

1 BIOLOGICAL PRODUCTION OF ACETIC ACID FROM
 WASTE GASES

 The present invention is directed to biological
 methods, processes, microorganisms, and apparatus for
5 producing products, materials, intermediates, and the
 like such as organic acids, single cell protein
 ("SCP"), hydrogen, alcohols, and organic acid salts
10 from the waste gas streams of certain industrial
 processes and more particularly concerns a process
 utilizing continuous gaseous substrate fermentation
 under anaerobic conditions to accomplish this
15 conversion.

 The conventional procedure for producing organic
 acids, alcohols, hydrogen and organic acid salts is
 chemical synthesis of petroleum-derived feedstocks.
20 The rapidly escalating cost of petroleum has generated
 considerable interest in producing these valuable
 commodities by fermentative processes that utilize
 renewable or waste materials as the feedstock. Single
25 cell protein is produced as a by-product of the
 fermentations to be used as an animal feed supplement.

 There is also growing concern over the massive
30 amounts of atmospheric pollutants and greenhouse gases
 produced by conventional industrial processes. The

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1 Environmental Protection Agency recently estimated
that over six million metric tons of carbon monoxide
and nearly four million metric tons of hydrogen were
5 discharged annually by the industrial complex. A
substantial portion of this waste carbon monoxide and
hydrogen is the result of carbon black manufacture and
coke production, roughly 2.6 million metric tons of CO
10 and 0.5 million metric tons of H₂. Large amounts of
carbon monoxide or hydrogen are also produced by the
ammonia industry (125, 144 metric tons of CO in 1991),
15 petroleum refining (8 metric tons per thousand
barrels), steel mills (152 pounds per metric ton of
steel produced), and sulfate pulping of wood (286
pounds per ton of pulp). In 1991, the adipic acid
20 industry generated 40,773 metric tons of carbon
monoxide that was burned for fuel value or flared. In
many cases, these gases are discharged directly to the
atmosphere, placing a heavy pollution burden on the
25 environment.

Typically, the waste gases from the manufacture
of industrial products are released at low pressures
and temperatures. Current technology cannot utilize
30 these dilute gases under such conditions. Adapting

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1 existing technology to separate and recover hydrogen
or carbon monoxide from these waste streams would be
expensive and impractical.

5 In light of the foregoing, there is a need for a
cost effective and practical method, microorganism,
and apparatus for utilizing the above-described waste
gases and for producing products, materials,
10 intermediates and the like such as organic acids,
alcohols, hydrogen and organic acid salts by other
than chemical synthesis of petroleum derived
feedstocks.

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SUMMARY OF THE INVENTION

In accordance with the present invention,
20 products, materials, intermediates, and the like such
as organic acids, alcohols, hydrogen, single cell
protein and/or organic acid salts are produced from
the waste carbon monoxide, hydrogen, and/or carbon
25 dioxide of industrial processes, thereby reducing
environmental pollution while at the same time saving
energy and chemical feedstocks.

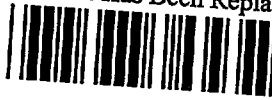
30 In accordance with an exemplary process of the
present invention, the desired components of the

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1 dilute gas mixtures are introduced into a bioreactor
containing one or more cultured strains of anaerobic
bacteria that utilize the waste gas components by a
5 direct pathway to produce a desired compound. The
compound is recovered from the aqueous phase in a
separate vessel or vessels, utilizing a suitable
recovery process for the compound produced. Examples
10 of recovery processes include extraction, distillation
or combinations thereof, or other efficient recovery
processes. The bacteria are removed from the aqueous
phase and recycled to avoid toxicity and maintain high
15 cell concentrations, thus maximizing reaction rates.
Cell separation, if desired, is accomplished by
centrifugation, membranous ultrafiltration, or other
20 techniques.

The principal object of the present invention is the
provision of a process and/or microorganism for the
production of products, intermediates, materials, and
25 the like such as organic acids, hydrogen, single cell
protein, alcohols, and/or organic acid salts from
carbon monoxide, hydrogen, and/or carbon dioxide.

Another object of the present invention is the
30 provision of methods, microorganisms and apparatus for



1 the production of items such as organic acids,
alcohols, hydrogen, single cell protein and/or salts
from the waste gas streams of industrial processes
5 such as oil refining, carbon black, coke, ammonia, and
methanol production.

A still further object of the present invention
is the provision of a process for producing acetic
10 acid and/or ethanol from a waste gas stream of
identical composition to that found in the manufacture
of carbon black.

15 Yet another and more particular object of the
present invention is the provision of a method,
microorganism and apparatus involving continuous
gaseous substrate fermentation under anaerobic
20 conditions to accomplish the conversion of waste gas
streams of certain industrial processes into useful
products such as organic acids including acetic acid,
alcohols, hydrogen, single cell protein and organic
25 acid salts.

Other objects and further scope of the
applicability of the present invention will become
apparent from the detailed description to follow,
30 taken in conjunction with the accompanying drawings

1 wherein like parts are designated by like reference numerals.

Fig. 1 is a schematic diagram of a process for
5 the production of acetic acid from waste gas.

Fig. 2 is a schematic diagram of a process for the production of CMA from waste gas.

Fig. 3 is a schematic diagram of a process for
10 the production of ethanol from waste gas.

Fig. 4 is a schematic representation of a continuous fermentation system in accordance with an embodiment of the present invention.
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Fig. 5 is a graphical illustration of cell concentration (OD) versus time.

Fig. 6 is a graphical representation of acetic acid (HAC) versus time.
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The term "waste gas" or "waste gas streams" as used herein means carbon monoxide and hydrogen mixed with other elements or compounds, including carbon
25 dioxide, nitrogen and methane, in a gaseous state and which are typically released or exhausted to the atmosphere either directly or through combustion. Normally, release takes place under standard
30 smokestack temperatures and pressures. Accordingly,

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1 the processes of the present invention are suitable
for converting these atmospheric pollutants into
useful products such as organic acids, alcohols and
5 organic acid salts. These products include, but are
not limited to acetic, propionic, and butyric acids;
methanol, ethanol, propanol, and n-butanol; plus
salts, such as calcium magnesium acetate (CMA) and
10 potassium acetate (KA).

