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(54) Title: PROCESS FOR THE DISPOSAL OF MUNICIPAL WASTE AND MANUFACTURE OF FUEL ALCOHOL (57) Abstract A process for the conversion of cellulose from municipal waste has been developed. Significant features are: (1) the use of concentrated hydrochloric acid at moderate temperatures with mechanical action to hydrolyse the cellulose to glucose; (2) recovery of the acid from the hydrolyzate by electrodialysis to provide concentrated sugar solutions for fermentation; and (3) continuous distillation of the ethanol produced.		

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PROCESS FOR THE DISPOSAL OF MUNICIPAL WASTE AND
MANUFACTURE OF FUEL ALCOHOL

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FIELD OF INVENTION

The present invention relates generally to resource recovery and more particularly to the manufacture of fuels, such as ethanol, or chemicals, such as furfural, from undesired waste products from, for example, a municipal waste dump.

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BACKGROUND OF THE INVENTION

Municipal solid waste has typically been disposed of in a land-fill, and, more recently, by incineration. These traditional methods unfortunately not only pollute the earth and often the atmosphere but also waste a large and valuable source of alternate energy. In many large urban areas moreover, incineration rules are strict while only a limited amount of land-fill space is available. The remaining open waste dumps are therefore overflowing to crisis proportions. The current "garbage crisis", particularly in the large urban areas, has accelerated the search for a better method of disposal of municipal solid waste. this has sparked an interest in the recovery and reuse of waste materials, such as cellulose.

Cellulose is the raw material of numerous types of manufactured goods such as paper, cardboard, rayon, celluloid or cellophane and is the chief

component in the walls of plants and trees. Cellulosic content of municipal waste varies with the source of the waste: department stores discard vast amounts of paper and cardboard; restaurants throw away mostly food, cans, and plastics; domestic garbage comprises a combination of food and packaging products. One ton of waste typically contains over 1/2 ton of cellulose. Besides paper materials, other major sources of cellulose include cotton, wood chips, sawdust, straw, corn stover, bagasse (residue of sugar cane), rice hulls and peanut shells. Most cellulosic materials contain three primary components: cellulose, hemicellulose, and lignin.

Cellulose has a very tightly bonded crystalline structure and has the chemical formula $C_6H_{10}O_5$. The crystalline nature of cellulose makes it very difficult to separate the molecules. However, a mineral acid, acting as a catalyst only, will break up the cellulose fiber chain, and permit each individual molecule to combine with one molecule of water, H_2O , forming a molecule of sugar, glucose $C_6H_{12}O_6$. With weak acid this hydrolysis action is very slow and incomplete except at high temperatures.

However, at elevated temperatures degradation of the resultant glucose becomes significant, typically preventing the attainment of glucose yields of over 50%. Concentrated acids, by contrast, cause rapid decrystallization of the cellulose, permitting facile hydrolysis at moderate temperatures (15 minutes at

50°C) and yields almost quantitative amounts of glucose.

5 Hemicellulose is a combination of simple or mixed polysaccharides, including polymers of hexoses (such as mannose, galactose and glucose), pentoses (such as xylose and arabinose) and sugar acid.

10 Hemicellulose has a much lower molecular weight than cellulose and is amorphous rather than crystalline; its molecules separate easily and they can therefore be easily hydrolyzed. The hexose sugars from glucomannans are fermentable with the glucose from the cellulose.

15 However the 5-sugar xylose from xylans is not fermentable by most ordinary yeasts. To make use of the xylose from the hemicellulose xylan, the xylose can be separately accumulated and, using a special yeast in a batch operation, be converted to ethanol or, it can be converted to Furfural, using heat and weak acid.

25 Furfural is the most important member of the family of heterocyclic compounds known as Furans and is characterized by a doubly unsaturated ring of four carbon atoms and one oxygen atom. Furfural can be oxidized to furic acid, reduced to furfuryl alcohol and converted to furan by decarbonization. Corncobs, 30 bagasse, cottonseed hulls, oat and rice hulls are major sources of furfural. Furfural is an important chemical intermediate and a selective solvent in the refining of 35 fuels. Furfural and other tetrahydrofuran compounds may be used as a selective solvent for separating saturated from unsaturated compounds in petroleum

lubricating oils, gas, oil and diesel fuel, as well as vegetable oil. Furfural may also be used as an ingredient in resins (particularly of the phenol-aldehyde types), as a decoloring agent for wood resin, as a resin solvent and wetting agent in the manufacture of abrasive wheels and brake linings and in the manufacture of synthetic rubber.

Since the hemicellulose hydrolyses first into sugars, these sugars are in longer contact with the acid and at high temperatures rapidly begin to be burned or caramelized, while the cellulose is not yet broken down. The higher the temperature during the reaction, the worse this problem becomes and an even larger quantity of sugar is lost. If reaction time is shortened, or the temperature lowered, the reaction of the cellulose material is less complete, thereby losing sugar from this source. Strong acid and low temperatures are the solution to this problem.

Lignin is the cementing material between adjacent cell walls of plants and trees and is a branched polymer macromolecule having three-dimensional, randomly linked polyphenolic units. The general aromatic character of lignin, as well as the prevalence of covalent carbon bonds, prevents reversion to monomers during processing of lignin and cellulose from the "woody" fibrous cell walls of plants. Lignin is generally unaffected by acid at moderate temperatures (50° C or below) and will remain as an insoluble residue along with other insoluble paper

components such as coatings, fillers, etc. after the hydrolysis process.

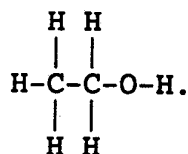
Glucose is a carbohydrate which occurs widely in nature in the food chain and can be obtained from cellulose by breaking the glycosidic bonds of cellulose by the addition of water, in the presence of an acid catalyst, creating a "hydrolysis" reaction. During hydrolysis, the polymer chain is shattered (depolymerized) and each cellulosic molecule picks up a water molecule and becomes a simple sugar or monosaccharide. Water (H_2O), combined with cellulose ($C_6H_8O_5$), results in glucose (a simple sugar - $C_6H_{10}O_6$). At the same time, the xylose polymers become xylose (a five carbon sugar). Lignin and acetic acid are also released. The usual source of glucose is the hydrolysis of starch, which is amorphous and branched and thus easily converted to glucose. The starch is usually obtained from corn. Once cellulose has been converted to glucose, the glucose may be more easily converted to many commercial and industrial products, including refining into pure sugar, or dextrose. When converted to glucose and then fermented and distilled, the product is ethanol alcohol. A pound of cellulose has the energy equivalent of one third of a pound of gasoline.

When cellulose is converted to glucose using acid as a catalyst, the initial product is a solution containing the glucose, water and acid. If done at high temperatures, this mix requires immediate

separation of the acid from the solution. Most successful commercial acid hydrolysis processes employ either sulfuric or hydrochloric acid as a catalyst. Removal of the acid from the sugar solution prevents further chemical reaction which could decompose the sugar into undesirable products and the acid becomes available for reuse in further processing of cellulose. The cellulose feedstock used in most past commercial processes was primarily sawdust or wood chips. Some types of cellulose convert to sugar faster than others.

Acid hydrolysis is a method used to break down cellulosic material into individual molecules. Mineral acids acting only as a catalyst fractures the chain of molecules allowing them to combine with water molecules. The acid is neither crystalline combined nor consumed in the process. The major factors affecting acid hydrolysis are acid strength and temperature. High acid concentration results in a high sugar yield. High temperatures must be avoided to prevent degradation of the sugars into undesirable by-products.

Ethanol (ethyl alcohol) may be produced by adding yeast to a sugar/glucose solution with an appropriate concentration of water. In the absence of oxygen, the yeast will ferment the sugar to alcohol. Ethanol has the empirical formula C_2H_5OH and is structurally depicted as follows:



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The compound ethanol is a carbonyl group and is a hydroxy derivative of hydrocarbons. Ethanol is the primary alcohol of all the alcohol groups, as opposed to the secondary and tertiary groups. All of these alcohols comprise a very wide and important segment of organic chemistry and are extensively used in industry worldwide.

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There are two primary markets for ethanol: the chemical and the fuel industry. The fuel industry provides by far the largest market and is rapidly growing. The chemical industry uses industrial grade ethanol which must be processed and refined to very high standards of purity for use in the production of solvents, detergents, pharmaceuticals, toiletries, cosmetics, plastics, paints, disinfectants, and in food and drug processing.

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Ethanol is usually sold as a blend with gasoline in the United States, although it is often used 100% as a fuel (neat) in Brazil. This blend is called "gasohol" and consists of 10% ethanol and 90% gasoline. The ethanol increases the octane rating, combustion efficiency, and overall engine performance. Ethanol produces minimal pollution -- it does not add net carbon dioxide to the atmosphere and is easily transported and stored. The demand is expected to

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double or triple within the next five years. Over one billion gallons of ethanol is expected to be produced in 1991. But these ethanol sales are in spite of the high cost. High cost is the chief constraint to the sales and use of ethanol sales reaching their full potential.

Almost all ethanol in the United States is made from corn starch, it breaks down into sugar for fermentation very easily, but it is also very expensive. Corn costs at present about \$2.50 per bushel. A bushel of corn is sufficient to make 2 1/2 gallons of ethanol. This means that the raw material alone for a gallon of gasoline costs \$1.00. If gasoline sells for \$1.10 per gallon, it is almost impossible for ethanol to be really competitive.

Substitute cellulose separated from municipal solid waste as a raw material that not only doesn't cost anything but which actually may pay a "tipping" fee to be used and an entirely different picture is created.

But the substitution of cellulose for ethanol manufacture on a major scale requires great improvements in the acid hydrolysis process - a tremendous increase in the conversion yield, a great improvement in the conversion time, and a big reduction in the cost of separation of the acid catalyst from the resulting sugar syrup. Cost has been the major obstacle to the use of cellulose as the ingredient for ethanol.

The critical step in the conversion of the cellulose in wood, agricultural residues, or municipal solid waste to ethanol or other chemicals via a glucose intermediate is the hydrolysis of the crystalline lignified cellulose to the glucose. Despite many decades of research, each of the three recognized methods of cellulose hydrolysis has until now suffered from a severe limitation that has prevented its economic use on a commercial scale.

