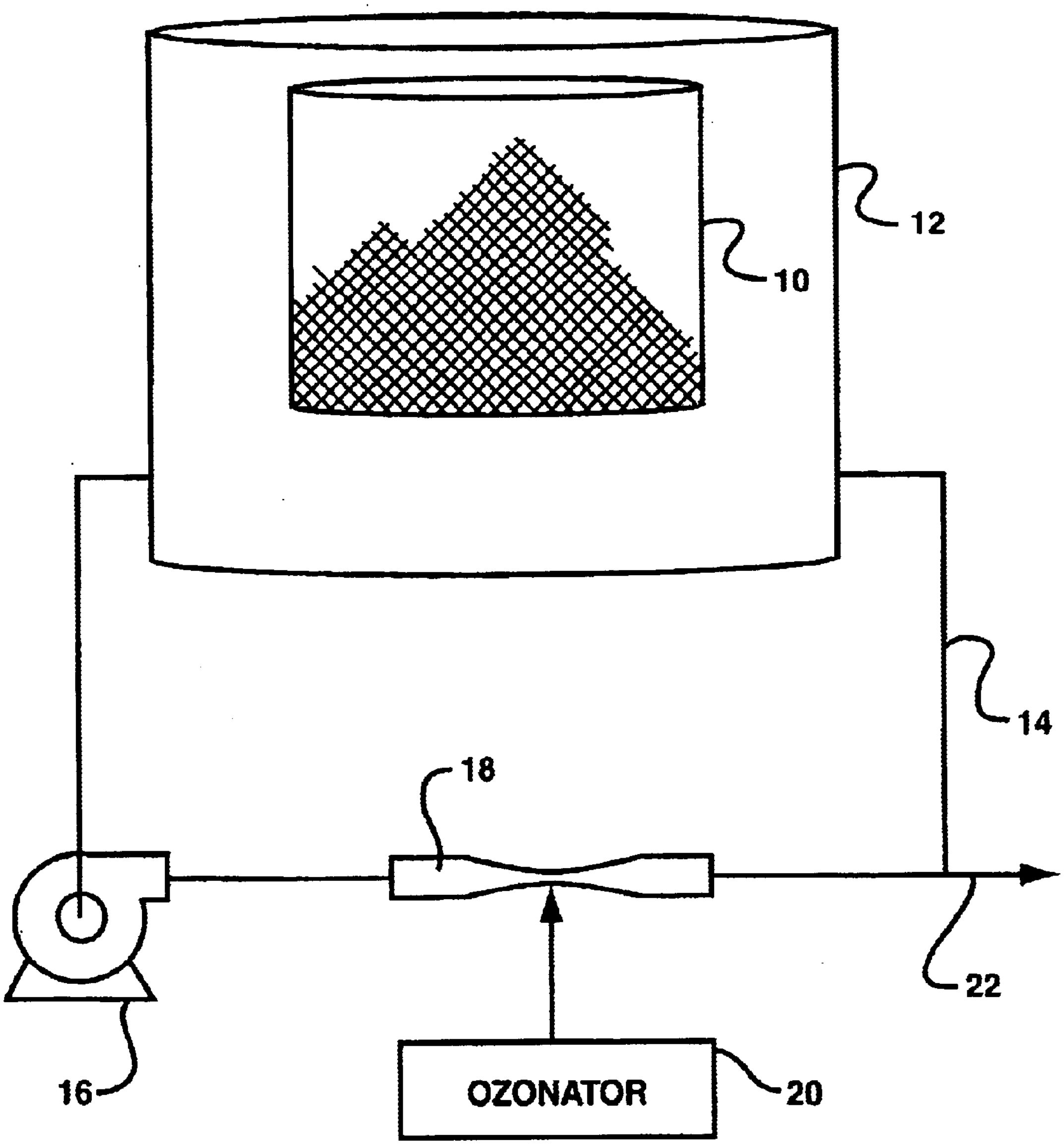

FIG. 2

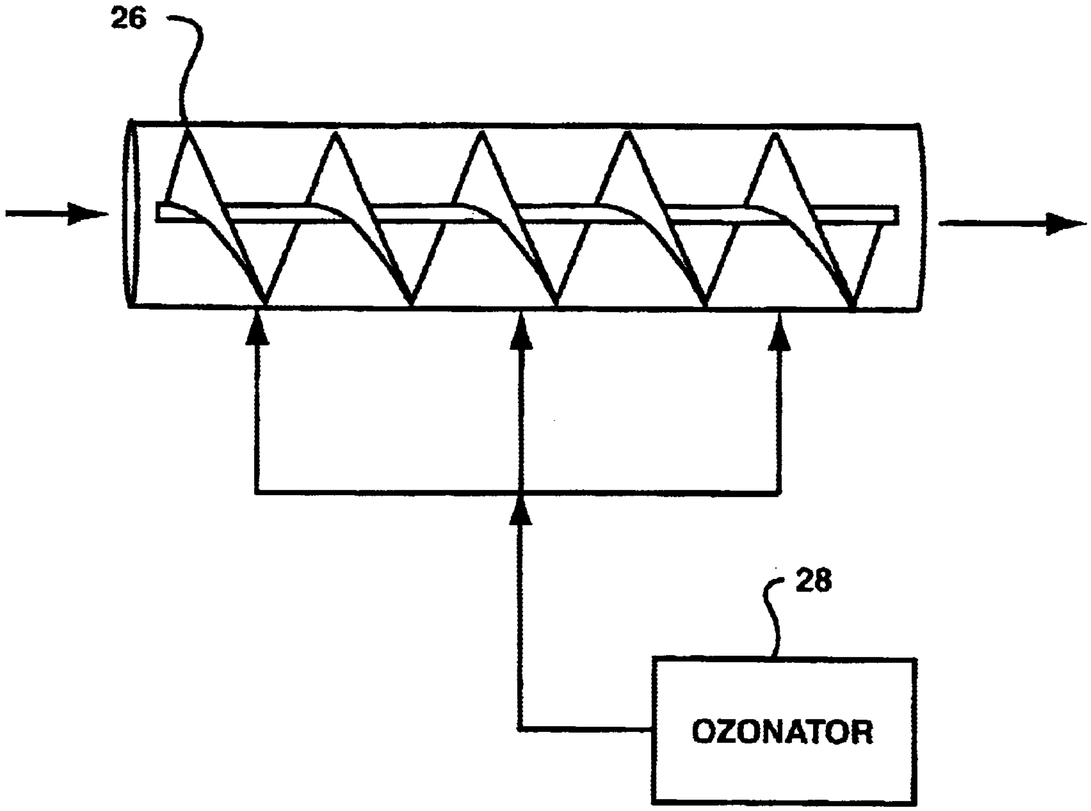

FIG. 3

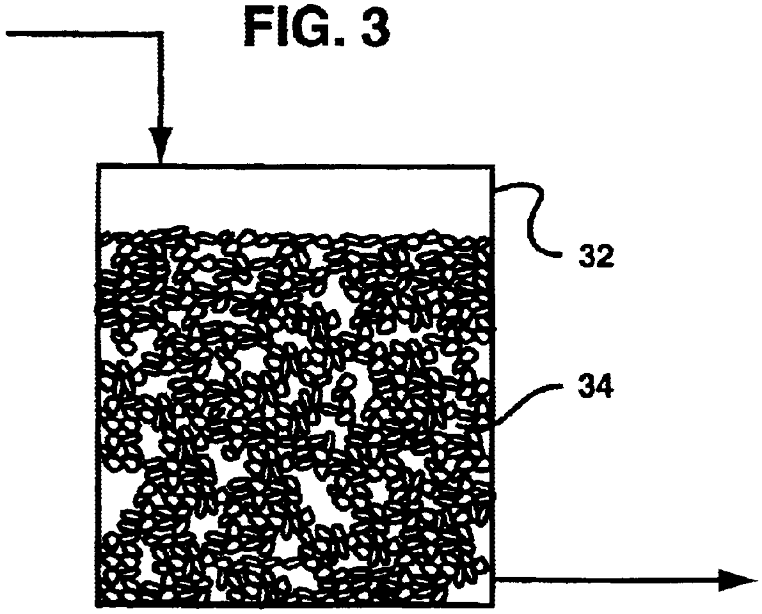

FIG. 4

PROCESS FOR OZONATING AND CONVERTING ORGANIC MATERIALS INTO USEFUL PRODUCTS

BACKGROUND OF THE INVENTION

Virtually all types of human activities generate various types of waste or by-product materials. Many of these materials can be processed to yield substrates that are or may be readily converted into a useful product. Such conversion is desirable for at least three interrelated reasons. First, conversion reduces the load of material that ultimately must be disposed of via traditional waste management methods; second, conversion saves natural resources by more fully utilizing raw products; and third, conversion not only may save energy but may in fact contribute to the supply of energy yielding materials.

Waste has varied forms and characteristics. In terms of the regulation of waste disposal pursuant to federal statutes, rules and regulations, many waste materials are characterized as municipal solid waste pursuant to 42 USC 691 et seq. Other categories of waste materials include animal waste either as it exists in confined animal production facilities or as it may be found in confinement ponds or lagoons. Other wastes from specific industries that may, but are not necessarily included as municipal solid waste, include materials produced during food processing and rendering, wood and timber processing, and chemical and petroleum manufacturing and processing.

A need currently exists for an improved process and system for disposing of waste materials. In particular, a need exists for a process that can recycle and/or convert the materials into useful products.

SUMMARY OF THE INVENTION

In general, the present invention is directed to a process and system for producing useable products from organic materials, such as waste materials. For example, in one embodiment, the process of the present invention is directed to producing ethanol from organic waste materials. In this example, the process includes the steps of first collecting waste materials from various sources. The organic waste materials may include lignocellulosic materials, proteinaceous materials, carbohydrate materials, chitin waste materials, household garbage, restaurant waste, agricultural and forestry waste, petroleum or chemical manufacturing waste, or waste water. Any organic-bearing compound that can be oxidized may be used as a starting material. Waste materials can be pre-separated into organic and inorganic materials. If necessary, the waste materials can first be reduced into a smaller size by any of a variety of means such as shredding or grinding. Further, water can also be added to form a slurry that can be subsequently treated. In this slurry, organic materials exist in suspension and/or in true solution.