Anaerobic bacteria which are known to convert
carbon monoxide and water or hydrogen and carbon
dioxide into alcohols and acids and acid salts
15 include *Acetobacterium kivui*, *A. woodii*, *Clostridium*
aceticum, *Butyribacterium methylotrophicum*, *C.*
acetobutylicum, *C. formoaceticum*, *C. kluyveri*, *C.*
20 *thermoaceticum*, *C. thermocellum*, *C.*
thermohydrosulfuricum, *C. thermosaccharolyticum*,
Eubacterium limosum, *C. ljungdahlii* PETC and
Peptostreptococcus productus. Anaerobic bacteria
25 known to produce hydrogen from carbon monoxide and
water include *Rhodospirillum rubrum* and
Rhodopseudomonas gelatinosa.

More specifically, bacterial species such as
30 *Acetogenium kivui*, *Peptostreptococcus productus*,

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1 *Acetobacterium woodii*, *Clostridium thermoaceticum* and
2 *Eubacterium limosum* produce acetate by the reaction:



5 Many anaerobic bacteria are also known to
6 produce acetic acid from H_2 and CO_2 . These bacterial
7 isolates include *A. kivui*, *P. productus*, and
8 *Acetobacterium* sp., which utilize homoacetic
9 fermentation by anaerobically oxidizing hydrogen and
10 CO_2 according to the equation:



15 *Acetobacterium woodii* and *Acetoanaerobium*
16 *noterae* produce acetate from H_2 and CO_2 according to
17 the above reaction, but in addition to acetate, *A.*
18 *noterae* produces some propionate and butyrate.
19 Another chemolithotrophic bacteria, *Clostridium*
20 *aceticum*, produces acetate from CO_2 using a glycine
21 decarboxylase pathway.

25 Some bacteria, like *A. kivui*, *P. productus*, and *A.*
26 *woodii*, produce acetate from either CO and H_2O or H_2
27 and CO_2 . *P. productus* gives particularly fast rates
28 of conversion and demonstrates high tolerance to CO ;
29 however, this organism shows a preference to follow
30 Equation (1) over Equation (2).

1 In addition to these listed bacteria, two strains
of an additional clostridia which produce acetic acid or
ethanol from CO and H₂O or H₂ and CO₂ have been isolated.
5 One is a *Clostridium ljungdahlii* ERI2 rod-shaped, gram
positive, non-thermophilic anaerobe which gives superior
acetic acid yields and operates at a low pH, which
greatly enhances the recovery of the product. C.
10 *ljungdahlii* ERI2 carries out a vigorous acetogenic
fermentation of glucose. It also infrequently forms
spores and carries out a primarily acetogenic
15 fermentation of hexose or H₂:CO₂. It is motile with
peritrichous flagellation. This new strain of C.
ljungdahlii, referred to as ERI2, was isolated from a
natural water source and was deposited on December 8,
20 1992, with the American Type Culture Collection (ATCC),
Rockville, Maryland, accession no. 55380.

In preparing the products of the present invention,
"mixed strains" of the bacteria enumerated hereinabove may
25 be utilized. By mixed strains, it is meant a mixed
culture of two or more anaerobic bacteria. This mixed
strain, when utilized in the process described herein,
produces organic acids (such as acetic acid and the like)
30 or salts thereof, alcohols, hydrogen, SCP, etc.

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1 In the development of the present invention, new
strains of anaerobic bacteria have been isolated which
enact this conversion with high efficiency. In
5 addition, modifications to the fermentation conditions
can result in the production of ethanol instead of
acetic acid in some strains. Depending on the specific
microorganism(s) utilized, variables which must be
10 considered in forming products from waste gases include
nutrient constituents and concentrations, medium,
pressure, temperature, gas flow rate, liquid flow rate,
15 reaction pH, agitation rate (if utilizing a Continuously
Stirred Tank Reactor), inoculum level, maximum substrate
(introduced gas) concentrations to avoid inhibition, and
maximum product concentrations to avoid inhibition.

20 In accordance with an exemplary embodiment of
the present invention and as shown in Figure 1 of the
drawings, a first step in the conversion process is
the preparation of nutrient media (10) for the
25 anaerobic bacteria. The content of the nutrient media
will vary based on the type of anaerobe utilized and
the desired product. The nutrients are constantly fed
to a bioreactor or fermenter (12), consisting of one
30 or more vessels and/or towers of a type which includes

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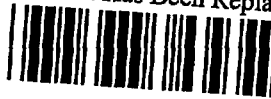


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1 the Continuously Stirred (CSTR), Immobilized Cell
(ICR), Trickle Bed (TBR), Bubble Column, Gas Lift
Fermenters, or other suitable fermentation reactor.
5 Within bioreactor (12) resides the culture, either
single or mixed species, of anaerobic bacteria
utilized in the gas conversion process. For the
CSTRs, TBRs, Bubble Columns and Gas Lift Fermenters,
10 these bacteria live dispersed throughout the liquid
phase of the reactor, but for ICRs, the bacteria
adhere to an internal packing medium. This packing
15 medium must provide maximal surface area, high mass
transfer rate, low pressure drop, even gas and liquid
distribution, and must minimize plugging, fouling,
nesting and wall channeling. Examples of such medium
20 materials are ceramic Berl saddles, Raschig rings or
other high performance packings.

The waste gases (14) are continuously introduced
into the bioreactor (12). The gas is retained in the
25 bioreactor (12) for the period of time which maximizes
efficiency of the process. Exhaust gases (16),
containing inerts and unreacted substrate gases, are
then released. The liquid effluent (18) is passed to
30 a centrifuge, hollow fiber membrane, or other

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1 filtration device (20) to separate out microorganisms
that are entrained. These microorganisms (22) are
returned to the bioreactor (12) to maintain a high
5 cell concentration which yields a faster reaction rate
(cell recycle).

A next step in the process is separation of the
desired biologically produced product(s) from the
10 permeate or centrifugate (24). In the embodiment
depicted in Figure 1, the permeate or centrifugate
(24) is passed to an extraction chamber (26) where it
is contacted with a solvent (28). The solvent (28)
15 should have a high distribution coefficient for the
desired end product, a high recovery factor, low
toxicity to humans, low toxicity to the bacteria,
20 immiscibility with water, appropriately high boiling
point, and form no emulsion with the bioreactor
constituents. The distribution of solute between
solvent and aqueous phase will determine the
25 thermodynamic feasibility and the amount of solvent
required to remove the end product. Typical solvents
include secondary and tertiary amines in a suitable
solvent, tributyl phosphate, ethyl acetate, tri-octyl
30 phosphine oxide and related compounds in a suitable

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1 co-solvent, long chain alcohols, hexane, cyclohexane,
chloroform, and tetrachloroethylene.