For hydrolysis with dilute acids at elevated temperatures the limitation is the reduced yield of glucose (50-60%). Hydrolysis with concentrated acids at moderate temperatures can provide quantitative yields of glucose, but the recovery of the acid has until now been too expensive. Enzymatic hydrolysis also provides high glucose yields, but it is not effective on lignified cellulose without an expensive pretreatment.

Concentrated acid hydrolysis of cellulose is effective on any substrate without pretreatment, can provide almost quantitative yields of fermentable glucose, affords more concentrated solutions for fermentation, takes place in minutes, and affords a relatively reactive lignin residue with potential by-product value. In contrast, neither dilute acid hydrolysis nor enzymatic hydrolysis can claim more than two of these attributes.

A critical drawback of concentrated acid hydrolysis processes has been the cost of recovery of

the acid. Most development work has been based on halogen acids because of their volatility. In an economic analysis of a hypothetical integrated wood hydrolysis plant using concentrated HCl, it was determined that over 35% of the operating costs and almost 40% of the capital costs were related to HCl recovery and loss. A more recent evaluation of concentrated halogen acid (including HCl and HF) hydrolysis processes confirmed that they are all expensive because of the high cost of acid recovery.

Our recent research has been directed at overcoming the recovery problem by the use of lower energy membrane separation technology. After simulation studies showed potentially large savings in recovery costs by electrodialysis, the feasibility of the concept was demonstrated experimentally. Further improvements with advanced membranes are described below.

It is therefore the object of this invention to find a superior and less costly method of utilizing cellulose from the vast amounts of municipal waste, as well as cellulose waste of all kinds - agricultural and wood wastes.

It is another object of this invention to produce ethanol, furfural, carbon dioxide, lignin and cattle feed from waste, both municipal and agricultural, using an environmentally benign process which obviates toxic air emissions or effluent discharges.

Yet another object of the invention is to produce these by-products as well as sugar in the course of producing ethanol.

5 An additional object of this invention is to use certain of these by-products from the conversion process as fuel to make the operation self sufficient in both steam and electricity, if the economics
10 dictate.

A further object of the invention is to reduce the cost of ethanol below that of gasoline by
15 reducing conversion time and conversion rate through improved reactor mixing and design, reducing burnt, or caramelized, sugars, and reducing unconverted
cellulose.

20 Another object of this invention is to reduce the high cost of separating the acid catalyst from the sugar syrup.

25 Still another object of this invention is to develop a continuous system from start to finish, eliminating the costly and time consuming "batch" methods normally used for acid hydrolysis and
30 fermentation.

SUMMARY OF THE INVENTION

35 These and other objects of the invention, which will become apparent hereafter, are achieved by applicant's PROCESS FOR THE DISPOSAL OF WASTE AND MANUFACTURE OF FUEL FROM WASTE BY RECYCLING AND

CONVERTING WASTE TO USEFUL BY-PRODUCTS, which generally comprises: (1) separation for further treatment of cellulosic material feedstock from waste material brought to a processing facility; (2) an acid hydrolysis process using an acid catalyst to convert the feedstock into simple sugars which can be fermented into ethanol via a continuous operation; (3) recovery of the acid from the hydrolyzate by electrodialysis to provide concentrated sugar solutions for fermentation and to recycle the acid catalyst; and (4) continuous fermentation of the sugars combined with the continuous distillation of the ethanol produced.

Intermediate steps in the disclosed and claimed process will create commercial sugar and cellulosic by-products such as lignin, furfural, carbon dioxide and cattle feed. By-products of the cellulosic conversion process can also be burned for the production of steam and electricity.

The invention will be better understood by the Detailed Description of the Preferred Embodiment in conjunction with the appended drawings, of which:

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow chart for the production and separation of cellulose from solid waste;

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Figure 2 is a graphical drawing of the production and separation of cellulose from solid waste;

Figure 3 is a perspective view of a primary disk screen;

Figure 4 is a cross sectional view of screen disk elements of a primary disc screen;

Figures 5 is a perspective view of an air table used in conjunction with the waste separation system;

Figure 6 is a perspective view of a primary shredder;

Figure 7 is a perspective view of an air knife used in conjunction with the waste separation system;

Figure 8 is a flow chart of the acid hydrolysis process;

Figure 9 is a perspective view of a twin screw extruder used for acid hydrolysis;

Figure 10 is a cross-sectional view of an electrodialysis unit;

Figure 11 is a schematic of a Delta-t continuous fermentation/distillation system; and

Figure 12 is a flow chart depicting the production of ethanol and also various by-products which may be obtained.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment of the present invention of conversion of municipal waste or other undesirable waste products to fuel, such as ethanol, involves generally the steps of:

- 5 (a) separating from municipal solid waste
the usable cellulosic feedstock;
- (b) baling the feedstock (optional);
- 10 (c) using an acid hydrolysis process to
convert cellulosic fibers of the
feedstock to sugar;
- (d) separation of HCl catalyst and
impurities from the sugar syrup; and
- (e) using a yeast fermentation system to
convert the sugar into ethanol.

15 In addition to ethanol production, by-
products of the cellulosic conversion process can be
used for the production of energy, such as electricity,
by:

- 20 (a) anaerobically digesting biodegradable
sludges left from the cellulose
conversion process and ethanol
production;
- 25 (b) producing electricity and heat energy
from the methane gas produced from the
anaerobic digestion;
- 30 (c) using diesel/gas generators to provide
electricity; and
- (d) burning lignin to produce steam and
electricity.

35 Other by-products such as lignin, furfural, carbon
dioxide, acetic acid, or cattle feed may also be
produced.

WASTE SEPARATION

The process of separation of commercial and residential waste for ultimately the production of ethanol is schematically depicted in Figure 1 and graphically depicted in Figure 2 and begins once the waste is delivered onto a "tipping" floor via collection vehicles. The tipping floor, is designed to handle a high volume of trucks and solid waste and usually has a series of traffic lights over an entry door. These lights are controlled by operators located in a main control room overlooking the tipping floor to control the flow of trucks and front end loaders and other traffic. Once refuse is dumped onto the tipping floor, its movement will be controlled by front end loaders which will perform a rough sorting of the refuse before feeding it into the waste separation system where large unprocessable materials (e.g., appliances such as refrigerators and stoves, etc...) will be separately handled and removed. The remaining refuse will be placed onto an infeed apron conveyor 200, as depicted in Figure 2, for feed into a process stream.

The infeed apron conveyor 200, such as one manufactured by Beloit-Rader, regulates the amount of material entering the separation system and elevates the solid waste to a primary disc screen 300. The conveyor 200 is equipped with a variable speed motor which will regulate conveyor speed from 0 to 50 feet per minute. Bag rippers (not shown) placed along the

infeed apron conveyor 200, facilitate opening of plastic trash bags, which, of course, contain a significant percentage of municipal solid waste, to
5 expose their contents for separation.

Several preliminary sorting operations will be performed at the conveyor. One such operation is simply "hand sorting" (not shown) -- i.e. removing
10 large pieces by hand. A flat/round separator (not shown) is also employed to separate out large flat pieces from the process of stream. Once the large
15 pieces are sorted out of the stream, easier access is provided to a magnet (not shown) which removes the non-cellulosic, metallic content waste. A hysteresis unit (not shown) may also be used at this stage to remove
20 the non-ferrous metals. Additional hand sorting (not shown) may be performed with respect to the diverted flat pieces.

The next step involves advancing the material
25 over primary disc screens 300 (see also Figures 3 and 4) which function as classifiers to sort the raw refuse into two (2) separate product streams. Primary disc
30 screens 300 have variable speed hydraulic drives which rotate the screen disks 310 (see Figure 4) to optimize their performance. The overflow from the disk screen will be material having a diameter of greater than 5
35 inches and will typically comprise paper and plastic products, while the underflow typically will comprise cans, glass and waste and grass clippings with other fibrous materials.

An underflow belt 320 (below the Primary Disk Screens) (Fig. 2), such as one manufactured by National Resource Recovery Systems, Inc., will move sufficiently slowly to allow hand picking of recyclable materials. Material underflow discharged from the Primary Disc Screen is transported on the underbelt and passed through a magnetic field 330, where a drum-type magnet 340 will be used to remove ferrous materials. The ferrous products typically comprise about 4% of the total material feed.

A secondary underbelt 350, such as one manufactured by National Resource Recovery Systems, Inc. will receive material underflow from a second disc screen 360 similar to the primary disc screen. The refuse falling onto this screen will typically comprise broken glass, ceramics, dirt and small organic materials such as grass clippings. The glass particles from the secondary belt will be recovered by an air table density separation system 400 comprising a series of air tables (see Figure 5).

The material from the Primary Disc Screen overflow will be discharged onto a slow moving shredder feed belt 500 (see Figure 2), which will allow hand sorting of non-processable materials and the option of gathering up of cardboard and mixed paper. The material moving along the shredder feed belt will be fed to the primary shredder 600 (see Figure 6). If the cardboard and mixed paper are removed, they could be shredded and fed directly to the hydrolysis operation.

The primary shredder 600, such as one manufactured by National Waste Recovery Systems, Inc., is located in a separate primary shredder building 700 and may be employed to reduce the oversize screen products, which are mostly non-cellulosic, into uniform sized particles. A final ferrous removal magnet (not shown), used in conjunction with the primary shredder, will extract the remaining amounts of iron still present in the prepared feed stock.

The shredder building 700 will be equipped with pressure reduction (blow out) explosion containment walls. The blow-out wall design will aid in rapid pressure relief in the event of an explosion. The building should be equipped with Hydrocarbon sensors which will detect explosive and most toxic gasses. This detection system will be connected to the electrical system to stop material movement, preventing its return into the screening building where operators are present. The shredder building should have limited access and precautions should be taken not to allow operators inside during normal operations. The building should be equipped with plant air, water, intercom, phone, electrical outlets (to include welding plugs) and television monitoring equipment.

The shredded material will then be passed over five air tables (single air tables are depicted in Figures 2 and 5), such as one manufactured by Beloit-Rader, each of which are actually air classifiers which permit the further recovery of the glass products

through density separation and permit light materials (such as grass clippings) to be vacuumed off the screen bed and into a cyclone separator. Each air table will facilitate removal of the heavy materials which will primarily comprise "grids" - i.e., metals, dirt, rock and ceramics. The air table will also separate the heavy glass fraction from the waste. The glass material will comprise a mixed color of clear, amber and green and will be used for the manufacture of fiber glass. A manual aluminum hand-picking station will follow the air tables and precede the air knife equipment as also shown in Figure 8. Each person on the aluminum picking station will be capable of picking an average of 40 to 50 cans per minute.

