Biomass-based Fuel Cells for Manned Space Exploration

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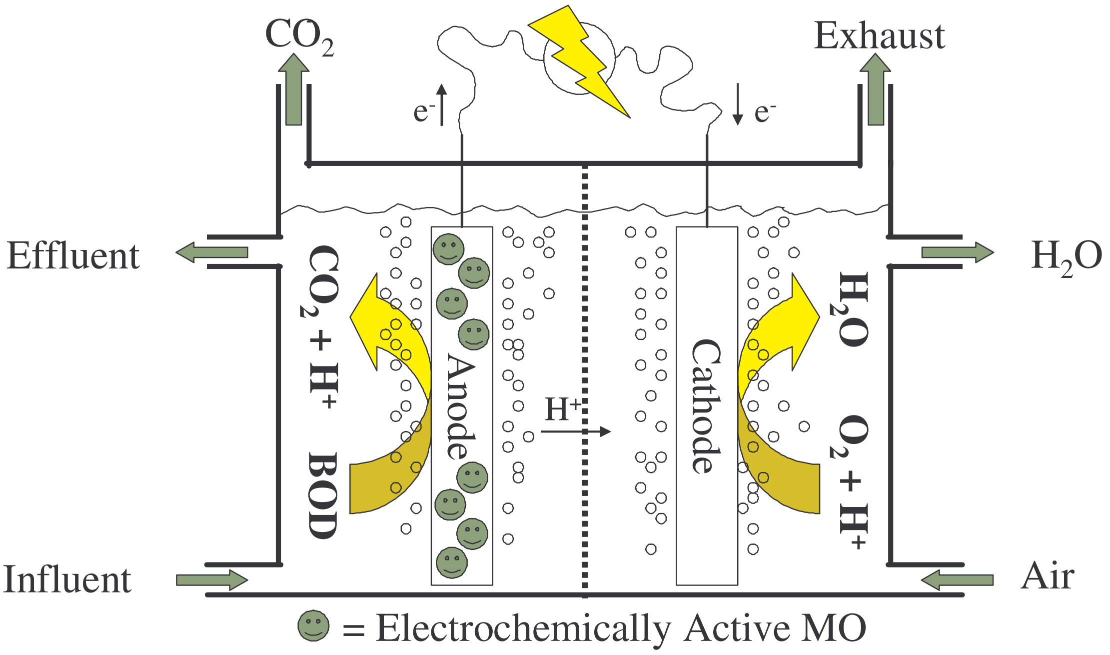

Final Report
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Index

1 Introduction

1.1 Scope of the research

This report describes the outcome of the activities as performed in the project “Biomass-based Fuel Cells for Manned Space Exploration” as performed by Wageningen University. Objective of the study is the exploration of the possible routes for the production of fuels from organic waste for power production using fuel cells. A fuel cell is a device that directly converts chemical energy into electricity, without combustion. The fuel cell is thus able to deliver electricity in a clean and efficient manner. The fuel cell consists of two compartments separated by some type of ion exchange membrane. Figure 1 shows a schematic representation of a chemical fuel cell.

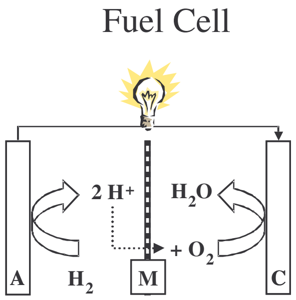

Figure 1 A schematic representation of a chemical fuel cell

In the anodic compartment (A) hydrogen is split into protons and electrons. The electrons leave the anodic compartment via the anode (A), the protons via the membrane (M). In the cathodic compartment the protons and electrons react with oxygen to water at the cathode (C).

A Chemical Fuel Cell (CFC) is based on chemical reactions at the anode and cathode. Hydrogen is the typical fuel for a CFC as chemically only limited catalytic possibilities are available. To use waste as an energy source it must be first transformed into a suitable gaseous fuel. This can be done using chemical processes (thermochemical, photochemical, photocatalytic) or biologically (digestion, biophotolysis, photofermentation, dark H_2 fermentation, light H_2 fermentation). After further treatment this produced gas can be used as fuel for the fuel cell.

A Microbial Fuel Cell is basically a CFC but it uses a microbial reaction at the anode. The microorganisms degrade the waste and transfer the released electrons to the anode. The organism can directly transfer the electrons to the electrode and/or can use some type of redox mediator. Microorganism can degrade a wide variety of substances

In the study we explored the possibilities of the production of fuel for the CFC and for the MFC from organic waste. The organic waste that is used is assumed to be produced during a 600 days manned space mission with 6 persons. In this study hydrogen and methane are regarded as fuels.

1.2 Outline

This report consists apart from the introduction of five main chapters.

Chapter 2. Design

This chapter describe the principles that have been use to focus the research.

Chapter 3. Feedstock and Hydrolysis (Kirsten Steinbusch)

This chapter defines the waste produced during a long term mission. Based on the composition of the waste the hydrolysis reactor and its products are defined. The composition of the waste is estimated based on the expected ESA menu during long term missions.

Chapter 4. Dark Fermentation (Kirsten Steinbusch)

This chapter describes the possibilities to generate hydrogen via fermentation from the waste.

Chapter 5. MFC for electricity and electricity (Rene Rozendal)

The use of an MFC for electricity and hydrogen production are described. Both individual systems and a combined system are described.

Chapter 6. Heterotrophic photofermentation. (Sebastiaan Hoekema)

The use of light for the production of hydrogen from the waste under Martian conditions is explored.

Chapter 7. Discussion. (Bert Hamelers)

Next to new material, in this report all progress reports so far are merged, together with the presentations at the mid-term meeting.

1.3 Legend

COD	Chemical oxygen demand. Analytical quantification method for the total organic carbon content which can be chemically oxidized
HRT	Hydraulic retention time
Fermentation	Fermentation is a microbiological pathway in which a redox reaction occurs in the absence of any added terminal electron acceptors. In this energy yielding process organic molecules serve as both electron donors and acceptor.
Methanogenesis	Microbial process in which methane is formed
MFC	Microbial fuel cell
Precursor	Chemical component serving as a reactant for a conversion. In this research it is the basis for the fuel production step.
SRT	Solid retention time
VFA	Volatile fatty acids as acetic acid and butyric acid

2 Design approach

As indicated in the project proposal the conceptual design for the fuel processing systems will be performed using a methodological design procedure. Methodological design can be framed in the general idea of rational problem solving. Problem solving is defined as a process with at the start a problem (How to get fuel from waste?) and at the end a successful solution to the problem, being a plan for a technical installation like an anaerobic digester. Rational expresses the assumption that by following some rules, this design process becomes more efficient, i.e. better solutions are found and/or these are faster found. Some of the issues raised by methodological design are quite self-evident. However, the deeper implications of these self-evident issues are often overlooked.

2.1 Background on Design

The procedure used here is based on the work of Pahl and Beitz (Cross, 2000). This method can be considered as a classic one and as such is widely applied, discussed and researched. In a conceptual design the following phases can be distinguished:

Problem Clarification
After a thorough problem formulation and analysis, objectives should be determined that describe what the design should achieve or bring about. If possible the objectives should be linked to performance specifications. Apart from the objectives also the relevant constraints must be identified at the start, like acceptable cost, product requirements, emission standards and safety standards. All these elements are recorded in the specification of the design process. Care should be taken again that this happens in a so-called solution neutral way, to keep all solutions options open. A solution neutral description prevents exclusion of solutions without consideration.

Function Analysis
The purpose of this step is to identify the essential functions of the design object using the function analysis method. This method aims at making a description of the functions that the design object should have, based on the input and output of the system. At the start, the design object is represented as a single black box with the appropriate inputs and outputs. Different types of inputs/outputs can be considered, mass, energy and information. Inputs can be determined from the problem formulation (the current situation) while the outputs can be determined from the objectives (the desired situation).
Functions can be found by describing in a solution neutral way the transformation from the input into the output. Functions thus relate the input to the output of the design object and typically consist of a noun and verb. The function thus focuses on what must be achieved and not on how this should be done. It should be emphasised that this process of determining function is not unique. Starting from the highest level with one black box, one starts dividing the functions into sub functions. This is necessary as most non-trivial design tasks have complex solutions. This division can be visualised by connecting blocks representing the sub-functions. The connections reflect the relationships between the subfunctions, in our case flows of energy, mass and information. By relating, these sub-functions the black box has been opened and made transparent. This process can be repeated until a certain level of refinement is reached.

Structure & Working Principle Selection
As a result of the function analysis method, we end up with a number of function structures. We have to make a decision on which are the most promising structures. Each function must now be connected to a working principle. The next step is to transform function structure into a structure with working principles. Working principles are physical principles that can be used to achieve a certain function. A working principle is not yet an apparatus but a physical principle that is determining an apparatus family. For instance sieving is a principle that can be done with many different types of sieves.

System Design & Evaluation

After the working principles have been selected the design, can be worked out further. In this phase final decision regarding the final lay-out are made. When the design has been set, the (expected) functioning can be evaluated. This can be done via calculations, simulation and/or prototype evaluation. To asses the value of the design, the expected performance has to be judged with the objective and criteria set earlier.
This part describes the results of the first three steps taken i.e Problem Clarification, Function analysis and Working Principle Selection. Step 4 System Design & Evaluation will be worked out per techniques in separate chapters.

2.2 Problem Clarification

Objective
During a long term space mission organic waste is produced. This waste comes from three different sources, plant and food remains, human faeces and organic trash like paper. It is known that this waste can be digested and the produced biogas can be converted into electricity via a fuel cell. The objective of the design is to identify better performing alternatives for the generation of fuels and electricity from the organic waste generated during a space mission. The system must be more energy efficient than the AD-SOFC system and should comply with the appropriate constraints.

Constraints
There are three most important constraints:
Those arising from the physical surroundings in space.
Light intensity & wavelengths
Absence or Presence of Gravity
Those arising from the fact that we are working with a closed system i.e. everything needs be virtually reused.
Maximal reuse
Small and light weight as possible
Minimal Emissions (odors, toxicants, pathogens)
Robustness

Those arising from the amount and nature of the available biomass
This latter constraint is discussed more in detail in the second part of this report

2.3 Function Analysis

The starting scheme for the function analysis is given below,a and basically says we need something to transform waste into useful energy.

Waste Input → CONVERSION → Energy Output

The waste input will be been defined in the next chapter. There are four types of energy carriers that could be envisioned, H2, Alcohol(s), CH4 and Electricity. As alternatives to CH4 we will consider hydrogen and electricity. Alcohols are left out as alcohol production is much less efficient as methane formation. The main reason is that the separation of ethanol from water by distillation needs a relative high heat input. This makes the overall energetic efficiency lower than that for the others.

Based on this consideration a basic scheme has been set up:

Biomass→Pre-treatment→Precursor Formation→Fuel Conversion→Fuel

After per-treatment, the waste must be first converted into a limited number of pre-cursors. This step is necessary as the waste has such a wide variety of components. Some kind of chemical homogenization is necessary. The precursors are the building blocks for the actual conversion in the energy carrier This scheme will be the basis for further elaborations including the working principles.

2.4 Working Principle Selection

Two important groups of working principles can be distinguished the thermochemical processes and the biological processes. Thermochemical processes are less efficient at small scale, as they run in general at high temperatures and high pressure. At small scale these processes lose relatively a lot of energy as heat. This makes that these processes have a highly unfavourable energy balance. Therefore the principal focus will lie at biological processes as these processes run at near ambient temperatures and normal pressures.
The following processes will be dealt with:
Feedstock and Hydrolysis (Chapter 3, Kirsten Steinbusch)
Dark Fermentation (Chapter 4 Kirsten Steinbusch)
MFC for electricity and electricity (Chapter 5 Rene Rozendal)
Heterotrophic photofermentation. (Chapter 6 Sebastiaan Hoekema)

3 Hydrolysis & Feedstock

3.1 Feedstock

Feedstock determines the reactor design of the recycle system and as a result the amount of fuel that can be produced from it. One set of data is used for the design of t all reactors. The data are retrieved from other life supporting Mars mission studies. The data of the waste composition are retrieved from a scenario of a NASA study on solid waste during a 600 days manned space mission. In this scenario 40% of the menu will contain grown food, for a 6 person crew this will be 4 kilogram of wet weight. The NASA study calculated for each plant the amount of inedible plant waste per person per day [1]. This report is further based on listing of ESA of 10 plants grown for the food menu during the space mission to mars. The suggested plants are wheat, tomatos, lettuce, potatoes, soy beans, spinach, union, rice, kale and spirulina. According to this menu and the data retrieved from the NASA study it is calculated that 9.715 kg wet inedible biomass per crew per day is produced. The average water content of the waste is 0.91 meaning a total waste content of 0.836 kg dry biomass per day. Based on a detailed composition of the plant residues [2], the total amount of different types of biomass waste can be calculated. In Table 1 the specified composition in the three main macromolecules (protein, hydrocarbons and fat) is written, to calculate in a later stadium the possibilities for fuel conversion.

