PLAS
CARB

INNOVATIVE PLASMA BASED TRANSFORMATION
OF FOOD WASTE INTO HIGH VALUE GRAPHITIC
CARBON AND RENEWABLE HYDROGEN

REPORT TO DISCUSS UPGRADING OF BIOGAS FOR FEED TO A PLASMA REACTOR
PROJECT DELIVERABLE D4.1

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Abstract :

PlasCarb is an EU-funded project with the aim of transforming biogas (mainly methane and carbon dioxide) generated by Anaerobic Digestion (AD) of food waste, into high value graphitic carbon and renewable hydrogen. The biogas is first upgraded to biomethane and then fed to an innovative low energy microwave plasma reactor and downstream separator, to generate and then separate the carbon from an off-gas containing hydrogen which is then processed further.

This report considers the separation techniques available to purify and upgrade the biogas to a methane-rich stream with a specification suitable for feeding to the PlasCarb plasma reactor. Specifically contained within this report is a discussion of results from an Aspen Plus process model for a high pressure water scrubber system, and experimental results from a lab-scale trial of a membrane unit, both of which are processes to remove carbon dioxide from the biogas. The outcome of this report is a decision on which unit operations for purification and upgrading of biogas should be taken forward to pilot plant trials and then main plant trials.

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1. OBJECTIVES

PlasCarb is an EU-funded project with the aim of transforming biogas (mainly methane and carbon dioxide) generated by Anaerobic Digestion (AD) of food waste, into high value graphitic carbon and renewable hydrogen. The biogas is first upgraded to biomethane and then fed to an innovative low energy microwave plasma reactor and downstream separator, to generate and then separate the carbon from an off-gas containing hydrogen which is then processed further.

The purpose of this report is to identify, from desk based investigation, the techniques available to purify and upgrade Biogas generated by an Anaerobic Digestion (AD) plant i.e. to increase the stream purity and methane (CH_4) content such that a purified and upgraded Biogas stream may be fed to a novel Plasma reactor. In the Plasma reactor, CH_4 is converted into high value graphitic carbon and an off-gas containing Renewable Hydrogen.

The techniques identified in the desk-based investigation are then ranked in order of techno-economic performance including ease of scale-up (or scale-down).

The most suitable unit operations are then either trialled on laboratory scale equipment, using 50 Normal litres per hour (Nlph) biogas mimicked by mixing cylinder Carbon Dioxide (CO_2) and cylinder CH_4 , or modelled using Aspen Plus process modelling software. This lab trial and modelling work identifies which unit operation(s) are suitable to take forward to pilot plant trials. The pilot plant scale is 5-6 Nm3/h (5000 – 6000 Nlph) raw biogas.

Note that investigation into the separation of Renewable Hydrogen from the off-gas stream forms part of a future report (PlasCarb D4.3, due October 2015).

2. UNITS OF MEASUREMENT

Normal litres per hour (Nlph), although it looks like a volumetric term, is in fact a mass term. The mass flowrate (kg/h) is converted to a pseudo volumetric flowrate (Normal m3/h) by dividing by the density (kg/m3) of the biogas at "Normal" conditions of temperature and pressure (NB 1 m^3 = 1000 litres). This density is a constant as the temperature and pressure are set at the stated reference, or "Normal", conditions. However, "Normal", does have to be defined as Normal temperature can be 0 °C, 15 °C, 20 °C or 70 °F and Normal pressure can be 1 atm or 1 bara. In this report, as the flowmeter being used to measure the feed stream to the Plasma reactor is an American instrument, Normal conditions are 21.1 °C (70 °F) and 1 atm (1.013 bara).

3. BACKGROUND

Biogas for the PlasCarb project is to be taken from an AD plant run by GAP and sited in Gateshead, North East England. Feedstock to the AD plant is the result of collections from food manufacturers, restaurants and households (separated collections) within 35 miles of the plant [1].

The annual variability of such Biogas is given in Table 1 below [1]:

Table 1: Biogas Composition results

Component	CH_4 (%v/v)	CO_2 (%v/v)	O_2 (%v/v)	H_2S (ppm)
Yearly min	56.73	31.87	0.13	0
Yearly max	63.25	40.26	1.79	34.70
Yearly avg	58.42	37.67	0.50	21.18

Note that this composition is the minimum/ maximum/ average values of one year's daily readings taken from a Biogas sample point downstream of an activated carbon bed and glycol chiller. The Hydrogen Sulphide (H_2S) content is therefore already lower than that in the raw Biogas stream where 200 – 600 ppm is more typical [1]. Similarly the water vapour content of the stream (not quoted) is lowered to the saturation value at the chiller exit temperature rather than the (higher) saturation value in the warmer Biogas storage dome, which is at ambient temperature.

The PlasCarb process requires a high purity methane (CH_4) stream as feed to the novel Plasma reactor. The purity requirement for the feed stream is given in Table 2 below [2]:

Table 2: Plasma reactor feed stream specification

Component	CH_4 (% v/v)	CO_2 (% v/v)	O_2 (% v/v)	H_2O (vapour) (% v/v)	H_2S (ppm)
	95 (min)	2 (max)	2 (max)	2 (max)	5 (max)

The difference in specification between Tables 1 and 2 defines the PlasCarb project requirement for biogas purification (removal of H_2S), drying (removal of water vapour) and upgrading (generally meaning to increase calorific value of gas stream by increasing CH_4 levels within the gas i.e. removing CO_2).

4. BIOGAS PURIFICATION (REMOVAL OF H_2S)

4.1 Dangers of H_2S

H_2S is a very toxic, flammable gas. It is pungent (rotten egg odour) and irritates the eyes, nose and throat. It rapidly destroys the sense of smell; odour is unreliable as a means of detecting H_2S. H_2S can cause unconsciousness and death. It is heavier than air and may accumulate in low-lying areas.
The workplace exposure limits (WELs) for H_2S are 5 ppm (8-hour time-weighted average TWA) and 10 ppm (15 minute TWA) [3].
Short-term (acute) symptoms and effects of H_2S are given in Table 3 below [4]:

Table 3 Acute Symptoms/ Effects of H_2S exposure vs concentration (ppm)

Concentration (ppm)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odour threshold (when rotten egg smell is first noticeable to some). Odour becomes more offensive at 3-5 ppm. Above 30 ppm, odour described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

Reducing H_2S concentrations to < 5 ppm is important from a Health and Safety standpoint.

4.2 Effect of H_2S levels on Carbon product quality

PlasCarb trials on the prototype Plasma system have shown that at high ppm levels of H_2S in the Plasma reactor feed, elemental sulphur is deposited on the Carbon product as well as remaining as H_2S in the gaseous phase [2]. There is therefore also a process requirement to reduce H_2S levels to <5 ppm.

4.3 Corrosive Effect of H_2S levels

H_2S has a corrosive effect on downstream equipment e.g. Combined Heat and Power (CHP) engine and pipework [8]. Even at low concentrations, H_2S can cause piping corrosion, gas engine pitting and clogged piston rings [11] and to avoid this it has to typically be reduced to between 200-500 ppm [8]. High levels of H_2S would similarly affect the PlasCarb plasma reactor, filter and other downstream equipment. Reducing H_2S for equipment protection is a less onerous requirement than that of health and safety and product quality.

4.4 Biogas Purification Techniques

There is an existing industrial requirement to remove H_2S from biogas, therefore there are numerous academic studies [5], [6], [7]; a large amount of general information much of it from European-funded projects [7]-[13]; and a raft of commercial information [14], [15], [16], [17] reported in the literature on this subject. Biogasmax [12] gives a table of eight H_2S reduction/ removal technologies which include the main techniques outlined below:

4.4.1 Biological Desulphurisation

Biological desulphurisation uses indigenous (i.e. already present) sulphur-oxidising bacteria e.g. thiobacillus denitrificans [11] or sulfolobus [10] to oxidise Hydrogen Sulphide to elemental sulphur by the equation

$$2n(H_2S) + n(CO_2) + light \rightarrow 2nS + n(CH_2O) + n(H_2O)$$

Typically 500+ ppm concentrations are reduced to <50 ppm [11] though the levels quoted by GAP are higher than this at 200 – 600 ppm. Air is added to the digestate/ gas storage tank typically at 2-5% which allows oxidation of H_2S to elemental sulphur and water [11]. Safety measures are required to ensure biogas concentration remains above Higher Explosive Limit (15 v/v% for methane) so that a flammable atmosphere is not created [9] i.e. the mixture is too rich to burn. The bacteria population can't respond to fluctuating H_2S levels in biogas as seen at GAP [1] and so a larger H_2S polishing stage (where the H_2S concentration is reduced to be within specification) is likely to be required.