The nutrients and materials in the aqueous phase
5 (30) pass back to the bioreactor (12) and the
solvent/acid/water solution (32) passes to a
distillation column (34), where it is heated to a
10 sufficient temperature to separate the solvent (28)
from the acid and water (36). The solvent (28) passes
from the distillation column (34) through a cooling
chamber (38) to lower the temperature to the optimum
15 temperature for extraction, then back to the
extraction chamber (26) for reuse. The acid and water
solution (36) passes to a final distillation column
(40) where the desired end product (42) is separated
20 from the water and removed. The water (44) is
recirculated for nutrient preparation.

Figure 2 shows a process for the production of
the road deicer calcium magnesium acetate (CMA) (46),
25 from waste gas (48). The process is identical to the
acetic acid process of Figure 1 through solvent
extraction. That is, identical organisms, nutrients
and process conditions are used in continuous
30 fermentation, including the reaction vessels.

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1 Similarly, cell recycle by hollow fiber membrane,
centrifugation or other filtration device is
identically employed in the process. Finally, the
5 extraction of acetic acid in an extraction chamber,
followed by recycle of the acid-free medium, is
employed.

10 After extraction, the process for producing CMA
differs greatly from the acetic acid production
process of Figure 1. In the CMA process the solvent
(50) containing acetic acid and a small amount of
15 water is sent to a reaction vessel (52) for CMA
production. The water content of the solvent stream
is dependent upon the solvent used for acetic acid
extraction. Again, solvents such as secondary and
20 tertiary amines in a suitable co-solvent, tributyl
phosphate, ethyl acetate, tri-octyl phosphine oxide
and related compounds in a suitable co-solvent, long
chain alcohols, hexane, cyclohexane, chloroform and
25 tetrachloroethylene may be employed with varying
success. The reaction vessel (52) for CMA is most
suitably a Continuous Stirred Tank Reactor (CSTR),
although other reactor systems may be employed. A
30 mixture (54) of dolomitic lime and magnesium oxide in

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1 water is added to the solvent containing acetic acid
and water. Reaction occurs to produce CMA in aqueous
solution at or below the saturation level.

5 The CMA, water and solvent (56) are then sent to
a settling device (58) to separate the aqueous and
solvent phases. The solvent phase (60) is returned to
the extraction chamber for recycle. The CMA/water
10 (62) is sent to drying/pelletizing (64) to produce a
pelletized CMA product.

Potassium acetate (KA) can be produced as an
15 alternative product by substituting caustic potash (or
potassium oxide) for the dolomitic lime. Since KA is
produced as a 50 percent aqueous solution, drying and
pelletizing are not required.

20 Figure 3 shows a process for the production of
ethanol from waste gas. As in Figure 1, waste gas
(66) and nutrients (68) are fed into a reactor (70)
containing a culture of microorganisms. The reactor
25 may be any of the types described above in the
narrative of Figure 1. The organism used in the
ethanol production process must be capable of
producing ethanol in place of acetic acid/acetate. In
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1 general, a low fermentation pH of 4.0 - 5.5 is
 required, coupled with a nutrient limitation.
 The bacteria listed hereinabove which are capable of
5 operating at these reduced pH levels can be used in
 this process of ethanol production.

 Waste gas is fed into the reactor containing the
 culture of organisms capable of ethanol production
10 along with the required nutrients. Ethanol is
 produced as the product in a similar fashion as in
 Figure 1. Cell recycle (72) may be used to enhance the
15 cell concentration in the reactor, but this operation
 is not required to make the process work. The
 permeate (74) from the cell recycle apparatus
 containing dilute ethanol in medium is sent to
20 distillation (76), where the water (78) and ethanol
 (80) are separated. 95 percent ethanol exits the top
 of the distillation column and water (spent medium)
 exits the bottom of the column. The spent medium is
25 sent back to the reactor as water recycle. The 95
 percent ethanol is sent to a molecular sieve system
 (82) to produce anhydrous ethanol (84).

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1 Thus in accordance with the present invention it
is now possible to produce valuable organic acids,
alcohols, or organic acid salts by a gaseous substrate
5 fermentation, not only reducing consumption of
valuable chemical feedstocks, but also removing
hazardous atmospheric pollutants from the waste gas
streams of many industries. Previous processes to
10 derive these chemicals biologically were based on
fermentation of sugars.

In the processes described hereinabove, it is
preferred that the process is conducted at higher than
15 1 atmosphere. Preferably, it is preferred that it be
conducted at pressures up to 30 atmospheres and more
preferably up to 20 atmospheres and most preferably up
to 15 atmospheres.
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The following specific examples are submitted to
illustrate but not to limit the present invention.
Unless otherwise indicated, all parts and percentages
25 in the specification and claims are based upon volume.

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EXAMPLE 1

PRODUCTION OF ACETIC ACID FROM CARBON BLACK

WASTE GASES

5 This example is directed to a process utilized
to convert waste gas of a composition which matches
that of the furnace exhaust of carbon black
manufacture to acetic acid. The waste gas has a
10 composition of about 13 percent carbon monoxide, 14
percent hydrogen, and 5 percent carbon dioxide, with
the remaining 68 percent largely nitrogen with traces
of oxygen and sulfur compounds. The waste gases are
15 produced as the result of partial oxidation of gas or
oil with insufficient air to form amorphous carbon,
with about 1.2 pounds of carbon monoxide produced per
20 pound of elemental carbon. These waste gases form a
serious atmospheric contamination problem and also
represent a valuable chemical feedstock resource not
presently being recovered.

25 In the development of the present process, two
distinct routes to produce acetic acid from carbon
black waste gases were studied. The direct route
converts CO and H₂O or H₂ and CO, directly into acetic
30 acid according to Equations (1) and (2), respectively.

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- 1 An indirect route involves the conversion of CO and
H₂O into H₂ and CO₂ by the water gas shift reaction,
followed by production of acetic acid from H₂ and CO₂.
5 This indirect route was found to be a less efficient
utilization of the technology.

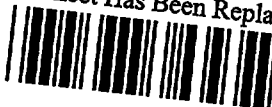
The acetogens tested are summarized in Table 1.
Among these bacteria that produce acetic acid directly
10 from CO, *A. kivui* and the newly isolated strain, *C.*
ljungdahlii ERI2, show far superior rates for both CO
and H₂ utilization. Further experimentation proceeded
using these two anaerobic bacteria.

15 There are obvious advantages to the bacteria
utilizing carbon monoxide and hydrogen simultaneously.
This would afford the most efficient use of the waste
gases and remove the greatest amount of atmospheric
20 pollutants.