Once the slurry or solution containing the organic waste materials is prepared, the slurry is contacted with ozone. The ozone is present is an amount sufficient to convert at least a portion of the organic waste materials into a medium capable of being converted further by an organism, such as being converted into a fermentable medium. For most applications, the ozone should be fed to the aqueous solution at a concentration of at least 0.01 ppm. Desirably, for most applications, the ozone is fed at a concentration close to saturation. In order to increase the amount of ozone that is dissolved into the slurry/solution, the slurry/solution can be cooled if desired. In order to maximize oxidation after

dissolution of ozone, the slurry/solution may be warmed to increase the rate of degradation of ozone to molecular oxygen and free radical oxygen.

During ozonation, the organic waste materials are oxidized and degraded into less recalcitrant materials. Complex carbohydrates such as cellulose are oxidized into a mixture of smaller molecules including sugars. Before, during or after ozonation, a base, such as a metal hydroxide, or an acid, can be added to the slurry to adjust the pH of the solution. By the ozonation process, the slurry is converted into a medium that is capable of sustaining biological metabolic processes.

After ozonation, the medium can be separated from any undissolved solids. Next, the medium is contacted with organisms which are capable of using the medium to produce a product. In one embodiment, microorganisms are contacted with the medium which causes the medium to undergo fermentation. For instance, microorganisms can be selected so as to produce ethanol from the fermentable substrate. The ethanol can then be collected and used as desired. Ethanol is known to be an effective energy source.

In order to collect the ethanol, the ethanol can be separated from the remainder of the aqueous solution. For instance, the solution produced after fermentation can undergo a distillation process for isolating the ethanol. One skilled in the art will recognize that there are many other ways of collecting products including centrifugation, temperature fractionalization, chromatographic methods and electrophoretic methods. Some products may be gaseous and can be collected by typical gas collection methods.

In another embodiment of the present invention, instead of being converted into ethanol, the oxidized waste materials can be converted into a hydrocarbon gas, such as methane. For example, a genus of methane-producing bacteria is Methanobacterium. In this embodiment, the converted medium can be fed directly to the methane-producing organism or, alternatively, the medium can first be converted into ethanol and then fed to the methane-producing organism. Once produced, the methane can be collected in various ways and used as desired.

It should be understood, however, that the process of the present invention can be used to produce other useful products through bioconversion in addition to alcohols and hydrocarbon gases. For example, the products produced by bioconversion of the substrate can be altered by varying the organisms used in the system. The organisms contacted with the slurry can be carefully collected in order to optimize process conditions. The organisms can be, for instance, bacteria, yeast, fungi, algae, genetically engineered microorganisms, or tissue culture. Both prokaryotic and eukaryotic organisms or mixtures thereof can be cultured in the ozonated substrate. The product may be intracellular or extracellular in nature. The product may be particulate, liquid or gaseous. The product may be miscible or immiscible in water. Other products that can be formed according to the present invention include other alcohols, aldehydes, ketones, organic acids, purines, pyrymidines, alkanes, alkenes, alkynes, ethers, esters, amines, proteins, amides, cyclic and aromatic compounds, enzymes, pigments, lipids, phospholipids, peroxides, gums, pharmaceuticals such as vitamins, microbial cellulose and other polymers.

Any of the oxidized and converted organic materials that are not used in the process can be fed to a plant system, such as an algae system, and used for irrigation and/or as a food source. The plant system can also remove inorganic and/or heavy metal substances. If necessary, prior to being fed to the plant system, the aqueous solution containing the converted organic materials can be reozonated.

Other features and advantages of the present invention will be apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

A full and enabling disclosure of the present invention, including the best mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figures in which:

FIG. **1** is one embodiment of a flow chart of a process for converting organic waste materials into a useful product;

FIG. **2** is one embodiment of a process for ozonating organic waste materials;

FIG. **3** is an alternative embodiment of a process for ozonating organic waste materials; and

FIG. **4** is one embodiment of a process for contacting ozonated waste materials with microorganisms for causing fermentation or another metabolic process.

Repeat use of reference characters in the present specification and drawings is intended to represent same or analogous features or elements of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations and their equivalents.

The present invention is generally directed to a two phase method that converts predominantly organic waste materials, such as animal waste, into useful byproducts. Following certain mechanical processing, the first conversion of the waste requires contacting the selected waste material with a strong oxidant to degrade organic materials to a bioconvertable substrate. The second conversion comprises respiration, fermentation, or photosynthetic metabolism of the substrate by an organism to yield a specific product. For example, complex plant hydrocarbons such as lignocellulose constitute a significant portion of dairy waste (fecal material). Ozonation of dairy waste oxidizes the complex hydrocarbon to a substrate that includes simple saccharides. The saccharides can be bioconverted by microorganisms such as yeast or bacteria to yield an alcohol (ethanol) which is a useful industrial/commercial product. It should be understood, however, that many other waste materials may be processed according to the present invention and many other various useful products can be formed.