Table 1 Composition of the inedible grown plant material.

Vegatables	Inedible biomass kg/p	water content	proteins	Celmat	hydrocarbons	HydroC	Fat
wheat	1.070	0.92	0.86	35.95	37.49	73.44	1.63
tomatos	0.170	0.92	1.68	1.31	8.16	9.47	0.69
lettace	0.001	0.95	0.01	0.01	0.02	0.02	0.00
Potato's	0.306	0.9	2.85	5.75	19.16	24.91	0.40
soy beans	-	0.9	-	-	-	-	-
spinach	0.008	0.9	0.19	0.09	0.35	0.44	0.03
union	0.034	0.9	0.46	0.39	2.07	2.46	0.02
rice	-	0.9	-	-	-	-	-
Kale	0.030	0.825	0.73	0.80	2.68	3.49	0.12
Spirulina	-		0.00	0.00	0.00	0.00	0
Total for 1 person	1.619	0.91	6.76	44.30	69.92	114.23	2.89
Total for 6 persons	9.715	0.91	40.58	265.83	419.55	685.38	17.35

* - the exact amount is not known and is not taken into account during the calculations of energy content of waste

The total organic waste that has to be recycled is the inedible grown plant material combined with trash, paper and faeces from the astronauts. In table 2 the total estimated solid waste stream for a 6 person crew during a 600 day exploration mission is listed. The composition is different from the Mid-Term report as agreed upon during the meeting. Table 2 shows the estimated organic waste stream with a wet content of 76.6 percent. The waste stream is subdivided into macromolecules proteins (41g), hydrocarbon (2529 gram) and fat (17 gram). The subdivision is made because the degradation of macromolecules is different from each other.

Table 2 Total estimated organic solid waste stream for a 6 person crew during a 600 day exploration mission

Biological waste	**Composition**				
6 crew members per day	dry matter g	water %	proteins g	celwall g	fat g
Faeces	225	75		214	
Inedible plant biomass	836	91	40,6	685	17,4
Trash	560			530	
Paper	1164			1100	
Total dry weight	**2785**				
Total wet weight	**11913**	**76,6**	**41**	**2529**	**17**

3.2 Hydrolysis

3.2.1 Principle

The aim of the overall reactor design is the production of fuels from organic waste, and in particular from human excrements, during manned space exploration. The expected amount of waste and its composition during manned space mission with a 6-person crew is assessed in previous chapter. The waste gathered for processing consists of faeces, biomass not-edible plant residual and packing material. The waste stream is grinded into small particles. The particles consist of different macromolecules. Macromolecules are protein, carbohydrates, lipids and have all a polymeric structure. The macromolecules can not directly be utilised by organisms to produce fuels. First the maromolecules have to be converted into soluble monomeric or dimeric organic molecules. This solubilisation step is called hydrolysis and is accomplished by enzymes. Enzymes help catalysing the conversion of complex structures of polymers into monomers of dimers. Hydrolysis is the first step in anaerobic digestion. Anaerobic processing of organic waste is called digestion.

Digestion consists of four stages: hydrolysis, acidification, acetogenesis and methanogenesis (Figure 2). In each step the macromolecules are further broken down in eventually methane. In this study methane is not regarded as the only fuel. Electricity and hydrogen via dark fermentation and phototrophic fermentation are also taken into consideration as energy source. In this research the last two steps of digestion acetogenesis and methanogenesis are coupled in one step fuel conversion. The hydrolysis step should be designed in a way precursors are generated for fuel conversion.

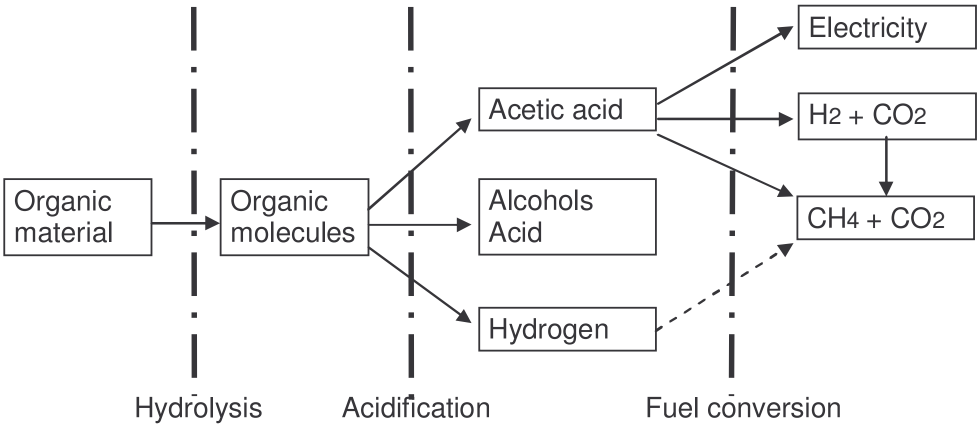

Figure 2 Schematic conversion of organic material into fuels as H2, CH4 and electricity

As described above waste contains different macromolecules such as proteins, lipids and carbohydrates. Each feedstock has a different composition of these macromolecules. Ten Brummeler formulated a more general composition for municipal solid waste which is shown in Figure 3 [3].

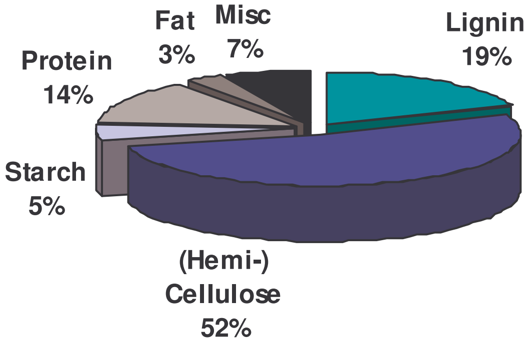

Figure 3 General composition of municipal organic waste [3]

The question is; "How to obtain from such a mixed waste composition one fuel?". Hydrolysis of each polymer will lead via diverse routes to different components as shown below:

Protein → polypeptide → peptide→ amino acids → VFA

Lipids → glycerol + fatty acids → VFA

Carbohydrates → sugars → VFA and H_2

The intermediate products of hydrolysis and acidogenesis can function as precursors for further conversion. The precursors for the fuels (H_2, CH_4) and electrical power as regarded in this report are listed in Table 3. In the microbial fuel cell a variety of organic components can be used as precursors for electricity and hydrogen production. As one can see from Figure 2 the two fuels are formed out of the same substrate, acetate. Acetate is needed for methane production, for the microbial fuel cell as well as for phototrophic hydrogen fermentation. Competition for acetate is therefore a point of attention in the design. Dark fermentation refers to the hydrogen formed in the acidification step and is generated from carbohydrates.

Table 3 Potential conversion processes and required precursor

Fuel	Process	Precursor
Methane	Methanogenesis	Acetate, H_2 and CO_2
Hydrogen	Acidification (pre-treatment)	Carbohydrates
	Phototrophic fermentation	Acetate
	Bio-electrochemical MFC	Divers
Electricity	Bio-electrochemical MFC	Divers

Hydrolysis is the rate limiting step in anaerobic digestion. In practice hydrolysis can be described by an empirical first order relation, but only when biomass is completely available for biodegradation. The amount of surface available for the hydrolysis is the most important parameter which determines the rate under limiting biodegradability [4].

$$\frac{dX_{\deg radable}}{dt} = -k_h \cdot X_{\deg radable}$$

$X_{degradable}$ = concentration degradable substrate (kg/m3)
t = time (days)
k_h = first order hydrolysis constant (day-1)

When the particle size is large and only the surface is available for organisms, a long solid retention time (SRT) is needed to be sure the particles would be fully hydrolysed. Longer SRT results in a larger reactor. In this way is the hydrolysis constant an important parameter for reactor design. As first order hydrolysis constant seems system and substrate specific, the use of literature values for the constant is therefore not accurate. Experiments with specific organic waste during space mission need to be done, to determine the biodegradability and the exact hydrolysis constant. Based on the experimentally determined hydrolysis constant the reactor can be designed properly. In order to give an indication of solubilisation of waste, hydrolysis rate constant has been adapted from other literature studies with comparable organic waste composition.

In case of fuel generation it is important to separate the fuel conversion process from the hydrolysis process. The process design should therefore consist of at least two coupled bioreactors. Other advantages for two-stage system are:

- Volume reduction
- Outcompeting methanogenic activity

In space the most important physical parameter is mass. Mass reduction is a very important design criterion. The mass is also determined by the amount of solids and water in the reactor. There are two types of digestion systems dry and wet. This is determined by the percentage of Total Solids (TS) in the system. Wet systems have TS of 15-25% and dry system more than 30%. The choice in between wet or dry digestion system is quickly made. A dry digestion system with low water content and high percentage of Total Solids (TS) of the solid waste has the advantage of smaller reactor volumes and need less energy for heating. As a result dry two-phase digestion system is selected as potential waste conversion system

Methanogenesis is found in the Melissa project to be more effective when digestion proceeds in two reactors [5]. The biogas yields are higher in a two-phased digestion process. Especially in space mission were efficiency should be >90% for complete recycling. High efficiency in hydrolysis is reached at high solid retention times. If only one reactor is used the volume is very large. In case of a two-phased system, a combination of high HRT and a low SRT reactor decreases reactor volumes [5]. Acetate is precursor for H_2 and electricity generation with the MFC and for phototrophic hydrogen production. The hydrolysis compartment for the conversion of those fuels will be equal. Normally during digestion a stable process is reached if no intermediary products as VFA are accumulating. If the rate of hydrolysis is higher than the methanogenic rate, accumulation of VFA and hydrogen may lead to irreversible acidification of the digestion. It effect is preferred for the production of precursors. Applying a high HRT will prevent growth of methanogens in the hydrolysis compartment on VFA.

3.2.2 Reactor type

There are several types known of two-phase dry digestion: batch and continuous systems. Each system can be operated at thermophilic and mesophilic conditions. The two-phase digestion systems employ a dry fermentation stage followed by a liquid methanogenic stage. A number of different systems have been developed that use this configuration and they have been variously described as "leach-bed" or percolation systems. A number of systems have been described but most apply the same principal: Biothane-AN system; IBVL process and ADTECH system [6].

SeBaC is a two-phase system which is applied in space mission simulations. SeBaC [7] Sequential Batch Anaerobic Composting is a leachbed high-solid reactor in which the leachate is pumped without dependence upon gravity. SEBAC ran with a BMP of 0.3 L CH4/g VS and a retention time of 15 days. The maximal conversion was 85%. Assuming that no intermediary products as VFA are accumulating, the hydrolysis constant for the SEBAC reactor is 0.126 d-1.

In this research is chosen for a continuous reactor to reduce the reactor volume. Separated storage of waste is not necessary and biomass can directly be fed into the reactor. The reactor type is a plugflow reactor with a liquid crosscurrent. Process water is percolated through the waste, hydrolysis takes place and the resultant percolate is fed into the fuel conversion reactor. Effluent from the methane reactor is recirculated through the hydrolysis reactor to reuse the water. Figure 4 contains a schematic overview of the reactor configuration. With the crosscurrent an optimal distribution of enzymes excreting organisms is obtained over the new added biomass.

