Report on Gas Treatment Options and Applications for biologically produced Hydrogen

BioTecH2

IMPRESSUM

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1 INTRODUCTION

Hydrogen is an important component of the future energy supply. A well-developed hydrogen economy requires not only available production processes but also end use options as well as storage and distribution options of hydrogen [1]. Several methods of obtaining hydrogen exist. By anaerobic digestion the retrieval of energy rich streams of specially sourced and waste biomass is used to produce hydrogen. Conventionally the fermentation of biomass has been performed in order to retrieve biogas, containing methane (CH_4). Methane rich biogas could subsequently be burned, for heat and electricity, or be upgraded further for the distribution in local gas grids.

In the German-Dutch research project BioTecH$_2$ the FH Münster (FHM) in cooperation with H2-bv, PlanET Biogastechnik GmbH and Bio-energiecluster Oost-Nederland aims to implement the process for hydrogen production, called dark fermentation, and evaluate different ways of usage. The fermentation process can be divided into two separate stages. The first stage creates organic acids, hydrogen (H_2), carbon dioxide (CO_2) and a few other constituents. The second stage further digests the liquid substance with organic acids into methane and carbon dioxide. Figure 1-1 gives a schematic overview of the fermentation process. Compared to conventional fermentation, the two stage system has the potential to extract more of the energy present in the organic waste [2]. Additionally, the hydrogen produced can be upgraded and used in fuel cells, representing a more use full energy carrying substance, when compared to the conventional retrieval of only methane.

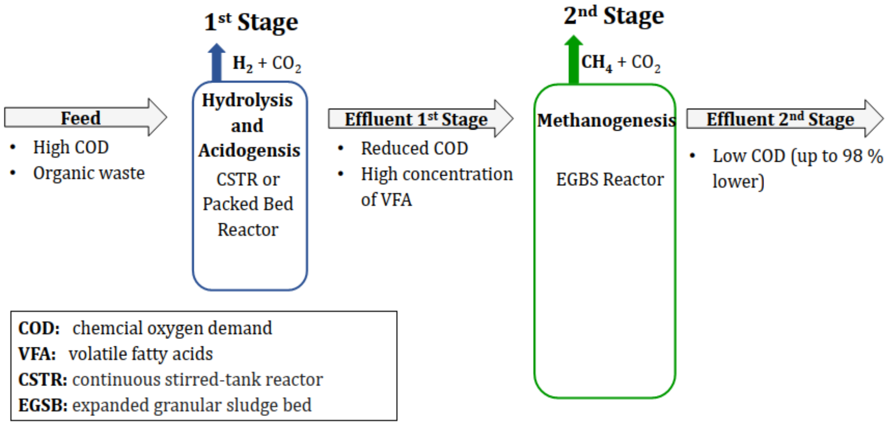

Figure 1-1: Two-stage digestion of organic waste into H_2, CH_4 and CO_2

The hydrogen gas mixture produced during the two-stage anaerobic digestion possibly needs to be purified in order for use. This document aims to give insight into the purification of the created hydrogen gas mixture and the accompanying applicability to the process of BioTecH2. The recovered gas composition found in BioTecH2 consists of 30-50% hydrogen (H_2), 50-70 % carbon dioxide (CO_2), 0-5000 ppm hydrogen sulfide (H_2S) and trace amounts of ammonia (NH_3). The report will end with a recommendation for the purification of the hydrogen gas mixture created by the two-stage anaerobic digestion involved in BioTecH$_2$.

2 Hydrogen Quality

The ISO has established a few standards for hydrogen purity demands depending on various use cases. The hydrogen quality specifications are given in ISO 14687:2019 [3]. These standards get updated every 5 years. The latest addition from 2019 includes gas specifications for applications such as hydrogen as a rocket fuel and most importantly the specification for hydrogen as combustion application for home appliances and combustion engines. The different types and grades are described by the ISO standard. The grades are described in Table 2-1.

