Annexes

Annex A: AHPD Pilot plant at the Energy Transition Centre (EnTranCe)

Two years ago, Bareau started a pilot plant at the EnTranCe testing ground, financed by Gasunie, GasTerra and Groningen Municipality and facilitated by Rijksuniversiteit Groningen and Hanzehogeschool (image 2). In addition, the AHPD process has been extended with hydrogen dosage to develop a Power-to-Gas technology; the AH_2PD process based on secondary sewage sludge. The complete system is optimised in order to produce green gas with 'Slochteren' quality and CO_2 dissolved in water, in one single step. Several parts of the process have been internationally patented. A scientific committee supervised the progress at EnTranCe. During the research period 2015-2017 at EnTranCe testing ground, the following results have been achieved:

- The AHPD process is stabilised at 52^{o} C whereby an optimal green gas composition is achieved at a maximal gas production and sludge reduction.
- Hydrogen dosage is much more efficient at high pressure when compared to atmospheric circumstances; with this AH_2PD process 100% H_2 conversion and 98% methane purity is achieved.
- With external carbon dioxide dosage in combination with hydrogen dosage, the production capacity AH_2PD is significantly increased. The autogenerative pressure build-up allows for the gasses to efficiently dissolve and mix, resulting in lower energy consumption; an important cost element in the conventional aerobic technology.
  Using the pressure build-up, residual sludge is dewatered to over 50% dry substance, being sufficient for autogenic combustion.
- In the sequential water treatment, heavy metals such as sulphur, phosphate and nitrogen are removed and recovered if need be.
  The AHPD reactor, the ultrafiltration and the process automation have been up-scaled to a "single stack" practice level.
- Together with our suppliers we have developed a large scale AHPD installation to a preliminary draft, including a cost estimate with +/- 10% accuracy.

Image 2: AHPD pilot plant EnTranCe testing ground and recovered phosphate (struvite)

Annex B: Elaboration of the research findings

Bareau's AHPD-pilot plant contains a functional wet contents of approximately 800 litres, an hydraulic retention time (HRT) of eight days, a sludge retention time of over thirty days and is stabilised in continuous operation at 19 bar pressure and 52^{o} C. The added substrate is converted into methane$_{(g)}$ and carbon dioxide $_{(aq)}$ after which the water phase, via ultrafiltration, as permeate, containing dissolved gasses and salts, is drained from the system. Because the substrate particles and the bacteria are being separated in the same way as if in a membrane bioreactor, the sludge retention time is much longer than the hydraulic retention time of the system. As a result, only a relatively small installation with a high conversion return is needed. Because of thermal isolation and, amongst others, making use of the biological warmth, the heat demand is minimal. The AHPD process is fully automated and runs in permanent operation by remote control. Feedstock is an ample 100 litres secondary sludge (sewage plant Zuidhorn) a day, with a dry substance level of approximately 2,0 - 2,6 g TSS/l.

We have tested both ceramic (Atech) and synthetic (Pentair) ultrafiltration membranes.
The ceramic membranes show a better removal of dissolved COD: 98% removal resulting in a permeate concentration of 200 – 300 mg COD/l, compared to 90% COD removal in a permeate concentration of 2.000 – 3.000 mg/l when using synthetic membranes.
This is caused by the smaller pore diameter of the ceramic membranes. In addition, ceramic membranes are more robust, easier to backwash, while a higher anaerobic sludge concentration can be applied (approximately 4 g TSS/l, compared to 2 g TSS with synthetic membranes). Depending on the pressure, temperature and the composition of the added feedstock, the AHPD installation produces a gas quality of 85% – 95% methane, whereby the simultaneously produced carbon dioxide, hydrogen sulphide, nitrogen and phosphate dissolve in the water phase. In an automated process, the fermented sludge is continuously removed from the installation and is, based on the built up pressure, dewatered to a dry substance level of 53%. The conversion of the provided dry substance amounts to 60-80%, depending on the substrate.

In the period 2010 – 2017 various (combinations of) substrates were tested such as primary sludge, kitchen waste, glycerol from a bio-diesel factory and black water from a vacuum sewage. These tests show that all substrates that are conventionally fermentable are very well suited for AHPD treatment. An important insight is that the AHPD bacteria population 'simply' converts carbon hydrates, proteins and fats into carbon dioxide and methane according to the known mechanisms[1], whilst the chemistry of the AHPD system is being influenced by the gas-law and the consequences thereof. The AHPD technology makes use of this in a practical manner. As an example, the relatively high temporary buffer capacity of the system is a result of the (under pressure) dissolved high quantities of weak acideous carbon dioxide.

Dissolved carbon dioxide is, under pressure, linked to -amongst others- hydrogen sulphide and ammonium, whereby a better gas separation occurs than 'just' based on Henry's law. Partially as a result of this, the pH of an AHPD process is relatively stable.

[1] See for instance: Anaerobic Digestion Model No 1.

The engineering design of the pilot plant is executed by Bareau and meets all current safety requirements such as the PED inspection and the Atex directives; the pilot plant has been certified by Lloyds on all parts. Based on the functional design and Bareau's P&ID's, Terberg Control Systems built the automation, which is now in function.