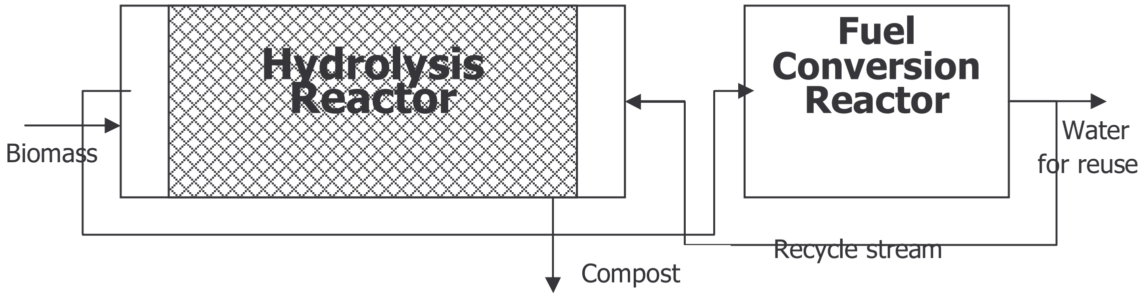

Figure 4 Configuration of plug-flow hydrolysis reactor connected with a fuel conversion reactor with recycle stream

3.2.3 Key design issues

The following design issues will be considered:

- Hydrolysis rate
- Solid retention time
- Loading rate
- Max. VFA concentration

Hydrolysis rate
The limiting conversion rate is the most important key issues for the design of a biological reactor. The hydrolysis rate is regarded as the most crucial rate of the total process, since the hydrolysis reactor precedes fuel conversion. Concluding from the previous part of the chapter, waste can be subdivided into macromolecules: carbohydrates, proteins and lipids. Each macromolecule needs different enzymes to hydrolyse the different bondings in the macromolecules. As a result no general hydrolysis rate exists and the most accurate hydrolysis rate can only be obtained by determining it during experimental research. In order to be able to design the reactor in this report, hydrolysis rates are adapted from literature.

The biodegradability of waste can be expressed by the maximum biogas that can be produced from the waste. It is expressed in the chemical oxidation demand (COD) of the converted biogas divided by the total COD of the waste. Biogas consists of methane and carbon dioxide. With biochemical methane potential assays the extent and rate of anaerobic conversion can be estimated. Chynoweth tested different types of waste feedstocks expected on space missions on their biochemical methane potential [7]. The feedstocks were obtained from various NASA laboratories and contractors. Anaerobic biochemical methane potential assays with these feedstocks resulted in methane yields ranging from 0.23 to 0.30 l/g VS added. The conversion efficiencies of tested materials ranged from 50-83%. Hydrolysis rates can be calculated from the BMP data assuming that there is no accumulation of intermediary products. The estimated hydrolysis rates ranged from 0.22 for rice to 0.069 for news paper. Previous BMP assays of Chynoweth with municipal solid waste (MSW) resulted in k_h of 0.13-0.16 d-1 [7]. In the present study the smallest rate is taken into account by the design of the hydrolysis compartment of the reactor. The waste material used in the mission with the smallest hydrolysis rate is paper 0.069 d-1 at a temperature of 35 ºC [7]. During the space mission to mars is 1.1 kg of paper is produced per day. Temperature influences the hydrolysis rate, a relation described by the Arrhenius equation. Operating at a higher temperature 50ºC the hydrolysis rate is increased to 0.21 d-1. This is agreement with the findings of Veeken et al. [8]. They found first order constant ranged from 0.03-0.15 d-1 at 20ºC to 0.24-0.47 d-1 at 40 ºC.

SRT

The solid retention time is determined by the hydrolysis rate and biodegradability. Time in Equation 1 is in this design equal to the solid retention time.

Equation 1 $$C = C_0 \cdot e^{-k_h \cdot t}$$

C = concentration organic matter (g COD/l)
C0 = Concentration of organic matter time zero before processing (g COD/l)
kh = hydrolysis constant
t = time

The SRT is calculated for the hydrolysis rate at 35 and 50 ºC with a biodegradability of 75%. The SRT is higher at lower temperature (20.7 days) than at 50ºC (6.5 days). Increasing temperature is crucial to this design, to out-compete methanogenesis and have a sufficient degradability. Based on these findings, a thermophilic hydrolysis/acidification reactor is chosen.

Loading rate

Table 4 Maximal acidification of biological waste calculated per macromolecule in gram acetate per day

Substrate	Structure formula[1]	COD/VS g/g	Loadingrate g/d	Loadingrate g COD/d
Carbohydrates	$(C_6H_{10}O_5)_n$	1,19	2529,1	3009,7
Protein	$C_5H_7NO_2$	1,42	40,6	57,6
Fat	$C_{57}H_{104}O_6$	2,90	17,4	50,3
Acidification products				3117,6

[1] Structure formula of the macromolecules are obtained form Angelidaki [9]

Table 4 shows the maximum of amount of acidification products that can be formed in a waste stream is 3.12 kg COD per day. The distribution of the COD among the acidification products varies and is depending on sludge loading and temperature, particularly in the thermophilic range. During acidification of glucose under mesophilic conditions mainly butyrate and acetate are produced, while under thermophilic conditions the main products are lactate and ethanol [10]. Although Shin found that also thermophilic conditions (55ºC) acetate and butyrate are main products during acidogenesis of food waste. According the results of Shins research is acidification product formation depended on HRT, pH as well as OLR. It was found that increasing OLR increased the total amount of final VFA and hydrogen. Operating at pH 5 and low HRT resulted in increased lactate formation. The ideal product from the hydrolysis reactor for fuel conversion is acetate. Concluding from the experiments of Shin a high SRT and pH of 5.5 or higher should be applied in the hydrolysis reactor. The exact composition of soluble acidification products stays unknown until experimental determination. For this report the product distribution of the operating CSTR on food waste is taken into account for further calculations. During operation of a OLR of 8 g VS/k/d, HRT of 5 and a pH of 5.5 86.1% of the COD was recovered in the soluble acidification products with 62.42% butyrate, 24.5% acetate, 1.61 propionate and 1.95 lactate. In the research of Shin in total 95.8 % of the COD could be recovered from the waste. During space mission not only food waste will be used as substrate, but plant residues which have a dense structure of cellulose and lignin. The efficiency is expected to be less. Chynoweth reported conversion efficiency of 50-85% using plant residues of rice, tomato's, wheat, peanut and potato [7]. Assumed for the space mission is a maximum degradation efficiency of 75%. This will be degraded into VFA, the rest will serve as compost material.

Maximum concentration

The hydraulic retention time (HRT) can be calculated from the solid retention time (SRT), the loading rate and the maximum VFA concentration in the liquid phase of the hydrolysis reactor. High VFA concentration contributes to inhibition of the microbial process due to the very low pH (<5). Maximum achieved VFA concentrations in previous researches at which the hydrolysis reactors still operated are 8000 mg/l [7] and 5000 mg/l [11]. In this design 5000 mg VFA /l is taken as the maximum concentration of the leachate coming from the hydrolysis reactor. The product composition is already posed in the previous paragraph, 5 g VFA/l is recalculated into 8,102 g COD/l. While applying a load of 3117.6 g COD/d a liquid recycle stream is needed with a flow of 10.35 l/h to keep below the maximum VFA concentration.

Table 5 Effluent composition and concentration of the hydrolysis reactor

VFA	VFA fraction%	gCOD/g VFA	g/l COD
butyrate	0,690	1,810	6243,4
acetate	0,271	1,070	1808,9
propionate	0,018	1,511	48,6
lactate	0,022	1,066	1,1
Total	1		8102,0

Reactor size and flows

The 75% degradation of paper is reached in 6.5 days calculated with the first order kinetics at 50 ºC. The kinetics are valid to describe degradation when no rate limiting step in biodegradability occurs. Applying an SRT of 8 days a margin for the biodegradability is taken. The reactor volume can be calculated from the total waste present in the system during 8 days loading of 11.9 kg: 95.2 kg, approximately 100 litres. This yields a solids retention time of SRT= 8 days and for the liquid a hydraulic retention time HRT= 100/10.35= 9.6 hours. The out flow composition is listed in table 5. Hydrogen is produced during acidification. Acidification is also called dark fermentation. This will be discussed in the next chapter.

3.2.4 Robustness and process conditions

The plug flow reactor is designed in a way that waste is processed continuously. Reaching a steady-state will lead to a sustainable process for a long time. Bacteria are not exposed to temperature and oxygen variations as occurs while operating in batch systems. In a batch system it takes some time before steady state is reached. Loss of microbiological activity is also prevented by using a continuous system. The two-phase digestion is proposed as alternative for the one-phase digestion because of its stability and control of the process [12].

pH shock

Hydrolysis is accomplished by enzymes, which are very sensitive to pH. Solubilisation of macromolecules is strongly affected by pH. The degradation behaviour on the three important organic polymers proteins, lipids and carbohydrates followed each a different trend with respect to pH changes [13]. Hydrolysis and acidification of proteins and carbohydrates are not promoted by acidogenic conditions [14]. High HRT is needed to stabilize the pH, to not irreversibly disturb hydrolysis and acidification. The pH should be at least 5, otherwise product composition will change more to instable products as propionate and lactate [15, 16]. The control of pH can prevent complete acidification.

Toxicants

During anaerobic digestion no nitrogen is removed. In two stage designs with attached growth, greater resistance toward inhibiting chemicals is achieved. A two times higher OUR could be applied in a two-stage reactor for waste yielding 5 g NH4+ /l before ammonium inhibition occurred. It was stated that two-stage processes can be treated with a C/N ratio of below 10 compared to one-stage processes which should have a ratio above 15. Urine is an important nitrogen source, can be excluded from the waste decomposition and directly used for irrigation. Part of the water is reused and added to the hydrolysis system. Post treatment is necessary to prevent accumulation of toxic components in the system.

Long-term behaviour

Zoetemeijer reported that both mesophilic and thermophilic separate acidification of glucose is possible; both processes are very stable [10]. Research with long operating systems reveals that thermophilic acidification can operate stable. A trickling biofilter reactor operated for stably at 55-64 ºC for 234 days on glucose [17]. A thermophilic CSTR reactor running on industrial sugar wastewater operated for 212 days and produced VFA and hydrogen [18]. The pH was maintained at 6.8 and the HRT was varied in the range of 0.5 to 3 day. No methanogenic activity was measured, probably due to the low HRT.

Variable load
The degree of VFA production, COD solubilization and organic substrate degradation primarily depended on HRT for complex substrates. The biodegradability of the three major constituents of wastewater increased with HRT, carbohydrates, proteins and lipids [19]. Carbohydrate was readily degraded at all loading rates, but degradation of protein and lipid decreased with the increase in loading rate. A study with thermophilic acidification of dairy wastewater in the up flow reactor also showed that the degree of acidification decreased with the increase in chemical oxygen demand (COD) loading rate [19].

Temperature
Temperature influences the biological process in various ways. Temperature is an important factor determining biological growth. Generally, growth rate increases by a factor of 2 to 3 is found by thermophilic (55ºC) and their mesophilic homologues (35ºC) [20]. Temperature influences the hydrolysis constant intensively [8]. Just as the pH temperature also temperature affects the activity of the enzymes. Every enzyme has its own temperature optimum. Temperature also changes the solubility of the substrate when lipids concerned. This makes the lipids more accessible to enzymes [21].

Advantages of thermophilic treatment
- High VFA
- Pathogens removal
- higher metabolic rates
- Small reactor volume
- Very low excess sludge production

Disadvantages
- High sensitivity during start
- High energy requirement

Infection and competition
There is no competition for polymers as substrate for micro-organisms. Polymers are not directly used as substrate for organisms. Polymers are hydrolysed by excreted enzymes of organisms into edible pieces (monomers) which are consumed by the organisms.

3.3 Conclusions

For generation of fuel precursors, hydrolysis and acidification steps of a plug flow reactor is designed with a liquid crosscurrent. With the design and the waste composition as described in the previous chapter a liquid effluent stream is created of 10.4 litres with a concentration of 5 g total VFA/l. The SRT is 8 days, resulting in a reactor size is 100 litres when not over dimensioned. Resulting in a HRT of 9.6 hours, which should be enough to prevent product inhibition.