Biological desulphurisation is being used by GAP as the first stage of H_2S reduction.

4.4.2 Dry Oxidation – Granular Activated Carbon

Dry oxidation gives higher purities up to <1 ppm [12]. Granular Activated Carbon (GAC) is commonly used, whereby the activated carbon is impregnated by other chemicals e.g. potassium iodide, sulphuric acid. GAC beds can be disposed of or regenerated off-site and are robust to the presence of water so there is no requirement to pre-dry the biogas, however drying the biogas will increase bed life as removal of water will remove the H_2S dissolved in this water thereby reducing the bed load [18].

This technology is being used by GAP as the second (polishing) stage of H_2S reduction.

See also section 6 below.

4.4.3 Dry Oxidation – Iron Oxide/ Hydroxide

Dry oxidation can also be achieved using Iron Oxide or Hydroxide pellets/ grains within a bed:

H_2S is adsorbed onto the internal surface of Iron Oxide or Hydroxide pellets/ grains and reacts to form iron sulphide (slightly endothermic, optimal reaction 25 to 50 °C, water vapour is released). Iron oxide is recoverable by regenerating the pellets using air to form sulphur (note that this is an exothermic reaction, mass can self-ignite). However, the elemental sulphur then formed coats the iron oxide pellets and thus limits the pellet life. Commonly units are run with two beds, one on duty, one on regeneration. Alternatively, a bed may be run until fully loaded then replaced. Often used as a polishing unit, residual H2S concentrations <1 ppm are achievable [12]. Such commercially available products include FerroSorp® S [17].

4.4.4 Liquid Phase Oxidation - Scrubbing

Many of the scrubber technologies included below are also successful in upgrading the raw biogas i.e. removing CO_2 (see section 6 below), since CH_4 is comparatively inert and both H_2S and CO_2 are more soluble in the chosen solvent i.e. they are absorbed preferentially.

Liquid Phase Oxidation is a physical absorption process using a packed bed and a solvent in counter-current flow (i.e. a scrubber); pressurised raw biogas (typically 7-10 barg) [12] is fed to the base of the packed column and flows upwards and the liquid phase solvent is distributed at the top of the column and flows downwards either under pressure or by gravity. A scrubbed, CH_4-rich stream leaves the top of the scrubber and a "dirty" solvent stream leaves the base. If the solvent is to be regenerated, this would happen in an atmospheric (i.e. lower pressure) regeneration column where the CO_2/ H_2S is desorbed; the lean (clean) solvent is re-pressurised and returned to the scrubber and the de-pressurised desorbed gas stream is vented. This vent stream may be passed through an activated carbon bed before release to atmosphere.

Solvents in common use are:

- High Pressure Water - clearly there is no need to pre-dry the gas before scrubbing.
- Sodium Hydroxide (NaOH or Caustic) - usually controlled to circa 50 ppm H_2S although lower H_2S levels achievable
- Polyethylene Glycol (e.g. Selexol) - also removes water; regenerated by stripping with steam or inert gas.

Chemical absorption occurs where there is the formation of reversible bonds between solute and solvent, such as with a solvent of an aqueous solution of amines (either mono (MEA)-, di- or tri-ethanolamine); low pressure; no requirement to pre-dry. See also section 6.2 below.

4.4.5 Other methods

An aqueous solution of an alkaline salt (typically sodium, potassium or calcium hydroxide) may be used which has the advantages of operation at low pressure with no requirement to pre-dry.

Iron salts can also be used which create a precipitate of iron sulphide $Fe_2(SO_4)_3$ e.g. liquid iron chloride may be injected directly into the feedstock mixing tank at 4g/ litre feedstock, this also reduces odour [8]. In addition to the advantages of a low pressure system with no requirement to pre-dry, there is low CapEx (tank and dosing pump) and ammonia removal. Disadvantages are a high operation cost (OpEx) i.e. cost of iron chloride and inability to achieve low residual ppm H_2S.

Liquid reagents are commercially available e.g. BgPur [27]. Raw, saturated biogas is introduced and dispersed as micro-bubbles into a vessel containing the liquid reagent. The reagent absorbs H_2S and makes it available for reaction with oxygen to produce elemental sulphur as crystalline solids (the reagent is not consumed in the process but acts like a catalyst). The dispersed micro-bubbles in the tank allows it to act like a flotation cell to remove the crystalline sulphur solids.

An interesting and novel technique is Biofiltration using cow manure digestate [24]. A reduction in H_2S levels of 1500 ppm to 300 ppm is reported. There is no requirement to pre-dry the raw biogas.

4.5 Conclusion

GAP will be using air injection to bring typical levels of H_2S in the raw biogas to an average of 266 ppm (maximum 578 ppm) [1] followed by an activated carbon bed polishing filter to achieve the required specification of < 5 ppm. Due to the anticipated total low loading level, it is not expected that the GAC bed will require regeneration within the project lifetime.

5. BIOGAS DRYING (REMOVAL OF WATER VAPOUR)

5.1 Biogas Drying Techniques

Saturated biogas contains 6.8% water at 40 °C (268 g/h at the biogas flowrate required to give 50 Nlpm to the Plasma reactor). The stored biogas will cool to ambient temperature with an associated lower dew point. The Plasma reactor requires <2% water (approx 38 g/h or less at 50 Nlpm Plasma feed flowrate, from the project Mass and Energy Balance) so drying of saturated purified gas is required. Drying can be achieved by:

- Absorption which is a bulk process where a substance (in this case, water) is captured and distributed throughout the whole of the absorbent e.g. contacting with glycol or hygroscopic salts which may be regenerated by drying at high temp.
- Adsorption which is a surface-based process where the substance (water) is only distributed through the surface of the adsorbent by the adhesion of atoms, ions or molecules to create a surface film e.g. silica gel or aluminium oxide which may be regenerated by drying at high temp and high pressure.
- Chilling which lowers the dew point of the biogas – a cold gas holds less water vapour than warm gas hence when the biogas is chilled e.g. using glycol heat exchanger, the excess water vapour condenses out as free water.

Note that water vapour can have either a detrimental impact on downstream unit operations e.g. reducing GAC bed life as discussed above, or a positive impact e.g. stabilisation of amine-containing CO_2 adsorbents to increase CO_2 uptake over the number of regeneration cycles [19]. Depending on the techniques chosen, the drying stage should be sited immediately downstream of the biogas take-off or immediately upstream of the plasma reactor.

5.2 Conclusion

GAP will be using a glycol chiller with an assumed set point of 4 °C on the chilled biogas outlet. This will give a water content of <21g/h at Plasma reactor feedrate of 50 Nlpm which is <2% v/v (<38 g/h) which is within specification. The location of the chiller will be dependent on the upgrading technology chosen and the recommended chiller location is an outcome of this report.

6. BIOGAS UPGRADING (REMOVAL OF CO_2)

The plasma reactor requires Biogas upgrading which, in this application, means increasing the proportion of methane in the stream by removing CO_2. Biogas upgrading is established technology at plant scale (available at >50 Nm3/h but more typically above 500 Nm3/h biogas – see Table 4) and is covered extensively in the literature.

The most common solutions for separation of CO_2 from CH_4 [9] [12] [19] are

- Adsorption : pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA)
- Absorbtion: scrubbing technologies; physical absorption or chemical absorption
- Membrane separation: high pressure and low pressure

Cryotechnology [20] is also available and is based on the fact that CO_2, H_2S and all other biogas contaminants may be separated from CH_4 due to the fact that each contaminant liquefies at a different temperature-pressure domain [29]. The biogas is cooled to a very low temperature until the CO_2 liquifies out and can be separated. The triple point of CO_2 (where it exists as a solid, liquid and gas) is 216.55 K (-56.6 °C), 5.19 bar [33] so below this point, CO_2 will separate out as a solid.
Cyrotechnology is less common industrially [10] [13] due to complex equipment requirements (high Capital Expenditure or CapEx) and cost of running (high Operating Expenditure or OpEx). For this reason, this option may be discounted at this stage, as it is in much of the literature [10].

More esoteric separation technologies are discussed by Sam Wong and Rob Bioletti [32] e.g. Electrical Swing Adsorption, but are not available for utilisation by this project.