As used herein, waste(s) refers to any substance that is no longer desired in its present state or location. One embodiment of a general flow diagram of the process of the present invention for converting waste materials is illustrated in FIG. **1**. Waste material **100** is pretreated and mixed with water to form a slurry **106**. The slurry **106** is ozonated thereby converting some of the slurry to a substrate or medium **110**. Substrate **110** is either prepared for commercial distribution **116** or is further processed by contact with an organism(s) **112** yielding a product **114**. If prepared for commercial distribution as shown in **116**, the product can be dried if desired. The dried ozonated product can be used in many useful applications, such as a fertilizer, even when not later contacted with organisms for bioconversion.

As will be described in more detail below, many and various diverse products can be produced according to the present invention. Depending on the product formed or created, the product can be collected, further processed as necessary, packaged, and then used as desired. For example, in one embodiment, the product formed according to the present invention can be ethanol which can be distilled and used as an energy source. In another embodiment, the process of the present invention can be used to produce methane or another hydrocarbon gas.

As shown, according to the present invention, various waste materials are first collected. The organic waste materials are particularized, if necessary, and placed in water to create a slurry, and subsequently contacted with ozone. If desired, the waste materials can be pre-sorted or preseparated prior to contact with ozone. For example, in one embodiment, inorganic materials, such as glass, metal, etc can first be removed prior to contact with ozone.

The ozone oxidizes the waste materials into a substrate that can sustain biological metabolic processes such as fermentation, respiration or photosynthesis. In particular, once contacted with ozone, the organic compounds are converted into substrates such as saccharides (sugars), that can be used as a growth medium for organisms. Alternatively, the oxidized waste can be contacted with a selected enzyme for conversion into a useful product.

After ozonation, the substrate is either collected for further processing or directly contacted with one or more specific organism or enzyme. As used herein, "organism" refers to any prokaryotic or eukaryotic organism including macro- and microorganisms and tissue culture. An organism used in the present invention can be a plant, a protista such as bacteria, a monera, or a fungus. The present invention also encompasses the use of genetically engineered organisms and microorganisms. The organisms carry out growth and metabolism thereby yielding a cellular product. As used herein, a cellular product refers to any intracellular or extracellular product produced by any respirative (aerobic or anaerobic), fermentative, photosynthetic or any similar growth process. In general, fermentation can be defined as an ATP-generating metabolic process in which organic compounds serve both as electron donors (becoming oxidized) and electron acceptors (becoming reduced). Respiration is an ATP-generating metabolic process in which either organic or inorganic compounds serve as electron donors (becoming oxidized) and inorganic compounds serve as the ultimate acceptors (becoming reduced). Photosynthesis refers to the conversion of energy from light to chemicals.

In accordance with the present invention, the organisms used in the process can be carefully selected so as to promote the production of a desired product. For example, in one embodiment, organisms can be selected that will convert the organic waste materials into ethanol. The ethanol produced according to the process can be collected and used. For example, ethanol is known as an effective energy source.

Various organisms can be used to convert the oxidized waste materials into ethanol. As described above, the organism can be a prokaryotic or a eukaryotic organism. One example of a bacterium that is known to produce ethanol from hydrocarbons is *Zymomonas mobilis*. An example of a yeast that is known to produce ethanol is *Saccharomyces cerevisiae*. It should be understood, however, that various other organisms known to produce ethanol can also be used in the process of the present invention.

It should be understood, however, that besides ethanol-producing microorganisms, other organisms can be selected so as to produce other types of microbial products. Such products include, but are not limited to, other alcohols such as alcohols containing one to nine, or greater, carbon atoms. Particular examples of alcohols that can be produced according to the process of the present invention include propanol, butanol, pentanol, hexanol, heptanol, octanol and nonanol. Besides alcohols, other products that may be produced include alkanes, aldehydes, ketones, organic acids and the like. The products described herein are presented as examples but not as limitation of the potential bioconversion products of organism growth on substrate.

The process of the present invention can also be used to form pharmaceuticals. Such pharmaceuticals can include vitamins, such as vitamin C. Other products include microbial cellulose and other useful polymers. Further, the process can also be designed to promote the production of lactic acid. Lactic acid can be used to produce, for example, biocompatible polymers. Other bioconversion processes include but are not limited to a two stage conversion process using yeasts with Acetobacter or Gluconobacter species for producing acetic acid. Growth of Propionibacterium on carbohydrates yields propionic acid. Microbial protein may be produced by growth of microorganisms on the oxidized substrate. Bacteriocins, unique antimicrobial proteins, may be produced by a wide variety of prokaryotic microorganisms grown on the substrate.