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4 Dark fermentation

4.1 Introduction

Hydrogen can be generated in a number of ways, for example through fossil fuel processing, biological production or by electrolysis using solar power. In this study the biological production of hydrogen is potentially more attractive, since now biomass is used as the raw material. Two possible ways of biological hydrogen production are the photosynthetic and fermentative route. The possibilities of both routes for the described waste stream during a long term manned-space mission are discussed within this report. In this chapter the possibilities of fermentative hydrogen production are outlined.

Principle of the process

There are different names used to describe biological hydrogen fermentation. It is known as dark fermentation or acidification in digestion process. However all names refer to the same process: the conversion of carbohydrates to hydrogen and acids. As discussed in the previous chapter during hydrolysis polymers are hydrolysed into monomers and dimmers. For example starch is converted into glucose molecules. The next step in the digestion process is acidification in which glucose is converted to hydrogen and acids. Both processes hydrolysis and acidification in current design take place in the same reactor.

The reactor is already designed so less attention will be paid to design issues. This chapter will focus more on the description of the hydrogen production process and points out the possibilities and the limitations of dark fermentation.

Bio-conversion of biomass to produce hydrogen has been demonstrated using anaerobic fermentation of high-strength wastewater, solids waste, containing compounds like molasses, glucose, crystalline cellulose, peptone, and starch (polymer or monomer hexoses) [21]. Theoretically four mol of hydrogen can be made from one mol a hexose as glucose, if 2 mol of acetate are produced (Equation 2). When butyrate is the main fermentation product only 2 mol of hydrogen are produced (Equation 3).

Equation 2 $C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CO_2 + 2\ C_2H_4O_2$

Equation 3 $C_6H_{12}O_6 \rightarrow 2\ H_2 + 2\ CO_2 + C_4H_8O_2$

During digestion organic material such as glucose can be converted into a variety of products: VFA as acetic acid, alcohols and hydrogen (Table 1 in the previous chapter). Production of hydrogen is depended on the product formation. In practice high H_2 yields are associated with a mixture of acetate and butyrate fermentation products, and low H_2 yields are with propionate and reduced end products which are alcohols and lactic acid [22]. Experimental yield for waste treatment have been found in literature from 0.5-2.5 mol H_2/mol hexose [23]. Though acetate production is favourable for hydrogen production, in practice butyrate is mostly the main product 60-70% [23]. Product formation during fermentation is influenced by the organisms and the applied process conditions as pH, temperature, retention time and reactor type, which can be controlled [24]. For example alcohol is formed at reducing conditions as high hydrogen concentration [25]. To prevent alcohol formation and stimulate acetate and hydrogen formation, elevated hydrogen pressure should be prevented and removal of hydrogen is needed. Final products of fermentation (acetate, hydrogen, and CO_2) are the precursors of methane formation (methanogenesis). In order to produce hydrogen, hydrogen consumption by methanogenesis must be prevented as well. As already discussed in previous chapter this can be achieved by working at low pH, low HRT and SRT.

Hydrogen production with the available substrate from the waste material at space missions is feasible due to the high hydrocarbon content from the paper and wheat and potato's residues. It is demonstrated that hydrogen was produced during co-digestion of comparable substrate food waste and sewage sludge [26]. Though hydrogen is hardly produced from protein and lipid, the relationship between carbohydrate concentration and protein concentration during co-digestion indicated that protein might even enhance hydrogen production potential. The maximum specific hydrogen production potential of 122.9 ml/g carbohydrate-COD was found at the waste composition of 87:13 (food waste: sewage sludge) van the VS concentration of 3%. The metabolic results revealed that hydrogen production was accompanied by butyrate production. Fermentation efficiencies ranged from 17.8-73.8% depending on the sewage content with probably hydrolysis capacity. Earlier research using municipal solid waste had a maximum hydrogen production potential and hydrogen production rate in the range of 49-298 ml H2/g carbohydrate-COD and 17-142 ml H2/g VSS/h, respectively [27]. For the design of the reactor for the space mission is based on results of a comparable study using food for thermophilic hydrogen production [28]. The results are discussed in the previous chapter and used for the reactor design. In this design 86.1% of the COD was recovered in the soluble acidification products with 62.42% butyrate, 24.5% acetate, 1.61 propionate and 1.95 lactate. In total 95.8 % of the COD could be recovered from the waste. The other 9.7 % of the COD was found in hydrogen production: 2.2 mol-H2 was yield per mol-hexose consumed. The hydrogen production was related to the concentration of total organic acids (TOA) which was strongly dependent on that of butyrate. This indicates that the reaction was mainly a butyrate fermentation.

4.2 Key design issue

The overriding key design issue id the hydrogen removal

Hydrogen removal
As hydrogen concentration increases, the production of hydrogen is repressed and metabolic pathways switch towards production of other metabolites such as lactate, ethanol, acetone, butanol or alanine. It is recommendable to remove hydrogen produced before it inhibits further production of hydrogen [29]. There is another advantage of an appropriate hydrogen removal. It can also prevent methanogens from using hydrogen for methanogenesis [29]. There are several methods to remove hydrogen such as gas sparging using nitrogen or nitrogen and argon, stream stripping by evaporation sparging with fuel cell exhaust gas [22], and membranes made of silicone, palladium-silver, synthetic polyvinyl-trimethyl silane [29]. A study carried out by Mizuno [30] showed that gas sparging with nitrogen increased in 68% the hydrogen yield. Some studies show that sparging with argon increases residual NADH and this is expected to increase production of hydrogen, but no measures of hydrogen yields were available with this method [29]. Groenestijn [31] performed an experiment to compare different methods of removal of produced hydrogen in high-rate bioreactors. The methods are absorption of H_2 in metals (eg. Palladium or nickel lanthanides), stripping by boiling, stripping with a recirculating gas and stripping by evaporation at a large surface. Palladium cannot be used because of the amount required and high costs (€ 30,000/kg), while nickel lanthanides are much cheaper but their absorption properties are affected by water and sulfides. Stripping by boiling has the disadvantage that bacteria may not survive the boiling process and that huge steam production is needed. With respect to the method of stripping with a recirculating gas, it needs energy to introduce the gas in the reactor and, if N2 and CO2 are used, hydrogen has to be separated before using it in fuel cells. This separation has high costs. Finally, the study of Groenestijn showed that stripping hydrogen by evaporation was the most economically feasible method because much lower amounts of steam are required compared to stripping by boiling and separation of H2O of hydrogen is much easier. An appropriate hydrogen removal technique for space application should be further studied as different decision factors have to be taken into account. .

4.3 Design

Hydrogen can be produced in the hydrolysis/acidification tank as described in the previous chapter. It is advisable to remove the hydrogen from the reactor to produce also more oxidised products as acetic and butyric acid. In this way product composition is depended on the removal of hydrogen. The product composition is linked to the hydrogen production. The theoretical hydrogen yield is 2 mol per mol butyrate and 4 mol per mol produced acetate. The product composition is already posed in the previous paragraph. COD is converted into 62.42% butyrate, 24.5% acetate, 1.61% propionate and 1.95% lactate. The hydrogen yield that is taken into the design calculations is 2.2 mol/ mol hexose [28]. The amount of hexose can than be calculated from the carbohydrates in the daily waste stream. From table 2 in chapter 3 the daily carbohydrate loading rate is 2.529 kg/d-1 of which. From the total amount of carbohydrates 75% is biodegradable and is converted into10.5 mol of hexoses. With the estimated yield of 2.2 this results in 23.2 mol of hydrogen per day. If the total amount of hydrogen is removed from the reactor 0.95 m3 biogas is produced per day (60% (v/v)). Before usage of the hydrogen in fuel cells, the carbon dioxide should be removed from the biogas.

4.4 Robustness & Conditions

The following conditions have effect on the robustness of the system. The conditions are related to bacteria performance in generating H2 from waste material.

pH-shock
The control of pH is a crucial factor to hydrogen production. It is reported that pH below 5.0 inhibits hydrogen production [26]. It can be found in different literatures that the optimum range for bacteria-growth is between pH 6-7 [22].

Toxicants
Accept for product inhibition itself no literature was found about other components in waste that influence hydrogen production. The maximum VFA concentration is set on 5 g/l in the previous chapter. As it is a biological process it is sensitive to xenobiotics. Medication of crew members can disturb or even completely inhibit hydrogen production via faeces. Antibiotics for example should be prevented from entering the system.

Long-term behaviour
Hydrogen production has been studied extensively at laboratory scale. The majority of research has been conducted on pure cultures with expensive pure substrates or to a much lesser extent mixed cultures in solid or wastewaters. Experience on sustainable long term hydrogen production processes is still missing. Information about long-term behaviour could not be found in literature.

Variable load
Butyrate is the major product during acidification. An organism that produces predominantly butyrate is the C. butyricum. This clostridium is a spore-former and forms spore in extreme conditions as heat or food shortage. The advantage is that such a species is able to survive extreme conditions. Spore formation in conditions when other bacteria continue growing is a disadvantage. In case of irregular feeding rate to a reactor inoculate is strongly selected for non-spore forming bacteria for example the propionate forming bacteria. Hydrogen is not formed in the propionate production from glucose. Because of the slow release of monomers by the slow hydrolysis from the waste stream this would not be the case in the plugflow reactor. A continuous stream of monomers supply the hydrogen producing bacteria [22].

Temperature
Most of the biological processes are operated at an ambient temperature of 30-40°C and normal pressure. Under higher temperatures, thermophilic operation is also possible and optimum temperature is 52°C. Under thermophilic conditions, Clostridium and Thermoanaerobacteria become dominant at thermophilic conditions (40-60 oC). Optima for mesophilic organisms are reached at 37 °C and for thermophilic bacteria about 52 °C [21]. Temperature selects spore forming bacteria as Clostridium. They can easily survive a temperature shock of 80 degrees Celsius, though time is needed to grow the organisms again. In case of temperature shock the retention time of the solids 8 days may be not sufficient to completely convert the organic waste into the design waste stream.

Infection and competition
Hydrogen production by a wide range of bacterial species, pure and mixed, defined, cultures grown on sterile medium, and undefined enrichment cultures grown in non-sterile conditions, has been reviewed by Nandi and Sengupta [20]. From an engineering point of view a process using a stable enrichment culture yielding hydrogen from non-sterile organic wastes is required [22]. Mixed cultures enriched form natural environments are reported to contain mostly clostridia. The organisms are naturally selected from the organisms that are already present in the organic waste material. While operating in space a limited contact is wanted with the processing of the organic

waste and humans. One could doubt if a good natural selection can take place in the reactors. However faeces are already a good source of different mixed cultures. In case of mal functioning of the reactor, the reactor can be restarted with new inoculation with conserved mixed cultures, which easily can be taken during the flight.

4.5 Conclusion

Biological treatment of waste has a lot of advantages for space applications: low energy use, low volume and low manpower requirements. However the disadvantage of biological processes is that they are sensitive to shock loading, pH and temperature variations. During reactor design most of the shock loadings can be prevented, but still not all risks can be excluded. As it is a bacterial process it will always be sensitive. However evaluating of biological waste processing for long term space missions turns out to be very positive these systems [32]. Generating fuel as hydrogen, electricity and methane are biological processes as well. In this way the generation of fuels has no potential higher risks for malfunctioning then other biological waste processing methods.

4.6 References

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5 Bio-electrochemical systems for the production of hydrogen and electricity during space missions

5.1 Introduction

The bio-electrochemical processes investigated by the laboratories of Wageningen University are based on the application of electrochemically active micro-organisms. These electrochemically active micro-organisms are capable of converting biodegradable material in wastewater to carbon dioxide, protons and electrons. Either by direct contact with the electrode surface or aided by an (excreted) electron shuttle, the electrons are transferred to the electrode at a high energy level. This electrode is called the biological anode and can be applied for driving several bio-electrochemical processes (figure 5).