Bench Scale Operation of the Described Process to Produce Acetic Acid

25 As shown in Figure 4 of the drawings and in
accordance with one embodiment of the present
invention, a bench scale continuous conversion system
is shown to include a BioFlo IIC fermentor (150) from
30 New Brunswick Scientific Co., Inc., Edison, NJ. The

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1 fermentor (150) is equipped with an agitation motor,
pH controller, foam controller, thermostat, dissolved
oxygen probe, nutrient pump, and 2.5 L culture vessel.
5 The working volume is variable (1.5-2.0 L). Other
variable operational parameters include medium feeding
rate (Dilution rate), gas flow rate (Gas retention
time), agitation (rpm). The vented or exhaust gases
10 exit the fermentor (150) through a condenser fixed to
a vented hood via a water trap and a sampling port.

The culture broth (152) is recycled through a
15 cross-flow hollow fiber module (154) by a peristaltic
pump (from Cole Parmer). The recycling rate is about
80-100 mL/min. The hollow fiber module (154) has the
following characteristics; the surface area is 0.35
20 ft², the pore size is 0.2 um and the lumen diameter is
1 mm. The permeate (156) is pumped to a storage tank
(158) (Feed storage). The culture cells are returned
to the fermenter along line (155).

25 A counter-current acetic acid extraction system,
including two stage mixer and settler components
includes first and second mixers (160) and (162) and
first and second settling tanks (164) and (166). The
30 permeate (168) from storage (158) is pumped to mixer



1 (160) through a flow controller (170). The solvent
(172) is pumped to mixer (162) from solvent storage
(174) through a flow controller (176). Both mixer
5 (160) and mixer (162) are equipped with a stirring
mechanism to achieve good mixing of aqueous phase and
solvent phase. The mixture of both phases from the
mixers (160) and (162) is led to settlers (164) and
10 (166), respectively. The phase separation is
accomplished in the settlers. The aqueous phase (178)
from settler (164) is pumped to mixer (162), the
solvent phase (180) from settler (164) is pumped to a
15 separator (182), the aqueous phase (184) from settler
(166) is pumped to raffinate storage (186), and the
solvent phase (188) from settler (166) is pumped to
20 mixer (160). The raffinate is recycled to the CSTR 50
along a line (190). This recycle line (190) is
partially bled at (192) to remove inhibiting factors.

The solvent (180) loaded with acetic acid is
25 pumped to a distillation flask (194) through a
preheater (196). The distillation flask (194) is
equipped with two thermocouples (196) and (198) to
monitor and control temperature in the liquid phase
30 and gas phase. The heating temperature for

1 distillation is set to achieve maximum vaporization of
the acetic acid. The acetic acid vapors are condensed
in a condenser (100) and collected in a flask (102).

5 The stripped solvent (104) is pumped through a cooling
coil (106) to solvent storage (174).

A bench scale operation of the described process
as diagrammed in Figure 4 was fabricated in the
10 laboratory to determine quantitative yields under
optimized conditions. The nutrient mixture fed to the
culture was as follows:

- 15 1. 80.0 ml of a salt, composed of
- | | |
|---|----------|
| KH_2PO_4 | 3.00 g/L |
| K_2HPO_4 | 3.00 g/L |
| $(\text{NH}_4)_2\text{SO}_4$ | 6.00 g/L |
| NaCl | 6.00 g/L |
| $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ | 1.25 g/L |
- 20 2. 1.0 g of yeast extract
3. 1.0 g of trypticase
- 25 4. 3.0 ml of PFN (Pfenning) trace metal

solution

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	1500 mg
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	100 mg
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	30 mg

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1		H ₃ BO ₃	300 mg
		CoCl ₂ * 6H ₂ O	200 mg
		CuCl ₂ * H ₂ O	10 mg
5		NiCl ₂ * 6H ₂ O	20mg
		NaMoO ₄ * 2H ₂ O	30mg
		Na ₂ SeO ₃	10 mg
		Distilled water	1000 ml
10	5.	10.0 ml of B vitamins	
		Pyridoxal HCl	10 mg
		Riboflavin	50 mg
		Thiamine HCl	50 mg
15		Nicotinic acid	50 mg
		Ca-D-Pantotheinate	50 mg
		Lipoic Acid	60 mg
20		P-aminobenzoic acid	50 mg
		Folic acid	20 mg
		Biotin	20 mg
		Cyanocobalamin	50 mg
25		Distilled water	1000 ml
	6.	0.5 g of Cysteine HCl	
	7.	0.06 g of CaCl ₂ .2H ₂ O	
	8.	2.0 g of NaHCO ₃	
30	9.	1.0 ml of Resazurin (0.01%)	

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1 10. 920.0 ml of distilled water

For use with *A. kivui*, the nutrient solution was pH adjusted to 6.6, whereas for the new strain, *C.*

5 *ljungdahlii* ERI2, the pH was adjusted to 4.9. The ability to operate at a lower pH is a great advantage in acetic acid recovery. The solution was then sparged for 20 minutes with a 20% CO₂ and 80% N₂,
10 atmosphere, then transferred anaerobically and autoclaved for 15 minutes.

Numerous experiments were carried out with both Continuous Stirred Reactors (CSTR) and Immobilized
15 Cell Reactors (ICR). The results obtained are exemplified in the following data.

20 CSTR Experiments Utilizing the bacterial Strains *A. kivui* and *C. ljungdahlii* ERI2

The bench scale system operating with the CSTR and the anaerobic bacteria, *C. ljungdahlii* ERI2 and *A.*
25 *kivui*, consisted of a New Brunswick Scientific Bioflo IIC fermenter, a hollow fiber membrane unit for cell recycle, and extraction and distillation columns. Nutrient mixture was fed into the bioreactor at a rate
30 of 3.2 cubic centimeters per minute. Capacity of the

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1 reactor was 2.5 liters, within which a constant fluid
level of 1.5 liters was maintained. The fluid was
agitated at variable rates of up to 1000 revolutions
5 per minute with gas introduced at a rate of
approximately 500 cubic centimeters per minute.
Optimal gas retention times were in the range of three
minutes. The gas feed varied with its uptake by the
10 bacteria, which was in turn a function of the cell
density.

