

Anaerobic biotechnology for industrial wastewater treatment

*Here is an overview of the scientific principles
and technological concepts and
a description of several installations*

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Microbiological formation of methane has been occurring naturally for ages in such diverse habitats as marshes, rice paddies, benthic deposits, deep ocean trenches, hot springs, trees, cattle, pigs, iguanas, termites, and human beings (Mah and Smith, 1981; Steggerda and Dimmick, 1966; Prins, 1979; Balch et al., 1979). In the past decade, interest in anaerobic biotechnology has grown considerably, both in the harnessing of the process for industrial wastewater treatment and in the bioconversion of crop-grown biomass to methane (Sheridan, 1982; Chynoweth and Srivastava, 1980).

Our fundamental understanding of anaerobic biotechnology is growing at a rapid rate. In the past five years, there has been a surge in research interest, specifically in methane bacteria. Significant research contributions have been made by U.S. and European microbiologists. This surge of interest, supported by advances in process en-

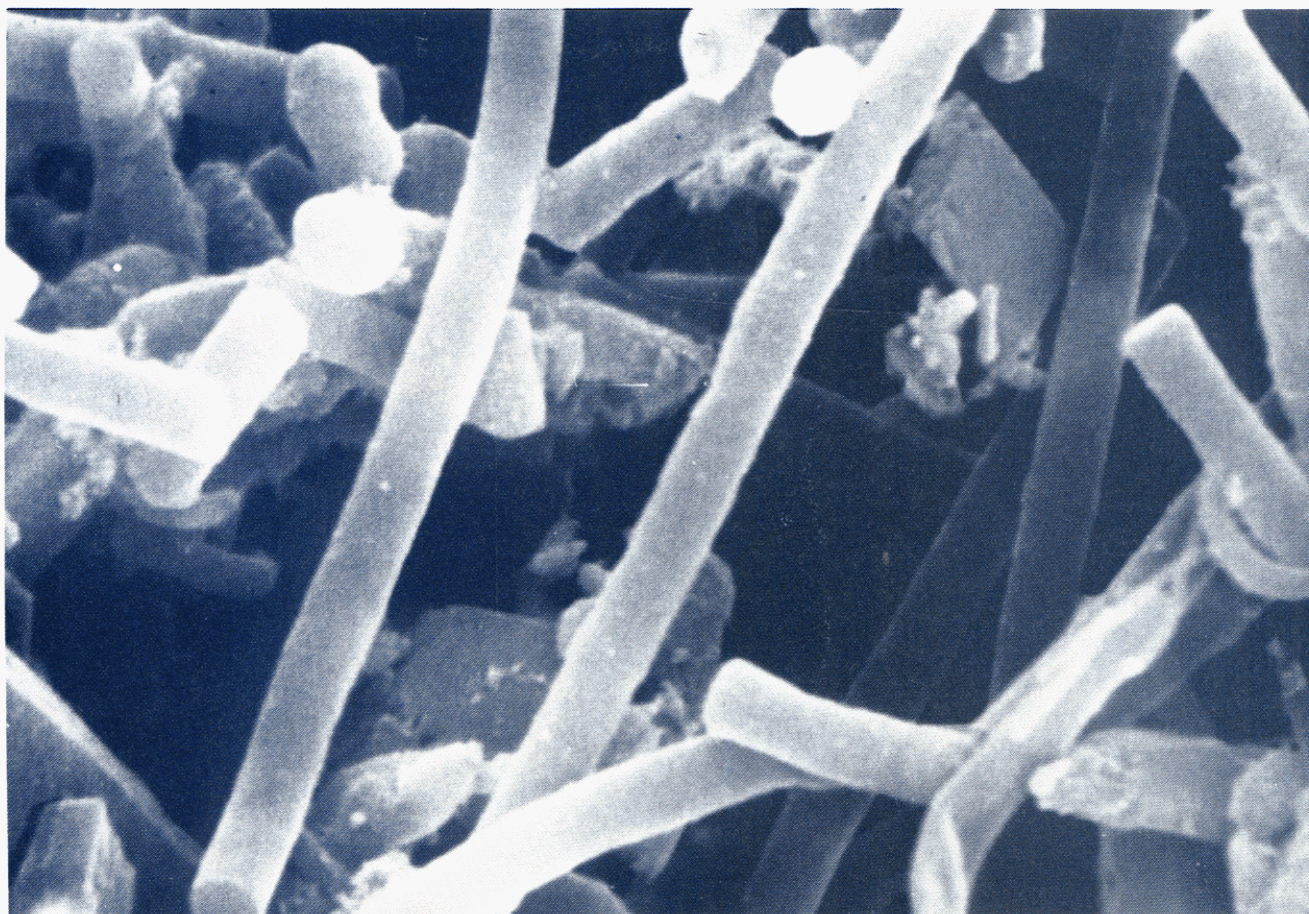
gineering, has been translated into numerous treatability studies of various industrial wastewaters. The fruition of this activity has been manifested in the commissioning of a growing number of full-scale industrial wastewater anaerobic treatment installations—over 60 in the U.S. and Europe (not counting anaerobic lagoons).

Initially, the anaerobic digestion process was applied primarily to complex feedstocks, such as municipal wastewater sludges, which contained a wide range of nutrients and alkalinity sources. Other candidate feedstocks considered for anaerobic treatment were food-processing wastewater, such as the effluent from meat-packing plants (Steffen and Bedker, 1961) and sugar beet operations (Lettinga et al., 1980). It was found that these wastewaters contain readily degradable organics and that the carriage water has a normal complement of inorganic ions such as those commonly found in surface or groundwaters. Still other candidate feedstocks now being studied are the nominally deionized wastewater arising from evaporative condensates such as pulp and paper mill black liquor evaporation condensate, coal conversion condensates, and deionized

industrial process wastewaters. More research is required to ascertain how to satisfy all inorganic nutrient requirements of this latter class of feedstocks.

Emerging data on inorganic nutrient requirements for anaerobic treatment point to the crucial role of inorganic ions, especially trace metals, in stimulating anaerobic microbial metabolism. In retrospect, it appears that an inherent lack of iron, cobalt, and nickel in past treatability studies of various industrial wastewaters may have been the cause of negative results. In addition, it is now evident that these trace metals are so vital that their lack casts doubt on the validity of many microbial kinetic studies reported in the literature on various substrates. Ignorance of these trace-metal requirements may well have delayed field application of anaerobic treatment for industrial wastewaters by at least a decade or more, because of the adverse publicity which resulted from process failures. Preliminary evidence is also pointing to an unusually high requirement by some of these microorganisms for un-ionized hydrogen sulfide.

The majority of industrial wastewaters that appear to be good candi-



Methane makers. Electron micrograph of methanogenic bacteria

dates for anaerobic treatment now require new phases of inquiry. The basic question is no longer whether an industrial wastewater can be anaerobically biodegraded to methane, since most organics are amenable to anaerobic treatment, but rather *at what rate* it is degradable. Also, to what *degree* is it degradable? Do chronic or sporadic toxicants enter the wastewater? Are the required nutrients provided? Will the process adequately accommodate variable flows and organic loads? These and other relevant questions must now be addressed for the rational exploitation of the process.