Other products of the present invention can include purines, pyrimidines, proteins, phospholipids, lipids, beta glucans produced from yeast, enzymes and pigments. One skilled in the art will recognize that these products may be integral components in the cell structure or, in some instances, particularly for the enzymes and pigments, may be excreted from the cell. Cell products may be the cells themselves such as valuable tissue culture organisms. Additional cellular products can include alkanes, alkenes, alkynes and cyclic versions of these. Esters, amines, amides, cyclic and aromatic compounds, alkanes, alkenes, alkynes, and gums may be produced by a variety of organisms. Ethers, although less common, are produced by certain organisms. Peroxides, such as hydrogen peroxide are produced by certain bacteria. Phospholipid is produced by many organisms, particularly in cell bound membranes. A variety of lipids, including hydroxybutyrate and hydroxyvalerate are produced by eukaryotic and prokaryotic organisms. These lipids have commercial value as starting materials for further syntheses. A number of organisms including but not limited to bacteria, yeast, fungi, and algae, produce pigments of commercial and scientific importance. Certain of these pigments are of use in research or in commercial manufacturing.

A wide variety of aromatic compounds are produced by growth processes of a variety of prokaryotic and eukaryotic organisms. Commercially valuable gums are produced by growth of organisms including but not limited to *Xanthomonas* sp. which produces xanthan gum. A number of enzymes may be produced by growth of selected prokaryotic and eukaryotic organisms on the substrate including but not limited to: amylases produced by species of *Aspergillus, Rhizopus* and *Bacillus*; catalase produced by species of *Micrococcus* and *Aspergillus*; cellulase produced by *Trichoderma* and *Aspergillus*; β-galactosidase (lactase) produced by *Kluyveromyces marxianus* and Aspergillus; invertase produced by *Saccharomyces cerevisiae* and *Candida utilis;* and lipase produced by *Aspergillus, Rhizopus, Penicillium* and *Candida*. Using eukaryotic organisms to bioconvert the substrate can yield a wide variety of products including pigments from algae, single cell protein from yeasts, DNA and RNA and other complex polymeric compounds. One skilled in the art will recognize that the above mentioned products may be produced as a result of respirative, fermentative or photosynthetic metabolic and anabolic pathways. The preceding bioconversion processes described herein are presented as examples but not as limitation of the potential bioconversion processes of organism growth on substrate.

As mentioned above, in one embodiment of the present invention, the oxidized waste materials can be fed to various plants, such as algae, for harvesting products produced by the plants. For example, in one embodiment, once the materials are oxidized, the oxidized medium can be fed to red algae, also known as *Rhodophyta*, in order to produce pigments. Specifically, red algae are red due to the presence of the pigments Phycocyanin and Phycoerythrin. Both Phycocyanin and Phycoerythrin fluoresce at a particular wavelength. Thus, the pigments are particularly useful for research. In addition, red algae contains high vitamin and protein content, making it attractive as a possible food source for animals and/or humans.

Besides red algae, another plant that can be grown from the oxidized medium is *Gelidium purpurascens,* which is a bright red seaweed. *Gelidium purpurascens* can be used as a source of agar for bacterial media, foods, etc.

Another useful substance that can be obtained from algae, such as Rhodophytes and Kelps is alginate. Alginates are gum-like substances that can be used in many useful and diverse applications. For example, alginates have an affinity for water and are commercially important in the production of paper, toothpaste, beer and frozen foods.

In still another embodiment of the present invention, the oxidized waste materials can be fed to an organism for the production of hydrocarbons, such as methane gas. As the methane gas is produced, the gas can be collected and used as a fuel source. For example, in one embodiment, the oxidized waste materials can first be converted into ethanol as described above. Once produced, the ethanol can then be fed to a microorganism which is adapted to convert ethanol into methane. An example of a genus of methane-producing bacteria is *Methanobacterium.*

In some applications, it should also be understood that the oxidized waste materials can be fed directly to a microorganism for the production of hydrocarbon gases.

Any recalcitrant organic waste molecule of biological or synthetic origin can be processed and converted according to the present invention. In other words, any organic material that can be oxidized may be used to produce cellular products as described above. Such organic waste materials can include municipal solid waste, restaurant and/or other food waste, discarded cotton products, animal waste materials, sewage, petroleum refining wastes, chemical manufacturing wastes, old tires, proteinaceous wastes, carbohydrate-containing wastes, lipid-containing wastes, pesticides, and waste water. Further, the organic waste materials can include any complex organic compounds such as lignin and lignocellulosic materials, proteinaceous materials such as cheese whey, any carbohydrates, lipids, chitin and chitosan materials, food processing plant waste, gums such as guar gum, oat hull, barley, hay, corn stover, corn stillage, bagasse, paper pulp, paper sludge, softwood and hardwood residues, and the like.

Depending upon the materials being processed, in one embodiment, the waste materials can first be pre-separated for removing, for instance, inorganic materials from the materials to be processed. Besides being pre-separated, the materials can also be sized prior to being contacted with ozone. For example, the waste materials can be ground, milled or pulverized as desired. Reducing the size of the waste materials will create more surface area to facilitate processing.