The liquid from the bioreactor was passed to the
hollow fiber membrane at a rate of 55 to 70
15 milliliters per minute. From the hollow fiber
membrane, permeate was gathered at a rate of 1.5
milliliters per minute. Analysis of this permeate
20 indicates the acetic acid/acetate concentration at
this stage to range in excess of 20 grams per liter.
Operating at a pH of 4.9, 42 percent of this product
was in the acid form using *C. ljungdahlii* ERI2. For
25 *A. kivui*, the acid yield was only 1.4 percent.
Results of various runs for the two bacteria,
including conversion rates and product yields are
summarized in Tables 2 and 3.

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1 ICR Experiments Utilizing the Bacterial Strain C.
ljungdahlii ERI2

5 An Immobilized Cell Reactor (ICR), consisting of
a 2 inch outside diameter by 24 inch tall glass tube
packed with fabric to support the cells and Enkamat
7020 as an immobilizing medium was also tested in the
acetic acid production process. With C. ljungdahlii
10 ERI2 as the acetogenic anaerobe, 100 percent of the
carbon monoxide and 79 percent of the hydrogen were
converted at a gas retention time of 20 minutes.
Acetic acid concentrations in the removed liquid were
15 approximately 6.0 grams per liter. Results of the ICR
studies are summarized in Table 4.

The ICR has a certain attractiveness on an
20 industrial scale in that the energy costs to operate
the reactor are reduced significantly. The proper
selection of packing materials, solution phases, and
pressures may yield production approaching that of the
25 CSTR.

Acetic Acid Recovery

Various solvents were tested for recovering
acetic acid from the permeate, the results are
30 summarized in Table 5. Tributyl phosphate was

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1 identified as having both a high distribution
coefficient and a high boiling point. The solvent and
permeate from the cell separator were commingled in a
5 two stage extraction process. Alternatively, an
extraction column could be used. Permeate was
introduced into a 3 liter flask where it was mixed
with incoming solvent. A ratio of 1 part solvent to 1
10 part permeate worked well and gave high recovery
rates. The combined fluids were passed from the mixer
to a 4 liter settling chamber where the solvent/acetic
15 acid mixture separate as a lower density phase from
the water and nutrients. Retention times of
approximately 15 minutes were used in the settling
tanks. The lower density phase was extracted and fed
20 to a distillation flask. The raffinate was passed
from the first settler to a second mixer where it was
contacted again with solvent, then removed to a second
settling chamber. This allowed for more complete
25 extraction of the acetic acid; acid recovery increased
from 82 percent to greater than 96 percent using
tributyl phosphate. The solvent/acetic acid mixture
from this settler was returned to the first mixer,
30

1 while the raffinate of water and organics was passed
back to the bioreactor.

The distillation unit was a 5 liter flask with a
5 boiling mantle. A common distillation column, with
reflux, could be used for complete acid recovery.
Because of the high boiling point of tributyl
phosphate, nearly complete recovery is accomplished in
10 one step. The solvent/acetic acid mixture was heated
to 120 degrees C, with the acetic acid collected
overhead in a condensing coil. In this single stage
system, distillation efficiencies of 70 percent were
15 achieved.

Solvent mixtures were also tried and
distribution coefficients of mixed solvents are
20 summarized in Table 6.

EXAMPLE 2

PRODUCTION OF ACETIC ACID FROM CARBON BLACK WASTE GASES

25 AT HIGHER PRESSURES

Mass transport in the cellular reactions can be
further enhanced by operating the system at increased
pressures. Simple batch experiments were carried out
30 to test the dynamics of this system. It was found that

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1 reaction rates increased in linear proportion to the
pressure, with a corresponding reduction in effective
retention time. Another advantage to operating at
5 increased pressure is that reactor volume can also be
reduced in linear fashion, i.e. operation at 10
atmospheres pressure requires a reactor with one tenth
the volume of a reactor operating at 1 atmosphere.
10 Figures 5 and 6 show the increase in cell density and
acetic acid concentration, respectively, with the
increased pressure. This acetic acid concentration
far exceeds typical batch concentrations for a batch
15 reactor at atmospheric pressure.

EXAMPLE 3

PRODUCTION OF ACETIC ACID FROM CARBON BLACK WASTE 20 GASES WITH SURFACTANTS

Mass transport is also increased by the use of
surfactants. Table 7 presents the results of carbon
monoxide uptake tests performed on *C. ljungdahlii* ERI2
25 in the presence of various commercial surfactants. In
each case, the control value of 100 (percent)
represents CO uptake in batch fermentation, and the
sample value, the percentage of the control in batch
30 fermentation in the presence of the surfactant.

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TABLE 1

ACETOGENIC BACTERIA TESTED FOR CO, H₂, AND CO₂

CONVERSION

5 Bacterial Route Simultaneous Consumption of CO and H₂

Direct Route

P. productus No

E. limosum No

10 A. noterae No

C. aceticum No

C. thermoaceticum No

15 S. sphaeroides No

A. woodii Yes

A. kivui Yes

C. ljungdahlii ERI2 Yes

20 Indirect Route

R. gelatinosa No

R. rubrum No

25

30

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Table 2. Summary of ERI2 Experiments in the CSTR with Cell Recycle

Gas Reten. Time (min)	Liquid Dilution Rate (hr ⁻¹)	Agitat. Rate (rpm)	Percent Gas Conversion		Dry Cell Weight Conc. (g/L)	Product Concentration		Specific Productivities	
			CO	H ₂		HAC (g/L)	ETOH (g/L)	(g/L hr)	(g/g hr)
9.30	0.056	750	80.75	74.5	2.3	9.7	0.07	0.43	0.13
9.28	0.055	750	82.1	72.0	3.32	9.56	0.094	0.52	0.16
6.14	0.061	750	73.6	46.5	4.11	12.78	0.125	0.78	0.19
6.4	0.08	750	74.8	49.6	5.02	12.98	0.125	1.05	0.19
4.74	0.087	750	68.5	37.2	4.79	12.38	0.125	1.08	0.23
4.91	0.10	750	68.8	50.2	4.53	10.73	0.05	1.08	0.24
4.05	0.102	750	65.5	58.1	5.27	11.49	0.076	1.17	0.22
3.98	0.103	900	74.3	67.9	6.17	12.73	0.1	1.31	0.21
2.89	0.117	900	66.1	33.9	5.91	11.69	0.04	1.38	0.23
3.28	0.105	1000	74.6	51.3	7.30	12.83	0.13	1.35	0.18
3.22	0.125	1000	73.1	54.0	10.25	13.57	0.08	1.71	0.17
2.65	0.13	1000	68.9	44.0	11.0	14.63	0.12	1.90	0.17
2.3	0.134	1000	66.0	38.7	11.1	20.59	0.113	2.77	0.25
2.7	0.11	1000	72.7	67.7	8.37	25.62	0.27	2.88	0.34
2.4	0.11	1000	68.6	63.3	9.88	25.82	0.36	2.95	0.30
2.55	0.122	1000	72.1	67.4	9.82	25.62	0.72	3.12	0.32
3.0	0.13	1000	76.6	73.3	12.4	22.33	0.52	2.90	0.23