Recently, attention has been given to the isolation of mutant forms of methanogens (Baresi, 1983). There is also interest in genetic manipulation of methanogens. However, McCarty (1982) has warned that if a single microorganism were developed that were capable of converting a carbohydrate all the way to methane, the consequences could be devastating. Such an organism does not now exist, but if it were created and became established in cattle having a rumen-type digestion system, it could potentially lead to malnutrition of such cattle by converting a portion of their food supply to methane. Presently, carbo-

hydrate conversion to methane requires several microorganisms, and diversion of an animal's food supply to methane gas is minor. Feed supplements further minimize diversion of feed to methane.

The potential market for anaerobic biotechnology is vast, but a sizable hurdle of user confidence must be overcome to win that market. Our improved understanding of the microbial consortium involved and significant developments in reactor design are now laying a strong foundation for the development of efficient and reliable anaerobic biotechnology for treatment of a wide variety of industrial wastewaters. Proper engineering design and acclimation can often accommodate inherent toxicity and minimize the need for nutrient supplementation, while producing an effluent of suitable quality.

Anaerobic vs. aerobic biotechnology

The common alternative to anaerobic biotechnology for treatment of industrial wastewater is the aerobic biological process. The major factors for comparison are electrical power usage, methane gas production, and excess microbial cell production, which has an associated disposal cost. The

comparison shown in Table 1 is based on a ton of chemical oxygen demand (COD) (organic pollution) destroyed.

The net operating cost differential between anaerobic and aerobic treatment is approximately \$160 per metric ton less for the anaerobic process (assuming \$0.06/kWh, \$4.50/10⁶ Btu for methane, and \$100/ton of dry cell mass disposal costs). This cost differential may be as high as \$250 for some industries (McDermott, 1983).

Typical petrochemical, cheese-making, corn wet-milling, and pharmaceutical plants have the potential of producing in excess of \$500,000/y of methane alone from anaerobic treatment of their industrial wastewaters. Rarely, however, is the value of the methane end product from a given effluent sufficient to be the sole justification for selecting anaerobic biotechnology. Rather, the reduced cost of excess cell disposal or reduced electricity consumption are the contributing factors favoring adoption of anaerobic biotechnology.

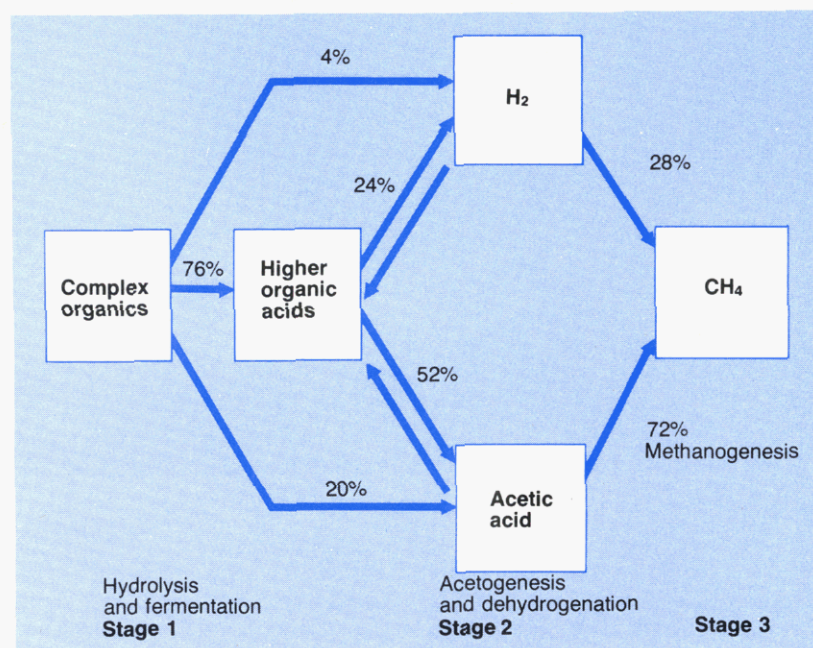
The anaerobic bioconversion process

The bioconversion of the organic feedstocks in industrial wastewaters to methane is accomplished by a consor-

TABLE 1
Comparison of anaerobic and aerobic biotechnology per metric ton COD destroyed

	Anaerobic	Aerobic
Electricity	—	1100 kWh
Methane	1.1×10^7 Btu	—
Net cell production	20–150 kg	400–600 kg

FIGURE 1
The three stages of methane fermentation^a



^a Shows the percentage flow of the energy content of complex organic materials through each stage into methane, as represented by the chemical oxygen demand. From McCarty (1981)

tium of bacteria comprised of chemoheterotrophic, nonmethanogenic bacteria and methanogenic bacteria (Mah, 1981). Complex organics are first hydrolyzed by the chemoheterotrophic nonmethanogens to free sugars, alcohols, volatile acids, hydrogen, and carbon dioxide. Subsequently, the alcohols and volatile acids longer than two carbons are oxidized to acetate and hydrogen by obligate (limited to a certain condition of life), proton-reducing organisms (acetogens), which must exist in symbiotic relation with hydrogen-utilizing methanogens (McInerney et al., 1979). In the last step, acetate and hydrogen are converted to methane by the methanogenic bacteria (Mah, 1982). McCarty (1981) has quantified this model, which is shown in Figure 1.

An obligate, syntrophic (nutrient exchange between two organisms) relationship exists between the acetogens, which convert the higher vola-

tile acids to acetate and hydrogen, and the hydrogen-utilizing methanogens. The hydrogen partial pressure must be maintained at an extremely low level to enable favorable thermodynamic conditions for the conversion of volatile acids and alcohols to acetate. Under standard conditions of 1 atm of hydrogen, the free energy change is positive for this conversion and thus precludes it. For example, the free energy change for conversion of propionate to acetate and hydrogen does not become negative until the hydrogen partial pressure decreases below 10^{-4} atm. McCarty (1981) has graphed this relationship (Figure 2). It is therefore obligatory that the hydrogen-utilizing methanogens maintain these extremely low hydrogen partial pressures in the system; otherwise, the higher volatile acids, such as propionic and butyric, will accumulate in the system. Fortunately, the hydrogen-utilizing methanogens in this physiological

partnership are adept at this and normally perform this "service" with ease to permit the reaction to proceed efficiently all the way to methane production. This phenomenon of interspecies hydrogen transfer, which is crucial to anaerobic biotechnology, is a very interesting symbiosis discovered by Bryant et al. (1967).

The free energy for the conversion of acetate to methane is so low (-28 kJ/mol) that a debate over whether acetate could serve as the sole substrate for methanogenesis lasted for years (Zeikus et al., 1975), and was finally demonstrated by Smith and Mah (1980) in pure culture. This low free energy was considered to be inadequate for adenosine triphosphate (ATP) production, which is the energy carrier for bacterial metabolism. It is now suggested that ATP production in methanogens is coupled to electron transport instead of substrate-level phosphorylation (Thauer et al., 1977). However, the mechanism coupling methane production and ATP synthesis still remains a mystery (Zeikus et al., 1977).