6.1 Adsorption Technology

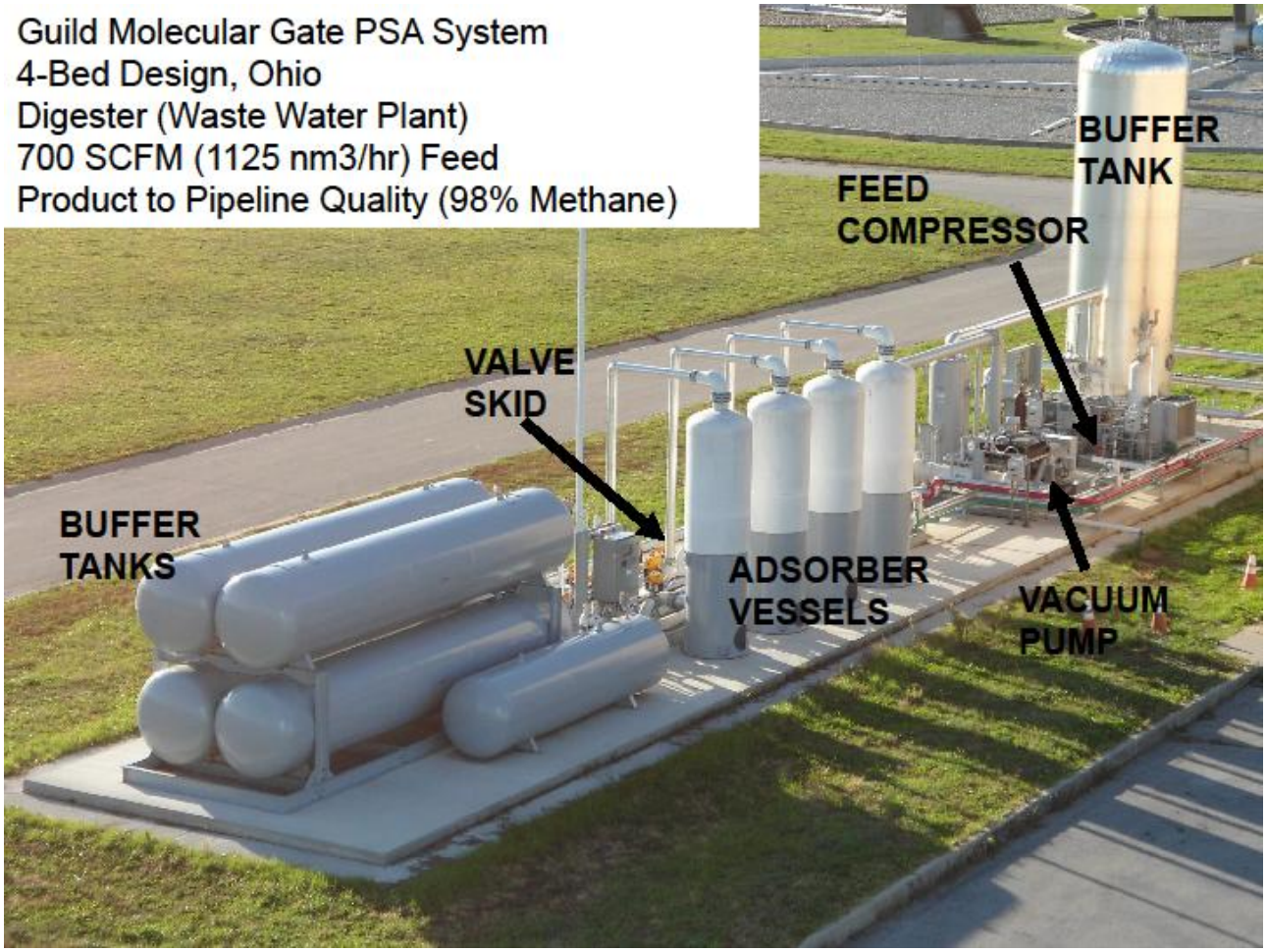
As explained above in Section 5, adsorption is a surface phenomenon. The PSA technique uses a series of vessels containing carbon molecular sieves at sequentially decreasing pressure and potentially different mesh sizes. For industrial scale units there are often four beds in series [9] (see Figure 1) and the gas pressure released from one vessel is used by the next thus reducing compression requirements. The species to be removed (e.g. water vapour, CO2) are adsorbed into cavities of the carbon sieve at high pressure and then desorbed at low pressure to regenerate the molecular sieve (hence, “pressure swing”). Note that the molecular sieve material is commonly poisoned by H_2S i.e. H_2S is adsorbed irreversibly so this species must be removed in advance. Typical operating pressures are 4-7 barg [12]. At smaller scale, a more usual configuration is one bed on duty and one bed on regeneration.

Zeolites are a common microporous material that have been used historically, which exhibit extremely narrow pore size distributions in the range of 0.5-2nm. Zeolites and related crystalline molecular sieves have an intrinsic limit on their pore dimension and accessibility owing to the pore templates available for their synthesis [21]. There is chemisorption at surface and physical adsorption in inner pores.

Porous polymer beads and other macroporous materials with pore sizes between 50 and 1000 nm allow for easy access to the pores at the cost of selectivity [21], so there is high slippage.

These drawbacks have led to the development of mesoporous materials which have an intermediate pore size range between 2-50 nm; narrow pore size distributions and high surface areas; and framework/ wall substitutions with various metal oxides including silica [21].

Figure 1 PSA system showing typical industrial scale [23]



6.1.1 Adsorption technology (PSA) at Pilot Plant Scale

A number of companies manufacture PSA units commercially [19] and these were contacted with the aim of building a test rig at lab scale. None of the companies were able to provide a unit at the lab scale required (50 Nlph, equivalent to 0.05 Nm3/h) and many were not able to provide a unit at the pilot plant scale (5.2 Nm3/h); however two companies, Sysadvance and Neo Zeo, were able to provide units at a usable scale. See table 4 below.

Table 4 Manufacturers of PSA units contacted and scale available

Company	Homepage	Scale (Nm3/h)
Carbotech	www.carbotech.info	> 35
Cirmac	www.cirmac.com	50-5000
ETW Energietechnik	www.etw-energy.com	Not suitable for pilot plant scale
Guild	www.moleculargate.com	>120
Mahler	www.mahler-ags.com	500-5000
Strabag	www.strabag-umweltanlagen.com	>1200
Xebec	www.xebecinc.com	Spec sent, not suitable for pilot plant scale
GTS	www.gastreatmentservices.com	No response
Sysadvance	www. sysadvance.com	20 Nm3/h test rig available
Neo Zeo	www.neo-zeo.com	5-6 Nm3/h test rig available

A zero-prototyping approach was considered for the PSA unit at lab scale (50 Nlph) by building an Aspen model to represent the unit. However, the isotherms required to populate such a model PSA block to give meaningful results are not available in Aspen Plus Dynamics; modelling these from first principles is discussed in the literature [22] but is beyond the scope of this report. Aspen Adsorption software is required for such modelling and this specialist software programme was not available to the author.

Sysadvance are a Portugese-based company which has a "Methagen" upgrading plant housed in a 40 foot (15m) shipping container, which can process 20 Nm3/h raw biogas. This uses vacuum PSA (VPSA) technology which can also remove significant quantities of Nitrogen e.g. from landfill gas, however this is not present in AD biogas. Furthermore, this technology is not appropriately scaled to the pilot plant trials at 5-6 Nm3/h.

NeoZeo is, "a technology company focused on Biogas Upgrading solutions with technological and scientific innovations to achieve best quality and efficient process optimization of Upgrading Biogas into Biomethane - renewable vehicle fuel and power source. NeoZeo biogas upgrading plants have modular design… and are based on Pressure Swing Adsorption (PSA) technology and imbedded uniquely developed adsorbent materials for improved cost- and operational efficiency… with raw biogas flow of 100-500 Nm3/h"[26].
NeoZeo also have a trial unit of 5-6 Nm3/h for rental which, although greater than the lab trial requirements of 50 Nlph, is scaled to the pilot plant trials which is the required output of this work package. Also, units are available for future up-scaling.

A flowsheet of the NeoZeo PSA biogas upgrading process for pilot plant trials is given in Figure 2 below. The bed pressure profile over a full adsorption and regeneration cycle is given in Figure 3.
For biogas consisting only of methane and carbon dioxide (i.e. biogas mimicked using cylinder CO_2 and CH_4), the upgraded stream is high in methane (CH_4 >97%, CO_2 <3%). For raw biogas, a methane purity of >95% is more realistic and this is still within specification as plasma reactor feed. OpEx (energy consumption) increases with an increased purity requirement.

To conclude, test data is available from NeoZeo which, from a process point of view, supports trialling a PSA unit at pilot plant scale (5-6 Nm3/h) as one of the chosen methods to upgrade biogas to the high purity CH_4 stream required as feed to the plasma reactor, without the requirement to trial or model at lab scale.