Table 3. Summary of *A. kivui* Experiments in the CSTR with Cell Recycle

Gas Reten. Time (min)	Liquid Dilution Rate (hr ⁻¹)	Agitat. Rate (rpm)	Percent Gas Conversion		Dry Cell Weight Conc. (g/L)	Product Conc. (g/L)	Specific Productivities	
			CO	H ₂			(g/L hr)	(g/g hr)
5.0	0.058	750	67.8	44.2	4.00	16.15	0.96	0.24
4.4	0.958	750	65.7	38.5	4.8	16.63	0.94	0.19
4.3	0.058	900	71.3	40.7	4.5	17.03	0.99	0.21
3.72	0.058	900	69.0	37.3	5.14	19.16	1.13	0.22
3.72	0.076	900	70.3	41.1	5.28	16.17	1.21	0.23
3.2	0.076	900	66.4	41.4	5.71	16.85	1.23	0.23
2.8	0.076	900	61.5	29.1	5.00	16.16	1.22	0.23
2.8	0.076	1000	67.5	36.3	5.8	18.58	1.62	0.29
2.8	0.11	1000	70.2	41.6	5.9	18.4	1.84	0.36
2.2	0.11	1000	64.0	28.0	7.2	16.5	2.1	0.3

Table 4. Fabric ICR Performance with ERI2

Liquid Dilution Rate (hr)	Gas Retention Time (min)	H ₂ Conversion (%)	CO Conversion (%)	Cell Concen. (g/L)	Product Concentration	
					HAC (g/L)	ETCH (g/L)
0.23	4.83	38.62	54.66	.125	3.221	.778
	7.41	49.15	70.87	.120	2.690	.620
	11.66	51.31	80.61	.067		
	13.61	56.87	83.93	.064	2.099	.201
0.17	6.39	48.15	73.27	.161	3.382	1.366
	11.21	68.96	92.82	.143	3.189	.495
	55.64	83.13	98.27	.112	.813	.058
0.12	6.26	43.89	70.76	.094	3.864	1.629
0.09	7.87	42.40	73.72	.095	4.423	2.733
	19.82	59.63	92.92	.102		
0.03	22.14	55.01	94.21	.071	4.878	2.631
	29.00	78.60	100	.018	5.604	2.743
	60.48	83.33	100			

Table 5. Acetic Acid Distribution Coefficient Study

<u>Solvent</u>	<u>Equilibrium Aqueous Acetic Acid Concentration, g/l</u>	<u>Acetic Acid Distribution Coefficients</u>
Hexane	6.559	0.0
Decane	5.968	0.08
Chloroform	5.128	0.09
Kerosene	4.648	0.11
Hexadecane	5.866	0.13
Dodecane	4.654	0.13
Dodecyl acetate	5.787	0.15
Dibutyl phosphate	4.615	0.18
Oleyl alcohol	5.114	0.28
Trioctylamine	3.785	0.31
Undecyl alcohol	4.528	0.40
Ethyl acetate	4.550	0.41
Ethyl butyrate	4.665	0.42
Dexyl alcohol	3.890	0.42
Octanol	4.358	0.45
Nonyl alcohol	3.470	0.55
2-ethyl-1-hexanol	3.308	0.77
3-methylcyclohexanol	2.110	1.26
Cyclohexanone	2.702	1.66
Tributyl Phosphate	1.657	2.38

Table 6. Distribution Coefficients of Mixed Solvents

<u>Solvent Mix</u>	<u>Distribution Coefficients</u>	<u>Percent Increase</u>
Oleyl Alcohol (10cc)	0.17	
Oleyl Alcohol (10cc) + Cyc (1cc)	0.31	72
Oleyl Alcohol (10cc) + TBP (1cc)	0.29	61
Oleyl Alcohol (10cc) + Cyc (2cc)	0.45	150
Oleyl Alcohol (10cc) + TBP (2cc)	0.42	133
Oleyl Alcohol (10cc) + Cyc (3cc)	0.36	100
Oleyl Alcohol (10cc) + TBP (3cc)	0.42	133
Oleyl Alcohol (10cc) + Cyc (4cc)	0.35	94
Oleyl Alcohol (10cc) + TBP (4cc)	0.40	122
Oleyl Alcohol (10cc) + Cyc (6cc)	0.52	188
Oleyl Alcohol (10cc) + TBP (6cc)	0.63	261
Oleyl Alcohol (10cc) + Cyc (7cc)	0.69	283
Oleyl Alcohol (10cc) + TBP (7cc)	0.74	311

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TABLE 7. CO CONSUMPTION BY ER12 IN THE
PRESENCE OF SURFACTANTS

	Control*	With Surfactant
5 DNAP (0.1%, v/v)	100	0
Nondiet P-40 (0.1%, v/v)	100	0
Tergitol NP-10 (0.1%, v/v)	100	0
Tergitol Min Foam 1X (0.1%, v/v)	100	0
Tergitol TMN-10 (0.1%, v/v)	100	0
10 Triton X-15 (0.1%, v/v)	100	0
Triton X-100 (0.1%, v/v)	100	0
Triton X-114 (0.1%, v/v)	100	0
Triton N-101 (0.1%, v/v)	100	5.83
Triton X-405 (0.1%, v/v)	100	7.82
15 Tergitol 8 (0.1%, v/v)	100	12.15
Triton N-42 (0.1%, v/v)	100	42.90
Witconol NS-500K (0.01%, w/v)	100	79.08
Tween 85 (0.1%, v/v)	100	82.16
20 Witconol H-33 (0.1%, v/v)	100	90.12
Witconol 6903 (0.1%, v/v)	100	92.39
Tween 80 (0.1%, v/v)	100	97.15
Arlacel 83 (0.1%, v/v)	100	97.43
Span 80 (0.1%, v/v)	100	99.12
25 Tyloxapol (0.1%, v/v)	100	104.86
Witconol 5906 (0.1%, v/v)	100	108.42
Span 85 (0.1%, v/v)	100	124.85
W-1 (0.001%, w/v) First time	100	105.89
Second time regas	100	0
30 Brij 96 (0.004%, w/v) First time	100	107.98
Second time regas	100	0