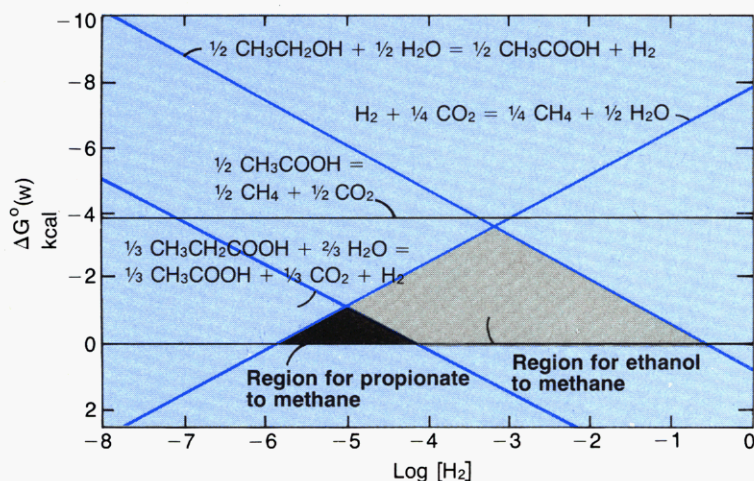
In anaerobic environments, sulfate reduction to hydrogen sulfide is energetically favored over methane production for both hydrogen and acetate substrates. The half-saturation constant (K_s , that substrate concentration that causes the microorganisms to metabolize at half of maximum rate) for hydrogen metabolism by methanogens has been reported to be $6.6 \mu\text{M}$, whereas it is only $1.3 \mu\text{M}$ for sulfate reduction (Kristjansson et al., 1982). Likewise, the K_s for acetate is reported to be 0.2 and 3 mM for sulfate reducers and methanogens, respectively (Schonheit et al., 1982). Thus, for limiting hydrogen and acetate concentrations, sulfate reduction is favored over methanogenesis. For that reason, industrial wastewaters containing high concentrations of sulfates, sulfites, or thiosulfates pose special problems ascribable to the resulting elevated concentrations of hydrogen sulfide. The BOD concentration and pH of the wastewater are crucial factors because they control the gas stripping of hydrogen sulfide (Figure 3). With high sulfate concentrations in the wastewater, it could be possible to operate the anaerobic process for the specific purpose of producing hydrogen sulfide rather than methane as the end product of waste stabilization.

Uniqueness of methanogens

Methanogens are often considered the key class of microorganisms in anaerobic biotechnology. In recent

FIGURE 2

Effect of hydrogen partial pressure on the free energy of conversion of ethanol, propionate, acetate, and hydrogen during methane fermentation^a



^a McCarty (1981)

years it has become evident that methanogens possess several unique features. Balch et al. (1977) have shown by means of 16 S rRNA (refers to a fraction of RNA) oligonucleotide catalog comparisons that methanogens are phylogenetically distinct from typical procaryotic microorganisms. Also the cell wall of methanogens does not contain muramic acid or true peptidoglycan as do other procaryotes except *Halococcus morrhuae* (Kandler and König, 1978). Consequently, they have been classified as members of the *Archaeobacteria* (Woese and Fox, 1977), a proposed new, phylogenetically distinct biological grouping.

Cofactors are ubiquitous in all microorganisms. However, at least three cofactors are apparently unique to methanogens, and recent literature is expanding this list. A recently discovered cofactor, 2-mercaptoethanesulfonic acid, has been found in all methanogens available in pure culture, except *Methanobacterium ruminantium*, which requires it for growth. However, this coenzyme has not been found in studies of a wide range of nonmethanogenic, eucaryotic tissues and procaryotic organisms (Balch and Wolfe, 1979).

Another organic compound apparently specific only to methanogens is factor 420 (F_{420} as designated by its absorption peak) (Cheeseman et al., 1972). The role of F_{420} is that of an electron transfer coenzyme (Tzeng et al., 1975). The structure of F_{420} has been tentatively identified (Eirich et al., 1978).

Recently still another coenzyme, F_{430} , has been discovered and is also designated by its absorption peak. There is evidence that this enzyme has a nickel tetrapyrrol structure (Diekert et al., 1980b). It is possibly another compound uniquely characteristic of methanogens (Whitman and Wolfe, 1980). Whitman and Wolfe also report that this compound contains substantial amounts of nickel and lacks other metals commonly associated with molecules of biological origin.

Diekert et al. (1980a) found that nickel was an essential component of factor F_{430} . Iron, cobalt, and molybdenum were not involved. F_{430} is the first nickel-containing biological compound of low molecular weight to be reported (Whitman and Wolfe, 1980). Recent evidence has been obtained that F_{430} may be a prosthetic group of 2-mercaptoethanesulfonic acid reductase. All methanogens investigated contained F_{430} (Diekert et al., 1981); F_{430} has thus far not been reported to be present in any non-methanogenic bacterium.

The obligate nickel requirement of methanogens is unusual even though it is not unique. The unusually high sulfur content of methanogenic cells, which has been reported to account for 2.6% of their total dry weight (Ronnöw and Gunnarsson, 1981), is also of note.

Overall rate-controlling step

A fundamental concern in process design is identification of the overall rate-controlling step. In anaerobic biotechnology, the rate-controlling

step in the overall process is related to nature of substrate, process configuration, temperature, and loading rate.

Raw cellulotics such as straw, corn stover, peat, and wood are mainly limited in the hydrolysis step by the lignin sheath surrounding the cellulose. The recalcitrance of lignin to anaerobic biodegradation severely limits the hydrolysis rate of raw cellulotics (Hobson et al., 1981).

Grease and lipid biodegradation may be rate controlling in some industrial wastewaters. It has been established that as the temperature decreases below 20 °C, grease biodegradation becomes nil, even though methanogenesis continues at a reduced rate (O'Rourke, 1968).

Food-processing industrial wastewaters are often high in starch and sugar content because of cooking operations. These simple organics are rapidly fermented to volatile acids. Consequently, the rate-controlling step is the conversion of the volatile acids to methane.

Since complex wastewaters containing organics have a continuous range of degradation rates, at low loading rates, the rate-controlling step may be acid formation, as is evidenced by low volatile acids concentrations. But as the loading rate increases, the methanogenesis stage may gradually become the rate-controlling step, as evidenced by an accumulation of volatile acids.