Once the waste materials have been selected and collected, the materials are ozonated. This process degrades the organic compounds contained in the materials into smaller organic compounds. In general, ozonation is carried out in an aqueous medium. As such, if desired, the waste materials can be combined with water prior to ozonation.

Many different methods can be used in order to contact the waste materials with ozone for decomposing the organic compounds. For example, in one embodiment, the waste materials can be contained within a tank and ozone can be fed toward the bottom of the tank and bubbled through the mixture. An example of this embodiment is described in the present inventor's prior application filed on May 27, 1999 and having U.S. Pat. No. 6,117,324, which is incorporated herein by reference in its entirety.

In another embodiment, if the waste materials are flowable, the waste materials can be fed through a line, such as a pipe, and contacted with ozone within the line. This embodiment is particularly well suited for use in continuous systems.

Another embodiment of a method for contacting the waste materials with ozone is illustrated in FIG. **2**. As shown, in this embodiment, the waste materials are placed in a porous container **10**. Porous container **10** can be constructed in various manners depending upon the size of the waste materials. For instance, the porous container can be made from a mesh or screen material or, alternatively, can be a solid structure with perforated walls.

As shown, porous container **10** is contained within a larger vessel **12**. Vessel **12** contains a liquid such as water which is circulated around a circulation loop **14** via a pump **16**. In this manner, the liquid flows through the porous container **10** causing organic compounds contained within the waste material to dissolve or be hydrated. Ozone is then fed into the circulation loop **14** for converting the organic waste materials into a fermentable medium. Residual ozone is transported via pump **16** back to vessel **12** where the ozone may contact organic compounds in container **10** to facilitate degradation of organic materials.

In this embodiment, in order to contact the solution containing the organic compounds with ozone, the system contains a venturi **18** in communication with an ozonator **20**. A venturi is generally described as a constriction that is placed in a pipe or tube that causes a drop in pressure as fluid flows through it. As shown in the figure, the venturi can include a straight section or a throat positioned in between two tapered sections. When used in the process of the present invention, the venturi draws the ozone into the main flow stream.

Using a venturi in the system of the present invention offers various advantages. For instance, the venturi allows the ozone to rapidly combine with the solution containing the organic compounds. Thus, a maximum amount of ozone can be dissolved into the solution. Further, better mixing between the ozone and the organic compounds is achieved using the venturi.

As shown in FIG. **2**, once the slurry has been ozonated to an extent desired, the resulting solution can be discharged from the system through discharge line **22** for further processing in accordance with the present invention.

Referring to FIG. **3**, still another embodiment of a system for treating waste materials with ozone is illustrated. In this embodiment, the system includes an auger **26** for receiving the waste materials. Auger **26** is configured not only to move the waste materials at a desired speed, but may also be is configured to reduce the size of the waste materials. As shown, the system further includes an ozonator **28** which feeds ozone into the auger to treat the materials. Ozone can be fed into the auger at a single location such as generally in the middle or, as shown, at multiple locations. Ozone also may be fed into the waste materials from one or more locations in the center of the auger shaft.

The embodiment illustrated in FIG. **3** is particularly well suited to ozonating waste materials that do not contain a substantial amount of fluids. For instance, the auger is well suited to receiving and sizing solid materials contained in a thick slurry.

In still a further embodiment of the present invention, ozonation of the waste materials can be carried out in a pressurized vessel. In this embodiment, a slurry or an aqueous solution containing the organic compounds can be placed in a vessel under pressure. Ozone can then be introduced into the chamber for breaking down the organic compounds.

The amount of ozone contacted with the waste materials will depend upon the particular application and the type of materials being treated. In general, the concentration of ozone contacting the waste materials should be at least 0.01 ppm. Preferably, however, greater concentrations of ozone are used during the process. For instance, for most applications, ozone should be fed at a concentration sufficient to saturate or to nearly saturate the slurry/solution with ozone.

The amount of ozone that it takes to saturate an aqueous solution depends upon the temperature and pressure of the solution. In general, greater amounts of ozone can be dissolved into the solution at lower temperatures. Thus, in one embodiment, the aqueous solution being treated in accordance with the present invention can be cooled prior to or during ozonation. For instance, in one embodiment, the temperature of the aqueous solution can be maintained below about 20° C., and particularly below about 15° C. The solubility of ozone in water at 20° C. is about 575 milligrams per liter, while the solubility of ozone in water at 10° C. is about 785 milligrams per liter.

In one embodiment, the solution or slurry being combined with ozone can first be cooled prior to or during ozonation. After ozonation, however, the solution or slurry can then be heated in order to cause the ozone to react more rapidly with the organic materials.

Similar to the concentration of ozone, the amount of time the waste materials are contacted with ozone also depends upon the particular application. For most applications, however, ozonation should continue until most of the organic compounds are broken down into smaller hydrocarbon species capable of being used in cellular processes. The length of time ozonation should occur in the process of the present invention can be determined using various methods. For example, in one embodiment, the maximum sugar potential of the waste materials can first be determined. Sugar potential can be determined by first pretreating a sample of the waste materials for different times in order to release the sugars and then conducting the Fehlings Test for reducing sugars on the sample. Once the maximum sugar potential for the waste materials is determined, the waste materials can be contacted with ozone at a concentration and for a time sufficient for the maximum sugar potential to be achieved.