The remaining material will be processed through the air knife 800 (see Figure 7), which is equipped with a hot air plenum 810 directly in front of the separation chamber. The air has different effects on different particles based upon particle weight and density and therefore serves as a classifier.

Once the work of the waste separation system is complete, the baling operation begins. Baling is necessary where the hydrolysis units and ethanol production units are in separate locations. The majority of the feed stock of the conversion plant will be compacted bales. An automatic baler is used to compress the high concentration of cellulose material into bales.

DESCRIPTION OF THE HYDROLYSIS PROCESS

5 A schematic flow sheet for the overall
process is shown in Figure 8. The process steps are
described in the following sections.

The lignocellulose from waste paper
comprising the raw material for the process will vary
10 in composition depending on its source and prior
treatment. Cellulose itself will be the most abundant
component, but will range from about 40% of
mechanically pulped softwoods (newsprint) to 75% of
15 unbleached kraft (linerboard) to 80% of bleached kraft.
Hemicelluloses differ greatly according to origin. The
glucomannans can vary from 3% in hardwood mechanical
pulps to about 10% in softwood chemical pulps to 17% in
20 softwood mechanical pulps. Xylans can vary from 8% in
softwood mechanical pulps to about 10% in softwood
chemical pulps to as high as 30% in hardwood mechanical
25 pulps. Lignin content can vary from 0% in bleached
chemical pulps to 6% in unbleached chemical pulps to
20% in hardwood mechanical pulps to 27% in softwood
mechanical pulps. The hydrolyzing acid is 45% HCl.

30 The requirements for the hydrolysis reactor
are that it bring together the cellulosic raw material
and the concentrated hydrochloric acid that will
35 hydrolyze it to sugars, have sufficient capacity for
the desired rate of production, provide adequate
residence time at the desired reaction temperature,

provide positive mixing and mechanical disruption of cellulose gels, and withstand corrosion from the acid.

5 Since the acid to cellulose ratio is a critical variable that must be minimized to achieve a reasonable size and cost for the acid recovery equipment, a stirred tank reactor is not suitable. Cellulose slurries can only be stirred up to
10 consistencies of about 15%. This upper limit corresponds to an acid to cellulose ratio of 5.7:1, which is prohibitive as far as recovery system cost is
15 concerned.

Furthermore, reaction kinetic studies have shown that in the absence of agitation to break up the swollen cellulose gels formed during decrystallization
20 of the cellulose, the hydrolysis reaction often stops short of complete conversion with only 50-60% of the cellulose hydrolyzed. With proper agitation, however, the reaction proceeds to over 90% conversion at rates
25 as much as 20 times greater than the diffusion controlled rates in the absence of agitation.

A Werner-Pfleiderer twin screw extruder is used to continuously mix, transport, and by inference
30 effect gel disruption of cellulose and water mixtures with a 2:1 liquor to cellulose ratio. This ratio is used in the acid recovery discussions below.

35 The reaction kinetic studies have also shown that over 90% of the cellulose is hydrolyzed in ten minutes at 50°C. A reactor residence time of 15

minutes at 50°C has been adopted to ensure that the hydrolysis does proceed to completion.

5 Although 40% HCl will hydrolyze cellulose,
increasing the concentration to 42-45% increases the
rate of the reaction and also ensures that it goes to
completion. The sugars liberated during the hydrolysis
10 bind some of the HCl, leading to the possible reduction
of the effective concentration to below 40% unless the
higher concentration is used. The cellulose is not
hydrolyzed all the way to glucose at this stage.
15 Instead the sugars are present in the form of
oligomers.

 The lignocellulose material, either the
separated fraction taken from municipal solid waste,
20 newsprint, food waste, or vegetable matter such as corn
stover or bagasse, must first be finely shredded. In
the preferred mode of continuous operation, using a
twin screw extruder reactor, this raw material is
25 forced by a "stuffer" or "packer" into a receiving
hopper of the reactor. The grinding fleights of the
screws draw the material into the barrel and begin to
crush it.

30 A continuous but closely controlled and
measured amount of hydrochloric acid flows into the
barrel and mixes with the cellulose. As the acid comes
35 into contact with the cellulose, the molecules of the
crystalline structure begin to dissociate.

 Water is already contained in the cellulose
(about 10% moisture content). The twin screws force

close contact, at the same time, of the three essential materials - water, acid, and cellulose. As the molecules of cellulose are broken free from the chain
5 by the acid, each loose molecule of the cellulose combines with one molecule of water. But some swollen, decrystallized cellulose forms a kind of jello and this substance sticks to and covers the inner fiber. This
10 keeps the acid from reaching these inner layers of cellulose. At this stage the shearing fleights of the screws begin to scrape off the jello and break it up, allowing the acid once again to touch fresh cellulose
15 and break its bonds. The jelly becomes oligomers and water soluble. The fresh cellulose surfaces are exposed and the action is repeated.

20 In the approximate ten minutes that cellulose takes to travel the length of the screw, almost 100% of the cellulose material has become sugar syrup, which is ejected at the end of the barrel along with lignin and
25 all of the hydrochloric acid added to the reactor. Lignin has not been affected by the acid at this low temperature and is not soluble in the sugar/acid mixture. The lignin must be separated from the mix and
30 the HCl must be separated from the sugars to permit fermentation and to reduce processing costs by recovery and recycling of the HCl.

35 The end product of the reaction in the reactor are sugar oligomer and 43% concentration of HCl solution. The hydrolyzate solution leaving the reactor contains all of the HCl added to the reactor. The HCl

must be separated from the sugars, to permit fermentation.

5 The hydrolyzate solution leaving the reactor
still contains all the HCl added to the reactor. This
must be separated from the sugars, not only to permit
fermentation, but also to reduce processing costs by
10 recovery and recycle of the HCl. The volatility of HCl
gas allows it to be stripped from the hydrolyzate at
reduced pressure. With pure water this can be carried
all the way to the azeotrope at 20.2% HCl. However,
15 the HCl binds to the sugars in the hydrolyzate as well
as the water leading to a reduction in HCl volatility
and an upward shift in the azeotropic composition in
addition to that which also occurs at the reduced
20 pressure. Compensation for reduced HCl volatility by
increasing the temperature in the stripper is limited
to the 50°C temperature adopted for the reactor to
prevent the degradation of the sugars that would occur
25 at higher temperatures.

 Stripping studies have quantified the
composition of stripped HCl solutions containing sugar.
Analysis of such a solution after stripping to constant
30 weight under reduced pressure at 50°C showed a residual
acid concentration of 35.7% (acid in water only). With
a starting composition of 900g HCl to 1100g water (45%)
sufficient to process 1000g cellulose at a 2:1 ratio,
35 the final composition of 200g HCl in 360g water
indicates that 78% of the original acid had been
stripped as a 48.6% solution (700g HCl in 740g water).

The HCl stripped from the hydrolyzate would be recycled as shown. Most of the acid would enter an absorption system such as a falling film absorber where it would concentrate the approximately 20% HCl solution recovered by the electrodialysis unit. The remaining HCl gas would be compressed sufficiently to bring the solution leaving the absorber up to the 45% concentration entering the reactor, as well as to maintain this concentration at the moderate temperature (50°C) in the reactor.

After stripping of HCl the hydrolyzate containing sugar oligomers and residual HCl must be freed of insoluble solids before it can be introduced into the electrodialysis unit. These solids will consist of lignin, unhydrolyzed cellulose, and inert materials such as ink, coating pigments, fillers, and dirt. Any trash that had not been previously separated from municipal solid waste would also be present. Removal of the solids can conveniently be accomplished by centrifuging. Some dilution with water is necessary here to reduce the viscosity enough to expedite sedimentation and to wash residual sugars from the sediment. Thus the acid concentration leaving the centrifuge will be less than 20%, which also conforms to optimum electrodialysis conditions. A filtration step to remove fines that might plug the electrodialysis membranes is also appropriate at this point.

Sugar oligomers and less than 20% concentration of HCl are then passed to the electrodialysis unit (see Fig. 10), which is typically the most expensive component of the hydrolysis plant. It may, however, prove cost effective to first use dialysis in advance of electrodialysis to save electricity. Dialysis is a concentration gradient-driven separation process. The dialysis system utilizes a unique ion exchange membrane permeable to anionic species and H^+ , but rejects other cationic species.

The dialysis technique is used to separate and purify acids from salts by selectively permeating acids through special anion permselective membranes driven by the concentration difference of the solutions. In this way hydrochloric and other acids can efficiently be recovered.

In dialysis, the feed solution is supplied to the dialysis unit at the bottom portion of one side of a vertical anion permselective membrane and made to flow upwards, while water is made to flow countercurrently through the top and flows downward on the other side of the membrane. The concentration of the acid in the feed solution drops when acid permeates to the water side with purified acid being recovered in the water stream. The almost pure acid/sugar mix continues to the electrodialysis unit.

Electrodialysis is an electric current driven separation process that utilizes specially designed,

thin ion exchange membranes for desalting,
concentration and ion separation. Electrodialysis may
be performed on a batch basis, a once-through
5 continuous basis, or a feed-and-bleed basis.

In the preferred continuous, once-through
operation, a feed stream is passed between a cation
permeable membrane that allows passage of positively
10 charged ions and an anion permeable membrane that
allows passage of negatively charged ions. Numerous
cell pairs (consisting of a cation permeable membrane,
15 a flow distribution spacer, an anion permeable
membrane, and another spacer) are arranged as a stack
in a plate and frame configuration between a positively
charged electrode and a negatively charged electrode.
20 When D.C. current is passed between the electrodes
through the solution, electrolytically disassociated
positive ions migrate toward the cathode, penetrate the
cation permeable membrane and enter the next cell where
25 migration is blocked by the anion-exchange membrane.
Negatively charged ions migrate toward the anode, pass
through the anion permeable membrane and enter the next
cell where migration is halted by the cation permeable
30 membrane. Thus concentration and dilution occur
alternately. Sugars leaving the electrodialysis unit
are still in oligomeric form and normally must be
35 hydrolyzed to monosaccharides before fermentation.