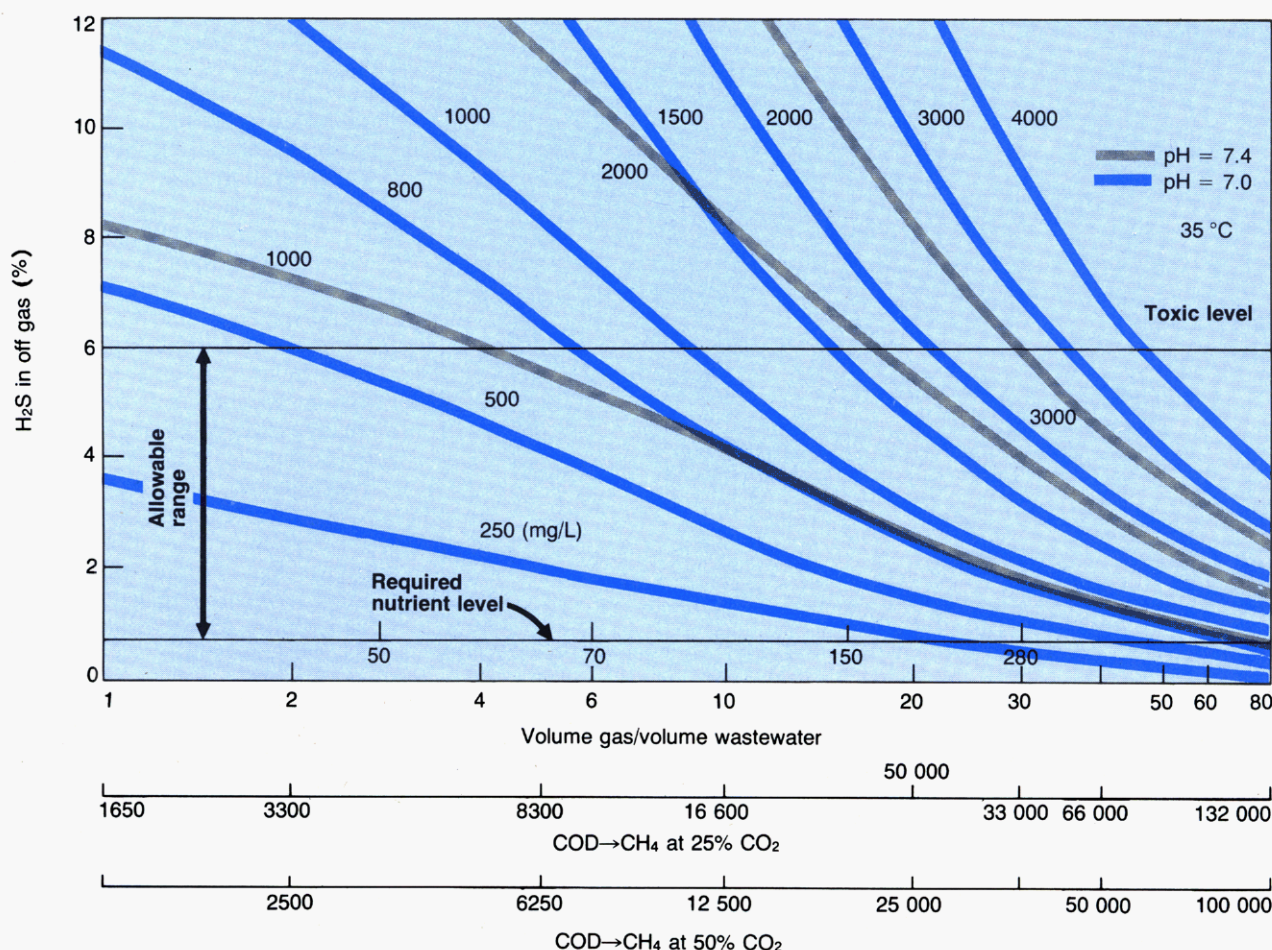
Nutrient requirements

Nitrogen and phosphorus. The nitrogen requirement for an industrial wastewater may be readily calculated, using the stoichiometry developed by McCarty (1972, 1974):

$$C_nH_aO_bN_c + \left(2n + c - b - \frac{9sd}{20} - \frac{ed}{4}\right) H_2O \rightarrow \left(\frac{de}{8}\right) CH_4 + \left(n - c - \frac{sd}{5} - \frac{de}{8}\right) CO_2 + \left(\frac{sd}{20}\right) C_5H_7O_2N + \left(c - \frac{sd}{20}\right) NH_4^+ + \left(c - \frac{sd}{20}\right) HCO_3^-$$

where: $d = 4n + a - 2b - 3c$, s = fraction of waste synthesized, $C_nH_aO_bN_c$ = empirical formula of organic being digested. Moreover, it can be shown that the nitrogen requirement for anaerobic treatment is only a small fraction of that required by aerobic processes. The phosphorus requirement is approximately 15% of

FIGURE 3
H₂S in off gas vs. V_g/V_w (or COD→CH₄)^a



^a Numbers indicate sulfide sources in wastewater (mg/L)

the nitrogen requirement (Speece and McCarty, 1964).

Trace nutrient requirements. Our lack of understanding of the trace nutrient requirements of methanogens has been a serious hindrance to the commercialization of anaerobic biotechnology. Since the methanogens are unique and in a separate class, it is not surprising that they have unique requirements. Consequently, attention only to traditional nitrogen and phosphorus nutrient requirements appears to be grossly inadequate for methanogens.

It appears that the cause of negative results in many anaerobic treatability studies of industrial wastewaters was not recalcitrant organics or inherent toxicity, but rather that trace nutrients were lacking. This phenomenon was manifested by an intractable increase in volatile acids concentration. Consequently, an adverse decision was then rendered on the appropriateness of anaerobic biotechnology for that industrial wastewater. Trace-metal

deficiency may be the reason why even food-processing wastewaters, which are among the most readily biodegradable candidates, could not support proper methane fermentation when anaerobic treatability studies on fruit cannery wastewaters were conducted at San Jose, Calif., in the 1960s.

In treatability studies of winery wastewater, Stander (1950) reported that reinoculation of the system to supply required nutrients was periodically required to maintain stable treatment. The reinoculum was from a system receiving domestic wastewater sludge. Van den Berg and Lentz (1970) also reported that continuous high loading rates of food-processing wastewaters required frequent reinoculation from another active digester. Yeast extract is a commonly used source of trace organic and inorganic nutrients. For the successful digestion of pear waste, van den Berg and Lentz (1971) reported that a minimum yeast extract supplement of 1.5 kg/m³ at all loading rates was required. Milor-

ganite at 5 kg/m³ could be substituted for yeast extract. The mineral fraction of yeast extract was significantly stimulatory. Mah et al. (1978) also found that the ash content of yeast extract stimulated methanogenesis, indicating the value of trace metals.

There is undoubtedly much more to be discovered about the nutritional requirements for all phases of anaerobic biotechnology. Iannotti and co-workers (1978) found that fermentative bacteria have fastidious nutrient requirements. In addition, in malfunctioning systems, increased levels of propionic and higher volatile acids are noted. This reflects a possible nutritional inadequacy in the acetogens responsible for conversion of the higher acids to acetate and hydrogen. This same condition of elevated levels of higher volatile acids could also be attributable to an inadequacy in the nutrition of hydrogen-utilizing methanogens, which must maintain hydrogen levels low enough to allow the conversion of the higher acids to be energet-

ically favorable. Elevated acetate levels reflect a microbial malfunctioning or an inadequacy in the nutrition of methanogens converting acetate to methane. A very complex interaction exists, which is considered to be synergistic for many organisms (Mah et al., 1976).

Four elements—iron, cobalt, nickel, and sulfide—have been shown to be obligatory nutrient requirements for methanogens to convert acetate to methane (Scherer and Sahm, 1981a; Speece et al., 1983; Speece and McCarty, 1964; Diekert et al., 1981; Hoban and van den Berg, 1979). This is a key conversion step, which gives rise to about 70% of the methane production from complex wastes (Jeris and McCarty, 1965). Molybdenum, tungsten, and selenium have also been reported as required trace metals (Scherer and Sahm, 1981a; Schonheit et al., 1979; Taylor and Pirt, 1977; Jones and Stadtman, 1977).

It becomes immediately apparent that the low-solubility product of the sulfide form of these trace metals indicates how tight the ecological niche is. Sulfide and trace metals appear to be mutually exclusive. However, the microorganisms produce and excrete substances extracellularly for the "harvesting" of required trace metals, which effectively chelate and transport trace metals into the cell (Emery, 1982; Heidinger et al., 1983). Synchronized "pulsing" of the additions of trace metals and sulfide at different time intervals may benefit the microorganisms, because both equilibria can be temporarily disturbed. This appears to allow the concentrations of the trace metals or sulfide to be elevated temporarily to concentrations that may allow "luxury" uptake by the methanogens to satisfy these nutrient requirements at least intermittently.

