Appendix 2: Biohydrogen

Hydrogen gas appears to be routinely evolved whenever organic materials undergo anaerobic decomposition, but before it can escape from the anaerobic environment, it is snatched up by the methane-forming bacteria and used to make CH_4, methane.

The factors which lead to the rapid formation of hydrogen are, therefore, little understood, since the hydrogen so rarely shows up— except in trace amounts— in the final biogas. Further, hydrogen, as a gas, is a more dilute energy source than methane. Where 12.5 liters of methane has 100 Calories (net) energy available, the same volume of hydrogen has only 30 Calories (net) energy available. So, why shoot for hydrogen when you can have methane?

A lot depends on what you intend to use your biogas for, actually. Not so great for an engine, but it may be quite useful in other applications. For example, hydrogen is desirable for its flame velocity, which is higher than that of methane (p. 96). So, mixed with the methane in your biogas, that hydrogen will make it easier to keep pilot lights lit, and easier to keep stoves burning.

Even so, very little research has been directed toward the production of hydrogen by anaerobic decomposition.

However, several things are known:

1. Hydrogen is produced during the first (acid) stage of anaerobic breakdown, but not, as far as is known, during the second stage.
2. Low pH seems to favor H_2 production, or possibly just its release, where it was otherwise dissolved in the slurry. Whether the mechanism is release or production is not known because the low pH data is based on studies of ordinary generators, where both stages of digestion are active simultaneously. Thus while low pH is related to an increase in H_2 in biogas, it may be that it merely inhibits the methane formers, which could then allow H_2 to get past them, rather than stimulating the production of hydrogen.
3. A high C/N seems to stimulate the production of H_2.
4. Substrates high in carbohydrates, such as cellulose, seem to stimulate H_2 production.

Omelianski (1902), an early pioneer in anaerobic studies, found that anaerobic cultures obtained from horse manure or soil, when heated to 75°C and held there for about 15 minutes, produced hydrogen when the culture was then kept at 35°C. He was apparently using cellulose as a substrate.

A. W. Shorger in his book, *Chemistry of Cellulose and Wood* (1926), recounts research from the *Journal of the Society of Chemistry and Industry*, v. 42, 1923, page 169. This research found that methane-rich biogas was produced more than 12 times as rapidly as hydrogen-rich biogas.

While H_2 may be evolved slowly, hybrid generation, which can separate the acid-forming stage from the methane-forming stage, may show some promise for H_2 production. In their cryptic, poorly written, tantalizing report, researchers at the University of Pennsylvania (1974) report that a gas of up to 10% H_2 was produced from the first (acid) stage reactor.

No lower methane production should come from a slurry used first to produce hydrogen and then methane. Chemically and biochemically, iron can replace hydrogen (as an electron donor), as reported by Thimann (1955), and thus both hydrogen and methane production should be compatible in the proposed hybrid generator. Should you try adding rust to your generator?

The key seems to be in finding the right culture, keeping the pH slightly acid, and keeping the acid modules warm. This last requirement throws us back into a hydrogen and fatty acids producing modular batch generator situation, but if hydrogen is what you want, this, apparently, is what you'll have to do.

Recently, other researchers have proposed and tested methods of producing hydrogen photosynthetically, and although it looks to be high tech, you're welcome to wade through it. The references, found in full in the bibliography, are Mitsui, 1974 and 1975, and Newton, 1976.

One final note: Travin and Buswell (1934) (see Bibliography), reported a biogas that was about 30% hydrogen by volume. By weight (and assuming the other 70% to have been CO_2) that is only about 2%. Not startling, but still, another reference for you.

Hydrogen-filled balloons from a compost pile? Another interesting fantasy— perhaps.