BioSNG Demonstration Plant

Summary of Technical Results

Results of test and experiments on the demonstration plant
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1.0 Introduction

BioSNG addresses the issue of decarbonising heat and transport, which together account for more than 70% of final energy use in the UK. It offers an affordable, low carbon alternative to fossil gas and could help provide a greener and more secure energy future. The widespread deployment of BioSNG will use the UK’s extensive gas network to help reduce carbon emissions from heat and transport without any disruption to consumers.

The BioSNG technology converts household waste into a grid compliant gas through the combination of gasification and catalytic conversion. Producing BioSNG would greatly expand the supply of renewable gas over and above existing solutions such as anaerobic digestion (AD). In total, AD and BioSNG have the potential to produce 100TWh of low carbon gas per annum, enough to meet one third of domestic heat demand.

The BioSNG Demonstration Project aimed to establish the technical, environmental and commercial feasibility of BioSNG production. National Grid Gas Distribution worked with Advanced Plasma Power, Progressive Energy and Carbotech to construct and operate a BioSNG demonstration facility. The results from this plant have validated the technical and commercial models of the process and enabled the development of the first BioSNG commercial plant, which will deliver gas to grid in 2018.

The funding and strategic backing for the project came from Ofgem’s Network Innovation Competition and the European BioEnergy Securing the Future ERANET programme.

It is anticipated that the results from the project will lead to the construction of larger scale commercial BioSNG facilities to serve regional needs across the country. These plants could make a telling contribution to the future of gas at an affordable cost and with significant reductions in greenhouse gas emissions.

The approach could help solve an issue facing governments, energy suppliers, policy makers and consumer groups across the world: how to decarbonise heat and heavy goods transport in a sustainable way through the development of technology that is commercially viable, affordable, and acceptable to consumers. It highlights National Grid Gas Distribution’s commitment to seeking economic and innovative ways to decarbonise energy, while making the best use of the existing UK gas network.

The benefits include contributing to the acceleration of a low carbon economy, the decarbonisation of heat and transport, and a marked reduction of waste volumes going to landfill. The economic benefits include new investment opportunities which will provide affordable energy for consumers, and the possibility of increased local control over waste processing linked to green energy production.

This document describes the experiments carried out in the demonstration plant. These results were used to develop designs of commercial BioSNG plants set out in the Summary of Plant Design1. The designs show the technical feasibility of BioSNG production and underpin the economic assessment set out in the Summary of Commercial Results2. It fulfils the requirements of Successful Delivery Criterion 9.5 set out in the Ofgem Project Direction for the project dated 13th December 2013.

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2.0 Executive Summary

The purpose of this project was to demonstrate the technical, environmental and economic feasibility of the thermal gasification of waste to renewable gas (bio-substitute natural gas or BioSNG) through the construction of a demonstration plant. The results from this facility have validated the technical and commercial models of the process and enabled the development of the first BioSNG commercial plant which is scheduled to deliver gas to grid in 2018.

Fundamentally, the project has confirmed that it is possible to produce methane from a mixed waste feedstock. The combination of an oxy-steam fluidised bed gasifier directly coupled to a tar cracking plasma unit delivers a high quality, raw syngas with very low levels of organo-sulphur compounds. The downstream gas processing and polishing techniques provide syngas of sufficient quality for catalyst operation, with no evidence of sulphur-induced catalyst degradation, nor any other contamination or deactivation.

![Figure 1 - BioSNG Demonstration Plant](image)

The fundamentals of a once-through methanation process train have been established on the demonstration facility. For the commercial plant, Amec Foster Wheeler are providing their Vesta process which relies on similar principles and can be supplied with appropriate process guarantees.

A foundational element to this project has been the development of validated process models to enable confident prediction of plant performance. The methanation process comprises a complex system of reactions as shown in Figure 2, and kinetic data was derived experimentally in order to develop the models.
Figure 2 – The Methanation Process

Following the successful construction and commissioning of the Demonstration Plant, the plant components were first tested individually, then integrated operation and testing of methanation and refining was demonstrated, both on bottled gases and on waste-derived syngas.

A key tool in evaluating and optimising catalyst operation was an offline testing rig which was built and operated in parallel to the Demonstration Plant and which enabled the partners to quickly and efficiently analyse catalyst performance across a range of tightly controlled variables. The effects of operating temperature, pressure reactant concentrations and diluents were assessed. Steam was shown to have an important role in process control and in reducing carbon deposition.

A series of operational runs were undertaken on the Demonstration Plant to explore its operating envelope and to verify results from the offline work. Methane was produced at rates which significantly exceeded the 51kWth design rating. Data from this testing were used to develop designs of commercial facilities.