Figure 2 PSA flowsheet for biogas upgrading for pilot plant trials

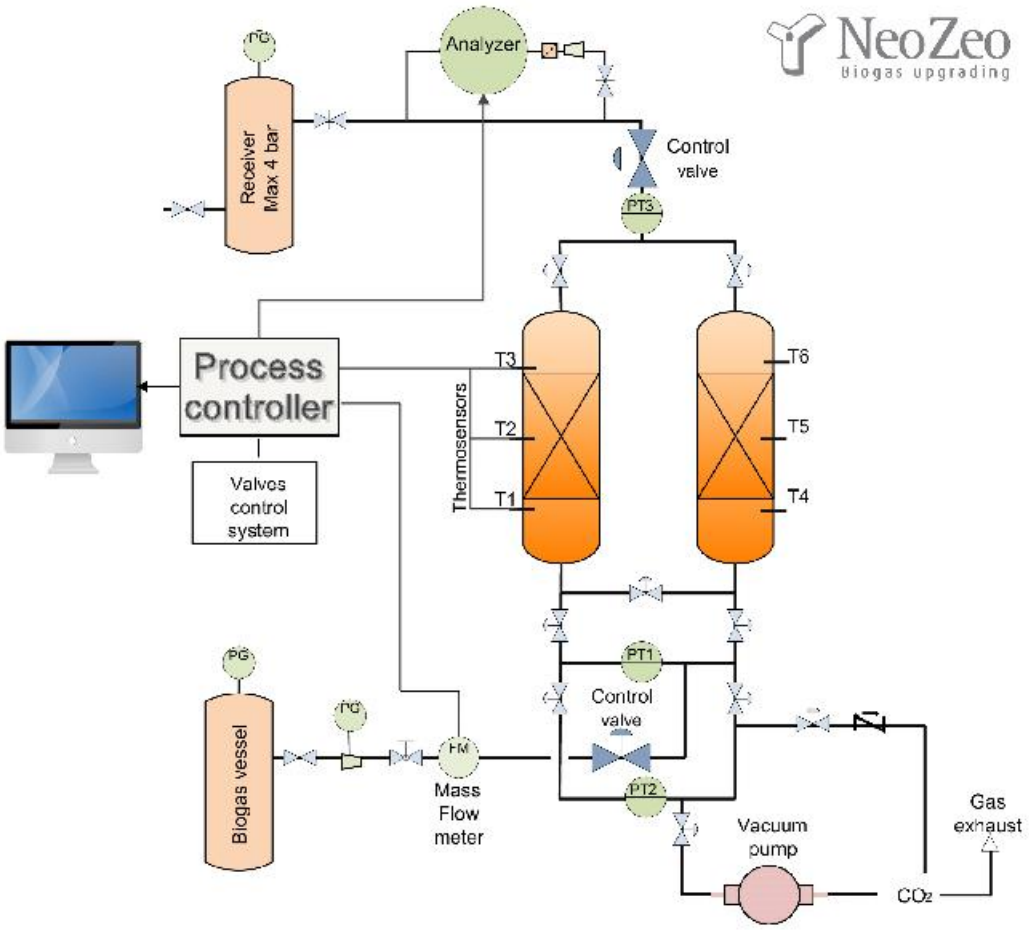


Figure 3 PSA bed pressure profile over complete adsorption and regeneration cycle

NeoZeo
Biogas upgrading

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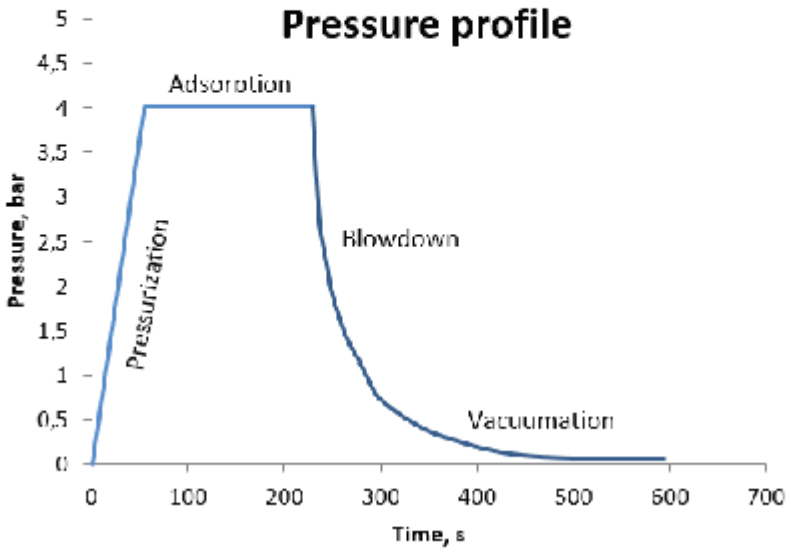

Process steps chart:

Steps	Time, s
Pressurization	50
Adsorption	190
Fast blowdown	50
Vacuumation	300

Process description:

Adsorbent – molecular sieve,

working pressure – 4 bars

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6.2 Absorption Technology

Absorption depends on different solubilities of various gas components in a liquid scrubbing solution – see Liquid phase oxidation in Section 4.4.4 above. This effect increases at increased pressure and reduced temperature.

To recap, water absorption removes H_2S as well as CO_2. Pressurised biogas (typically 7-10 barg) is fed to the base of a packed tower and, being buoyant, flows upwards to the top of the tower. Good scrubber design gives a uniform gas flow across the packed bed and avoids channelling. Pressurised water (again typically 7 -10 barg) is run counter-currently i.e. water is introduced at the top of the tower and flows downwards, wetting the packing which then provides a high surface area within the tower, and preferentially absorbing H_2S and CO_2 on contact with the gas stream. Saturated, scrubbed gas is taken off the top of the tower. The water stream containing the dissolved gases is taken off the tower base and may be regenerated in separate column by depressurising or stripping with air; the water is then re-pressurised and re-circulated. Water Scrubbing as an upgrading unit operation for the plasma reactor feed stream was modelled using Aspen Plus process modelling software and this is discussed in 6.2.1 below.

Other solvents are available e.g. Polyethylene glycol (commercially available as “Selexol”). An advantage in using this is that CO_2 is more soluble in glycol than in water, so less solvent is needed giving smaller columns and a smaller pumping requirement (i.e. lower CapEx and OpEx). CO_2, a weak base, reacts exothermally with MEA, a weak acid, to form a water soluble salt. The glycol is recovered and re-circulated.

Amine scrubbers are also used to upgrade raw biogas and literature indicates monoethanolamine (MEA) as the favoured amine solvent; both 9% [35] and 20% [29] are quoted as an optimum concentration. An obvious disadvantage is the toxicity of MEA compared to water. Inhalation of MEA vapour may cause irritation to the respiratory tract. Symptoms may include sore throat, coughing, respiratory distress, headache, lethargy, and narcosis. Exposure to higher concentrations may cause pulmonary irritation, and kidney and liver damage. Ingestion of MEA may cause mucosal burns of the mouth and oesophagus, abdominal pain, nausea, and vomiting. It may cause systemic poisoning with symptoms paralleling inhalation. Skin Contact may cause irritation, redness, burns, and pain. It may also be absorbed through the skin; symptoms may parallel inhalation.
Vapours and contact may cause severe irritation to the eye, burns, redness, pain, and blurred vision.
Prolonged or repeated skin exposure may cause severe irritation or dermatitis [34].
Because of this additional toxicological hazard versus water scrubbing, MEA scrubbing will not be considered further for this project and will not be modelled. However, Aspen modelling of MEA scrubbers is covered in the literature [36], including as a comparison to modelled membrane units [30]; here an MEA scrubber system has been modelled using the electrolyte- NRTL method to calculate the fluid transport and thermodynamic properties.

6.2.1 Aspen Plus Modelling of High Pressure Water Scrubber System

The applicability of high pressure water scrubber units to upgrading of biogas is discussed positively in the literature [29], [37], [38], [39] including at small scale. This unit operation was therefore considered further for the upgrading of biogas to Plasma reactor feed quality at pilot plant scale.

As there is a large amount of physical property data available on the interaction of water and CO_2, a zero prototyping approach was adopted to investigate the feasibility of using a water scrubber system to upgrade biogas for pilot plant trials. A high pressure water scrubber system was modelled in Aspen Plus process modelling software, starting with an Electrolytes metric template. Electrolyte- NRTL physical properties method was used to calculate the fluid transport and thermodynamic properties.

Initially the absorption column was modelled using a flash block for the system to converge and the model was then advanced using a Radfrac block to model the absorption column.