Table 2-1: Quality grades described by ISO 1468:2019 [3]

Type	Grade	Category	Applications	Clause
I Gas	A	-	Gaseous hydrogen; internal combustion engines for transportation; residential/commercial combustion appliances (e.g. boilers, cookers and similar applications)	7
	B	-	Gase hydrogen; industrial fuel for power generation and heat generation except PEM fuel cell applications	7
	C	-	Gase hydrogen; aircraft and space-vehicle ground support systems except PEM fuel cell applications	7
	D[a,b]	-	Gaseous hydrogen; PEM fuel cells for road vehicles	5
	E		*PEM fuel cells for stationary appliances*	6
		1	Hydrogen-based fuel; high efficiency/low power applications	
		2	Hydrogen-based fuel; high power applications	
		3	Gaseous hydrogen; high power/high efficiency applications	
II Liquid	C	-	Aircraft and space-vehicle on-board propulsion and electrical energy requirements; off-road vehicles	7
	D[a,b]	-	PEM fuel cells for road vehicles	5
III Slush	-	-	Aircraft and space-vehicle on-board propulsion	7

[a] Grade D may be used for other fuel cell applications for transportation including forklifts and other industrial trucks if agreed upon between supplier and customer.
[b] Grade D may be used for PEM fuel cell stationary appliances alternative to grade E category 3.

For this research the focus will be put onto Grade A, Grade B, Grade D and Grade E, especially Type I, as the gas state is the most commonly requested form of hydrogen. The C grade is also excluded from further examination, as the aircraft industry and aircraft/space-ground support systems are not a typical use case for bio-hydrogen.

The gas compositions of the quality grades of interest are described in Table 2-2. It is important to note that this table contains the most relevant constituents, which are directly applicable to the process employed by BioTecH_2. For the complete overview of the concentrations of all described constituents consult ISO 1468:2019 [3].

Table 2-2: Gas composition per hydrogen quality grades described by ISO 1468:2019 [3]

Constituents	Grade A	Grade B	Grade D	Grade E		
				Category 1	Category 2	Category 3
Hydrogen (H_2)	98,0%	99.90%	99,97%	50%	50%	99,9%
Impurities [ppm]						
Water (H_2O)	-	-	5	-	-	-
Hydrocarbons C_1-equivalent	100	-	2	10	2	2
Methane (CH_4)	With above	-	100	5%	1%	100
Oxygen (O_2)	a	100	5	200	200	50
Nitrogen (N_2)	a	400	300	-	-	0,1%
Carbon dioxide (CO_2)	-	-	2	b	b	2
Carbon monoxide (CO)	1	-	0.2	10	10	0.2
Total Sulphur S_1-equivalent	2	10	0.004	0.004	0.004	0.004
Ammonia (NH_3)	-	-	0.1	0.1	0.1	0.1
Formaldehyde (HCHO)	-	-	0.2	3	0.2	0.2
Formic acid (HCOOH)	-	-	0.2	10	0.2	0.2

[a] Combined water, oxygen, nitrogen and argon max 1,9%
[b] Included in total non-hydrogen gas

When considering the concentrations of constituents found in Table 2-2, it can be concluded that the gas composition in BioTecH2 could only suffices for grades E1 and E2 under near perfect circumstances due to the required 50% H_2. Therefore, in order to obtain any of the grades mentioned in Table 2-2, purification of the gas mixture is a requirement.

3 COMPARISON OF PURIFCIATION TECHNIQUES

To summarize the findings from the detailed report for hydrogen purification technologies a comparison table has been made, shown in Table 3-1. The following purification methods have been determined:

1 – Pressure Swing Adsorption (PSA)
2 – Vacuum (Pressure) Swing Adsorption (VPSA)
3 – Temperature Swing Adsorption (TSA)
4 – Flow-through Metal Hydride
5 – H_2-selective Membrane
6 – CO_2-selective Membrane
7 – Cryogenic Distillation
8 – Electrochemical Hydrogen Compressor (EHC)

It is however very important to explain the nuances that accompany these comparisons.