The technical feasibility of the separation
of hydrochloric acid from sugars in cellulose
hydrolyzates by application of membrane technology had

been demonstrated by earlier experiments. In that work, the permeability of disaccharides was found to be less than 1% of that of the acid, and acid flux in diffusion dialysis was only 6% of acid flux at optimum current density in electrodialysis. Critical parameters for economic feasibility were identified as acid to cellulose ratio in hydrolysis, current efficiency, and membrane service life.

Availability of an improved membrane system for recovery of acids, ASAHI GLASS type AAV membranes, stimulated research to optimize recovery by electrodialysis of HCl from the hydrolysis of cellulosic materials. The studies measured current efficiency as a function of acid and sugar concentrations, and provided such relationships as current efficiency vs. initial acid concentration; final acid concentration vs. initial acid concentration; yield of transferred acid vs. initial acid concentration; power/lb HCl transferred vs. initial acid concentration; and membrane area required vs. initial acid concentration.

Ideally the separation of HCl from the sugar in the hydrolyzates by electrodialysis should provide a maximum yield of recovered acid in maximum concentration at minimum power consumption with minimum membrane area. The experimental results made it obvious that these conditions cannot be met simultaneously. At the highest current efficiencies and resultant lowest membrane area requirements, the

final acid concentration in the concentrate solution is too low. At the highest final acid concentrations the percentage of acid transferred falls off and power consumption and membrane area are high.

Setting reasonable values for percentage of acid transferred of 90% (total acid recovery of 97.5% if 75% is recovered by stripping) and final acid concentration of about 20% permits the realization of a power consumption of about 0.50 KWHr/lb HCl transferred, current efficiency of about 0.60 Moles/F/Cell, and membrane area for transport of 24 tons/day HCl of about 32,000 sq. ft. at an initial acid concentration in the diluate of 15-16% in the presence of sugar. The HCl tonnage cited corresponds to 90% of the acid residue from stripping 75% of the HCl from a 2:1 ratio of 45% HCl to 120 tons/day of cellulosic waste. Under these optimal electrodialysis conditions and the 2:1 acid to substrate ratio, sugar solution concentrations as high as 60% are obtained.

The remaining independent operating variable is current density, the current per unit of effective area of the membrane through which the current passes. The experiments reported above were conducted at a current density of 116 mA/sq cm. The optimum current density may be determined from balancing initial and replacement membrane costs which fall with increasing current density against power costs which rise with current density. Without knowing the actual values for

capital, membrane, and power costs the site-specific optimum current density cannot be determined.

5 As HCl passes through the membranes, water is also transferred by osmotic forces. The volume of this acid and its associated water increases the volume of the recovery stream and decreases the volume of the hydrolyzate stream. Since the sugars are retained,
10 their concentration increases as already noted to as high as 60%. The HCl concentration in the hydrolyzate at the end of electrodialysis based on acid and water alone is about 3%.
15

The sugars leaving the electrodialysis stacks are still in oligomeric form and must be hydrolyzed to the monomeric sugars before fermentation. This
20 posthydrolysis is carried out with dilute acid at temperatures that will not cause serious degradation of the sugars. With 3% HCl at 100°C the posthydrolysis requires 4-5 hours. Only 30-45 minutes are needed at
25 120-125°C and an acid concentration of 0.5-1%. Higher temperatures cause decomposition of the sugars.

30 The solution of monomeric sugars resulting from the posthydrolysis is neutralized before fermentation. To the extent that calcium ions can be tolerated in the fermentation process lime would be the
35 cheapest base. Some ammonium hydroxide might be used to provide nitrogen for the fermentation.

The sugar solutions obtained have two additional significant advantages over those obtainable

from high temperature dilute acid hydrolysis beyond the improved yield. Since the processing temperatures are mild (not exceeding 50°C), the solutions are readily fermentable without the need for removal of inhibitors formed at high temperatures. And the high concentration of sugars allows significant energy savings in fermentation and ethanol distillation when coupled with the BIOSTIL or Delta-T process for ethanol production.

The CHEMATUR (Sweden) BIOSTIL or Delta-T (American) process is a continuous fermentation process for ethanol production, combining fermentation with simultaneous ethanol distillation. A concentrated substrate such as a 55% sugar solution is fed to the fermenter at a rate that maintains the residual sugars in the fermenter at a very low concentration. Immediate conversion of sugars to ethanol occurs, but the alcohol concentration is maintained constant at about 5% by ethanol removal from a circulating beer stream. Only a single fermenter is needed for continuous operation.

Fermented liquid (beer) is fed to a centrifugal yeast separator and the separated yeast slurry fraction is returned to the fermenter. De-yeasted beer enters a primary distillation column where about 90% of the ethanol is removed. The ethanol-water vapor (about 40% ethanol) goes to a rectification column. The exhausted liquid (weak beer) passes through a heat exchanger and cooler and is returned to

the fermenter. A minor stream passes to the stripping section of a beer column. Concentrated stillage is removed at the bottom of the stripping section.

5 The process permits the use of more concentrated feedstocks, provides a more concentrated stillage, and improves ethanol yields. Sugar losses are considerably smaller, glycerol formation is
10 inhibited, and yeast is recycled. In addition the operations are very resistant to bacterial infection, and can accept unpasteurized substrates.

15 Several by-products are produced or can be obtained by further processing in addition to the ethanol which is the principal product of the process. These include lignin, carbon dioxide, furfural and some
20 cattle feed.

 Depending on the proportion of mechanical pulp in the raw material, the lignin residue may
 comprise as much as 25% of the starting material. It
25 has been demonstrated that the lignin from concentrated HCl hydrolysis shows high reactivity to phenol. The phenolated lignin has excellent resin-forming
30 capability and shows superior performance as an adhesive component (15). However, if highly contaminated with other insoluble residue components the lignin may only be suitable for burning to provide
35 some of the process energy requirements.

 Carbon dioxide is a major by-product of fermentation, with about one pound produced for each

pound of ethanol. Its value varies with plant location.

5 Furfural is obtainable from the xylose that is not fermentable by *Saccharomyces*. For a raw material consisting entirely of hardwoods, the Furfural yield could be as high as half the ethanol yield. Even at lower xylose contents, Furfural can be a valuable
10 co-product. Furfural is produced by heating xylose in a weak acid solution.

Conventional ethanol production from grain
15 derives significant by-products credit from stillage. The stillage from the present process is not as abundant or valuable because the fermentation uses sugar rather than grain, the yeast is recycled, and
20 furfural production from xylose would modify the stillage.

Applicant's recognition that cellulose gel formation was changing the reaction kinetics to much
25 slower diffusion control, has permitted the application of mechanical disruption of the gels to drive the hydrolysis to completion at the higher rate. And instead of conducting the reaction for 4-6 hours at
30 ambient temperature, applicants have demonstrated that quantitative conversion with minimal degradation of glucose can be attained in less than 15 minutes at
35 50°C, permitting a continuous process configuration.

Complete recovery of HCl by distillation is difficult and expensive, especially for the final portions of the recovered acid that are tightly bound

to the sugars in the hydrolyzate. The use of
electrodialysis to recover this last 25% of the acid,
along with the reduction of the acid to substrate ratio
5 to 2:1 permitted by the mechanical processing in the
reactor, has reduced acid recovery costs while
providing sugar solutions as concentrated as 60%.

10 The availability of these concentrated sugar
solutions allow the use of a continuous BIOSTIL or
Delta-T fermentation and distillation process which
were designed for use with molasses or grain
15 feedstocks, and would not be applicable to dilute sugar
solutions from cellulose hydrolysis.

While the preferred embodiments and steps of
the invention have been described in detail, it is to
20 be expressly understood that modifications and
adaptations can be achieved with respect to the
invention without departing from the scope of the
invention as defined in the following claims.

25

30

35

I claim:

1. A process for manufacturing fuel from cellulosic
5 material in waste products, said process comprising the
steps of:

separation of cellulosic material from said waste
10 products;

hydrolyzing said material using a catalyst,
wherein said cellulose material and water in the
hydrolyzing processes combine to form a sugar solution;

15 continuously separating the sugar solution from
said catalyst; and

continuously fermenting said sugar solution to
convert said solution into alcohol fuel by distillation
20 using a continuous fermentation/distillation process.

2. The process of claim 1 further comprising the step
25 of baling said separated material.

3. The process of claim 1, wherein said fuel is
alcohol.

30 4. The process of claim 3, wherein said alcohol is
ethanol.

35 5. The process of claim 4, wherein said separation
further comprises an air table system.

6. The process of claim 5, wherein said separation further comprises an air knife separation system.

5

7. The process of claim 6, wherein said separation is at least partially performed by a primary shredder, wherein said shredder reduces oversized material into substantially uniform particles.

10

8. The process of claim 7, wherein said separation further comprises the step of extracting ferrous material from said waste by a magnetic means.

15

9. The process of claim 8, wherein said separation further comprises a sizing disc screen, wherein said screen regulates size of material passing through it.

20

10. The process of claim 9, wherein, said baling further comprises an automatic baler, wherein said baler compresses high concentrations of said cellulosic fibers into bales for said hydrolyzing process.

25

11. The process of claim 10, wherein said fermenting process further comprises feeding fermented liquid solution into a centrifugal yeast separator.

30

12. The process of claim 11, wherein said liquid solution is aerated and dosed to ensure adequate yeast growth.

35

13. The process of claim 12, wherein a separated yeast slurry fraction is returned to the fermenter.

5

14. The process of claim 13, wherein said separation process further comprises an infeed apron conveyor.

10

15. The process of claim 14, wherein said separation process further comprises a primary screen, said screen functioning as a classifier.

15

16. The process of claim 15, wherein said infeed apron conveyor further comprises bag rippers to facilitate the opening of bags of said waste material.

20

17. The process of claim 16, wherein said infeed apron conveyor elevates said waste onto said primary screen.

25

18. The process of claim 17, wherein said primary screen separates said material into a plurality of product streams, wherein one of said streams comprises underflow material transported to a primary underbelt.

30

19. The process of claim 18, wherein a second of said product streams comprises overflow material transported to a slow moving shredder feed belt.

35

20. The process of claim 19, further comprising a magnet to remove iron content from said material on said underbelt.

5

21. The process of claim 20, further comprising a secondary underbelt to receive underflow from a secondary disc screen.

10

22. The process of claim 5, wherein said air table separation system comprises a plurality of air tables wherein each of said air tables serves as a classifier.