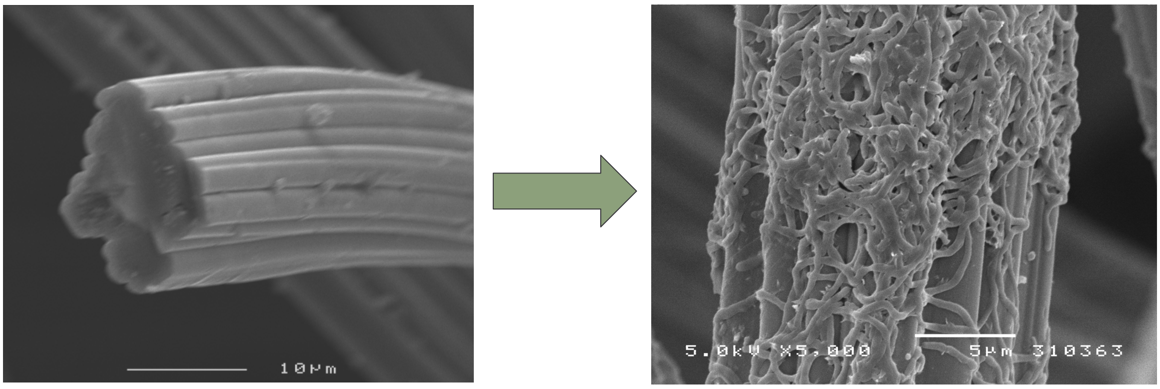

Figure 5. Biological anode. On the left: graphite fiber without electrochemically active micro-organisms; on the right: graphite fiber colonized with electrochemically active micro-organisms (source: http://www.geobacter.org).

At the moment two bio-electrochemical processes are investigated in depth in the laboratories of Wageningen University: the microbial fuel cell (for electricity production) and biocatalysed electrolysis (for hydrogen production). The latter is a novel process developed and patented by Wageningen University. For space application also a combined system can be developed that is both suitable for electricity and hydrogen production, depending on the demand. This system we call the multipurpose bio-electrochemical system.

The energy levels (=potentials at pH 7 vs. NHE) at which the electrons are released by the biological anode and accepted by the cathodes in the described bio-electrochemical processes are depicted in figure 6.

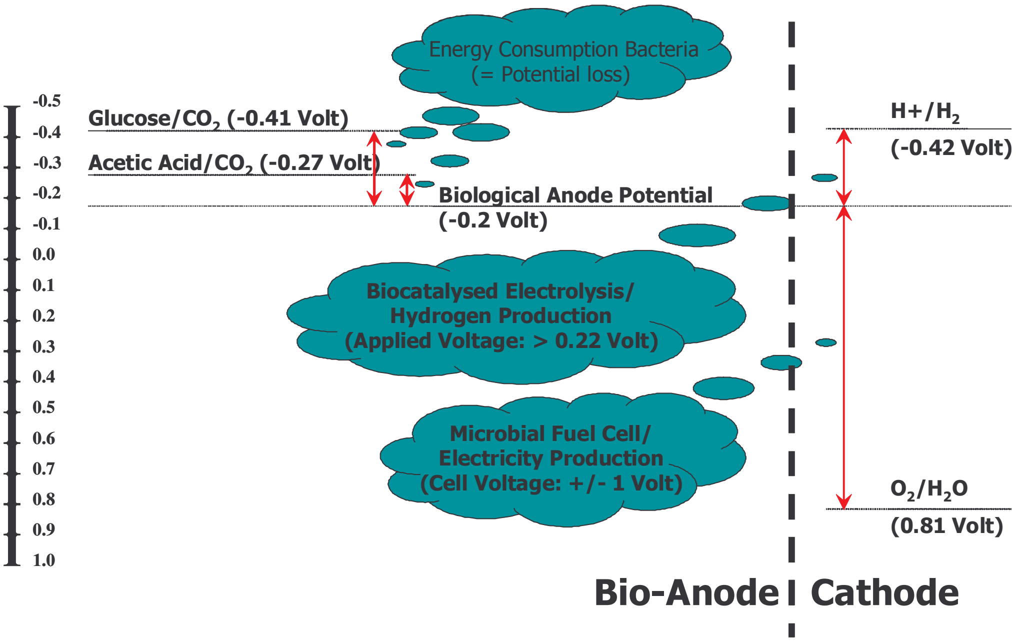

Figure 6. Typical potentials valid for the bio-electrochemical processes discussed in this report (i.e microbial fuel cell, biocatalysed electrolysis, multipurpose bio-electrochemical system).

Bio-electrochemical conversion processes (figure 7, 8 and 9) take place in an electrochemical cell. The anode compartment of this cell is continuously fed with wastewater. In the cell the oxidation of the biodegradable material at the biological anode is separated from the cathode reaction by means of a cation exchange membrane. Externally, the anode and the cathode are connected through an electrical circuit. While the released electrons flow from the anode to the cathode through the electrical circuit, an equal number of protons permeate through the membrane. At the cathode the protons and electrons are consumed by the cathode reaction (oxygen or proton reduction). Ideally, the gas stream leaving the anode compartment only consists of carbon dioxide. The gas stream leaving the cathode compartment consists of humidified air (microbial fuel cell) or pure hydrogen gas (biocatalysed electrolysis).

In the next three paragraphs the working principles of the three bio-electrochemical processes currently are explained in more detail.

5.2 Microbial Fuel Cell (MFC)

In the microbial fuel cell the biological anode is electrochemically coupled to an oxygen reducing cathode. In this way electricity is generated from the electrical circuit (figure 7).

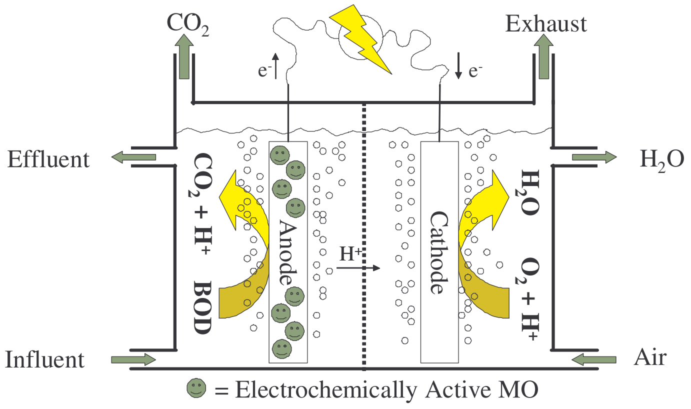

Figure 7. Schematic representation of the microbial fuel cell

In the case of acetate:

Anode: $CH3COOH + 2\ H2O \rightarrow 2\ CO2 + 8\ H+ + 8\ e-$

Cathode: $2\ O2 + 8\ H+ + 8\ e- \rightarrow 4\ H2O$

Overall: $CH3COOH + 2\ O2 \rightarrow 2\ CO2 + 2\ H2O$ + electricity

The overall reaction has a negative ΔG. Therefore power can be extracted from this reaction. Theoretically, about 1 Volt can be generated with the microbial fuel cell. In practice, due to losses in the cell, electricity is generated at 0.5-0.7 Volt. Currently, the typical power density of a microbial fuel cell is about 0.1 kW/m3 reactor volume. In about 5 years this will increase to over 1 kW/m3 reactor volume.

5.3 Biocatalysed Electrolysis (BCE)

In biocatalysed electrolysis the biological anode is electrochemically coupled to a proton reducing cathode. In this way hydrogen is generated (figure 8).

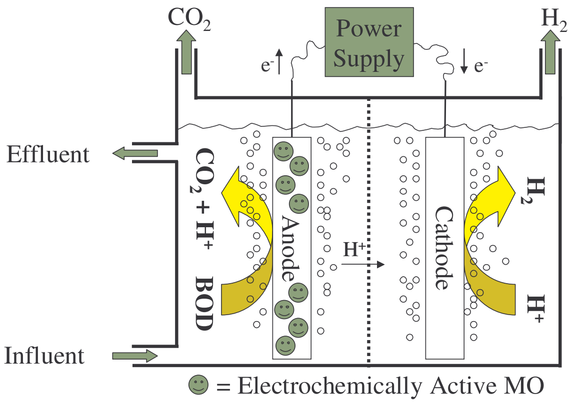

Figure 8. Schematic representation of biocatalysed electrolysis

In the case of acetate:

Anode: $CH3COOH + 2\ H2O \rightarrow 2\ CO2 + 8\ H+ + 8\ e-$

Cathode: $8\ H+ + 8\ e- \rightarrow 4\ H2$

Overall: $CH3COOH + 2\ H2O + \text{electricity} \rightarrow 2\ CO2 + 4\ H2$

The overall reaction has a positive ΔG. Therefore a small amount of electrical power needs to be provided to be able to drive this reaction. This input of electrical energy is provided by a power supply. Theoretically, an applied voltage of about 0.14 Volt is required (in the case of acetate). In practice, due to potential losses in the cell an applied below 0.5 Volt is sufficient. Still, the amount of electrical power required per amount of hydrogen is 3 to 5 times lower than that required for hydrogen production by means of conventional water electrolysis. Furthermore, biocatalysed electrolysis has several advantages compared to conventional fermentative hydrogen production from wastewater (table 6).

Table 6. Comparison of biocatalysed electrolysis with conventional fermentative hydrogen production.

	Biocatalysed electrolysis	Conventional fermentative hydrogen production
# reactors	1	2
Substrate	Biodegradable material in general (sugars, fatty acids, etc.)	Only sugars!
Pure culture required?	No	Yes
Inhibited by hydrogen itself?	No	Yes (pH2 > 20000 Pa)
Sunlight required?	No	Yes
Gas separation required?	No (product = pure H2)	Yes (product = H2/CO2 mixture)
Can H2 be produced at elevated pressure?	Yes (By electrochemical pressurization)	No (Separate compressor required)

Biocatalysed electrolysis is a novel hydrogen producing technology that was developed and patented by Wageningen University (WO2005005981 – priority date: July 2003). Recently also other researchers have recognized the potential of this configuration and refer to the technology as electrochemically assisted microbial production of hydrogen [33]. In the currently used laboratory system a volumetric hydrogen production rate of 0.02-0.3 m3/m3 reactor volume/day is achieved at an applied voltage of 0.5 Volt. In 5 years this will increase to over 10 m3/m3 reactor volume/day at an applied voltage of 0.3-0.4 Volt.

5.4 Multipurpose Bio-electrochemical System (MBES)

The working principle and conditions of the biological anode in the microbial fuel cell are identical to those in the biocatalysed electrolysis process. The electrochemically active micro-organisms do not notice the difference between the two systems. This allows for a combined system in which both electricity and hydrogen can be produced depending on the demand at a certain moment. We call this system the multipurpose bio-electrochemical system or MBES (figure 9a). Switching from electricity (figure 9b) to hydrogen production mode (figure 9c) is simply achieved by switching the system from power production to power consumption by switching the air flow in the cathode from on to off. This switch is performed in minutes. In this way biodegradable material can be efficiently dedicated to either electricity or fuel production.