Table 3-1: A table overview of the hydrogen purification methods

No.	H_2 purity	H_2 recovery	Typical feed gas	Resistance against contaminants	Application scale	Operational cost	Capital investment	Source
1	99.9999+%	50-95%	50-90% H_2 SMR, Syngas	Non-damaging, can hinder adsorption	All scales	Low-moderate	Moderate dependent on setup	[4–8]
2	99.99+%	50-95%	20-90% H_2 SMR, Syngas	Non-damaging, can hinder adsorption	All scales	Moderate	Moderate dependent on setup	[9–11]
3	99.99+%	50-90%	50-90% H_2 SMR, Syngas	Non-damaging, can hinder adsorption	Large scale	Very high	Moderate dependent on setup	[11]
4	99.99+%	75-95%	25-60% Bio-H_2	Non-damaging, can hinder	Small scale	Low	Moderate	[12, 13]
5	99.99+%	80-98%	20-90% H_2 All types	Dependent on specific type impact free to performance hit	Small scale	Low-moderate	Low	[14, 15]
6	99.99+%	80-98%	20-90% H_2 all types	Dependent on specific type impact free to performance hit	Small scale	Low-moderate	Low	[15–18]
7	85-99%	50-90%	10-90% H_2 all types	No impact	small scale	Very high	Very high	[19, 20]
8	98-99.99+%	80-98%	30-98% H_2 all types	Can cause irreversible damage	Small scale	Low	Low-moderate	[21–25]

High hydrogen purity is vital for many of the hydrogen grades specified in Table 2-2. Conventionally the adsorption-based technologies such as PSA, V(P)SA and TSA have been used on an industrial scale to produce high purity hydrogen. The feed gasses that have typically been purified with these technologies are of hydrogen concentrations of 50-90%. V(P)SA is able to extract hydrogen from gas mixtures as low as 20%. For these feed gasses the recovery rate is rather high, between 50-95%, dependent on the hydrogen concentration at the feed and the presence of contaminates. The addition of a vacuum in the VPSA process, on the adsorbents increases recovery and adds minor costs. Especially when compared to the operating costs of a TSA system, where large amounts of heat are used in the adsorption process. Due to new innovations regarding local and sustainable (bio) hydrogen sources new small-scale PSA and VPSA purification devices are entering the market to fill the need for small scale purification. Another type of adsorption-based technology are flow through metal hydrate reactors. These systems can be used for the continuous purification of hydrogen and can also be employed for storage. The technology especially caters to bio hydrogen, it is cheap and small scale. Currently the technology is still in development.

An older technology used for many years mostly at laboratory scale is cryogenic destillation. Making use of the distillation process at the very low temperatures required for condensing the gasses in a gas mixture, comes with high penalties in operational cost and investment cost. The purity of hydrogen that can be reached is not up to the highest gas standard without any additional pre-treatment. One of the main benefits is that low concentration hydrogen feed gas can be used as long as the boiling point of these gasses is not to close to that of hydrogen.

The demand for cheaper devices for the purification of hydrogen has sparked an interest in membrane technology, these membranes can be selective towards specific constituents, allowing the constituents to pass through their structure in various ways. The technology is cheap and yields high recovery. Additionally, it can be employed on low hydrogen concentration sources. For the purification of hydrogen from a mixture with carbon dioxide, one of the more common use cases, two types of membranes are used. The first, CO_2–selective membranes have a high purification degree filtering out more CO_2, the second, H_2-selective membranes are employed for a higher degree of hydrogen recovery. The concentration of hydrogen that can be achieved varies for these membranes, this is dependent on the size of the membrane and the pressures used. An EHC is a membrane technology for the purification and pressurization of hydrogen. The technology is based on similar principles to proton exchange membrane (PEM) fuel cell technology. The method obtains high selectivity and recovery even from low purity hydrogen sources, currently only employed at small scale. The main downside of the technology is its vulnerability towards contaminants, such as sulphur, that can irreversibly damage the membrane.