The iron and cobalt requirements of methanogens were reported over 20 years ago (Speece and McCarty, 1964), but the difficulty of providing adequate iron in solution was not adequately recognized. Apparently this is still a widespread problem. In recent years, Hoban and van den Berg (1979) have also noted that iron is required by methanogens at unusually high levels. Emery (1982) states: "Although iron is the fourth most abundant element in the earth's crust, all forms of life have a difficult problem in assimilating enough iron for their well-being."

Even domestic wastewater sludges and cattle manure feedstocks have been noted to respond favorably to supplemental iron additions. This was evidenced by a decrease in volatile

acids concentrations in a municipal sludge digester from the range of 4000 mg/L before iron supplementation to less than 400 mg/L after (Owen, 1981). Traditionally, these feedstocks had been assumed to be nutritionally adequate. Recently it also has become known that specific cobalt supplementation averted a progressive process failure in an industrial wastewater anaerobic treatment process.

The nickel requirement of methanogens is one of their distinct features, since nickel is generally not essential for the growth of bacteria (Diekert et al., 1980b). The apparently universal occurrence of nickel containing F_{430} in methanogens raises the question as to the source of nickel, since it has not generally been included in defined media (media in which all components are known). It appears that nickel has been supplied as a contaminant in other mineral salts and in yeast extract, as well as from contact with stainless steel fittings and syringe needles. Diekert et al. (1981) state that the high contamination level in defined media is the reason why the nickel requirement for methanogens has long been overlooked. Specific addition of nickel to acetate-utilizing methanogens has resulted in methane production rates in excess of 50 kg/m³-d, which is higher than any recorded in the literature (Speece et al., 1983).

Industrial wastewaters, in many cases, would have contact with stainless steel and, therefore, might possibly contain adequate nickel. However, an adequate supply of nickel should not necessarily be assumed, because it may be precipitated as a sulfide, and thus not be available in solution for bacterial nutrition. (This may also be true for other trace metals present in precipitated form.)

In spite of the fact that sulfide may adversely affect methane production by precipitating essential trace metals, and that it is in itself toxic at concentrations above 100 to 150 mg/L of un-ionized H₂S (Speece 1983), sulfide is required by methanogens. Dramatic stimulation has been demonstrated when sulfide is supplied to some species of sulfide-depleted methanogens.

As previously stated, the sulfide content of methanogens is unusually high when compared to aerobic microorganisms, reportedly 2.6%, which is about 50% greater than the phosphorus content. Since the methanogens contain such a large amount of sulfide, and only 4% of it can be accounted for by the mercaptoethanesulfonic acid content, a large

pool of sulfur compounds, primarily of low molecular weight, still remains to be discovered (Ronnöw and Gunnarsson, 1982). Methionine and cysteine obviously account for a large part of the sulfur. Optimal sulfide concentrations reported in the literature for methanogenic growth vary from 1 to 25 mg/L (Scherer and Sahm, 1981b).

Still, sulfide is the major sulfur source, although cysteine and methionine reportedly have been used. The sulfide must exist as un-ionized hydrogen sulfide to pass through the cell membrane. The pK of hydrogen sulfide is 6.85, which is also near the pH of normal digester operation. Therefore, un-ionized sulfide is approximately half of the total soluble sulfides in solution.

Head gas (gas in equilibrium with the liquid) is a better indicator of un-ionized hydrogen sulfide. If the un-ionized hydrogen sulfide concentration required for optimal growth of methanogens is 13 mg/L, this would correspond to approximately 0.5% hydrogen sulfide in the head gas at equilibrium. (This greatly exceeds the hydrogen sulfide level warranted for use in internal combustion engines fired with digester gas.) There is evidence that intermittent "pulses" of sulfide can satisfy the sulfur requirement of some methanogens.

In summary, the aqueous chemistry within an anaerobic system is quite complex and strongly tends to precipitate mutually essential trace metals and hydrogen sulfide. If domestic wastewater sludges have occasionally proven to be nutritionally deficient to support anaerobic digestion, that fact underscores the necessity of ensuring nutritional sufficiency in industrial process wastewaters, which are commonly even more nutrient restricted. This need is even greater in condensate wastewater streams, which are nominally deionized. The costs for trace metals and sulfide are minor, but the impact of their addition may be dramatic.

Toxicity

Although exceptions have been noted, methanogens are commonly considered to be the most sensitive to toxicity of all the microorganisms in the overall consortium for anaerobic conversion of organics to methane. Since it would be rare to find an industrial wastewater completely devoid of all potential toxicants, there is a commonly held belief that anaerobic biotechnology is not appropriate for treatment of most industrial waste-

waters. This assumption has greatly hindered widespread application of the process to industrial wastewater treatment. Some of the toxicants encountered in specific industrial wastewaters are:

- heavy-metal catalysts from chemical processes,
- pharmaceuticals (e.g., monensin) supplemented to animal feeds,
- detergents and disinfectants used in food equipment cleanup,
- solvents from degreasing operations,
- inhibitors formed as secondary products (e.g., cyanide in coking operations),
- toxic process stream leakage (e.g., formaldehyde), and
- chemical inhibitor treatments for food preservation (e.g., chlorophenyl isopropyl N-3 carbonate to inhibit potato sprouting).

However, anaerobic bacteria, like most microorganisms, can tolerate a wide variety of toxicants (Parkin et al., 1983; Speece and Parkin, 1983) and even biodegrade some of them (Stuckey et al., 1980; Bouwer and McCarty, 1983). Of singular significance is the fact that acclimation to toxicity and reversibility of toxicity are commonly noted (Parkin and Speece, 1982).

As a case in point, two full-scale anaerobic non-methane-producing treatment processes are operating on two bleached paper mill wastewater effluents in Finland for the specific purpose of biodegrading toxic chlorophenols formed during the bleaching process (Salkinoja-Salonen et al., 1982). The mutagenicity of the bleached paper mill effluents is also reduced by 85%, and 50 mg/L of chloroform is biodegraded in the anaerobic process (Hakulinen and Salkinoja-Salonen, 1982).

One of the main advantages of anaerobic biotechnology is the low synthesis rate of excess organisms. However, during start-up and also during recovery of lost biomass, the low synthesis rate becomes a major disadvantage. Therefore, since toxicity is often reversible, the inventory of biomass is still viable and eliminates the need for the prolonged periods of biomass inventory build-up required if the biomass were actually killed.

Immobilized cultures of methanogens have been temporarily exposed for 1–48 h to concentrations of toxicity on the order of 100 times the level required to stop methane production. But after the adulterated supernatant was replaced, full gas production recovered within 24 to 48 h (Speece and

Parkin, 1983). It should be noted that these high levels of toxicity are not normally encountered in industrial wastewater.

In another case, when acetate-utilizing methanogens were first exposed to 2.5 mg/L of chloroform, full recovery to the background rate of methane production required about two weeks. However, subsequent exposure to repeated injections of 2.5 mg/L of chloroform showed no inhibition whatever of methane production (Yang et al., 1980).