Once the electrolyte-based calculation for a Radfrac multi-stage water scrubber had run without errors or warnings, the recycle stream and regeneration column were added. The raw biogas flowrate was set at 6 Nm^3/h with a compostion as per Table 1 average values. The water feed stream was taken at 9 barg and ambient temperature (15 °C). See Figure 4 below for process flowsheet. Once converged, sensitivity analysis was run on scrubbed gas purity versus make-up water flowrate (see Figure 5) and scrubbed gas purity versus recycle flowrate (see Figure 6).

Figure 4 Aspen Plus process model of water scrubber system

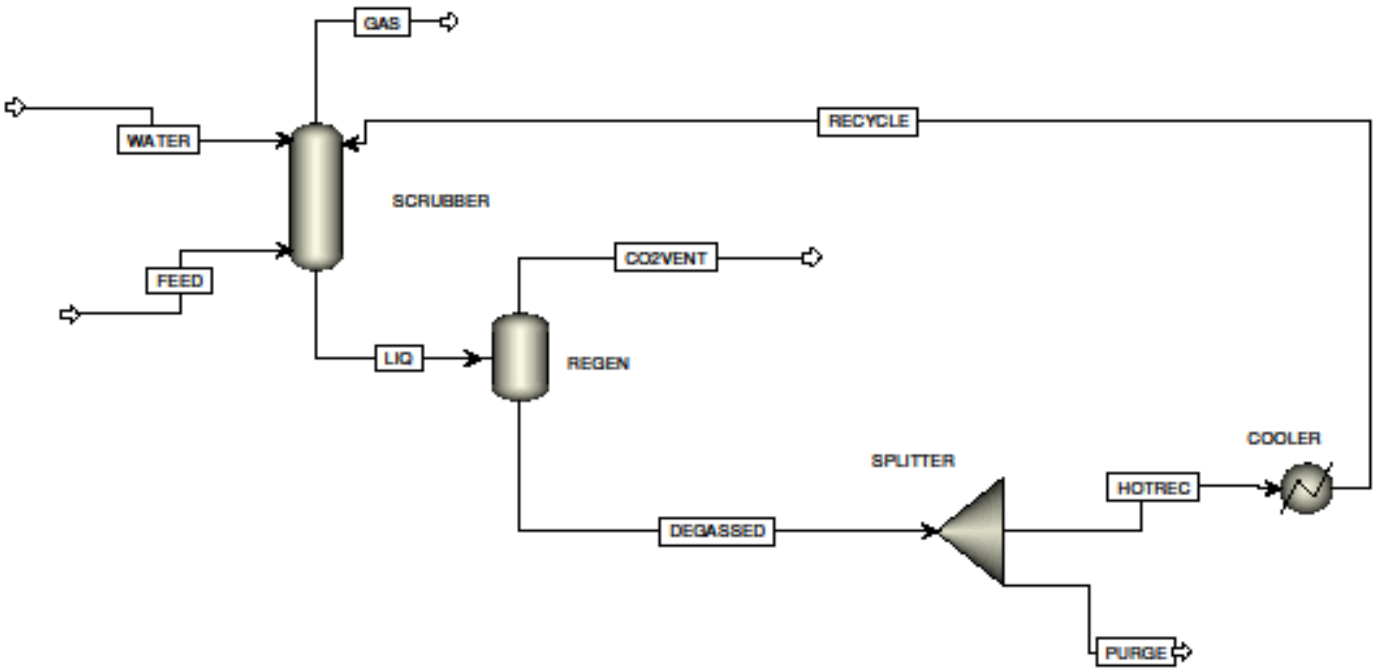
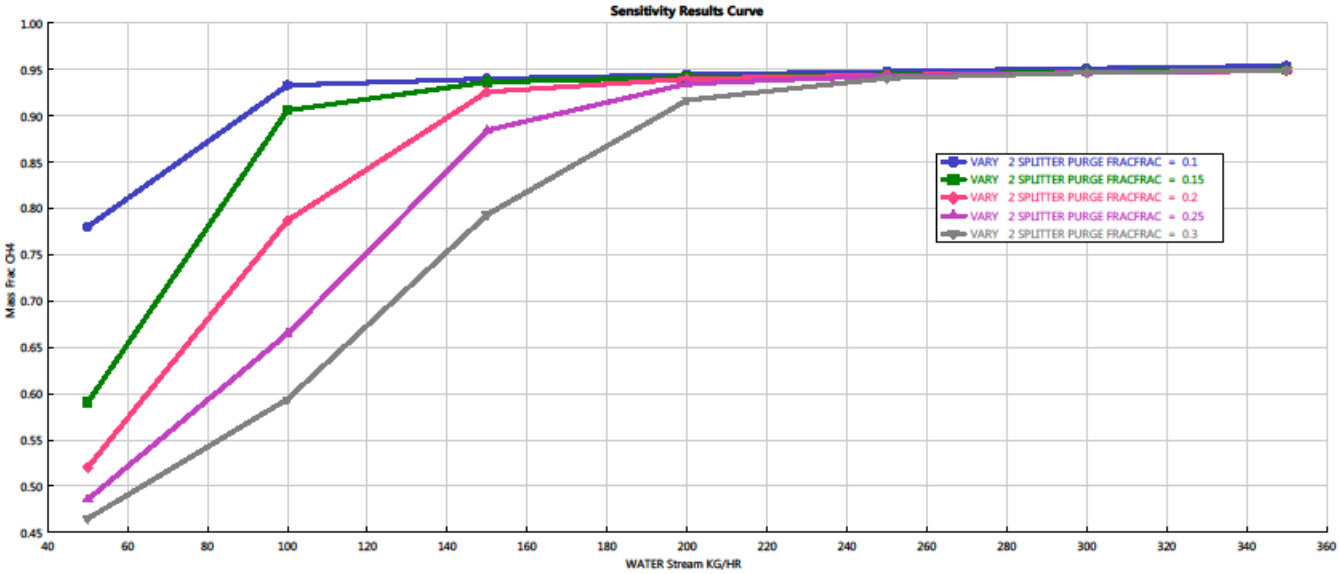


Figure 5 Sensitivity Analysis of Scrubbed Gas Purity versus Make-up Water Flowrate



It can be seen from Figure 5 that a high water make-up rate (>= 250 kg/h) is required to avoid build-up of impurities in the recycle stream, to achieve the required upgraded biogas specification of 95% CH_4.

Figure 6 Sensitivity Analysis of Recycle Flowrate versus Water Make-up

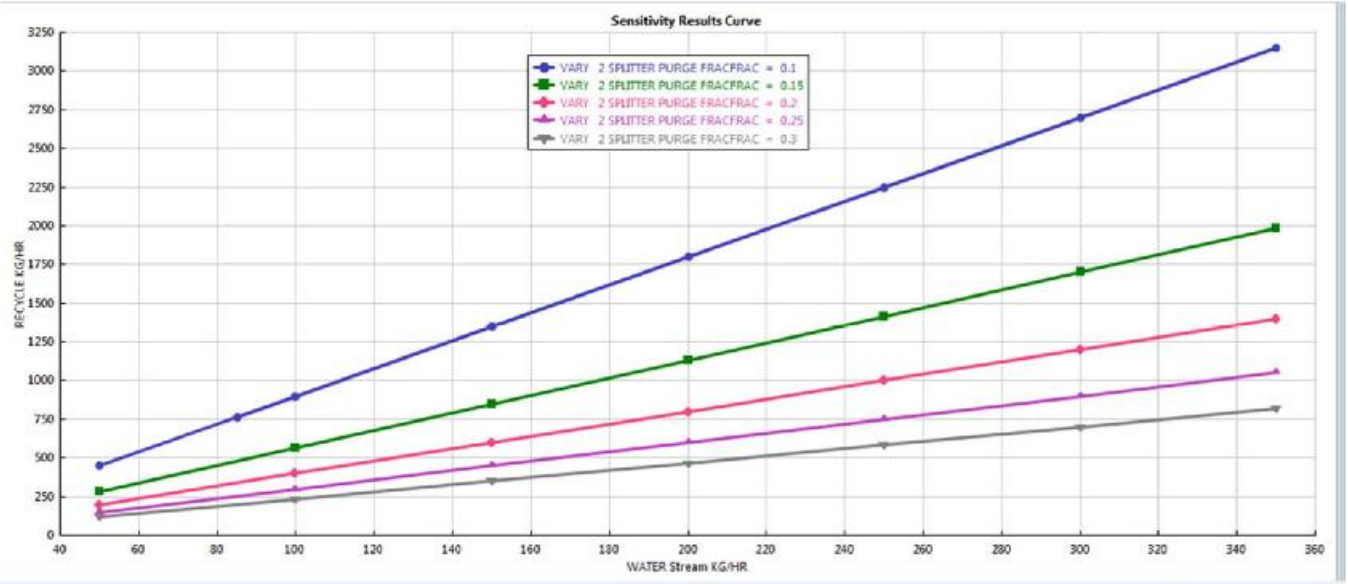


Figure 6 shows that the minimum required water make-up flow of 250 kg/h has an associated recycle flowrate of approx 600 – 2250 kg/h. As can be seen, a high splitter purge fraction of 0.3 results in the minimum recycle of 600 kg/h. This is for a biogas mass flowrate of 5.86 kg/h.