In an alternative embodiment, the amount of sugars can be monitored during the ozonation process by collecting periodic samples and conducting the Fehlings Reducing Sugar Test. The amount of sugar generated then can be plotted versus time of ozonation. A maximum amount of reducing sugar is achieved upon reaching a maximum peak or steady state as indicated by the plot. When the slope of the line indicates a decline in sugar content over time, it is indicative of additional ozone continuing to oxidize and, thereby destroy the newly formed sugars. Further ozonation may then result in the reduction of useful medium and degrade the quality of the resultant substrate.

Besides testing for sugars, it is also possible to determine how much ozonation is required in a particular application by testing for the amount of degradation of proteins in the waste materials. This can be tested by any of a number of methods including the Bradford method, gel filtration (molecular sieve, molecular size exclusion) methods and polyacrylamide gel electrophoresis methods. Similar tests to determine optimum ozonation can be conducted for other chemical moieties such as lipids.

During ozonation, the pH of the aqueous solution may have a tendency to alternatively decrease and increase with a gradual overall downward trend. Should the pH of the solution vary too greatly from neutral (generally between a pH of 5 and 9), subsequent cellular growth may be adversely affected depending on the organism cultured. Consequently, in some applications, a base or an acid can be added to the aqueous solution prior to or during or after ozonation to adjust pH to the optimum pH range for the microbial population.

Prior to or after ozonation, various enzymes can also be added to the aqueous solution to assist in breaking down the waste materials. For instance, if the waste materials contain cellulosic materials, cellulase enzyme can be added to the materials. The enzyme will break down cellulose increasing the availability of organic compounds that may be released during the process of the present invention. Other enzymes that can be added include lipases, proteases, amylases, and the like.

Once the aqueous solution containing the waste materials has been ozonated, the remaining solid materials can be separated, if desired, from the aqueous solution by a variety of means including but not limited to settling, centrifugation, and filtering. Separating the materials, however, can occur prior to ozonation or after contact with organisms.

As described above, once the slurry of waste materials has been ozonated, a solution is produced containing a growth medium (substrate) for organisms. The substrate can contain, for instance, sugars, proteins, lipids, inorganic compounds, minerals, vitamins, and other nutrients. In accordance with the present invention, the oxidized medium is then contacted with organisms and/or enzymes for carrying out the processes of growth, metabolism and bioconversion via fermentative, respirative, photosynthetic, or similar pathways. In accordance with the present invention, particular organisms can be selected for producing cells or specific end products that can be collected and used as desired. For example, in one embodiment, microorganisms can be selected that will convert the fermentable compounds contained within the aqueous solution into ethanol. The ethanol can then be collected and separated from the solution and used, for instance, as an energy source.

The particular organisms and/or enzymes selected for carrying out respiration, fermentation, photosynthesis and other cell processes will depend upon the particular application and the desired products. The organisms can be, for instance, yeast, fungi, molds, bacteria, algae or genetically engineered microorganisms or tissue culture or mixtures thereof.

The manner in which the organisms are supplied with the oxidized medium can also vary. For instance, in one embodiment, a batch system can used in which the aqueous medium is placed into a reservoir containing the organisms. The aqueous substrate can remain in contact with the organisms until microbial growth and metabolism has reached the desired endpoint.

In another embodiment, the ozonated solution can be fed through an immobilized culture of organisms. For instance, as shown in FIG. **4**, the ozonated solution can be fed to a packed tower **32**. Packed tower **32** can contain a packing material **34** in which the organisms reside or are bound to the outer surface. The ozonated solution (substrate) can be filtered through the packing material for carrying out fermentation and/or other growth processes. Depending on the cellular product produced, the resulting fluid or gas can be collected from the tower.

In still another embodiment, the organisms can be contained in an aqueous culture that continuously contacts the ozonated solution in a continuous culture, chemostat-type process. For example, in this embodiment, the ozonated solution can be fed into a chemostat chamber which contains a solution comprising organisms. Fermentation and other growth processes can occur within the chemostat chamber as the organisms conduct metabolism. Excess solution containing the desired organism and/or product can be collected.

After contact with the organisms, the cellular products can be separated from the aqueous solution, if desired. For instance, when producing ethanol, ethanol can be distilled from the remainder of the solution. In some embodiments, however, it may not be necessary to separate the microbial products from the remainder of the solution.

Depending on the product that is produced according to the present invention, various post processing steps can be carried out. For instance, depending on the product, the product can be collected, stored and packaged as desired. For example, in one embodiment, the product can be dried and then packaged prior to being shipped to a desired location.