In still another case monensin, a pharmaceutical added to cattle feed, at 1 mg/L completely inhibited methane production from acetate in unacclimated cultures. However, gradual acclimation has been demonstrated with no inhibition at 100 mg/L (Speece et al., 1979; Varel and Hashimoto, 1982).

Changes in the concentration of a toxicant can change the classification of the substance from toxic to biodegradable. For instance, formaldehyde or phenol are common disinfectants at high concentrations, but in the range below 400 and 2000 mg/L, respectively, these substances are readily converted to methane by anaerobic treatment. A coking operation wastewater containing 1000 mg/L of phenol, 2000 mg/L of ammonia, and 5 mg/L of cyanide was successfully treated by an immobilized-cell anaerobic system when iron was added to precipitate the cyanide.

A wide variety of candidate industrial wastewater feedstocks are amenable to anaerobic treatment. It is regrettable that this type of treatment is often precluded when the principal organics are toxic or the wastewater contains chronic or sporadic levels of secondary toxicity, since the anaerobic biotechnology may still be appropriate. In point of fact, the majority of industrial wastewaters successfully treated by anaerobic biotechnology have been toxic at various levels. However, when anaerobic treatment is adopted, proper attention must be paid to process design to ensure adequate solids retention time, flow regime, and recycling when needed.

Amenable substrates

The number of substrates that have proven amenable to anaerobic biotechnology is quite extensive. Generally if an industrial wastewater is treatable aerobically, it will be treatable anaerobically, although there are exceptions. For example, diacetone gulusonic acid reportedly biodegrades anaerobically but not aerobically

(Brandl, 1980), and monensin biodegrades aerobically but not anaerobically. However, these are relatively minor exceptions to a general pattern.

Table 2 is a partial list of organics that have demonstrated anaerobic biodegradation and that are potential components of industrial wastewaters. Only ultimate anaerobic biodegradation is implied by inclusion in Table 2. The rate of biodegradation is not documented in all cases.

Process configurations

The microbial biomass responsible for anaerobic biotechnology can be "packaged" in a variety of process configurations. Selection of the appropriate process configuration is critical to successful operation and warrants detailed consideration.

Each different configuration has implications for the ratio of solids retention time/hydraulic retention time (SRT/HRT). SRT is the fundamental design parameter of biotechnology systems. Maximal SRT is desirable for process stability and minimal sludge production. Minimal HRT minimizes the reactor volume and thus reduces capital costs. Forethought and proper design are required to prevent long-term plugging of the reactor with biomass or refractory components in the feedstock.

A major consideration inherent in anaerobic biotechnology is the relatively low synthesis ratio of the key class of microorganisms in the consortia—i.e., methanogens. Therefore, special attention must be paid to ensure efficient retention of the biomass in the system. With the relatively high synthesis ratio of aerobic organisms, an effluent suspended solids level of 500 mg/L may border on solids washout failure for a waste strength of 1000 mg/L BOD. However, for anaerobic systems a solids loss of 30 mg/L may border on washout for the same waste. Therefore, much more efficient solids capture must be provided with anaerobic biotechnology.

Anaerobic growth in a quiescent environment allows relatively large agglomerations of biomass clumps, described as "stringlike" biomass "globs" that accumulate in anaerobic filters, to develop (Young and McCarty, 1969), or the "granular" sludge reported to be in the upflow anaerobic sludge blanket (UASB, Figure 4) (Lettinga et al., 1980). It requires protracted periods to develop these large biomass agglomerations, which can be irreversibly dispersed in an instant in a high shear zone such as

TABLE 2

Organics amenable to anaerobic biotechnology

Acetaldehyde	Formic acid	Isopropyl alcohol	Giant kelp
Acetic anhydride	Fumaric acid	Propionate	Animal wastes
Acetone	Glutamic acid	Propylene glycol	Cheese whey
Acrylic acid	Glutaric acid	Protocatechuic acid	Pear wastes
Adipic acid	Glycerol	Resorcinol	Pectin wastes
Aniline	Hexanoic acid	Sec-butanol	Meat packing
1-amino-2-propanol	Hydroquinone	Sec-butylamine	Corn milling
4-amino butyric acid	Isobutyric acid	Sorbic acid	Dairy
Benzoic acid	Isopropanol	Syringaldehyde	Brewery
Butanol	Lactic acid	Syringic acid	Rum distillery wastes
Butyraldehyde	Maleic acid	Succinic acid	Wine distillery wastes
Butylene glycerol	Methanol	Tert-butanol	Guar gum wastes
Catechol	Methyl acetate	Vanillic acid	Water-soluble polymers
Cresol	Methyl acrylate	Vinyl acetate	Bean blanching
Crotonaldehyde	Methyl ethyl ketone	Corn	Pulp mill evaporate
Crotonic acid	Methyl formate	Potato	Coking mill
Diacetone gulusonic acid	Nitrobenzene	Sugar cane	H ₂ -CO pyrolysis
Dimethoxy benzoic acid	Pentaerythritol	Bagasse	Wool scouring
Ethanol	Pentanol	Peat	Tannery wastes
Ethyl acetate	Phenol	Wood	Yeast
Ethyl acrylate	Phthalic acid	Corn stover	Heat-treated activated sludge
Ferulic acid	Propanal	Straw	
Formaldehyde	Propanol	Water hyacinths	

a centrifugal pump. Once dispersed, the biomass does not readily reflocculate, and therefore is easily lost in the process effluent. Judicious choice of a recycle pump is thus required for success of the anaerobic contact process. This issue has been the major impetus for development of process configurations using immobilized cells. Figure 4 shows the various process configuration schematics.

Suspended, mobilized growth reactors. The first generation of reactors for anaerobic biotechnology applied to municipal sludge digesters consisted of continuously stirred tank reactors (CSTR) (some were not even mixed) with no solids recycle. Therefore, the SRT/HRT ratio was one. Subsequently, solids recycling was incorporated to increase the SRT/HRT (Torpey and Melbinger, 1967; Schroeffer and Ziemke, 1959); this modification was termed the anaerobic contact process. This type of reactor configuration lends itself to feedstocks containing refractory particulates that must be passed through the system. Meat-packing-plant wastewaters were the first major class of industrial wastewaters employing the anaerobic contact process (Steffen and Bedker, 1961).

Immobilized cell reactors. Process stability and economics dictate in-

creased SRT/HRT ratios. Immobilized cell reactors are a rational attempt to achieve these higher ratios. Many schemes have evolved. Coulter et al. (1957) and Young and McCarty (1969) used an upflow packed column. The packing material provided contact surface for biofilm development, reduced the Reynolds number to ensure low turbulence and efficient sedimentation, and thus allowed the retention of unattached biomass.

The first prototype anaerobic filter in the U.S. was an upflow packed reactor, which treated a wheat starch wastewater. It was located at Centennial Mills in Spokane, Wash. In the upflow packed reactor, less than half of the cell mass is attached to the packing as a biofilm; the majority is unattached as clumps of cells retained in the packing interstices (Young and Dahab, 1982).