15

23. The process of claim 22, wherein each of said air tables performs density separation.

20

24. The process of claim 23, further comprising a cyclone separator, wherein substantially light particles of said materials may be vacuumed off said primary screen and into said cyclone separator.

25

25. The process of claim 6, wherein said air knife system further comprises a hot air plenum in the form of a separation chamber.

30

26. The process of claim 25, wherein said hot air plenum generates water heat to help nuggetize film plastic from said waste material, wherein deformation of said film results in a greater bulk density film product.

35

27. The process of claim 6, further comprising an aluminum picking station located before said air knife separation system.

5

28. The process of claim 7, further comprising a light accept belt, wherein lighter of said substantially uniform particles are blown onto said lighter accept belt.

10

29. The process of claim 28, further comprising a heavy accept belt, wherein heavier of said substantially uniform particles are blown on to said heavier accept belt.

15

30. The process of claim 7, further comprising a housing maintaining said primary shredder.

20

31. The process of claim 1, further comprising by-products of said hydrolyzing step, where said by-products are used for production of energy.

25

32. The process of claim 31, wherein said energy is electricity.

30

33. The process of claim 32, further comprising an anaerobic digester, wherein said digester biodegrades sludge and facilitates said fermenting process.

35

34. The process of claim 33, further comprising diesel/gas generators to provide electricity.

5 35. The process of claim 1, further comprising by-products of said hydrolyzing step, wherein said by-product comprises furfural.

10

36. The process of claim 1, further comprising by-products of said hydrolyzing step, wherein said by-product comprises acetic acid.

15

37. The process of claim 1, further comprising by-products of said hydrolyzing step, wherein said by-product comprises carbon dioxide.

20

38. The process of claim 1, further comprising by-products of said hydrolyzing step, wherein said by-product comprises cattle feed.

25

39. The process of claim 1, wherein said catalyst is an acid.

30

40. The process of claim 39, wherein said acid is H_2SO_4 .

35

41. The process of claim 39, wherein said acid is HCl.

42. The process of claim 1, wherein said hydrolyzing step is performed with a twin screw extruder.

5 43. The process of claim 1, further comprising the step of centrifuging said hydrolyzate.

10 44. The process of claim 1, wherein said separating is performed by an electrodialysis unit.

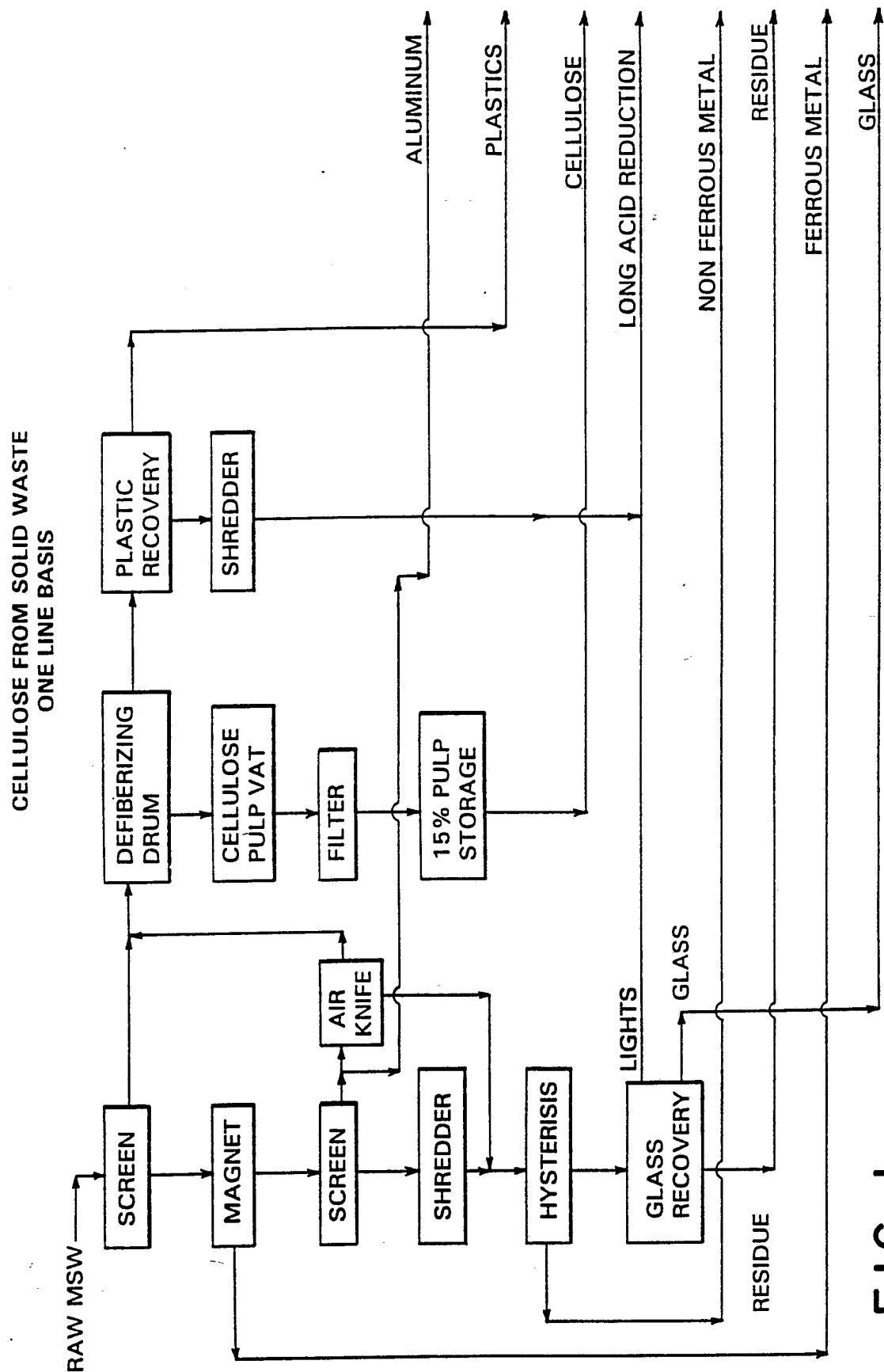
15 45. The process of claim 44, wherein said separating is also performed by a dialysis unit.

20 46. The process of claim 1, wherein said fermenting step is performed in a Delta-t unit.

25 47. The process of claim 1, wherein said fermentation step is performed in a Biostil unit.