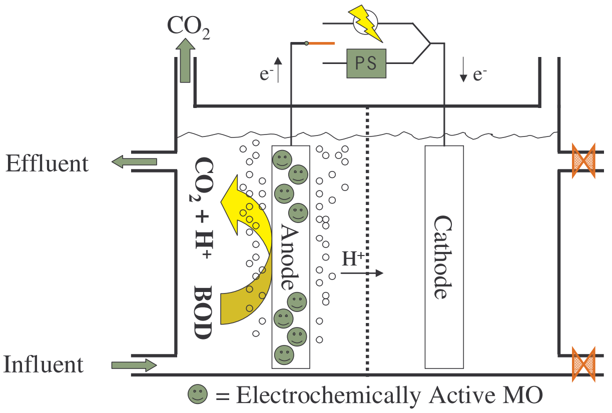

Figure 9a. Schematic representation of the multipurpose bio-electrochemical system

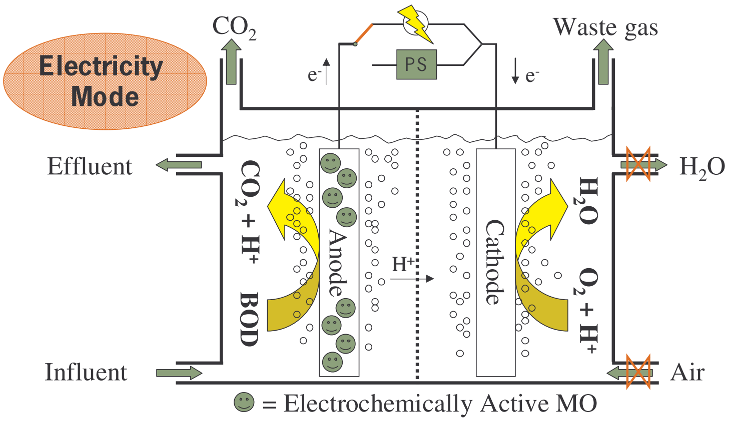

Figure 9b. The multipurpose bio-electrochemical system in the electricity production mode

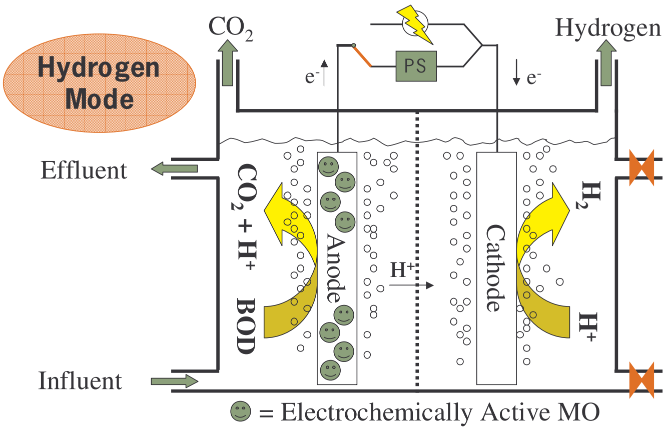

Figure 9c. The multipurpose bio-electrochemical system in the hydrogen production mode

5.5 Design

General remark

All three systems discussed above work with an identical biological anode. In fact, the electrochemically active micro-organisms do not experience a difference between being in an electricity producing electrochemical cell (microbial fuel cell) or in a hydrogen producing cell (biocatalysed electrolysis). Therefore, many of the characteristics (e.g. flow composition, robustness, conditions) are identical for all of the described bio-electrochemical processes. For this reason the design of the three bio-electrochemical processes are discussed together in the following paragraphs. Where necessary, the differences between the processes are discussed.
All reported gas flows are in volumes @ 298 K and 1 bar.

Potentials & Performance

As discussed in chapter 3 the effluent stream of the hydrolysis step has got a flow of 10.35 litre/hour and still contains 8.1 g COD/litre. This COD will mainly consist of acetate, propionate, butyrate and lactate. From literature is known that these substrates can be easily converted by means of bio-electrochemical conversion processes [34-39]. When converted, the following reaction stoichiometry applies for electricity (microbial fuel cell) and hydrogen production (biocatalysed electrolysis):

Electricity production (Microbial Fuel Cell):

Acetate (CH3COO-) + 2 O2 → 2 HCO3- + H+ + electricity

Propionate (C2H5COO-) + 3.5 O2 → 3 HCO3- + 2 H+ + electricity

Butyrate (C3H7COO-) + 5 O2 → 4 HCO3- + 3 H+ + electricity

Lactate (C3H5O3-) + 3 O2 → 3 HCO3- + 2 H+ + electricity

Hydrogen production (Biocatalysed Electrolysis):

Acetate (CH3COO-) + 4 H2O → 2 HCO3- + H+ + 4 H2

Propionate (C2H5COO-) + 7 H2O → 3 HCO3- + 2 H+ + 7 H2

Butyrate (C3H7COO-) + 10 H2O → 4 HCO3- + 3 H+ + 10 H2

Lactate (C3H5O3-) + 6 H2O → 3 HCO3- + 2 H+ + 6 H2

The Gibbs energy for these reactions (calculated according to [40]) are given in table 7. The theoretical voltages of these reactions were calculated from the Gibbs energy according to $\Delta G = -n \times F \times \Delta E$ [41] (ΔG = Gibbs Energy, n = # of electrons, F = Faradays number 96485 C/mol, ΔE = voltage).

Table 7. Gibbs energy and theoretical voltages for electricity and hydrogen generation from acetate, propionate, butyrate and lactate.

Component	Microbial Fuel Cell		Biocatalysed Electrolysis	
	Gibbs Energy ΔG (kJ/mol)	Theoretical Cell Voltage	Gibbs Energy ΔG (kJ/mol)	Theoretical Required Voltage
Acetate	-844.16	1.09	104.55	0.14
Propionate	-1479. 21	1.09	181.03	0.13
Butyrate	-2114.38	1.10	257.4	0.13
Lactate	-1322.48	1.14	100.58	0.09

As can be seen from table 7, the theoretical voltages for the various substrates vary only slightly. It is therefore common practice to generalize the theoretical voltages for COD. Typically one can say that one can theoretically produce electricity at a cell voltage of about 1.10 Volt and produce hydrogen by applying a voltage between 0.10 to 0.15 Volt. However, these values are theoretical values and in practise under operating conditions one will experience various potential losses in the system (a.o. potential losses associated with microbial energy consumption, ohmic losses, overpotentials associated with the cathode reaction). For calculation purposes we will therefore have to make a few assumptions. In the case of the discussed bio-electrochemical processes these assumptions are based on the expected performance in 5 years time:

Calculation assumptions:

Microbial fuel cell:
In future systems the cathode compartment becomes redundant by replacing it with a gas diffusion electrodes (air cathode[37, 39, 42, 43]) directly attached to the anode compartment (figure 6).
Achievable voltage under operating condition: 0.6 Volt
Volumetric performance: 1 kW/m^3 reactor volume
(current standard: 0.1 kW/m^3 reactor volume)
Overall efficiency (i.e. conversion of COD tot electrons): 90%[1]

Biocatalysed Electrolysis:
In future systems the cathode compartment becomes redundant by replacing it with a gas diffusion electrodes directly attached to the anode compartment (figure 9).
Required voltage: 0.35 Volt → Required energy input: 0.8 kWh/m^3 H_2
(by comparison: conventional water electrolysis requires > 4.5 kWh/m^3 H_2)
Volumetric performance: 10 m3 H_2/m^3 reactor volume/day
(current standard: 0.02-0.3 m^3/m^3 reactor volume/day)
Overall efficiency (i.e. conversion of COD tot hydrogen): 95%[3]

Multipurpose bio-electrochemical system:
Conditions in electricity mode identical to microbial fuel cell operation
Conditions in hydrogen mode identical to biocatalysed electrolysis

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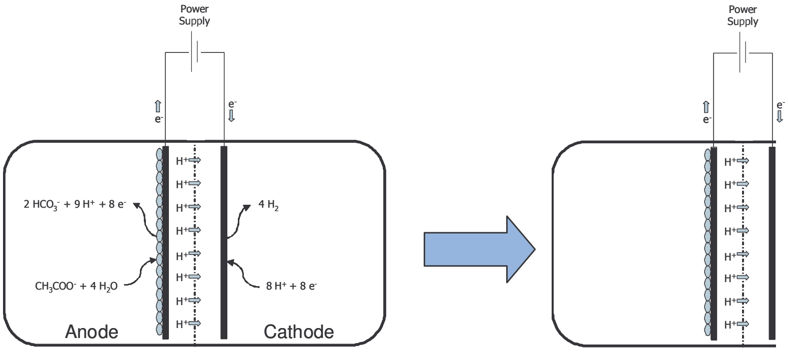
[1] Efficiency losses caused by methane formation in the anode compartment and aerobic conversion of COD due to oxygen diffusion through the membrane from cathode to anode during microbial fuel cell operation.

[2] Including additional required energy input due to diffusional loss of hydrogen through the membrane from cathode to anode (5%) and re-oxidation at the anode.

[3] Efficiency losses caused by methane formation in the anode compartment.

Figure 10. In future bio-electrochemical systems the cathode compartment becomes redundant by replacing it with a gas diffusion electrode (GDE). The cathode reaction then occurs directly in the gas phase.



Based on the assumption as mentioned above one can calculate that every kilogram of COD can be converted to 2 kWh of electrical energy in the microbial fuel cell or to 1.5 m3 of hydrogen gas in the biocatalysed electrolysis process (figure 11). In the case of the multipurpose bio-electrochemical system one can choose between making 2 kWh of electrical energy or 1.5 m3 at any point in time depending on the demand at a that time.

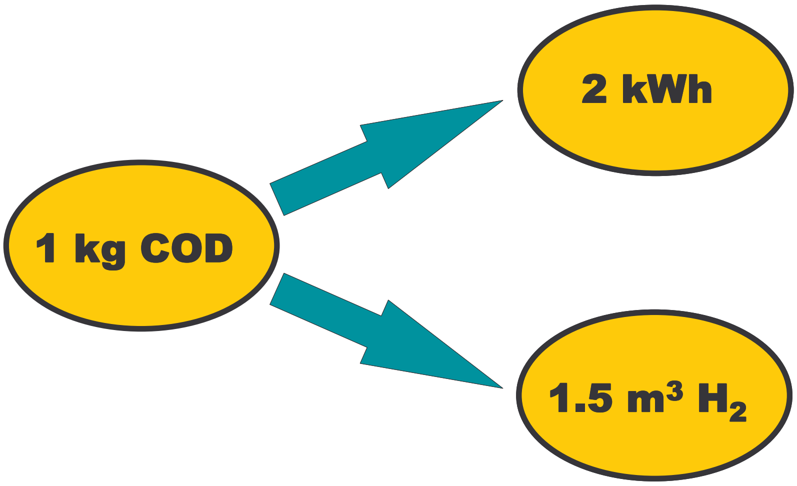


Figure 11. Bio-electrochemical conversion of biodegradable material (BOD) to electricity or hydrogen

Sizes

The effluent stream of 10.35 litre/hour leaves the hydrolysis step containing 8.1 g COD/litre. For the bio-electrochemical systems this gives a total load of approximately 2 kg COD per day. In a microbial fuel cell system (see above), this COD load will yield 4 kWh of electrical energy. In a biocatalysed electrolysis system this will yield 3 m3 of hydrogen gas per day at the expense of 2.4 kWh of electrical energy.

Based on the assumptions as made above a microbial fuel cell treating this COD load will have an approximate size of 167 litres. A biocatalysed electrolysis system will have an approximate size of 300 litres. The dimensions of the multipurpose bio-electrochemical system needs to be based on the largest of both systems and will therefore be also designed with a 300 litre volume.

Table 8 below summarizes the design values.

Table 8. Electricity production/consumption, hydrogen production and expected size of the bio-electrochemical processes.

	Microbial Fuel Cell	Biocatalysed electrolysis	Multipurpose bio-electrochemical system
Electricity (kWh)	4 (=production)	-2.4 (=consumption)	1. Electricity-mode: 4 2. H2-mode: -2.4
Hydrogen (m^3)	-	3	1.Elec-mode: - 2.H2-mode: 3
Reactor Size (litre)	167	300	300

An extra remark can be made regarding the required volume for biocatalysed electrolysis process. The current prediction of 300 litre is based on a volumetric hydrogen production rate of 10 m3 H2/m3 reactor volume/day at an applied voltage of 0.35 Volt. If electricity is sufficiently available the applied voltage can also be increased (e.g. to 0.5 Volt), thus increasing the energy investment per volumetric amount of hydrogen, but also increasing the volumetric hydrogen production rate and thus reducing the required reactor size.

An interesting option that applies to all three of the bio-electrochemical system is the integration of these systems with the hydrolysis step. Because the bio-electrochemical systems are able to operate perfectly within mixed microbial cultures (see 1.3.5), certain conditions can possibly be established at which the electrochemically active micro-organisms can form a consortium with the hydrolyzing micro-organisms [44]. Although this will probably increase the required volume for the bio-electrochemical systems, it will almost certainly reduce the volume of the complete system (including hydrolysis). More research is necessary to conform this.