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1 EXAMPLE 4

PRODUCTION OF CMA FROM CARBON BLACK WASTE GAS

 Carbon black waste gas containing about 14
5 percent CO, 17 percent H₂ and 4 percent CO₂, as the
 major components in N₂ is sparged into a 160L
 continuous stirred tank reactor, maintained at 6 atm
 37°C, and containing *Clostridium ljungdahlii* isolate
10 ER12 ATCC deposit 55380. The waste gases are produced
 as the result of partial oxidation of hydrocarbons
 with insufficient air to form amorphous carbon, with
15 about 1.2 pounds of carbon monoxide produced per pound
 of elemental carbon. These waste gases form a serious
 atmospheric contamination problem and also represent a
 valuable chemical feedstock resource not presently
20 being recovered. The gas retention time (defined as
 the ratio of the reactor volume to the gas flow rate
 at standard conditions) is maintained at 0.52 min. An
 aqueous liquid medium containing water, base salts, B-
25 vitamins, a nitrogen source and a sulfide source is
 fed to the reactor at a liquid dilution rate (defined
 as the ratio of the liquid flow rate to the reactor
 volume) of 1.05 hr⁻¹. The agitation rate in this
30 reactor is 322 rpm, the temperature is 37°C and the



1 operating pH is 5.03. Under these conditions, the
conversion of CO was 83 percent and the conversion of
H₂ was 54 percent. A hollow fiber membrane cell
5 recycle unit is used to maintain a cell concentration
of 10.5 g/L inside the reactor. The dilute acetic
acid/acetate product stream from the reactor
containing 13.2 g/L acetic acid/acetate is sent to a
10 three stage countercurrent extraction device, where it
is extracted with solvent. The solvent to feed ratio
is 1 to 4. The acetic acid in the acetic acid/acetate
product stream is 3.7 g/L. The acetic acid
15 concentration in the solvent leaving the extractor is
16.7 g/L. Water (medium) from extraction is sent back
to the fermenter as recycle.

20 Dolomitic lime/MgO is added to the acetic acid
directly in the solvent phase to form CMA. After
reaction the saturated CMA solution is sent to drying
and pelletizing 1.15 lb of CMA containing a Ca²⁺/Mg²⁺
25 molar ratio of 3/7 is formed per pound of acetic acid.

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1 **EXAMPLE 5****PRODUCTION OF ACETIC ACID FROM CARBON BLACK WASTE GAS**

Carbon black waste gas containing about 14
5 percent CO, 17 percent H₂, and 4 percent CO₂ in N₂ is
sparged into a 144 L trickle bed reactor operating at
1.58 atm, 37°C and containing *Clostridium Ijungdahlii*
isolate ER12 ATCC deposit 55380. A trickle bed
10 reactor is a column packed with a commercial packing
such as Raschig rings or Berl saddles in which liquid
and gas are contacted with each other due to flow
through the column. In the present example, the
15 liquid and gas both enter the column from the top in a
cocurrent fashion, although countercurrent flow (gas
entering the bottom, liquid entering the top) is
possible. The gas retention time is maintained at
20 0.46 min and the liquid medium dilution rate is 0.57
hr⁻¹. The liquid medium contains the same constituents
as in Example 1. Agitation in the reactor is provided
25 by liquid recirculation, using a recirculation rate of
60 gpm. The operating pH in the reactor is 5.05.
Under these conditions, the CO conversion is 57
percent and the H₂ conversion is 58 percent. A hollow

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1 fiber unit is used to maintain a cell concentration of
13.6 g/L inside the reactor.

5 The dilute acetic acid/acetate product stream
containing 6.4 g/L combined acetic acid/acetate and 2
g/L acetic acid is sent to a three stage
countercurrent extraction column. The solvent to feed
ratio is 1:4. The acetic acid in the solvent leaving
10 the extractor is 10 g/L. Water (medium) from the
extraction unit is sent back as recycle to the
reactor.

15 The solvent containing the acetic acid is sent
to distillation to recover the acid and solvent. A
vacuum solvent distillation column and an acetic acid
distillation column are used in the separation.
20 Glacial acetic acid is produced as the final product.

EXAMPLE 6

PRODUCTION OF POTASSIUM ACETATE FROM CARBON BLACK WASTE GAS

25 The carbon black waste gas of Example 4 is used
to make potassium acetate instead of CMA. All
fermentation and solvent extraction conditions remain
the same. Caustic potash (potassium oxide) is used to
30 react with the acetic acid to form a 50 percent

1 solution of potassium acetate directly in the solvent
phase.

EXAMPLE 7

5 PRODUCTION OF SCP FROM COKE OVEN WASTE GAS

A coke oven waste gas containing about 6 percent
CO, 2 percent CO₂, 57 percent H₂, 5 percent N₂, and 27
percent gaseous hydrocarbon is fed to a continuous
10 stirred tank reactor with cell recycle as described
previously in Example 4. The reactor is used to
produce a product such as dilute acetic acid or
ethanol. In addition, the cell concentration inside
15 the reactor is 13.6 g/L. These cells (microorganisms)
can be harvested to produce bacterial single cell
protein as an animal feed. A purge stream from the
20 reactor containing cells is sent to a dryer to process
dry single cell protein.

EXAMPLE 8

PRODUCTION OF H₂ FROM REFINERY WASTE GAS

25 Refinery waste gas containing about 45 percent
CO, 50 percent H₂, and 5 percent CH₄ is sparged into a
1L CSTR operating at 50°C and a few inches of water
pressure containing *Bacillus smithii* isolate ERIH2
30 which was deposited on March 18, 1993 with the

1 American Type Culture Collection, Rockville, Maryland
and given deposit accession no. 55404. The medium to
the reactor is 1.0 g/L corn steep liquor. CO in the
5 waste gas is converted along with water to CO₂ and H₂.
With a 90 percent conversion, the exit gas stream
contains 3.2 percent CO, 64.4 percent H₂, 28.8 percent
CO₂, and 3.6 percent CH₄. The CO, CO₂, and CH₄ are
10 removed from the gas stream by solvent extraction.