30

35



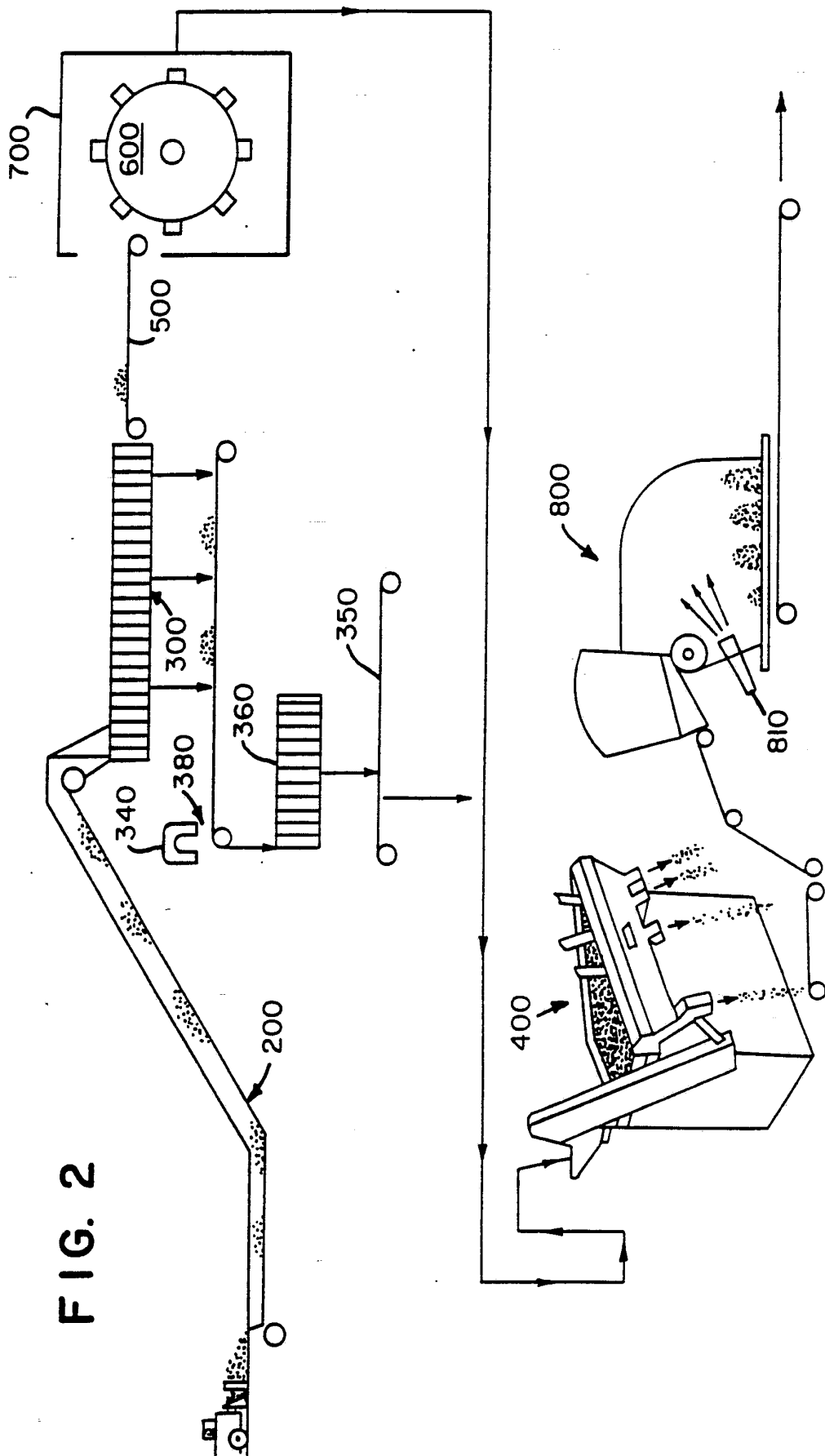


FIG. 2

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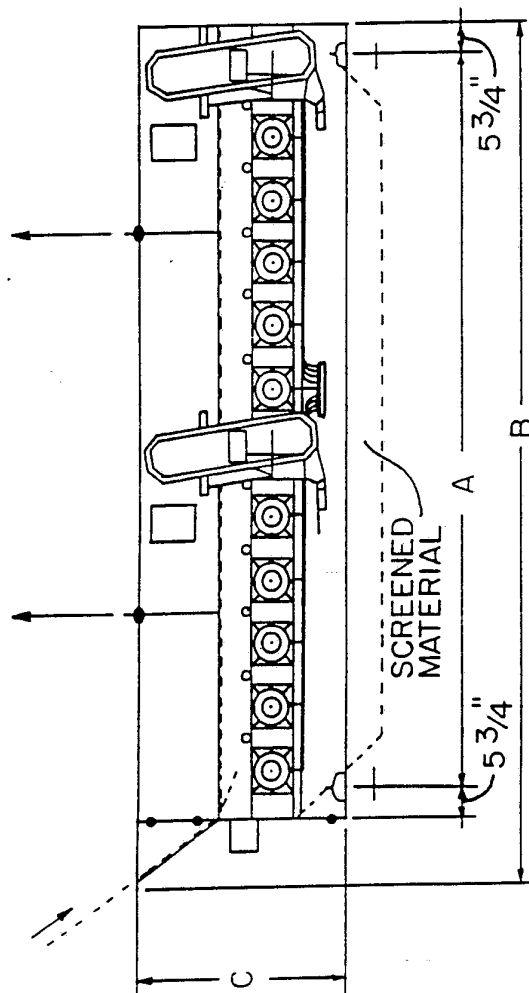
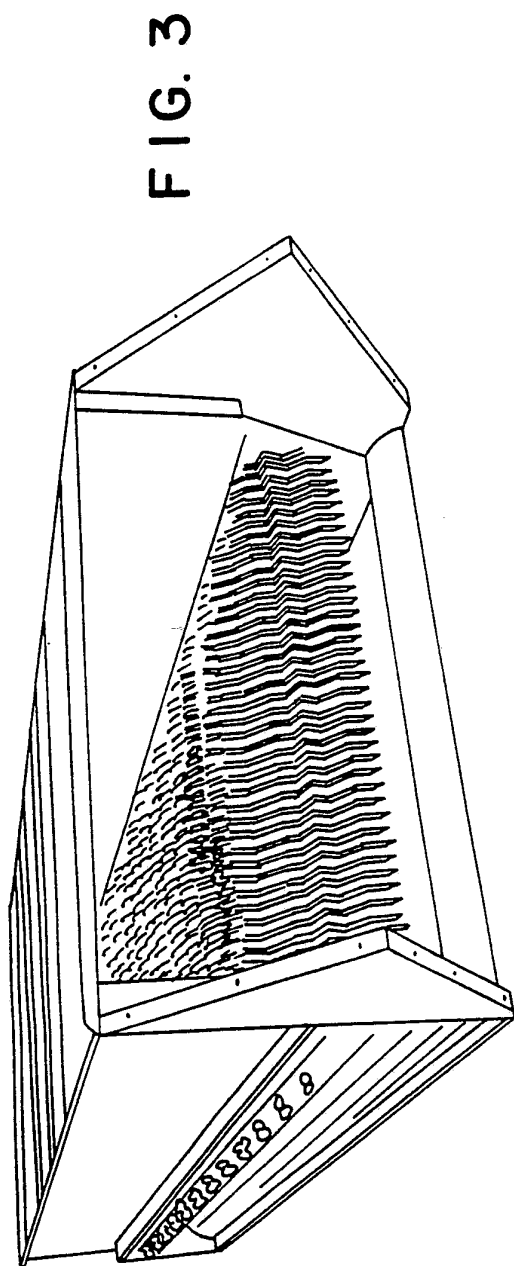


FIG. 4

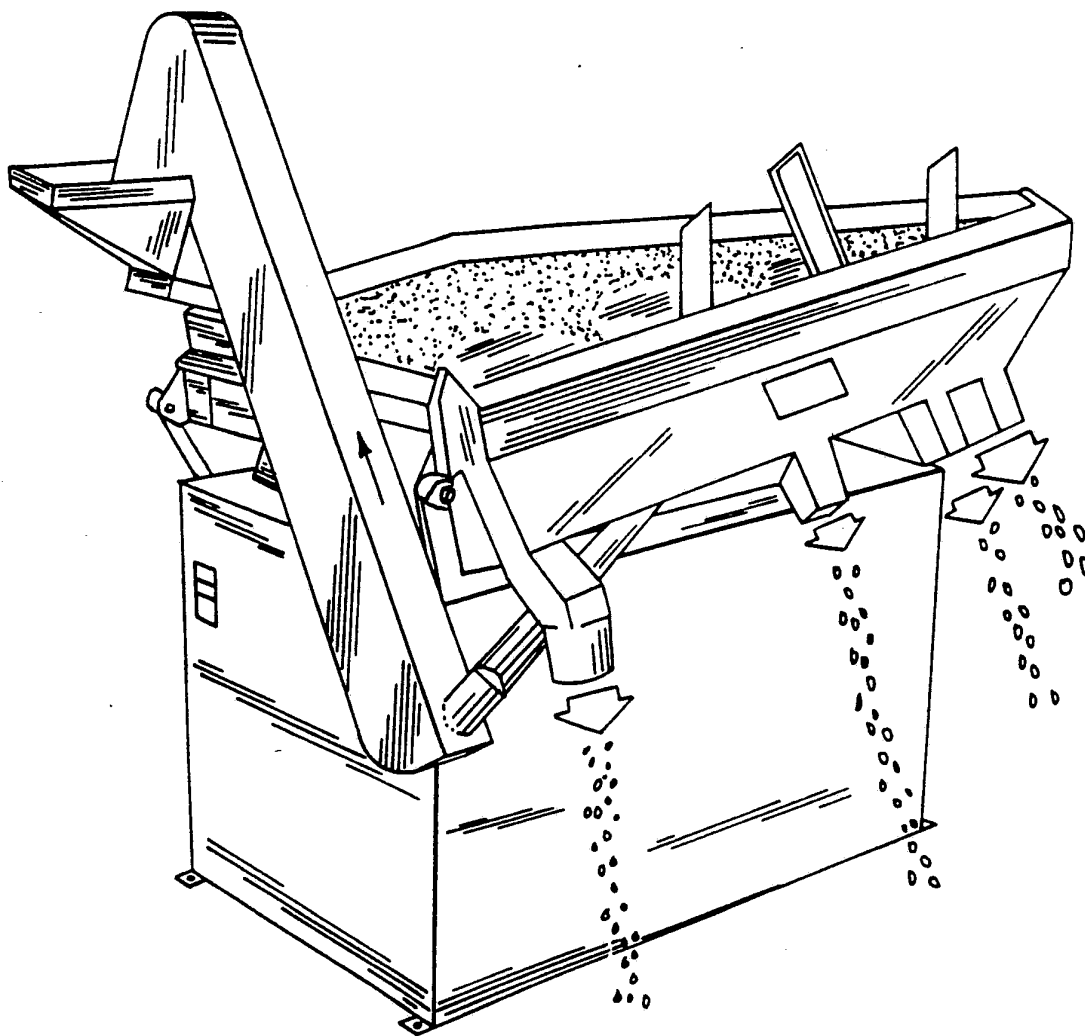


FIG. 5

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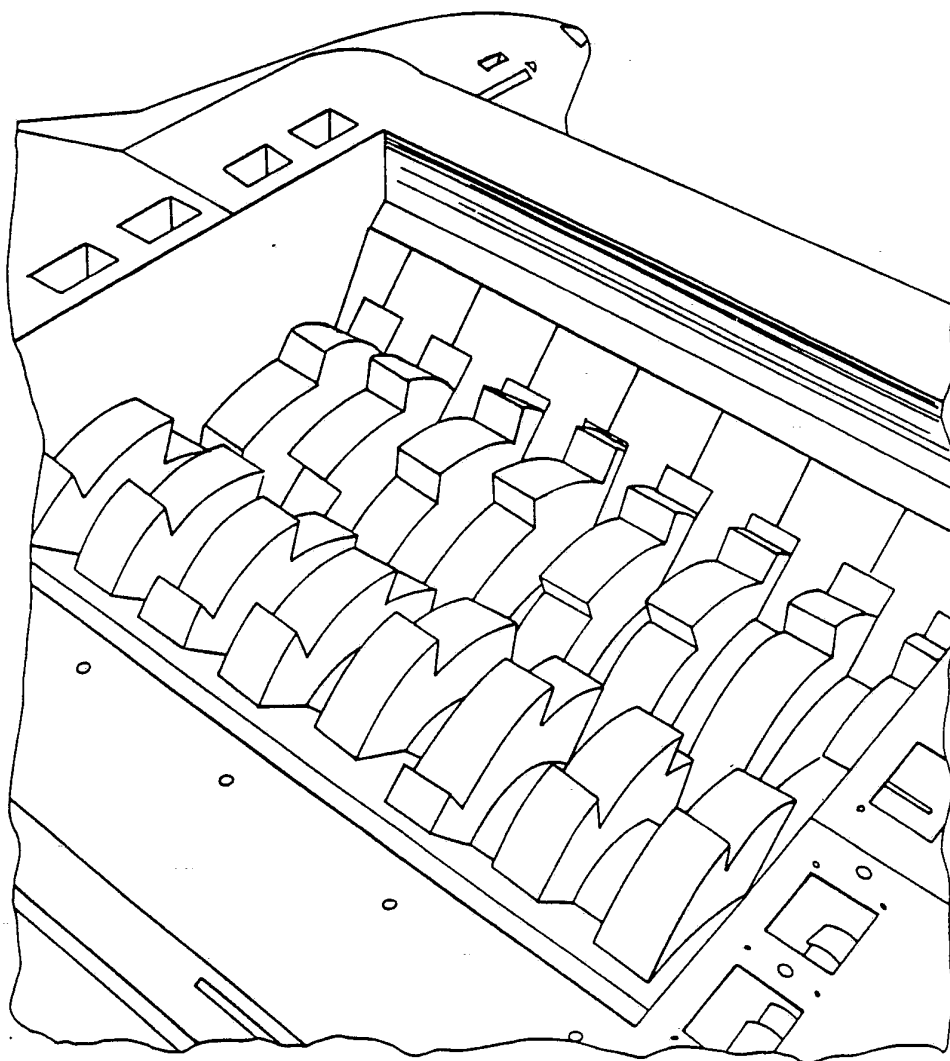