4 SEPARATION TECHNIQUES EMPLOYABLE BY BIOTECH$_2$

This section will explore the possibilities of purification of biohydrogen for gas mixtures from two stage anaerobic digestion. Many methods of hydrogen purification are summarized in Table 3-1. However, the single methods offer either insignificant hydrogen concentration increase or only offer this increase in concentration at an economically un-viable standard. The flow through metal hydride purification solution was largely aimed at the upgrading of biohydrogen, it was still proven to be insufficient as a standalone solution. The combination of two or more individual separation devices could combine into a system, that is capable of delivering the hydrogen purity demands, at an economically viable price point. There are several instances of these hybrid solutions having beneficial results [26, 27]. These hybrid solutions, if setup correctly, are able to combine the advantages of the separate solutions. Membrane systems have a high potential, as they are rather cheap to employ and offer very high recovery. Furthermore, they are able to separate out the contaminants such as H_2S, that impact a lot of purification systems negatively. It is however impossible to suggest a single combination of technologies, that is the most suitable to the gas composition of BioTecH_2. As these technologies improve continuously and commercialized solutions are still scarce. A suitable economically viable solution has to be realized by simulation and rigorous testing in order to be a conclusive candidate for upgrading the biohydrogen.

The composition of the gas mixture produced in the dark fermentation step of BioTecH_2 consists out of, 30-50% H_2, 50-70% CO_2 as the main constituents. Additionally, H_2S is present at values of 0-5000 ppm, NH_3 could possibly be present, but was not measured for. In order to comply to any of the ISO hydrogen standards mentioned, a reduction in CO_2 and H_2S content may potentially be needed to be achieve a sufficient gas mixture. The increase in hydrogen content and the reduction of the other constituents needs to be carried out in an efficient manner tailored to the desired grade. The proposed solutions to purifying the obtained gas mixture to the specific grades of hydrogen will be described in this section. However, these solutions are suggested based on the literature research and are there to give an indication of a particular system. Based on further exploration of a purification system the specific solutions of such a system can differ in practice.

Starting off with the gas mixture produced by BioTecH_2 it needs to be noted that all purification systems need to be based on a wide range of gas composition. This will ensure that there will not be a scenario, where the yielded gas mixture is not up to the desired grade. Furthermore, the sulphur content can be present in the gas mixture as high as 5,000 ppm. This value is significantly larger than the admissible amounts of any of the hydrogen grades specified in ISO 16487. The sulphur could have a substantial effect on the purification process, furthermore H_2S removal was not intensively studied for the purification methods. Therefore, a chemical removal of the H_2S from the feed gas would be preferable. By this removal there will be two main constituents remaining, H_2 and CO_2. Some purification methods can be excluded beforehand. Starting off the TSA and cryogenic distillation methods are very expensive to operate and could possibly only be employed at very large scales, this leaves these technologies in-competitive with respect to the other methods. Furthermore, the flow-through metal hydride system is still only used in laboratories and is not developed for the commercial scale, which leaves the technology inapplicable to the purification of real world biohydrogen purification.

To obtain a Grade A hydrogen gas mixture a hydrogen content of 98% needs to be achieved. There are a few combinations of purification devices that could yield this result. These methods would all preferably contain a H_2 selective membrane as a starting point, this is due to the high recovery rate the membrane provides, with the addition of it being a relatively cheap option. The retained gasses could than subsequently be further upgraded by a CO_2 selective membrane, a PSA, VPSA or an EHC. The CO_2 rich waste streams of this step can be reintroduced into the feed stream. However, this reintroduction should not significantly alter the hydrogen concentration of the feed, therefore an extra membrane should be added if the CO_2 rich off-gas needs to be presented at the feed.

The purification solution to obtain Grade B, Grade D and Grade E_3 are similar. Similar to the Grade A solution, a good starting point would be a H_2 selective membrane. The subsequent purification could be performed by either a PSA or VPSA. This is based on the H_2 purity demanded for these grades. Furthermore, the EHC's performance regarding H_2 purification is very high, however it especially tailors to upgrading a moderate hydrogen content (40% to 60%) up to 98%. The very high purity desired, especially with the H_2 and CO_2 mixture is hard to achieve. This implies that a hybrid purification setup could also benefit from a 3-step setup, with an EHC in the middle step. Again, similar to the Grade A setup, the waste streams of these purification devices could be reintroduced at the feed, with the help of membranes ensuring the concentration of hydrogen at the feed will not significantly be reduced.

To obtain a Grade E_1 or Grade E_2 hydrogen purity some light gas purification needs to be executed. The hydrogen content needs to be increased form 30% up to a minimal of 50%, this could be done with a H_2 selective membrane to ensure a good recovery of hydrogen.

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