It was therefore concluded that although successful at industrial scale, a high pressure water system is inappropriate technology for pilot plant trials.

Note that Zhao et al [29] use a 20% MEA scrubber on 90 lpm (5.4 Nm^3/h) biogas flowrate which is directly comparable with PlasCarb pilot plant trial rates, however the scrubber in question was a batch not a continuous unit.

6.3 Membrane Separation Technology

The principle of membrane separation is that some components of the raw biogas are transported [permeate] through a membrane whilst others are retained as their permeability rate through the membrane is slower or negligible. A cross-flow flowpath is used i.e. the mixed gas stream flows across the surface of the membrane. One (or more) species flows preferentially through the membrane and forms

the permeate stream. The other species flow(s) preferentially along the membrane and forms the retentate stream.

This differs from dead-end filtration, typically used to separate phases, where the whole gas stream flows through the membrane and the solid/ liquid phase is left on the upstream surface of the membrane and eventually blinds it.

Porous membranes can be constructed as hollow fibre modules, ceramic structures or sintered metal which give a large membrane surface per unit volume. Species diffuse from the upstream region of high pressure through the pores to the downstream region of low pressure. However, pressure drop across the membrane may have to be limited to avoid damage to the membrane structure.

Polymer membranes are dense, non-porous flexible films of synthetic polymer where the species transfer by a solution-diffusion mechanism. In other words, the gas dissolves in the polymer at the high-pressure side of the membrane. The gas then diffuses through the thin polymer film and desorbs or evaporates at the low-pressure side of the membrane and enters the pores of the support structure. Finally, the gas diffuses through the pores of the support material and flows out into the low pressure side. This flow may be encouraged by the use of a sweep gas on the low pressure side (to reduce the concentration of the diffused species and hence increase the flux) or by applying vacuum. The permeability is a direct function of the chemical solubility of the target component [i.e. the given molecular species] in the membrane [29]. The flux through the polymer (membrane) film is inversely proportional to the thickness, hence for high gas flowrates the film should be as thin as possible. Gas separation processes can operate at high pressures and so the membrane is supported by a porous structure that offers little resistance to flow. The thin membrane offers a desirable short path for diffusion for the target species, however in practice the membrane is not of uniform thickness because it penetrates partly into the pores of the supporting material [41]. Polymer membranes are used to industrial biogas upgrading, typically in multi-stage units, though there are fewer reference plants than for the other technologies discussed [10]. Membrane material and selectivity improvement is still a developing technology.

Membranes may be modelled in Aspen Plus. However, as the characteristics pertaining to specific commercially available membrane units are unknown and therefore unable to be modelled with any accuracy, this zero-prototyping approach was not adopted in this case. Instead, a membrane unit suitable for lab scale was identified, a rig was built and trialled and thus the membrane unit assessed for applicability at pilot plant scale.

Membrane separation technology is discussed further in Section 8 where the membrane rig trials are discussed and evaluated.

7. TECHNO-ECONOMIC ASSESSMENT OF BIOGAS UPGRADING (REMOVAL OF CO2) TECHNIQUES

There is a body of literature [12] [13] [19] [39] [44] considering the technological performance and CapEx and Opex of the biogas upgrading techniques discussed above. Much of this is at a larger, industrial scale though one report, Valorgas [44], looks specifically at small-scale biogas upgrading plants (nominally <50 Nm3/h). It is worth noting that this is still up to a factor of ten greater than the PlasCarb pilot plant scale.

A summary of the Valorgas report is presented by the author in the following tabular form:

Table 5 Summary of Valorgas information

Plant	Location	Nm3/h raw biogas	Nm3/h upgraded gas	CO2 removal technique	CH4 purity (%)	CapEx/ Nm3 biogas	OpEx/ Nm3 biogas
1	Finland	30-100		High Pressure Water Scrubbing	92-99		0.32
2	Hungary	50-100		High Pressure Water Scrubbing	>97		
3	Sweden		25	”Biosling” water scrubbing	94-97		
4	Austria	180	100	2-stage membrane	70->99		
5	**Austria**	**10**	**6**	**PSA**	**97**		
6	Austria	18					
7	Austria	22		PSA			
8	Austria	70		1-stage membrane			
9	Sweden	17		Water Scrubbing			0.37 (assuming 8000 h/y operation)
10	Germany	600		Low pressure amine scrubbing			0.4
11	Sweden	80		High Pressure Water Scrubbing	97		0.02 (this seems low)
12	India	20		Water scrubbing		0.42	

Case study 5 at Plucking, Austria is most representative of the PlasCarb requirement, unfortunately there is no associated techno-economic data within the report.
However, it can be seen that the chosen upgrading technologies for small-scale biogas upgrading plant are PSA, water scrubbing and membrane technology as discussed in Section 6 above.

As stated above, more techno-economic evaluation in the literature is at industrial scale which is indicative only at pilot plant scale. The Danish Technological Institute [19] has a matrix of technology available (PSA, scrubbing, membrane separation) vs OpEx which is summarised in Table 6 below; the range quoted reflects the range in scale at which the technology operates:

Table 6 Comparison of different commercial upgrading technologies

Cost/ Nm3 raw biogas etc	PSA	Water Scrubbing	Amine Scrubbing	Membrane separation
Electricity consumption kWh/Nm3	0.23 to <0.3	<0.25 to 0.3	0.1 to 0.25	0.18-0.2
Heat consumption kWh/Nm3	none	none	0.5-0.75	none
Max CH4 purity %	99	98.5	>99.5	98
H2S co-removal	Possible	yes	contaminant	possible

From Table 6, it can be seen that all the techniques are capable in theory of meeting the required PlasCarb plasma reactor feed specification. It can also be seen that membrane separation and PSA have the lower running costs. At pilot plant scale, these two unit operations also have the lower capital costs as can be deduced from a comparison of the flowsheets contained in this report (see Figures 2,4 and 8).

The Biogas to Biomethane Technology Review [10], [13] gives a table of typical investment cost i.e. CapEx and typical operational cost i.e. OpEx for a range of plant sizes, 100 m3/h biomethane being the smallest. This data is summarised in Table 7 below.

Table 7 Typical Investment and operational costs for 100 m^3/h Biogas upgrading plant

Cost (Euro/ m^3h^{-1} biomethane)	Water scrubbing	Amine scrubbing	PSA	Membrane technology
CapEx	10.1	9.5	10.4	7.3-7.6
OpEx	14.0	14.4	12.8	10.8-15.8

Table 7 shows that a membrane unit is economically the most favourable to run at pilot plant scale with regards to both CapEx and OpEx. A unit was identified for lab scale trials at 50 Nlph, to test whether a membrane rig is technically suitable for further trials at pilot plant scale.

By considering the CapEx and OpEx together, a PSA rig is economically the second more viable option to run at pilot plant scale. A PSA rig has been identified that has been shown to be technically suitable for the pilot plant trials at 5-6 Nm3/h and so this unit operation will be trialled at pilot plant scale in Q315 in task 4.3 of this project.

8. EVALUATION OF LAB SCALE MEMBRANE UNIT

Membrane manufacturers [19] were contacted, however only Pervatech [28] were able to supply a unit suitable to the lab scale flowrate of 50 Nlph and also at 5 Nm^3/h for pilot plant trials.

The membrane element supplied is hybrid silica coated on the inside of a support material, the substrate being aluminium oxide (Al_2O_3) with a gamma alumina intermediate layer. The element dimensions are 250mm (L) x10 mm (D) with an effective area of 0.005 m^2. Each element has 1 channel with 7mm inside diameter and 0.3-0.5 nm pore size.
Design temperature of the element is 150 °C, Design pressure is 10 barg. See Datasheet, Appendix (i). Operating temperature is 50 °C, operating pressure is 3-5 barg [28].

Note that high operating temperature usually decreases membrane selectivity but increases permeability of the target species according to Arrhenius equation (i.e. increase in diffusivity at higher temperature is greater than decrease in solubility at higher temperature) [41]. Because of this offset in desired results, the operating temperature was not changed during the trials but was left at the manufacturer's recommended value of 50 °C.