FIG. 6

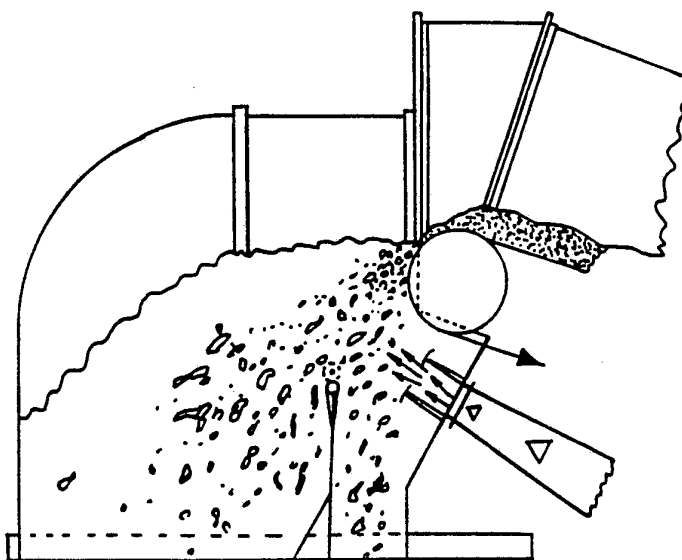
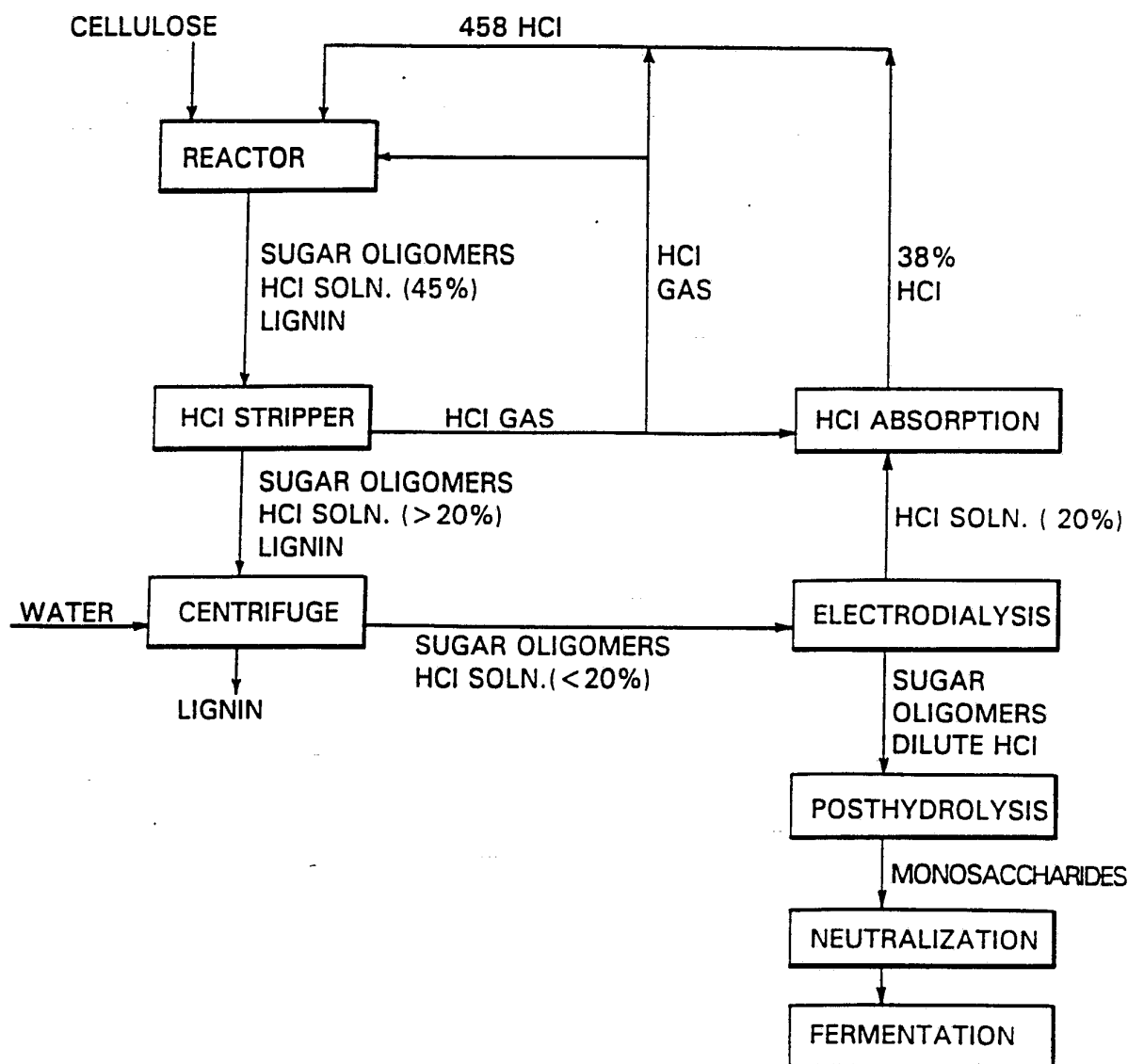


FIG. 7

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PROCESS FLOW SHEET FOR CELLULOSE HYDROLYSIS

FIG. 8

SUBSTITUTE SHEET

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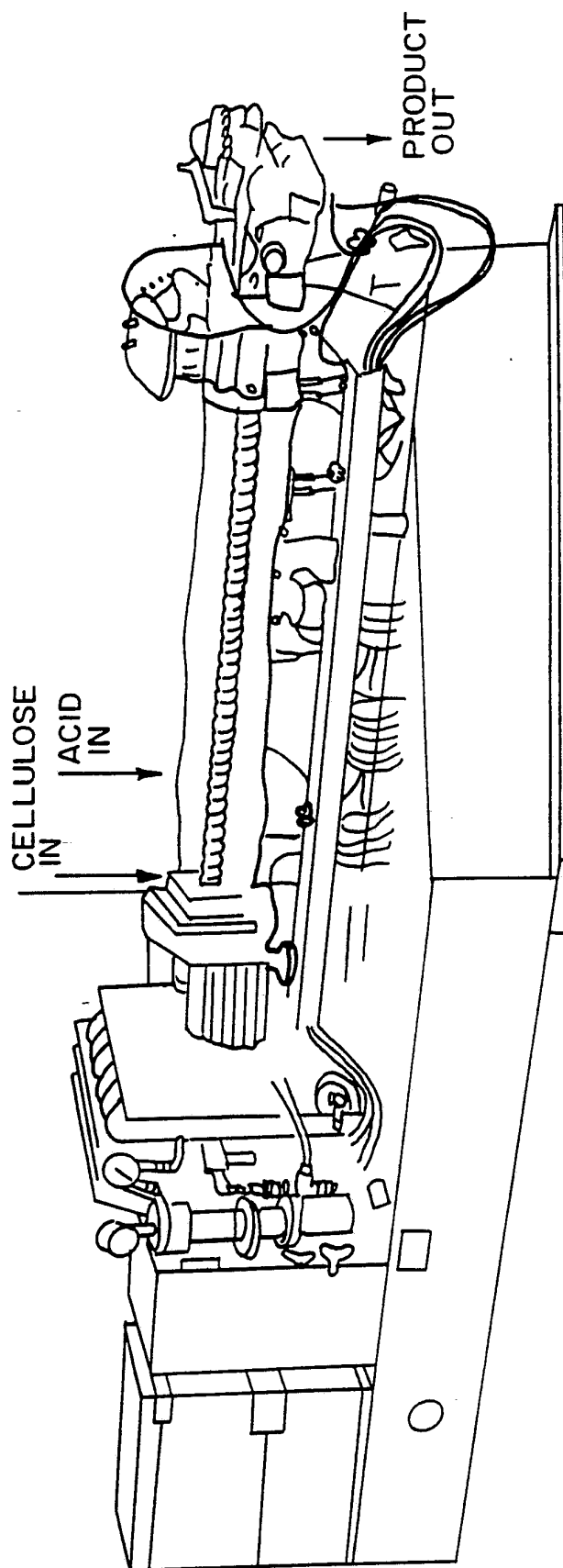