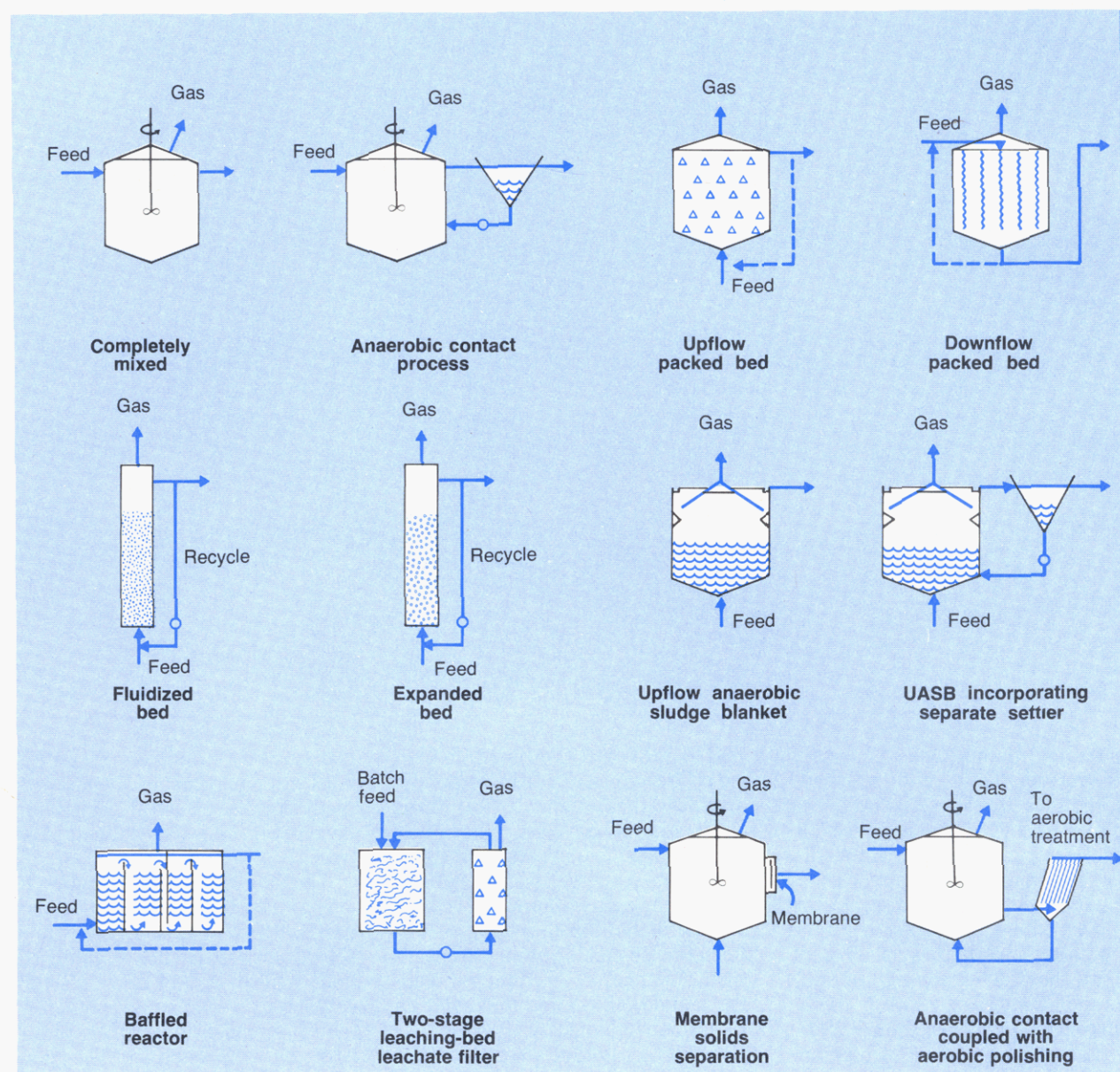
The concept of a downflow mode through a packed reactor was developed by van den Berg and Lentz (1979) to prevent accumulation of refractory particulates contained in the feedstock. The cell inventory is all in the biofilm attached to the packing. Any biofilm sloughs off discharges by gravity along with refractory particulates in the effluent. Either the submerged or unsubmerged option is available with the downflow mode.

Gas stripping of volatile toxicants (e.g., H₂S) is enhanced in the downflow mode because all of the gas produced passes through the influent wastewater.

The fluidized bed developed by Jeris (1982) incorporates an upflow reactor partly filled with sand. The upflow velocity is sufficient to fluidize the sand to fill about 75% of the reactor. A very large surface area is provided by the sand, and a uniform biofilm develops on each sand grain. The internal sand grain markedly increases the net density and settling velocity of the attached biofilm and ensures efficient cell retention within the reactor. The system readily allows passage of refractory particulates that could plug a packed bed, but requires energy for fluidization of the sand. A lower-density carrier, such as anthracite or high-density plastic beads, can be substituted for sand to reduce the fluidization energy requirements. Jewell (1982) has developed an expanded bed reactor that uses an upflow velocity less than that required for complete fluidization of the granular media.

The expense of the reactor packing material is considerable. McDermott (1983) estimates the packing cost is comparable to the tank cost. It may be on the order of \$350/m³ for a large prototype system (\$3 million for the

FIGURE 4
Reactor configurations for anaerobic biotechnology



Bacardi installation). In addition, concern over long-term plugging problems has fostered the development of "unpacked" reactors that still incorporate the immobilized cell feature. Lettinga et al. (1980) initiated the development of the first full-scale installation of an upflow anaerobic sludge blanket reactor (UASB) at the Central Sugar Manufacturing plant in The Netherlands. His laboratory studies had shown that he could develop a granular sludge on beet sugar wastewater with excellent sedimentation characteristics in an unpacked reactor. He also demonstrated that exceptionally high loading rates of up to $30 \text{ kg/m}^3\cdot\text{d}$ could be applied.

The mechanism by which the

granular sludge is developed is not well understood, nor is the phenomenon responsible for its rapid disintegration under some conditions. Recently, McCarty (1982) introduced a modification of the UASB called the baffled reactor. The multiple baffling of the reactor provides staging, enhances cell retention, and avoids the cost of packing material. Another modification of the process has been developed in France for sugar manufacturing and distillery wastewaters by the IRIS (Research Institute for Sugar Industry). The process combines a sludge bed and anaerobic contact process with an incorporated settler (Verrier et al., 1983).

Dynatech (Augenstein et al., 1977)

and the Institute of Gas Technology (IGT) (Chynoweth and Srivastava, 1980) both piloted a process configuration for solid feedstocks such as giant kelp or municipal solid wastes. A reactor is completely packed with the solid feedstock, through which a nutrient-supplemented water is percolated to leach out the solubilized organics. The leached effluent is then passed through a packed reactor containing a microbial consortium of acid fermenters, acetogens, and methanogens for conversion of the leachate to methane. This configuration effectively separates the liquefaction and methane formation stages to permit independent control of SRT in both phases. Two-phase digestion of liquid

feedstocks has been proposed, but is applicable only to simple feedstocks containing considerable amounts of easily hydrolyzable substrates (Cohen, 1983), in which case the methane formation stage is rate limiting.

Dynatech (Tracey and Ashare, 1983) and Dorr-Oliver (Li et al., 1982) have separately developed a reactor configuration comprised of a CSTR followed by a membrane filter for cell retention. The Dynatech system is a novel application of anaerobic biotechnology to convert a coal gasification waste gas stream containing hydrogen, carbon monoxide, and carbon dioxide to methane. The reactor operates at very high pressures, and the membrane filter is continually scoured with a jet stream of liquid reactor contents to avoid plugging. No prototypes of the CSTR-membrane filter process configuration have been constructed.