The high degree of correlation between model predictions, laboratory scale tests and Demonstration Plant results gives confidence in the thermodynamic and kinetic modelling and, therefore, the ability to predict performance of the commercial plant. This allows rapid assessments of different scales, configurations and feedstock types.

Heat loss on the Demonstration Plant was a significant issue. This was a result of scale, uncertainties over catalyst performance at the plant design stage and the impact of designing for experimental flexibility. Heat losses will be addressed in commercial plant design, with assurances secured from Amec Foster Wheeler.

A key element in delivering grid quality gas is the refining stage downstream of methanation. The facility provided demonstration of the efficacy of a single stage pressure swing adsorption (PSA) system for separation of carbon dioxide, as well as the potential to remove a proportion of residual hydrogen, nitrogen and carbon monoxide, although removal of these gases was associated with appreciable loss of methane to the tail gas stream. Whilst a PSA is feasible for this application, alternative separation techniques, such as chemical solvents, use heat to effect separation which offer the prospect of integration with the waste heat available from the methanation process and produce a high quality carbon dioxide.
stream that is suitable for industrial sales or storage.

In addition, this work has demonstrated the possibility of in situ low-level production of ethane and propane, offering potential environmental and economic benefits compared with conventional fossil propane enrichment.

Based on the work undertaken in this programme, a commercial plant, including the appropriate grid entry unit, will be able to meet the gas requirements of both the Gas Safety (Management) Regulations and Network Entry Agreement.

Operation of the Demonstration Plant has required development of a range of competencies within the operations team which are directly transferable to a commercial plant. In particular, this has required development of detailed safety assessments and provided extensive operational experience with regard to handling combustible gases at high temperatures and pressures, as well as safe catalyst handling. This invaluable experience will form the basis for safe operation in commercial facilities.
3.0 Background

3.1 Process Overview

BioSNG production is a five-stage process as shown in the Figure 3.

The stages are:

- **Fuel Preparation**: Drying, shredding and removal of recyclates from feedstocks to produce a fuel that is compatible with the thermal treatment.

- **Thermal Treatment**: Gasification of the prepared feedstock to produce a synthesis gas that can be converted into biomethane. For successful downstream processing, this gas must be low in tars and long chain hydrocarbons.

- **Cooling and Cleaning**: The synthesis gas will contain contaminants such as sulphur and chlorine compounds or heavy metals that would hinder the next stage. This requires a combination of wet scrubbing, activated carbon filtration and other polishing media to deliver reduction of contaminants to the parts per billion level necessary for successful operation.

- **Gas Conversion**: A combination of catalysed reactions comprising the water gas shift and methanation reactions is used to convert the syngas to natural gas.

- **Refining**: To meet the specifications for grid or transport applications, the product gas must be refined, primarily through the removal of carbon dioxide, as well as management of other components such as hydrogen and nitrogen. As with biomethane from Anaerobic Digestion pure methane currently requires dosing with propane to meet network entry calorific value requirements.

3.2 Technical approach to undertaking the project

A primary objective of the project was to establish the basis for the design and delivery of a commercial BioSNG plant. As shown in Figure 4, this was achieved through the construction, commissioning and operation of the Demonstration Plant in conjunction with an offline testing facility developed during the project. Together with the development and validation of analytical models, the underlying process was understood and optimised. This work underpinned the development of the commercial plant design. During the programme over 40 experimental test runs were performed in the various facilities, in addition to offshore testing work during the early part of the project.
Figure 4 - Basis for the Design & Delivery of a Commercial BioSNG Plant

In the course of the work a number of academic journal papers have been produced. The first of these is in press.
4.0 BioSNG Process and Facilities

4.1 Process Design Rationale

The production of substitute natural gas from coal is a well-established process, being practised for example at the Dakota synfuels plant in the USA for over 30 years. Production of BioSNG presents a number of issues demanding specific design choices and technical solutions.

The demand for low carbon solutions for heat and transport is receiving increased international attention, for example with the Gobigas project in Gothenburg and the Engie BioSNG research facility in Lyon. Both these facilities are focused on pure biomass feedstocks. In light of the dominance of waste in the UK bioenergy landscape as well as the wider economic attributes, this project is focused on waste-derived biomass.

BioSNG plants must be at a significantly smaller operational scale than coal to SNG plants (10-100MWth output compared with 1000MWth) due to the distributed nature of biomass and waste arisings and the lower energy density of the feedstock. This has important implications for many aspects of the plant design, specifically the gas processing and methanation approach.