FIG. 9

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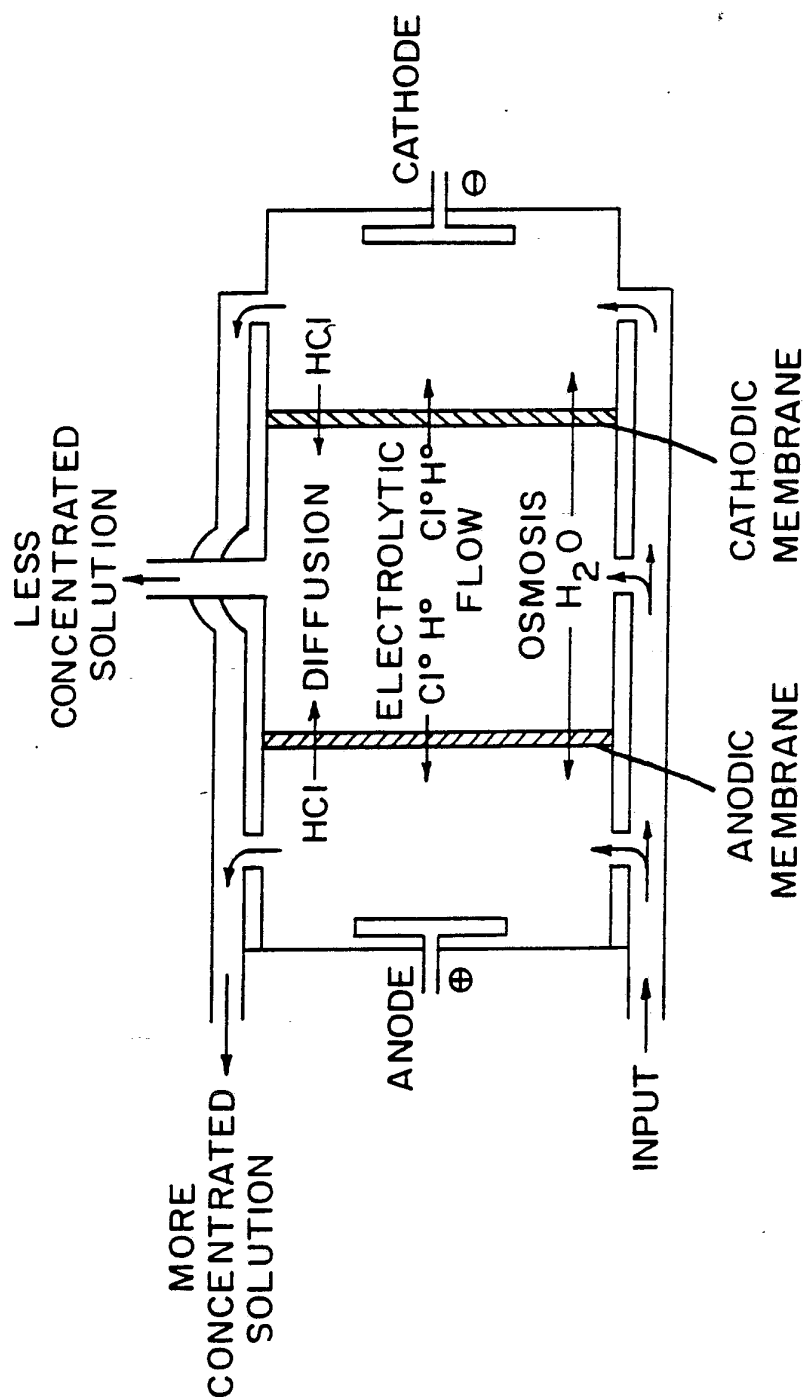
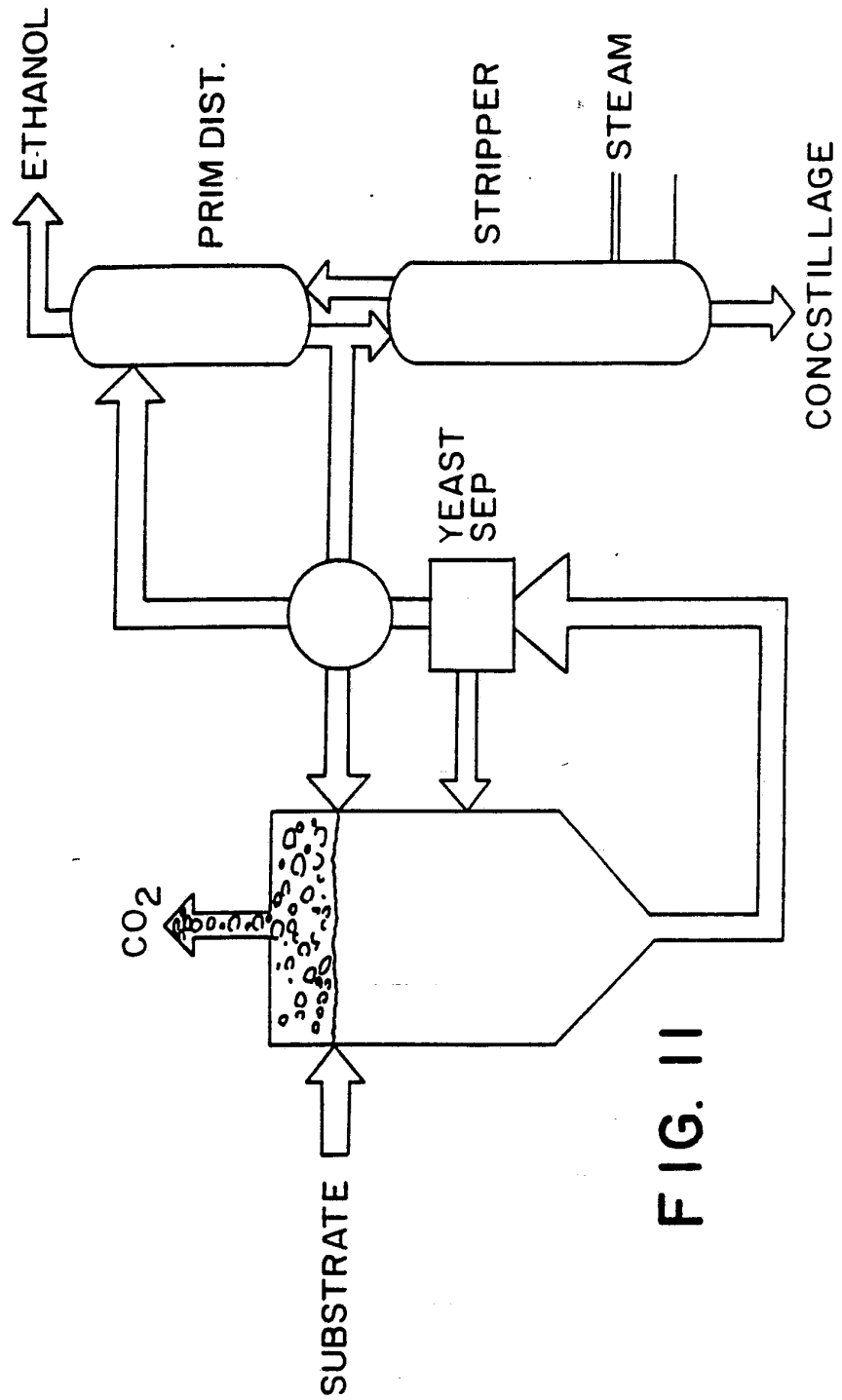


FIG. 10

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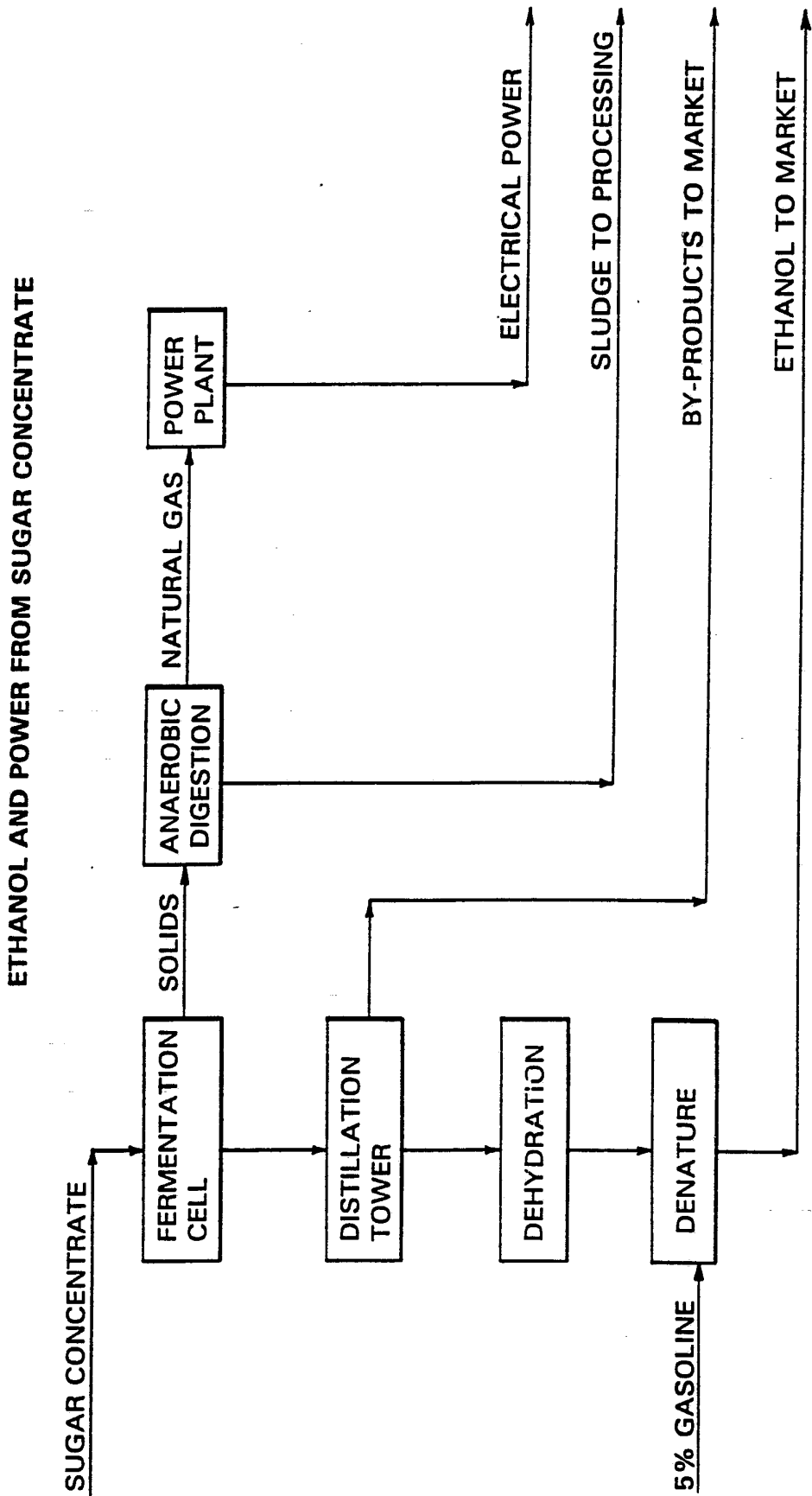


FIG. 12

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/07879

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): C12S 13/00; C12P 7/08 US CL : 435/262, 163		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	435/262, 163	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
APS Search terms: trash, cellulose, sugar, ferment, fungus		
III. DOCUMENTS CONSIDERED TO BE RELEVANT¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US, A, 3,711,392 (Metzger) 16 January 1973, see the Abstract.	44-45
Y	US, A, 4,237,226 (Grethlein) 02 December 1980, see entire document.	1-47
Y	US, A, 4,540,467 (Grube et al) 10 September 1985, see entire document.	1-47
Y	US, A 4,321,328 (Hoge) 23 March 1982, see entire document.	1-47
Y	US, A 4,842,877 (Tyson) 27 June 1989, See Abstract.	1-47
Y	Stafford et al, "Methane Production from Waste Organic Mattter" published 1980 by CRC Press, Inc. (Florida), see pages 192-195.	1-47
[*] Special categories of cited documents:¹⁶ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
03 FEBRUARY 1992		14 FEB 1992
International Searching Authority ¹		Signature of Authorized Officer ²⁰
ISA/US		Timothy J. Reardon