EXAMPLE 9

PRODUCTION OF OTHER CHEMICALS FROM CARBON BLACK WASTE 15 GAS

Carbon black waste gas containing about 14
percent CO, 17 percent H₂, and 4 percent CH₄ in N₂ is
sparged into a 1L CSTR operating at 37°C and a few
20 inches of water pressure. The medium in the reactor
is a basal salts mixture containing water, B-vitamins,
salts and minerals. The single or mixed culture in
the reactor produces a liquid phase product of
25 methanol, propanol, butanol, propionic acid, butyric
acid or other desirable product. The system is set up
essentially the same as in Example 6. Following dilute
product formation, the product is recovered in a
30 suitable product recovery system consisting of

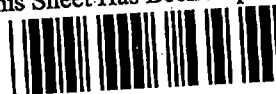
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1 extraction, distillation or other well-known product
recovery techniques. If multiple products are
produced, a stagewise product recovery system is
5 employed.

Thus, it will be appreciated that as a result of
the present invention, a highly effective improved
10 process for converting waste gases to acids, including
organic acids, e.g., acetic acid, alcohols, hydrogen,
SCP or organic acid salts is provided by which the
principle objective, among others, is completely
15 fulfilled. It is contemplated and will be apparent to
those skilled in the art from the preceeding
description and accompanying drawings that
modifications and/or changes may be made in the
20 illustrated embodiments without departure from the
present invention. Accordingly, it is expressly
intended that the foregoing description and
25 accompanying drawings are illustrative of preferred
embodiments only, and are not limiting, and that the
true spirit and scope of the present invention be
determined by reference to the appended claims.

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1 WHAT IS CLAIMED:

1. A process for producing a product selected
from the group consisting of an organic acid or salts
5 thereof, alcohol, hydrogen and SCP comprising
fermenting a waste gas containing CO and water or CO₂
and hydrogen in an aqueous nutrient media in a
bioreactor with an aerobic bacteria capable of
10 converting the waste gas system to said product to
produce a broth containing said product; removing
continuously a portion of said broth containing
product from said bioreactor; and recovering the
15 product therefrom.

2. The process according to Claim 1 wherein the
waste gas contains carbon monoxide and water.

20 3. The process according to Claim 1 wherein the
waste gas contains carbon dioxide and hydrogen.

4. The process according to any of Claims 1-3
wherein said waste gas is generated by an industrial
25 process.

5. The process according to Claim 4 wherein the
industrial process is the manufacture of carbon black
ammonia, methanol or coke or is petroleum refining.
30





1 6. The process according to Claim 1 wherein
said bacteria is of a species which produces an
organic acid or alcohol by anaerobic fermentation of a
5 carbon monoxide or a carbon dioxide gaseous substrate.

7. The process according to Claim 1 wherein
said bacteria is of a species which produces hydrogen
by an aerobic fermentation of a carbon monoxide or
10 carbon dioxide gaseous substrate.

8. The process according to Claim 1 wherein
said bacteria is of a species which produces single
cell protein by anaerobic fermentation of a carbon
15 monoxide or carbon dioxide gaseous substrate.

9. The process according to any of Claims 1-8
wherein said product is acetic acid, propionic acid,
20 butyric acid, methanol, ethanol, propanol, n-butanol,
hydrogen, single cell protein, or organic acid salts.

10. The process according to Claim 9 wherein
said organic acid salt is a salt of acetic acid.

25 11. The process according to Claim 10 wherein
said salt of acetic acid is calcium magnesium acetate
or potassium acetate.

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1 12. The process according to any of Claims 1-11
wherein said bioreactor is a continuously stirred tank
reactor, an immobilized microbial cell bioreactor, a
5 trickle bed bioreactor, a bubble column bioreactor, or
a gas lift bioreactor.

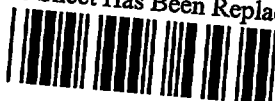
13. The process according to any of Claims 1-12
wherein said bioreactor is maintained at a pressure of
10 greater than one atmosphere.

14. The process according to any of Claims 1-13
wherein said recovery step includes separating said
product and said bacteria by passing said removed
15 broth containing product through a cell separation
unit, returning the bacteria to the bioreactor to
maintain a high bacteria concentration and producing a
20 bacteria-free, product-containing stream.

15. The process as recited in Claim 14 wherein
said separating is accomplished by centrifugation,
hollow fiber membrane filtration, settling or
25 ultrafiltration.

16. The process as recited in Claim 14 wherein
the process is conducted in the absence of any cell
separation.
30





1 17. The process according to any of Claims 1-13
wherein said recovery of said product is accomplished
by (a) contacting said removed broth containing the
5 product with a water-immiscible solvent having a high
affinity for the desired product in a counterflow
mixing vessel and then (b) optionally distilling the
product of (a) to recover solvent and product.

10 18. The process according to any of Claims 1-13
wherein said recovery of said product is accomplished
by distillation.

15 19. The process according to any of Claims 1-18
wherein said anaerobic bacteria is *Acetobacterium*
kivui, *A. woodii*, *Butyribacterium methyotrophicum*,
Clostridium aceticum, *C. acetobutylicum*, *C.*
20 *formoaceticum*, *C. kluyveri*, *C. thermoaceticum*, *C.*
thermocellum, *C. thermohydrosulfuricum*, *C.*
thermosaccharolyticum, *Eubacterium limosum*, *Clostridium*
ljungdahlii PETC, *Peptostreptococcus productus*,
25 *Rhodospirillum rubrum* or *Rhodopseudomonas gelatinosa*.

 20. The process according to any of Claims 1-18
wherein acid anaerobic bacteria is *C. ljungdahlii* ERI-
2 or *B-Smithlii* ERI-H2.

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1 21. The process as recited in any of Claims 1-
20 wherein said anaerobic bacteria is a mixed culture.

5 22. The process according to any of Claims 1-21
wherein the waste gas stream is generated from the
industrial process for making carbon black, and the
product is acetic acid or salts thereof.

10 23. A biologically pure culture of the
microorganism *Clostridium ljungdahlii* isolate ERI2.

 24. A biologically pure culture of the
microorganism *Bacillus smithlii* strain ERI-H2.

15 25. An isolated culture of *Clostridium*
ljungdahlii isolate ERI-2.

 26. *Clostridium ljungdahlii*, isolate ERI-2 ATCC
55380.

20 27. An isolated microorganism *Bacillus smithlii*
strain ERI-H2.

 28. *Bacillus smithlii* strain ERI-H2 ATCC 55404.

25 29. A mixed culture containing *Clostridium*
ljungdahlii, isolate ERI-2 ATCC 55380.

 30. A mixed culture containing *Bacillus*
smithlii strain ERI-H2 ATCC 55404.

30 31. The product prepared by any of the process
of Claims 1-22.