The chemistry and form of the feedstock, as well as scale of operation, means that unlike coal, it cannot be processed using established high intensity, high pressure entrained flow gasification. The available gasification technologies for this service tend to produce a syngas that contains a range of complex hydrocarbons (‘tars’) and inorganic contaminants such as hydrogen sulphide and hydrogen chloride, with some evidence with indirect gasifiers of tars containing covalently bonded sulphur and chlorine. At the modest commercial scale associated with biomass or waste fuelled facilities it is economically impractical to use conventional syngas scrubbing techniques to handle the entire range of contaminants found in the syngas.

The approach taken in the project comprises a primary fluidised bed gasification unit, ideally suited to the conversion of heterogeneous feedstock with low melting point components, and a second, high temperature syngas treatment stage, comprising an electric arc plasma converter. Together these constitute the Gasplasma® process. The high temperature in the second stage breaks down tars and sulphur bearing species such as thiophenes delivering a carbon monoxide and hydrogen-rich intermediary gas which can be treated by conventional dry and wet gas processing and polishing techniques to remove contaminant components to the parts per billion levels required for methanation catalysis.

Indirect gasification, an alternative approach taken in other BioSNG processes, offers the potential efficiency advantages of a syngas containing up to 15% methane, as well as low inherent nitrogen levels. However, this high methane content in this pyrolysis gas represents the gaseous end of a spectrum of complex and condensable hydrocarbons, including cyclic, polycyclic and sulphur containing organic species. Removal of large quantities of complex organics down to levels which can be tolerated by a catalyst is particularly challenging. The design approach here is to produce syngas inherently free of such complex hydrocarbons.

Methanation catalysts are highly sensitive to sulphur and other contaminants; the high reaction rates can generate very high heat fluxes which can lead to thermal degradation, localised coking and catalyst sintering. In coal-scale SNG facilities this is typically addressed by complex reactor design and recycling of product gas to minimise reactant concentration and remove reaction heat. In the light of the scale of waste and biomass facilities, the strategic approach here is for a simplified once-through reactor system with the
retention of carbon dioxide and use of steam as diluents to provide thermal buffering and moderation of the reactions. A detailed understanding of the thermodynamics and kinetics of the involved reactions is necessary to properly design and optimise such reactors and, more importantly, to limit the risks during up-scaling from laboratory over pilot to commercial scale. This understanding is a key output of this project.

Unlike production of a fuel gas for direct combustion, delivery of a grid quality gas requires low levels of inerts such as nitrogen and argon. These are difficult to separate from methane and therefore it is preferable to limit them at the gasification stage. The chosen design approach is to use high purity oxygen in the gasification process, thereby controlling the main potential source of nitrogen contamination in the product gas.

For this facility, gas upgrading, primarily the removal of carbon dioxide, has been effected using a single stage Pressure Swing Absorption (PSA) system. This approach has been adopted in upgrading of conventional anaerobic digestion biomethane facilities but also holds the potential for removal of other gaseous components such as hydrogen, carbon monoxide and nitrogen.

### 4.2 Demonstration Plant

The syngas used in the project is a waste-derived syngas from Advanced Plasma Power’s (APP) existing Gasplasma® pilot facility, located at Swindon, which is converted and refined in a new, dedicated conversion and conditioning plant. These are shown in Figure 5 and the process flow diagram, Figure 6.

![Figure 5 - The Major Components of the Pilot Plant](image-url)
The Gasplasma® process is a combination of two distinct thermal process steps. The first is a bubbling fluidised bed gasification process in which steam and oxygen are used to partially oxidise the waste derived fuel. In the second step, the crude syngas produced by the gasifier is exposed to high temperatures (around 1200°C) in a separate plasma arc converter.

Downstream of the plasma arc converter, the syngas is cooled to below 200°C in a heat exchanger prior to treatment to remove any residual particulates and acid gas contaminants (mostly, chlorine and sulphur based components). This includes a dry filter (incorporating a ceramic filter unit with sodium bicarbonate and activated carbon dosing), an alumina hydrolysis reactor to convert any residual COS to H₂S, and then an oxidative alkaline wet scrubber. This provides bulk removal of nitrogenous compounds, chloride, fluoride and sulphur gases which may be present prior to demisting in order to reduce entrained water. An iron oxide pellet guard bed is used for any residual sulphur scavenging. Slightly negative pressure (5–10 mbar) is maintained using an induced draft (ID) fan located after the wet scrubber.