The element is in a stainless steel 316L housing (code PVM-035) with EPDM O-rings suitable for CO_2 and flammables and ¼" FNPT connections for feed, retentate, permeate and sweep gas connections. See Equipment Datasheet, Appendix (ii).

A photograph of the experimental rig is given in Figure 7. A Piping and Instrumentation Diagram (P&ID) of the rig is given in Figure 8, showing the membrane unit and associated streams – CO_2 and CH_4 feed streams and N_2 sweep/ purge stream. The rig is located in an extracted fume cupboard with face velocity of 0.9 m/s and an audible alarm in case of extraction failure. Both CO_2 and CH_4 are supplied from a cylinder and are piped local to the fume cupboard via a Restriction Orifice Plate (ROP) to limit the maximum flow to within the Relief Valve capacity. There is also a Pressure regulator valve set at 5 barg, a suitably sized relief valve set at 6 barg and a local pressure regulator valve, on each line. Governing relief case is failure of the upstream pressure regulator. Prior to the membrane unit, the flowrate of each gas is measured using a rotameter; the gases are then mixed in suitable ratios to mimic biogas composition, and heated to 50 °C. After the membrane unit, a back-pressure control valve on the retentate stream (the stream which does not pass through the filter membrane) provides a suitable back-pressure to push gas though the membrane – the permeate stream.
The retentate flowrate and permeate flowrate are measured and the streams are sampled before venting to extract at the top of the fume cupboard.
According to the manufacturer, CO_2 passes preferentially through the membrane as the permeate, leaving a CH_4-rich stream as the retentate.
In order to encourage permeation, there is provision for a sweep gas to reduce CO_2 concentration on the permeate side of the membrane. The sweep gas used in this experimental rig is site Nitrogen (N_2) at a controllable flowrate at variable pressure (0-6 barg) connected onto the membrane housing, with the option of connecting a Variable Speed Drive vacuum pump to the permeate downstream of the unit. N_2 is also used to purge the membrane unit at the end of the experimental run.

Two sets of trials were run and the results of these are presented in Appendix (iii) and Appendix (iv) respectively. The first set of trials showed no selectivity for CO_2. In case of damage to the membrane element not visible to the naked eye, the membrane element was replaced and the trials re-run.
In the second set of trials, the second modified membrane did show selectivity for CO_2 at low permeate flowrate, however the mass of CO_2 removed in this case is small and so the composition of the retentate stream is virtually unchanged. When the back pressure on the unit is increased such that the permeate flowrate increases, then selectivity is lost and again the composition of the retentate stream is unchanged.

In conclusion, whilst membrane separation is a successful industrial method of upgrading biogas, lab trials concluded that membrane elements available at lab scale and pilot plant scale do not show sufficient selectivity to separate the biogas to give a 95% CH_4 purity stream.

Figure 7 Laboratory scale membrane unit (50 Nlph)

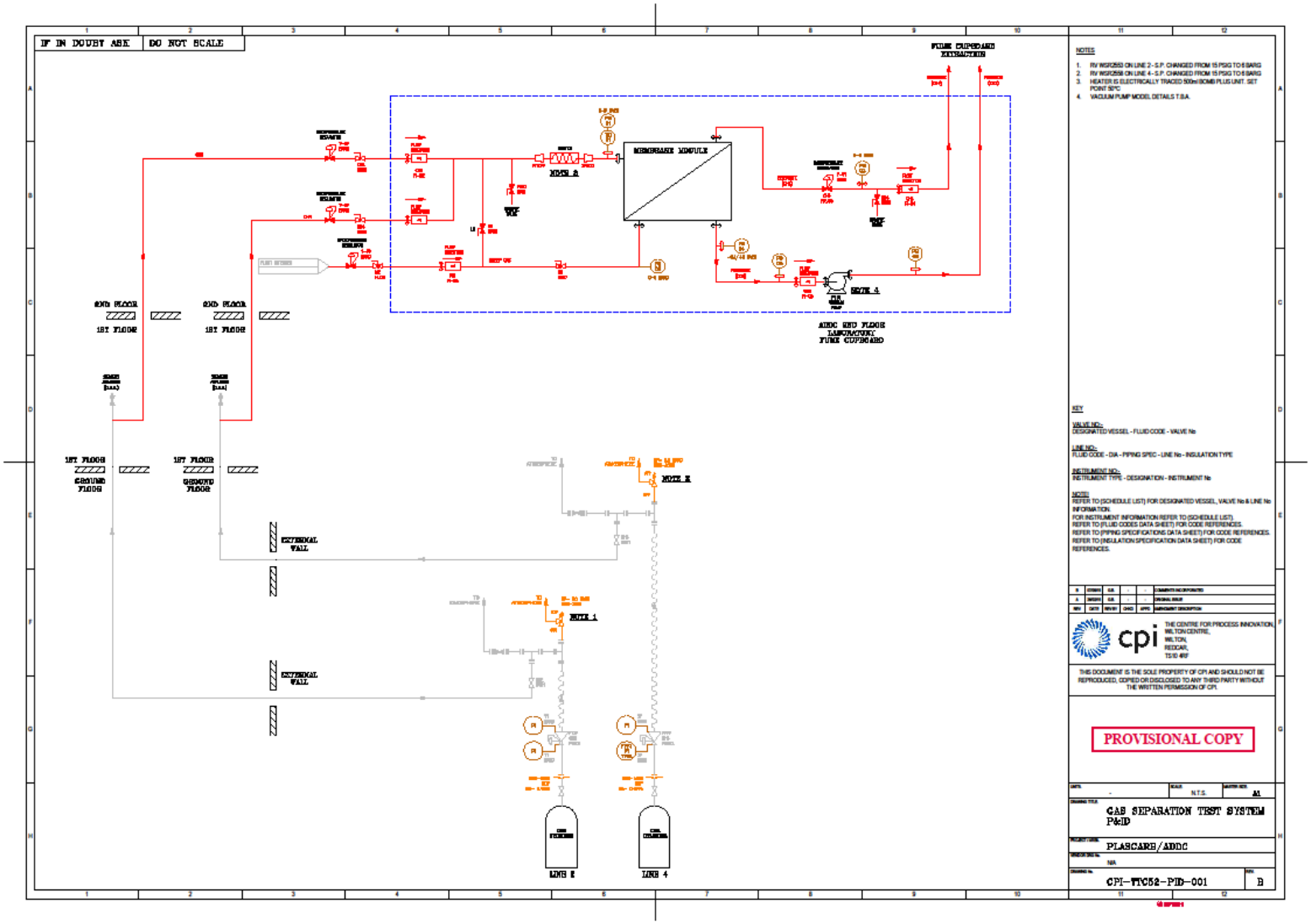


Figure 8 P&ID of Laboratory scale membrane unit and feed streams.

9. CONCLUSIONS

GAP will be using air injection to promote Biological Desulphurisation to bring typical levels of H_2S in the raw biogas to an average of 266 ppm (maximum 578 ppm), followed by an Granular Activated Carbon (GAC) bed polishing filter to achieve the required specification of < 5 ppm. The bacteria population can't respond to fluctuating H_2S levels in biogas as seen at GAP and so any additional load will be adsorbed by the GAC bed. However, the overall loading level is still anticipated to be low and it is not expected that the GAC bed will be regenerated in the project lifetime.

Test data is available from NeoZeo PSA that show that this technology should be trialled at pilot plant scale to upgrade the required raw biogas flowrate of 5-6 Nm^3/h to a 95% CH_4 purity stream.

A re-circulating high pressure water scrubber unit is not available for rental at the required pilot plant scale. Furthermore, from the Aspen Plus process model it can be seen that such a unit would have a degree of complexity and therefore high CapEx that is not appropriate for pilot plant scale. From the Aspen model, it can also be seen that the water make-up required to maintain the required 95% CH_4 purity is significant as is the flowrate of the pumped, cooled recirculation stream. Both these factors give a high OpEx.

Whilst membrane separation is a successful industrial method of upgrading biogas, laboratory trials have shown that membrane elements available at lab scale and pilot plant scale do not show sufficient selectivity to separate the biogas to give a 95% CH_4 purity stream.

To conclude, a PSA unit will be trialled at pilot plant scale (5-6 Nm3/h) as the chosen method to upgrade biogas to the high purity CH_4 stream required as feed to the plasma reactor.

GAP will be using a glycol chiller with an assumed set point of 4 °C to dry the biogas to <2% water vapour. Assuming that the pilot plant trials of the PSA unit are successful, then for full plant operation at Gateshead, this chiller will be located upstream of the GAC.