Flows

The effluent flow of the hydrolysis is the influent flow of the bio-electrochemical system. This flow is 10.35 litre/hr with a COD concentration of 8.1 g COD/l. In our laboratories, we have operated the biological anodes at concentrations as low as 20 mg COD/l without to much loss in performance of the system. With a safe margin the biological anode can be easily operated at an effluent concentration of 100 mg COD/l. This COD will consist of unconverted acetate, propionate, butyrate and lactate. Because the anode compartment in all the bio-electrochemical processes is anaerobic also reduced inorganic compounds are likely to be present in the effluent (e.g. NH4+, HS-). Depending on the pH in the system these compounds are also likely to be present as trace gases (as NH3 and H2S) in the anode waste gas stream, thus polluting the carbon dioxide. Also some methane (up to 5% of the COD) could be present in the anode waste gas due to some methanogenic activity in the anode compartment. To be able to recycle the nutrients the trace gases and the methane in the anode waste gas need to be converted to their oxidized (and soluble) forms again using aerobic post treatment ($H_2S_4 \rightarrow SO_4^{2-}$, $NH_3 \rightarrow NO_3^-$, $CH_4 \rightarrow CO_2$). This aerobic post treatment can simultaneously also be utilized to convert the remaining COD in the effluent of the anode compartment. A possible configuration of this aerobic post treatment can be that of a membrane bioreactor (MBR). The effluent of an MBR can easily be made suitable for human consumption again by nanofiltration (NF) and reversed osmosis (RO). If the anode waste gas is purified from trace gases and methane, pure carbon dioxide remains, which can be used to fertilize the crops. The gas stream leaving the cathode compartment consists of humidified air (microbial fuel cell) or pure hydrogen gas (biocatalysed electrolysis).

Table 9 below presents the flows and expected compositions in the bio-electrochemical systems based on the reaction stoichiometries

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[4] H_2S can also be treated separately by partially oxidizing it to elemental sulphur (S^0) using another biological process. This biological sulphur is known to be a good fertilizer and fungicide and can therefore be mixed with compost to improve the soil condition.

Table 9. Expected Flows and compositions in the microbial fuel cell and biocatalysed electrolysis; the values for the multipurpose bio-electrochemical system depend on the operation mode and can be adapted from the values for the microbial fuel cell and biocatalysed electrolysis.

Component	Microbial Fuel Cell		Biocatalysed Electrolysis	
	Flow (l/h)	Composition	Flow (l/h)	Composition
Anode Liquid Influent	10.35	8.1 g COD/l +nutrients	10.35	8.1 g COD/l +nutrients
Anode Liquid Effluent	10.35	0.1 g COD/l + nutrients	10.35	0.1 g COD/l + nutrients
Anode Gas Influent	-	-	-	-
Anode Gas Effluent	68	81 % CO2 / 19 % CH4 + trace gases	68	81 % CO2 / 19 % CH4 + trace gases
Cathode Gas Influent	Diffusion: 65 l O2/h	Air	-	-
Cathode Gas Effluent	Diffusion	Humidified Air	125	~100% H2

5.6 Robustness & Conditions

From the experience in our laboratories it is known that biological anodes can be operated stably for long periods of time. Some anodes in our laboratories were operated for over 5 months without a noticeable loss in performance. In our laboratories biological anodes have been operated in the pH range 5-9 and from literature it is known microbial fuel cells can be operated from 15 up to 70 °C [45].

Under the right conditions start-up of the system is fast and easy. A normal start-up usually does not exceed 5 days, but can be a lot faster (less than 3 days) if fresh effluent from the bio-electrochemical system is used as an inoculum. Furthermore, the micro-organisms responsible for the electron donation can be grown from almost any inoculum. From some studies it is known that the electrochemically active micro-organisms can even be grown from domestic wastewater [37]. It is thus expected that the faeces of the space crew is already suitable for inoculation. Therefore, in the case of an incident that kills of all the micro-organisms (e.g. spill of a toxic chemical in the water treatment system), the system can be restarted within a short period of time.

As the system operates on the principle of natural selection, mixed microbial cultures occur in the reactor. This allows for easy operation as no effort needs to be spent towards keeping the culture pure (e.g. influent sterilization). Furthermore, working with mixed microbial cultures also makes the system extremely flexible, as a mixed culture can easily adapt to changes in the influent conditions (variable load, different kinds substrates, concentrations, etc.). Laboratory studies have shown that electrochemically active micro-organisms are able to generate an electrochemical potential from many different substrates, varying from organic substrates like sugars[46-48] and fatty acids[39, 49, 50] to even inorganic substrates, like elemental sulphur[51]. In our own studies the electrochemically active bacteria have also shown to have a considerable flexibility with respect to periods of famine. Even after a week without feeding, current generation starts almost instantly upon re-addition of electron donor.

At the cathode side still some important challenges remain. Especially the development of well performing gas diffusion electrodes is most important for the future improvement of bio-electrochemical systems. Currently, especially the oxygen reduction reaction suffers from severe potential losses, thus limiting the performance of the microbial fuel cell configuration. Another challenge is the development of a gas diffusion electrode for the multipurpose bio-electrochemical system that is both suitable for performing the oxygen and proton reduction reactions. Interesting developments in that field are currently ongoing for regenerative hydrogen fuel cells[52].

5.7 References

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6 Photoheterotrophic Hydrogen Production

6.1 Principle

The high-grade re-use of organic waste fractions that are generated during a long term space expedition requires their degradation towards organic acids, as described previously. After this acidification step, converting these organic using photoheterotrophic bacteria is optional and yields a source for single cell protein (SCP), as was described in The Melissa progress report for 2002 (Melissa partners, 2003). We should state here that long-term toxicity effects should be performed before phototrophic purple non sulfur bacteria can be used as SCP in a human diet (Sasikala and Ramana 1995).

By using specific types of photoheterotrophic micro organisms for degrading the organic acids to SCP, the high-grade energy carrier hydrogen can be generated concomitantly. The conversion of for instance acetate to hydrogen can only be performed by phototrophic organisms, since it has a positive Gibbs free energy change. Purple non sulfur bacteria have a photo system that generates the energy that is required to use organic acids to produce both biomass and hydrogen with by photo-phosphorylation.

The ratio of hydrogen to SCP production can be altered by changing the parameters under which the bacterial culture is grown, depending on the requirement for both. This versatility and the ability of the system to convert part of the waste that is generated into an energy carrier that can be converted to electricity very efficiently (around 65 %) at low temperature (80 – 100 ºC) in a Proton Exchange Membrane Fuel Cell (PEMFC) are two major advantages of this system.

From literature it is known that solar light energy can be converted to hydrogen energy using purple non-sulfur bacteria with a 2 % energetic efficiency (Wakayama et al. 1998), while the theoretical optimum could be calculated from own estimations and literature data (Göbel 1978) to be 10.3 %. We refer to this efficiency of light energy to hydrogen energy conversion as photosynthetic efficiency or PE.

The proposed process layout is schematically represented in figure 12. The liquid stream containing the VFA’s (1) that were generated during the acidification step is transported to a buffer tank (2). This buffer tank is used to store the acidifier effluent that is generated during night time, as the photobioreactor (PBR) is not in operation during these hours. From the buffer tank, the liquid is pumped to the photobioreactor (3). Here, the VFA’s present are converted to biomass, hydrogen and carbon dioxide. This process is driven by photosynthesis taking place on the inside of the purple non sulfur bacterial cells that are present in the PBR. For this photosynthetic process to take place, irradiation, exemplified by the sun (4) is required. The PBR is assumed to be a continuous stirred tank reactor (CSTR) meaning that the effluent has the same composition as the reactor content.

The liquid that is removed from the PBR contains a minute concentration of VFA’s and a certain concentration of SCP in the form of biomass (5). The other products that result from this fermentation are gaseous. The off-gas contains about 90% of hydrogen, while the remainder is carbon dioxide with possibly traces of nitrogen and sulfur containing gases.

For most fuel cell applications, this hydrogen content will suffice. The gas stream can also be treated to yield 100 % pure hydrogen. There are various practical options for the construction of a gas separator (6) such as membranes through which only H2 permeates (Teplyakov et al. 2002).

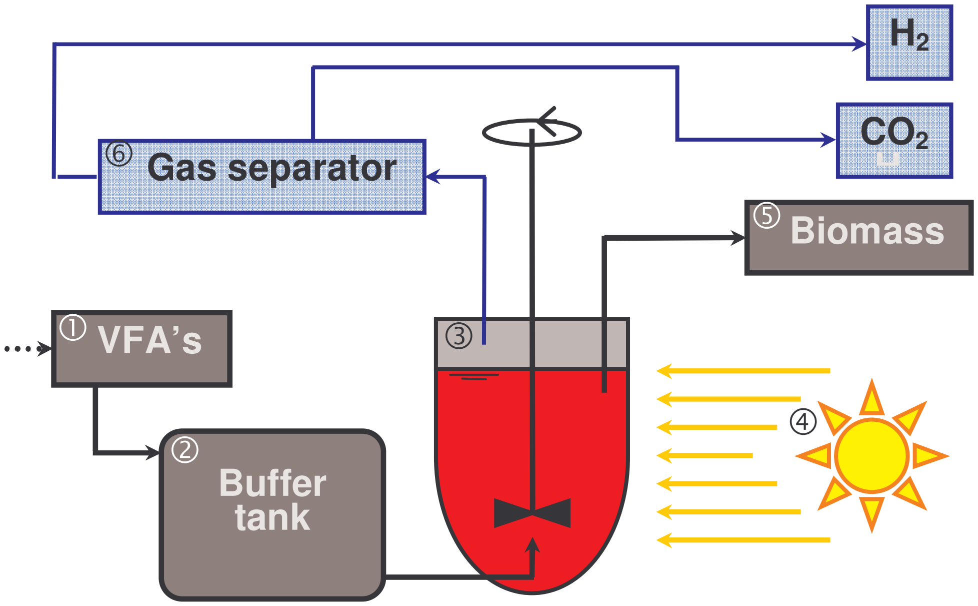

Figure 12 Schematic representation of the VFA conversion process towards hydrogen using photoheterotrophic fermentation.

Design issues

For simplification purposes we have calculated our photobioreactor dimensions by using several assumptions. We will state them here briefly, to indicate which factors might result in an alternate outcome of our calculations.

Related to the hydrogen producing capacity of the system

Since the UVB and UVC levels on mars are significantly higher then on earth, they might have an adverse effect on the viability or growth rate of the cultures. No data are available on the possibly adverse effects on culture survival or stability at these elevated UV levels but it seems improbable that it is a life limiting factor on the surface of Mars (Cockdell 1998). A thin water shield between the culture and the solar irradiation can easily remove this radiation. It seems unlikely that the current

Because purple non sulphur bacteria absorb only in the 400 – 950 nm spectral range, we define energy conversion efficiencies based on that spectral range. The spectral absorption characteristics of the Rhodobacter capsulatus NCIMB 11773 species that we use are displayed in figure 13.

The calculations were performed assuming a continuous and axenic ammonium limited culture of a purple non-sulfur bacterium in a photobioreactor. From our own experience, the specific hydrogen producing capacity is 0.5 mmol kg s-1, in this modus.

The VFA substrate to hydrogen conversion efficiency was assumed to be 80% of the theoretical stoichiometry (Sasikala et al. 1993). The residual carbon is converted to biomass and CO2. If this is preferred, the ratio of hydrogen to biomass production can be altered towards the generation of more biomass at the expense of the hydrogen yield.

Related to the Martian illumination conditions

The illumination of the Martian surface is calculated as a yearly average of the entire planet, as it is dependent upon its location as a result of the axial tilt of the planet (Appelbaum and Flood 1990).

The spectral composition of the extra-terrestrial standard solar irradiation spectrum provided by the US National Renewable Energy Laboratory (NREL) was used (NREL 2005). It is displayed in figure 11**Error! Reference source not found.** for the 400 - 950 nm range. This is the spectral composition that the planet receives outside its atmosphere. Local atmospheric conditions can have a pronounced influence on this spectral content.
We have not taken the opacity of the Martian atmosphere into consideration, since it is highly variable. We should note here however that dust-storms might have a large and negative effect on the illumination the Martian surface receives. This discrepancy can be as high as 73%, depending on the combination of the zenith angle and the optical depth of the Martian atmosphere (Appelbaum and Flood 1990).