Van den Berg and Kennedy (1983) made a comparison of reactor types, loading rates, and removal rates based on their work and values found in the literature. This comparison is shown in Table 3.

Full-scale installations

It is difficult to catalog completely all of the full-scale installations of anaerobic biotechnology. The proprietary installations, of course, are well documented by their respective sales managers. However, since the fundamental anaerobic process is not patentable, many installations have been designed, built, and operated without being recorded in an official tally. This is particularly true of the many anaerobic lagoon installations for treatment of effluents from meat-packing plants, feedlot operations, canneries, and the like. Nyns et al. (1983) report on 550 biogas methane digestors built in the past five years in the European community and Switzerland.

A number of proprietary anaerobic biotechnology processes are actively being marketed. Each has distinct features, but all utilize the fundamental anaerobic conversion to methane. Table 4 contains this summary of proprietary installations.

The ANAMET process uses an unpacked reactor, followed by a lamella plate separator (parallel plates to improve solids capture) for solids recycle, followed by an optional aerobic biological treatment polishing step. The ANITRON process incorporates a fluidized sand bed with a biofilm developed on the sand. The BACARDI process is a downflow submerged, packed-bed reactor. The CELROBIC

TABLE 3

Comparison of reactor types, loading rates, and removal efficiencies^a

Reactor type	COD loading rate kg/m ³ ·d	COD removal %
Contact	1-6	80-95
Upflow filter	1-10	80-95
Fluid/expanded bed	1-20	80-87
Downflow filter	5-15	75-88
Sludge bed	5-30	85-95

^a (van den Berg and Kennedy, 1983)

TABLE 4

Summary of anaerobic biotechnology proprietary installations

Company	Process name	No. of installations
AC-Biotechnical (formerly Sorigona)	ANAMET	U.S.—3, Canada—1; world—27
Dorr-Oliver	ANITRON	U.S.—2
Bacardi	BACARDI	U.S.—1
Badger (formerly Celanese)	CELROBIC	U.S.—3
Biomechanics	BIOENERGY	Europe—3
Ecolotrol	HY-FLO	U.S.—1
IRIS	—	Europe—7
Joseph Oat and CSM	BIOTHANE	U.S.—3, Europe—18

process is an upflow packed-bed reactor with an instrumentation package and solids inventory control technique. The BIOENERGY process uses the anaerobic contact principle with a cooling of the reactor effluent to decrease gasification in the settler and improve solids removal. The HY-FLO process is a fluidized sand bed with a biofilm developed on the sand. The BIOTHANE process uses an upflow sludge blanket contactor.

Ninety percent of the ANAMET installations are in the food industry, 50% are specifically sugar wastewaters, and two installations are for pulp and paper effluents. A fluid-bed anaerobic reactor has been operating for over a year at a yeast plant wastewater in Delft, The Netherlands. It is 1.4 m in diameter and 16 m high. A peculiarity of this installation is that at very high loading rates, hydrogen is formed at 10-18 m³ m⁻³ d⁻¹. Two of the three CELROBIC processes treat chemical process industry wastewaters containing methanol, acetate, methyl formate, acetic anhydride, propionate, butyrate, methyl ethyl ketone, methyl and ethyl acrylate, formaldehyde, acetate esters, butylene, glycerol, and pentaerythritol and produce approxi-

mately \$650,000-\$900,000/y worth of methane.

The Hercules Corporation has two full-scale anaerobic biotechnology installations at industrial plants in West Germany and Denmark. Construction of another full-scale process is planned later this year at a plant in France.

Enhancement of product

Biorefining is a concept proposed by Dynatech (Levy et al., 1981). Since methane has a relatively low market value per unit weight in comparison with other organic chemicals, the company proposes to block methane formation by a specific inhibitor: bromoethanesulfonic acid. This process would increase the volatile acids concentration. Kerosene would then be used to extract the four-carbon and higher volatile acids. Acetic and propionic acids are proposed for extraction by kerosene containing 20% tri-octylphosphine oxide. The harvested acids would be subject to a Kolbe electrolysis to produce a variety of organic chemical products, such as alkanes, alkenes, esters, and alcohols, which have much higher market values than equivalent methane. Related re-

search is also being conducted at the Solar Energy Research Institute (Chum, 1983).

The threshold volatile acids concentration must exceed 6000 mg/L before any other products can be harvested; therefore, the industrial wastewater BOD must exceed this concentration considerably. In addition, the daily tonnage of organics in the wastewater must exceed a certain threshold amount to provide an adequate scale for process economy. Thus, only relatively few industrial wastewaters are viable candidate feedstocks for such a process. A typical "corn slops" or cheese-whey wastewater might qualify, but cheese industry representatives thus far have indicated little interest in building and operating such a by-product recovery facility. Other industry representatives have expressed doubts concerning the commercial viability of the Kolbe electrolysis process, the purity of the organic chemicals produced, and the strength of a market for such limited quantities of product as would be available from even a large industrial wastewater feedstock.

The city of San Diego, Calif., has announced plans to build a chemical process for conversion of raw digester gas to methanol (*International Petrochemical Developments*, 1982), which has a higher market value than methane. The city of Modesto, Calif., operates a gas purification process to scrub digester gas of carbon dioxide and hydrogen sulfide, dry it, and compress it to fuel a fleet of municipally owned automobiles with the purified methane. During World War II, raw digester gas was a truck fuel in Germany. Landfill gas is being converted to electricity at a 2-MW facility in Durare, Calif. (*ES&T*, December 1982, p. 641A).

A well-balanced effort

Presently, there is a rather well-balanced effort in the areas of basic microbiology, bench and pilot plant studies, and full-scale installation evaluations. Historically, the effort has never been stronger in any of these three areas, which is indicative of the keen interest anaerobic biotechnology is enjoying. Future increases in the cost of electricity, sludge disposal, and methane should intensify this interest even more.

As more attention is paid to ensure an adequate supply of all required nutrients, especially the trace metals and sulfide, malfunctioning caused by elevated volatile acids concentrations should be minimized. In addition, as

more case histories of successful treatment of industrial wastewaters containing various toxic materials are documented, the robustness of the process will be demonstrated, and problems of incompatibility of the process with toxic substances will be surmounted. New process developments and reactor configurations should reduce the capital costs and increase process stability. Indeed, even now, anaerobic biotechnology is an appropriate process for industrial wastewater treatment. It has a solid scientific and engineering foundation, and the potential market for properly designed and operated systems is great.

Acknowledgment

Before publication, this article was reviewed and commented on for suitability as an *ES&T* feature by Edward D. Smith, U.S. Army Construction Engineering Research Laboratory, Champaign, Ill. 61820, and Edward H. Bryan, National Science Foundation, Washington, D.C. 20550.

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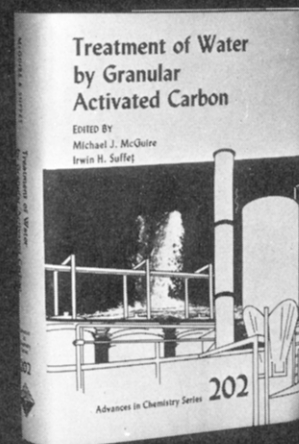
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