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APPENDICES

Appendix (i) Membrane Element Datasheet

PERVATECH

Datasheet: 1-Channel Hybrid Silica Membranes

The Pervatech hybrid silica membranes have hydrophilic characteristics, meaning that the water content of the feed passes preferentially through the membrane.

Membrane construction

Element sizes:	500 x 10 mm (L x D), effective area 0,01 m^2 (standard), 250 x 10 mm (L x D), effective area 0,005 m^2 (knock-out testing only) Each element has 1 channel with 7mm inside diameter.
Substrate material:	α-Al_2O_3
Intermediate layer:	Gamma alumina
Top layer:	Hybrid Silica coated on inside of the support tube
Pore Size:	0,3 – 0,5 nm

Limits of operation

Temperature:	150 °C
Pressure:	max. 10 bar
pH:	2-8,5

Handling, storage and cleaning

Handling

Always wear clean gloves when handling the membranes in order to prevent contamination with fungi. **Warning:** The membranes are brittle and cannot withstand shock, excessive vibration nor mechanical bending forces.

Storage

The membranes can be stored in a dry place under ambient conditions. To prevent the risk of fungi growth on the ceramic element the relative humidity should not exceed 60%.

Cleaning

At the end of the standard dehydration process flush the element with clean solvent or demineralized water (max. 50 °C). In some cases special CIP procedures might be applicable. Please consult Pervatech for more information or consult the separate cleaning datasheet.

Possible applications with hydrophilic membranes

- Breaking of azeotrope
- Removal of water from organics like Alcohols, A-protic solvents, DmAc, DMSO, DMF, ethyl acetate, NMP, Phenol, THF, AcN
- In situ dehydration of condensation reactions
- Dehydration of essential oils
- Separation of low mw from higher mw solvents (purification)

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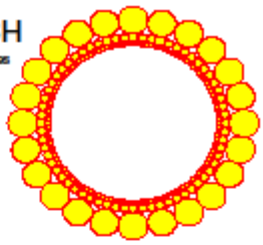
Appendix (ii) Membrane Module Datasheet

datasheet pvm-035, version 19-02-2013

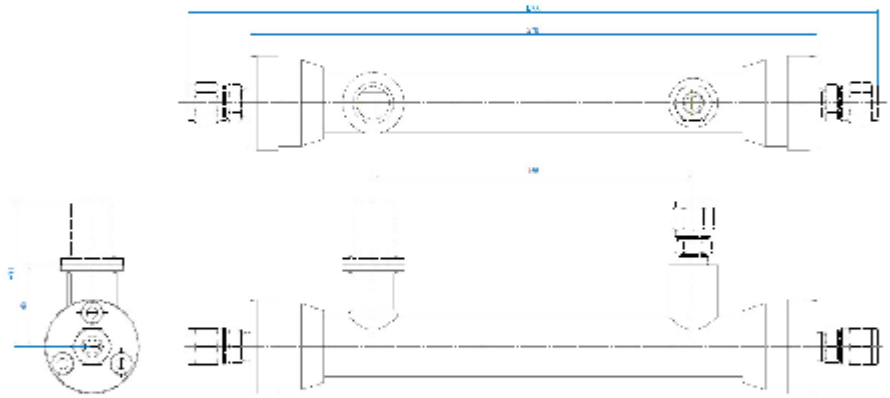
PERVATECH
selective ceramic membranes process design



Datasheet: PVM-035 module

The PVM-035 module is designed to hold one 25 cm ceramic tubular membrane element for use in pervaporation or vapour permeation applications.

Standard Membranes:	HybSi®, PDMS, Optimised Silica (see membrane data sheets)
Pressure housing:	SS316L
Membrane area:	0,005 m^2
Feed, Retentate conn.:	¼"FNPT
Permeate conn.:	NW16 KF
Pressure Gauge conn.:	¼"FNPT
Sealing of membrane tubes:	O-ring
O-rings:	10 x 3 mm, EPDM (standard) VITON – Kalrez (option)
Dimensions:	See figure



Limits of Operation

Max. process pressure:	5 bar
Max. process temperature:	Dependent on membrane type, See membrane data sheet
Vacuum:	The level of vacuum depends on the application but is typically 20 mbar.
Feed pump capacity:	Linear velocity of the feed to be high enough to guarantee turbulent flow inside the tube, this to prevent concentration polarisation and limit fouling.
Cleaning:	Depending on the specific membrane and nature of the fouling, see instructions in the membrane data sheets.

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Appendix (iii) Membrane Results Trial 1

Membrane trials			GC CH4 reading error +10%			date		27/04/2015
run no			1	2	3	4		5
cylinder P	barg		2	2	3	5		5
FI01					0.5	>1.4	>1.4	
FI02				0.6	0.3	1.4	>1.4	
FI03				0	0	0	>1.4	
FI04			0.5	0.4	0.95	0.5	>1.7	
PG01			0.2	0.2	0	1.7		2.7
T	degC		47.1	47.1	44.9	46.6		39.1
permeate 1	CH4 %		*78*	79.43		82.97		80.7
	corrected CH4		*70.2*	71.487		74.673		72.63
	CO2 %		*26.6*	**28.85**		**25.81**		**27.4**
	sum		*96.8*	100.337		100.483		100.03
permeate 2	CH4 %		80.23	79.19				
	corrected CH4		72.207	71.271				
	CO2 %		**28.68**	**28.67**				
	sum		100.887	99.941				
retentate 1	CH4 %		79.16	75.58				78.43
	corrected CH4		71.244	68.022				70.587
	CO2 %		29.49	34.14				**29.74**
	sum		100.734	102.162				100.327
retentate 2	CH4 %			74.68				
	corrected CH4			67.212				
	CO2 %			33.24				
	sum			100.452				
feed 1	CH4 %		79.76	80.2	72	87.2		*87.2*
	corrected CH4		71.784	72.18		78.48		*78.48*
	CO2 %		**29.7**	**28.51**	**34**	**20.7**		***20.7***
	sum		101.484	100.69		99.18		*99.18*
feed 2	CH4 %			78.37				
	corrected CH4			70.533				
	CO2 %			**29.23**				
	sum			99.763				
%selectivity for CO2		perm.	-3.4343434	-0.3810184		24.68599		32.36715
		retent.						43.671498

Conclusion: No selectivity for CO2 hence retrial with new membrane installed.

Appendix (iv) Membrane Results Trial 2

Membrane trials 2			GC CH4 reading error +4.85%			date	21/05/2015	22/05/2015
run no			1 (conditioning)	2	3	4	5	6
cylinder P	barg		2	2	5	5	5	5
FI01 (CH4)	ml/min		0.5	0.3	0.5	0.25	0.25	0.2
FI02 (CO2)	ml/min		0.3	0.1	0.3	0.1	0.25	0.15
FI03 (perm)	ml/min							
FI04 (ret)	ml/min	overreading	1.1	0.8	1.1	0.8	1.6	1.4
supply P	barg		2	2	4	4	4	3.5
T	degC		49.5	49.5	49	49	49	47
filter in PG01	barg			0.8			1.3	1.85
back P PG03	barg		0	0.7	0	1	1.15	1.8
feed 1	CH4 %		73.7	82.88	73.59	91.6	59.9	63.21
	corrected CH4		70.13	78.86	70.02	87.16	56.99	59.29
	CO2 %		33.46	22.88	34.1	15.2	49.8	45.06
	sum		103.59	101.74	104.12	102.36	106.79	104.35
feed 2	CH4 %		72.99	84.44				
	corrected CH4		69.45	80.34				
	CO2 %		35.37	22.87				
	sum		104.82	103.21				
retentate 1	CH4 %		71.76	81.8			59.9	57.47
	corrected CH4		68.28	77.83			56.99	53.91
	CO2 %		34.37	23.18			49.82	45.58
	sum		102.65	101.01			106.81	99.49
retentate 2	CH4 %			80.67				
	corrected CH4			76.76				
	CO2 %			22.31				
	sum			99.07				
permeate 1	CH4 %			67.04			22.34	45.69
	corrected CH4			63.79			21.26	42.86
	CO2 %			37.26			81.87	61.62
	sum			101.05			103.13	104.48
permeate 2	CH4 %							
	corrected CH4							
	CO2 %							
	sum							
%selectivity for CO2	perm.	n/a		62.885246	n/a	n/a	64.39759	
	retent.			1.6288525			0.0401606	

Conclusion: Membrane does show selectivity for CO2 however permeate flowrate is too small hence retentate composition not affected. When permeate flowrate increased then selectivity is lost.