In one embodiment, the microbial products can be separated from the solution and the remaining solution can be fed to plants for plant growth. For example, some waste materials such as animal waste contain relatively high concentrations of fertilizing nutrients, such as nitrogen, phosphorous and potassium. These nutrients are typically contained in the oxidized medium. A portion of these nutrients may be used by the organisms introduced to the medium. However, in the case of high fertilizing nutrient content, residual nitrogen, phosphorus and potassium compounds may remain in the spent medium. In accordance with the present invention, the spent substrate solution can then be fed to the plants that will beneficially remove these nutrients from the solution. If desired, the spent medium can be re-ozonated prior to being fed to the plants.

In general, the solution can be fed to any suitable plant or crop. In one embodiment, the solution can be fed to a wetland for use by any vegetation that may be present in the wetland. A wetland is typically defined as a foliage and vegetation area that is configured to accept runoff.

Alternatively, the solution can be fed to plants in a hydroponic system. A hydroponic system involves growing plants in a soil-less system, usually in a liquid medium that provides all essential minerals.

In still another embodiment, the solution can be used as irrigation water. For example, the solution can be sprayed over a field or, alternatively, used to irrigate plants grown in greenhouse flats or similar containers.

As described above, besides ethanol, various other fermentation and microbial growth products can be made according to the present invention. In general, the microbial product can be any cell bound or cell excreted product. For example, the process of the present invention can be used to produce lactic acid or pharmaceuticals. Other fermentation and microbial products that may be produced include other alcohols, aldehydes, ketones, organic acids, polyhydroxy compounds such as polyhydroxybutyrate and polyhydroxyvalerate, proteins and single cell proteins, enzymes and pigments. Cellular products can include the cells per se, pigments, phospholipids. Other cellular products can include esters, ethers, amides, amines, purines, pyrimidines, alkanes, alkenes, alkynes, cyclic and aromatic compounds, gums, microbial cellulose and other polymers.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

What is claimed is:

1. A process for producing useful products from organic materials comprising the steps of:

providing an aqueous solution containing organic materials;

contacting said aqueous solution with a gas comprising ozone, said ozone being contacted with said aqueous solution at a concentration of at least 0.01 ppm., said ozone being present in an amount sufficient to oxidize at least a portion of said organic materials into an oxidized medium;

contacting said ozonated aqueous solution with a microorganism, thereby converting said oxidized medium into a metabolic product; said metabolic product comprising a hydrocarbon gas; and

collecting said product.

2. A process as defined in claim **1**, wherein said aqueous solution is contacted with said ozone by flowing said aqueous solution through a venturi and feeding said ozone into said venturi.

3. A process as defined in claim **1**, wherein said hydrocarbon gas comprises methane.

4. A process as defined in claim **1**, wherein said microorganism comprises a bacteria chosen from the group of methanogenic bacteria and wherein said hydrocarbon gas comprises methane.

5. A process as defined in claim **1**, wherein said organic materials comprise food industry waste.

6. A process as defined in claim **1**, wherein said organic materials comprise animal waste.

7. A process as defined in claim **1**, wherein said organic materials comprise paper industry waste.

8. A process as defined in claim **1**, wherein said organic materials comprise petroleum refining waste.

9. A process as defined in claim **1**, wherein said organic materials comprise tire waste.

10. A process as defined in claim **1**, wherein said organic materials comprise municipal solid waste.

11. A process for producing methane from waste materials comprising of steps of:

providing an aqueous solution containing organic compounds;

contacting said aqueous solution with a gas comprising ozone, said ozone being present in an amount sufficient to convert at least a portion of said organic compounds into an oxidized medium;

contacting said ozonated aqueous solution with microorganisms, said microorganisms converting said oxidized medium into methane; and

collecting said methane.

12. A process as defined in claim **11**, wherein said aqueous solution is contacted with said ozone by flowing said aqueous solution through a venturi and feeding said ozone into said venturi.

13. A process as defined in claim **11**, further comprising the steps of:

monitoring the amount of metabolizable substrates in said aqueous solution during ozonation; and

ozonating said aqueous solution until the amount of said metabolizable substrates detected begins to decrease.

14. A process as defined in claim **11**, further comprising the steps of:

calculating a maximum amount of metabolizable substrates that may be produced during ozonation of said aqueous solution based upon the amount and type of organic compounds contained in said solid waste materials; and

contacting said aqueous solution with ozone in an amount sufficient to produce at least said calculated maximum amount.

15. A process as defined in claim **13**, wherein said metabolizable substrates comprise sugars.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,835,560 B2
DATED : December 28, 2004
INVENTOR(S) : Annel K. Greene

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [56], **References Cited**, U.S. PATENT DOCUMENTS, "5,011,599" reference, change "Kearney" to -- Keatney --.
OTHER PUBLICATIONS, "Finch, et al.", reference, change "Lambia" to -- Lamblia --.
Insert -- Byvn, et al., Gamma Irradiation and Ozone Treatment for Inactivation of Escherichia coli O157:H7 in Culture Media, Journal of Food Protection, 61:728-730, 1998. --.

Signed and Sealed this

Sixth Day of September, 2005

JON W. DUDAS
Director of the United States Patent and Trademark Office