The outlet of the ID fan defines the system boundary between the original Gasplasma® pilot facility and the new BioSNG Demonstration Plant. In order to separate the operation of the Gasplasma® and the BioSNG Demonstration Plants, the syngas from the Gasplasma® process is compressed and stored. The syngas is generated at approximately 0.05 barg pressure and is compressed to 50 barg through a four-stage reciprocating compressor, featuring interstage cooling with condensate removal. The compressed syngas is then supplied to the BioSNG gas store which comprises four identical gas storage vessels. These vessels are capable of holding approximately 1.2 tonnes of compressed syngas. Each vessel features inert gas purge, pressure relief and vent connections.

To produce BioSNG, the compressed syngas is fed from the store to the main BioSNG process plant where it is subject to a series of process operations designed to transform the syngas from a mixture of hydrogen, carbon monoxide and carbon dioxide to a methane-rich gas that can then be further purified to produce a gas transmission quality substitute natural gas (SNG). These process operations comprise:
**Pressure Let Down System.** This section of the plant receives syngas from the high-pressure store and a heater electrically heats the syngas before releasing the pressure to the required plant operating pressure (in the range 2 to 20 barg). This initial heating is required to prevent the formation of solid, frozen carbon dioxide in the process pipework due to Joule-Thompson cooling during pressure reduction.

**Gas Conditioning.** The syngas is then electrically heated by further heaters to 400°C and controlled flows of either steam or steam-forming deionised water are added. The steam-laden syngas is then electrically-heated to provide the feed gas to the water gas shift reactor at a temperature sufficient to initiate the reaction.

**Water Gas Shift Reaction.** The high temperature water gas shift reactor comprises a tubular reaction vessel with a suspended canister containing ferro-chrome catalyst beads. In this reactor the syngas components are combined to enhance the hydrogen content via the moderately exothermic reversible water gas shift reaction:

\[
\text{H}_2\text{O} \text{(g)} + \text{CO} \text{(g)} \leftrightarrow \text{H}_2 \text{(g)} + \text{CO}_2 \text{(g)}
\]

**Guard Bed.** The shifted syngas from the water gas shift reactor passes through a single guard bed tubular reactor containing a suspended canister of zinc oxide in which residual sulphur contaminants (principally hydrogen sulphide) are removed:

\[
\text{ZnO} \text{(s)} + \text{H}_2\text{S} \text{(g)} \rightarrow \text{ZnS} \text{(s)} + \text{H}_2\text{O} \text{(g)}
\]

**Methanation Gas Preparation.** Some or all of the cleaned, shifted syngas from the guard bed passes through a water-cooled heat exchanger to cool the gas to a temperature appropriate for that required for downstream methanation reactors.

**Methanation Reactors.** The cooled, shifted syngas is then fed to the methanation reactors. The gas can be sent to any or all of the three physically-identical methanation reactors. The reactors each contain a suspended canister containing differing catalyst beads, comprising nickel-based catalysts of differing activity. As the gas passes through these catalyst beds the hydrogen and carbon monoxide within the shifted syngas are reacted together to produce methane, thus:

\[
3\text{H}_2 \text{(g)} + \text{CO} \text{(g)} \leftrightarrow \text{CH}_4 \text{(g)} + \text{H}_2\text{O} \text{(g)}
\]

The water gas shift reaction given above and the Sabatier reaction:

\[
(4\text{H}_2 \text{(g)} + \text{CO}_2 \text{(g)} \leftrightarrow \text{CH}_4 \text{(g)} + 2\text{H}_2\text{O} \text{(g)})
\]

also have an influence on product formation in the methanation reactors.

Methanation is a highly exothermic reaction and leads to significant rises in temperature across the reactors. The methanation reaction chain includes a number of features specifically designed to mitigate and/or control this exothermic temperature rise (which reduces methane yield) including:

a) inter-reactor cooling through a water-cooled heat exchanger unit,

b) individual control of addition of inert ‘ballast’ gas to each of the methanation reactors,

c) individual control of fresh shifted syngas feed flows to each methanation reactor,

d) an ability to divert some or all of the product gas flow from the individual methanation reactors, so
bypassing downstream reaction stages,

e) an ability to cool the shifted syngas feed flows, and

f) the geometric arrangement of catalyst and inert bed material.

As the shifted syngas passes through the series of methanation reactors the concentration of methane rises steadily to approximately 30%, while the levels of hydrogen and carbon monoxide drop away to near zero levels.

**Product Gas Conditioning.** From the final methanation reactor the methanation product gas is cooled through a water-cooled heat exchange unit and thence passes to a knock-out pot where any condensed water droplets are removed from the gas stream.