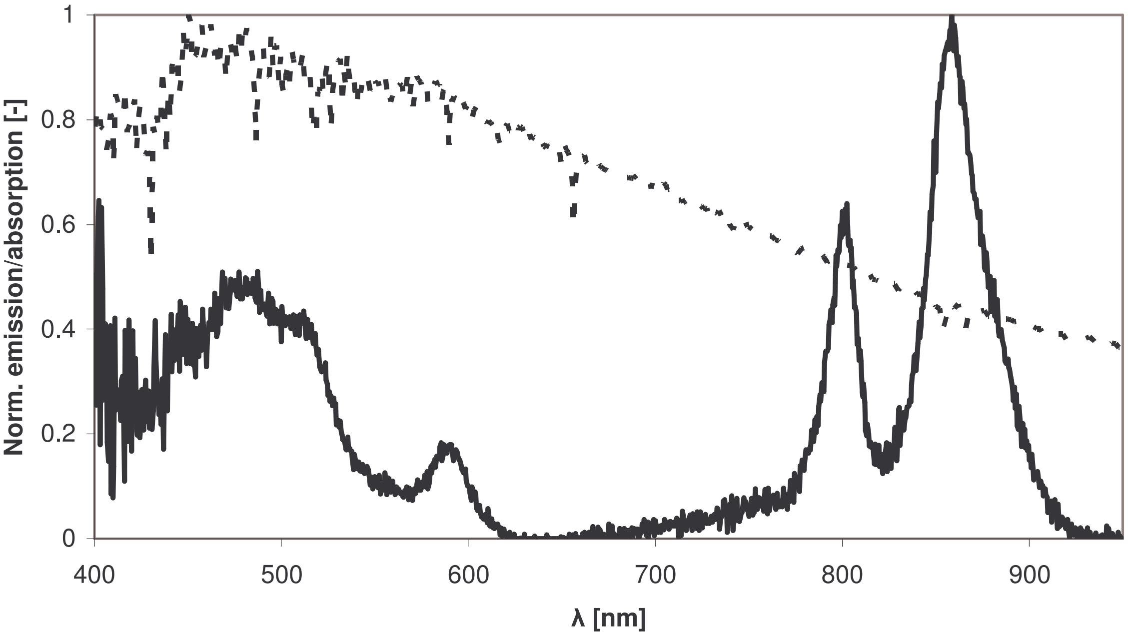

Figure 13 (---) Energy normalised extraterrestrial solar emission spectrum ASTM E-490-00 on Mars and (—) normalised *Rhodobacter capsulatus* NCIMB 11773 absorption spectrum

6.2 Design

Required hydrogen producing capacity
Resulting from the calculations performed under the acidification step, a continuous Volatile Fatty Acid (VFA) loading of 52 g h-1 in a 10.35 L h-1 flow is generated. The composition and concentration of the VFA's that are generated in the acidification step are displayed in Table , as well as the maximal stoichiometric amount of hydrogen that can be generated with them, assuming an 80% VFA to hydrogen conversion ratio compared to the maximal stoichiometry.

Table 10 Composition and concentrations in 1 litre of the acidification effluent and resulting hydrogen quantity

Compound	Concentration [mg L-1]	Concentration [mM]	Hydrogen yield [mmols]
Butyrate	3450	39.65	285.5
Acetate	1690	28.18	90.2

propionate	32	0.44	2.5
lactate	1	0.01	0.1
total	5173	68.28	378

One litre of acidification reactor effluent then maximally yields 378 mmols of H2. This results in a total required hydrogen producing capacity of 3.91 mols H2 h-1.

$$\frac{378 \cdot 10.35}{1000} = 3.91$$

Required surface area and volume
Theoretically, a PE of 10.3 % can be attained (own estimation and (Göbel 1978), based on the spectral composition of the solar irradiation as it is received by the Martian atmosphere and the efficiency at which the energy content of photons of various wavelengths can be used by the photosystem of purple non-sulfur bacteria to generate energy. Within the 400 - 950 nm range, the solar spectral composition does not differ significantly from the spectral composition of the solar irradiation that impings on the earths surface. It is depicted in figure 13. However, efficiencies in this range have never been reached in practise. We will therefore perform our further calculations based on two scenarios. Scenario 1 is based on this maximal, theoretical 10.3 % PE, while scenario 2 is more realistic, assuming a 2 % PE.
As the Sun-Mars distance is 1.52 times greater than the Sun-Earth distance, it receives a light intensity that is 2.3 times lower (1.522). As the beam irradiance on the earth's surface is 1371 W m-2, Mars receives 590 W m-2. This beam irradiance can be converted into an average illumination by taking the sun zenith angle and day/night cycling into account for each location on Mars. This results in an average illumination of the Martian surface with a light intensity of 97.5 W m-2 (Appelbaum and Flood 1990).

When the hourly production of 3.91 mols H2 h-1 is combined with the enthalpy of combustion (285 kJ mol-1) and the photosynthetic efficiency of either 10.3 or 2.0 %, we can calculate the surface area that is required for the complete conversion of the VFAs that were generated. The required surface areas for both scenarios are presented in Table IX.

Table IX Assumed PE, required solar energy, resulting reactor surface area and volume for scenarios 1 and 2

	scenario 1	scenario 2
PE (%)	10.3	2.0
required avg. solar energy [W]	3023	15493
resulting surface area [m2]	38	159
resulting reactor volume [m3]	1.09	1.09

Since during night time the system will not be in operation, a certain buffer capacity will need to be installed in order to temporarily store the VFA's that are generated during night time operation. Assuming an average day length of 12 h, half the daily production requires storage, which means a storage capacity of at least 125 litres is required.

For our Rhodobacter capsulatus species, a stable specific hydrogen producing capacity of 0.5 mmol kg-1 s-1 was registered. In order to produce 7.83 mols of H2 per hour during daytime, assuming a realistic biomass concentration of 4 g L-1, a reactor volume of 1.09 m3 is required, as also indicated in Table IX. The hydrolic retention time during daytime is 0.46 d-1 in this case.

6.3 Robustness & Conditions

pH-shock

It is generally recognized that purple non-sulfur bacteria grow best and produce hydrogen optimally at a pH between 6.0 and 7.0 (Maness and Weaver 2001). Mild pH-shocks in the range of 6 to 9 did not result in unrecoverable problems using a Rhodobacter sphaeroides sp. (Sasikala et al. 1991). Larger pH shocks however might result in unrecoverable damage.

Toxic compounds
Unfortunately, not much is known from literature regarding the response of hydrogen producing photobioreactors on toxic compounds. It is therefore impossible to predict how a culture of purple non-sulfur bacteria would respond to certain levels of toxic compounds.

Long-term behaviour
In our experience, photoheterotrophic hydrogen generation is a rather robust process that can be operated in a stable manner for more than a month. It will be possible from a technological point of view to design the process such that it can operate stabile for several years.

Variable load
In batch fermentations it is generally observed that hydrogen production continues from the initial substrate level until all carbon substrate is consumed. It seems therefore reasonable to assume that the systems operation will remain stable upon varying loading rate, provided that the dilution rate will not become extremely high and that toxicity levels for the organic acids applied are not reached. These upper levels typically lie at 100 mM (own observations with acetate) but may differ depending on the applied VFA.

Temperature
In general, purple non-sulfur bacteria have a clear optimum for growth at 30 ºC. Within the 20 to 45 degrees temperature range no unrecoverable damage to the system was observed when a Rhodobacter sphaeroides species was applied. It did result in retarded growth of the microbes (Sasikala et al. 1991).

Infection and competition
The system is sensitive to infection by methanogenic micro organisms, as these organisms can convert acetate to methane and carbon dioxide anaerobically. It is therefore required for stable operation that the feed stream does not contain these microbes. In the acidification reactor methanogenesis is prevented by the high temperature of 50 ºC applied. A temperature treatment of the acidifier effluent to 100 ºC will most probably be the most cost-efficient method to ensure the absence of methanogens in the PBR feed.

6.4 Concluding remarks

The required photobioreactor surface areas that were calculated in this study are rather large, resulting from the low light intensity that impinges on the Martian surface. However, the surface area of the photobioreactor can be made smaller, if the required light energy is first concentrated and then redistributed within it.
This concentration of light energy can be performed using Fresnel lenses or parabolic mirrors. Next, this concentrated light energy flux should be distributed inside the photobioreactor using a light distributing system consisting of optical fibres or light diffusing plates. The efficiency and economic feasibility of these systems are currently under investigation at the Process Engineering Department of Wageningen University.
This decoupled collection and distribution does not entail a reduced surface area requirement, but only a reduced surface area of the PBR.

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7 Discussion

Aim of this discussion is to determine the relative strengths and weaknesses of each process. Based on the earlier discussion on objective and constraints of the work (see 2.2), four items are of importance:

1. Fuel and Energy Production
2. Volumetric Productivity of the systems
3. Robustness
4. Recycling Extent & Plant choice

All systems are compared to a conventional anaerobic digestion system (AD) with respect to these items. In this report 4 alternative systems have been studied, dark fermentation (DF), bio catalyzed electrolysis (BCE), the microbial fuel cell (MFC) and the photofermentation (PF). All systems have the hydrolysis reactor (HR) as its pre-treatment system. Therefore this reactor is also shown in the tables although it contributes in itself not to the fuel production. The MFC produces electricity and no fuel as such; this system can therefore not be compared to the other systems.

In all cases it should be considered that this work is a desk studies, does not allow for final conclusions. The conclusions are more pointers for future research.

Fuel and Energy Production

Table 11 gives the daily production of the different systems.

Process	Product type	Amount mol/day	Input
AD	CH4	31.4	Heat
HR	VFA	16.9	Heat
DF	H2 CH4	23.2 19.8	
BCE	H2	112.0	2.4 kWh
PF	H2	93.8	40-160 m2
MFC	Electricty	**4 kWh**	

Table 11: Productivity of the different systems, note the different unit of the electricity production of the MFC.

We see that the alternative systems all produce hydrogen and in case of the DF also some methane. The DF as such is operated in the hydrolysis reactor and yields a gas with lowered hydrogen content. The methane in case of dark fermentation is produced in a separate reactor treating the effluent of the HR reactor. We see that the PF and the BCE give the highest hydrogen yield. The BCE is expected to have the highest hydrogen content in the gas. The inputs differ between the systems. Heat to heat up the water entering is needed in all cases and gives no difference between the systems. The heat is only mentioned at the AD and HR because there the initial heating takes place. The increased production of H_2 in case of the BCE and PF comes at a price, either electricity of surface area for the light catchments. If the energy is derived from solar panels, it would seem that the BCE has here an advantage as the photo efficiency of solar panels is higher than of the PF.

Volumetric Productivity

Table 12 gives the volumes and volumetric productivities of the different systems. We only can sensibly compare the hydrogen production. We see that it decreases in the order BCE, DF, PF.

Table 12: Volumes and van volumetric productivities of the compared systems

Process	Volume L	Productivty mol/L/day
AD	134	0.23
HR	100	
DF	100	0.23
	85	0.23
BCE	300	0.37
PF	1090	0.09
MFC	170	

Robustness

All systems are biological and have there own specific band of operation with respect to pH, temperature etc.. Compared to the AD system most system seems to have the same level of robustness. In retrospect this is no real surprise all except the PF are mixed culture systems operating under anaerobic conditions. Only the PF system which is a pure culture system, has the additional risk of contamination and thus performance deterioration.

Recycling Extent & Plant choice

For all systems the recycling extent is the same as this is basically determined by the hydrolysis reactor. A higher recycling extent would mean a much bigger HR. It seems to be more attractive to use either aerobic post-treatment or some physical-chemical system for the remaining material.

Another approach would be to look for different food ingredients. Plant choice could be based on a small hydrolysis rate and ahigh hydrocarbon content. For instance wheat gives a lot of non degradable material; other crop choice might be potatoes or sweet sorghum as a basic feedstock.