For the duration of six months, a batch experiment has been conducted whereby external hydrogen from gas bottles was added in dosage to the AHPD reactor. This extension of the AHPD process with hydrogen is called AH_2PD. The uptake and conversion of hydrogen and carbon dioxide to methane appears to be dependent of the dissolved carbon dioxide concentration, which shows that an AH_2PD process executes this conversion faster and therefore more efficiently in comparison to atmospheric circumstances.
The conversion of hydrogen is 100%, no hydrogen is detected in the gas phase anymore, while a methane level of 98% in the gas phase is reached. Because of lack of time, we have not been able to add hydrogen in dosage to an electrolyser in permanent operation. Therefore we have not been able to gain insight in the influence of various production speeds of hydrogen, which result from the variation in the excess electricity in relation to the dynamics of the AHPD process. This is still very high on our list of priorities.

After the membrane filtration, the pressure of the permeate is reduced to atmospheric circumstances, so dissolved acid gasses separate from the water phase. A conventional biological sulphur reactor biologically removes the hydrogen sulphide in the, subsequently, created gas flow. Because the permeate pH increases after this pressure reduction, phosphate precipitation with bivalent metals occurs in the phosphate reactor (packed bed). This spontaneous precipitation takes place outside of the AHPD reactor, whereby the recovery of raw materials is facilitated (see photo on the right hand side of image 2). The precipitate has a density of 2,1 to 2,4 (kg/l) and contains approximately 80% of the heavy metals (copper, led and zinc) from the supplied load together with 50% of the dissolved phosphate load. Therefore this makes the precipitation comparable to the struvite (magnesium-ammonium-phosphate) that occurs inside many conventional digesters in the fully fermented sludge, often caused by local pH increase resulting from a pressure reduction in, for example, the cavitation zone of a sludge pump.
Advanced P-removal is possible by dosing extra bivalent metal salts whereby both the quantity (50% is already precipitated) and the cost (no hydroxide needed to increase the pH) are significantly reduced.

In the last stage of the process, various ways of removing nitrogen are possible, the Anammox process being the most conventional one. We also consider the possibility of electrolyses of dissolved ammonium to nitrogen and hydrogen, after which the hydrogen can be reused in the AH_2PD-proces.

Annex C: Calculation of the final green gas production with the AHPD and AH_2PD technology.

Based on the starting point that the Netherlands produces 38 million CZV population equivalents (source: CBS 2016). The pressure on the Dutch communal treatments plants is, on average, 150 gram CVZ/i.e., amounting to an oxygen usage of 55 kg O_2 /i.e year with complete aerobe degradation. Taking into account that, in the anaerobe AHPD process, 50% of the carbon is converted to $CH_{4,}$ [[44/32]*55/2]*[16/44]= 13,7 kg CH_4/i.e./year can be produced at maximum. With a concentration of 90% CH_4 in the natural gas (the remaining 10% is carbon dioxide from the AHPD process), the maximum production is 23,6 Nm^3 green gas /i.e. year, based on the general gas law at 25^o C (nRT=PV).

The following parameters were used:

• Molecular weight of carbon dioxide:	44	grams/mol;
• Molecular weight of oxygen	32	grams/mol;
• Molecular weight of methane	16	grams/mol;
• Conversion 50% of the CZV to methane	55/2	kg/oxygen/i.e./year

Supposing that in the business case 'AHPD on DWA' 80% on average of the CZV is made available for AHPD, wherein at maximum 70% is being degraded anaerobically, 23,6*0,8*0,7= 13,2 Nm^3green gas/i.e. year can be produced at the utmost.

The maximum direct green gas production, to be achieved with conversion of all communal treatment plants to AHPD, herewith amounts to approximately 0,5 billion Nm^3 green gas on a yearly basis; about ten times more than the current – heavily subsidized – green gas production from sewage sludge. This potential production volume can be further increased, when adding the below plus factors:

- When the CZV from the domestic organic kitchen waste is also added to CZV from the wastewater for anaerobe AHPD treatment, the revenue doubles to approximately **1 billion Nm^3** green gas per annum.
- When the AHPD process is extended to AH_2PD and the remaining carbon dioxide with hydrogen is converted into methane, revenues will again double to **2 billion Nm^3** per annum.
- When animal manure, currently available, would also be treated with this technology, the potential even increases to **3 billion Nm^3 green gas per annum.**
- When externally produced carbon dioxide (decentralized from households and centrally from conventional power plants or drying plants etc.) is added, the production of methane can be further increased, provided that sufficient hydrogen is added.

  During the time that an average sewage plant is inactive (especially at night between 23.00 hours an 05.00 hours) and between morning- and evening peaks of the conventional wastewater flow (daily around 07.00 hours and 19.00 hours), the methane production can be significantly improved. Because methane production from hydrogen and carbon dioxide is roundabout ten times faster than methane formation from biomass and taking into account that we have at least six hours time for the hydrogen dosage, the potential can – again – increase with at least factor 6/24*10= 2,5 without additional investment in the production capacity.

Of course there are two conditions applicable in this case; ample availability of both carbon dioxide and of cheap energy. The total potential green gas production then amounts to 3 + (2,5*3) = approximately **10 billion Nm^3 green gas** per annum.

An AHPD installation will then, by daytime, operate as both water treatment plant and organic kitchen waste processing plant and, especially in the afternoon and at night, as a 'power-to-gas plant'.

For the required hydrogen production, taking the conventional production returns into account, an amount of electricity is needed of the same volume as the total Dutch power usage (source: CBS, CE Delft). Consequently, the whole Dutch power usage can be buffered per season with the AHPD / AH$_2$PD technology.

Finally, AHPD can be an efficient intermediate step in the production of bio-LNG.

All process steps mentioned have been thoroughly tested and proved by Bareau at the EnTranCe testing ground in de AHPD-pilot plant.