**Pressure Swing Adsorption.** The methanation product gas contains a mixture of primarily methane and carbon dioxide, with some residual nitrogen, hydrogen and carbon monoxide. This gas mixture is then passed to a pressure swing adsorption (PSA) unit where the gases are separated from one another to yield a methane-rich product stream and a carbon dioxide-rich tail gas stream.

The entire process has been designed to be automatically operated by a control system which monitors the process conditions and takes appropriate actions where necessary to ensure the process remains both safe and controlled.

The gas composition was continuously monitored using an IR Xenta 4210 analyser in the Gasplasma® facility, a Gasmet Fourier Transform Infrared (FTIR) Continuous Emissions Measuring System (CEMS) and Gas Data Click! gas analyser in the BioSNG facility and, in the PSA unit, a Siemens Ultramat 23 for CO/CO₂ and a Siemens Calormat for Hydrogen.

The plant was specifically designed to operate over a broad range of conditions, with flows of up to 51 kW (of thermo-chemical energy) of methane product gas and at reaction pressures of between 2 and 20 barg.

### 4.3 Offline Facility

Throughout the project, focused testing on smaller scale experimental facilities has been recognised as important. Such an approach enables tight control and easily changed experimental conditions (flux rates, gas compositions, pressures and temperatures), and quick change out of catalysts, so different configurations of very active catalysts can be easily trialled and replaced. Practically, gas volumes are much lower than in the Demonstration Plant and rapid cold start can be achieved.

During the course of this project, a new dedicated offline facility was developed in order to secure these advantages. Results facilitated further development of the kinetics of the process, validation of modelling, and, when combined with Demonstration Plant data, confidence in up-scaling from demonstration to commercial scale.

This plant is designed to be operated at a range of reactor space velocities up to 40,000 h⁻¹, taking feedstock derived from bottled gases, real syngas from the Demonstration Plant store, and steam, or mixtures of these. It enables accurate measurement and control of input flow and composition with inlet temperatures in the range 200°C to 450°C and operation up to 10 barg into a range of reactor geometries, with detailed instrumentation for temperature and gas compositions. The equipment is spread across two mobile skids, as shown below in **Figure 7** and the P&ID for the process, **Figure 8**.
Figure 7 – Offline Facility

Figure 8 - Offline Facility Piping and Instrumentation Diagram
5.0 Establishment of Reaction Kinetics for Process Modelling

An important element to this project has been the development of validated process models to enable confident prediction of plant performance.

5.1 Shift Catalysis

A range of offline test runs were undertaken to confirm the kinetics of the water gas shift reaction for this system using a high temperature iron oxide (Fe₃O₄) shift catalyst. This was achieved with a suite of tests using various concentrations of carbon monoxide and steam to establish the order of the reaction. Combined with literature data, the final rate equation was established as shown below.

\[ r_{CO} = 10^{1.16} \exp \left( \frac{-94 \pm 2}{RT} \right) \cdot p_{CO}^{0.91} \cdot p_{H2O}^{0.02} \cdot p_{CO2}^{-0.16} \cdot p_{H2}^{0.05} \left( 1 - \frac{1}{K \cdot p_{CO} \cdot p_{H2O}} \right) \]

Where \( r \) is the reaction rate (mol gcat\(^{-1}\) s\(^{-1}\)); \( R \) is the universal gas constant (kJ mol\(^{-1}\) K\(^{-1}\)); \( T \) is the reaction temperature (K); \( K \) is the equilibrium constant for WGS reaction, and \( P \) is the partial pressure of the gas component.

The derived rate equation was compared to experimental data from an earlier test, showing good agreement, with both curves approaching the equilibrium conversion for outlet temperatures above 350°C, as shown in Figure 9 below.

5.2 Methanation Catalysis

There is a complex range of interrelated reactions occurring during the methanation process. These are governed, not only by the thermodynamics, but critically, the reaction kinetics.

Testing work was undertaken both at Catal International Ltd., the catalyst provider’s facility, and subsequently on the offline facility developed as part of this project. The primary testing for the purposes of development of base kinetic data was undertaken using an 8% Nickel-Alumina (8%Ni-Al₂O₃) methanation catalyst with a surface are of 160 sq.m/g and packed with a bed voidage of 0.46.

The kinetic data sought included both the activation energy for the methanation reaction and the order of...
the reaction with respect to hydrogen and carbon monoxide concentration. It was found that, in order to properly model the reaction, it was necessary to consider steam methane reforming, water gas shift and reverse water gas shift reactions, all of which took place simultaneously with methanation in the reactor. These key reactions, along with others in the system are shown below in Figure 10.

Figure 10 - The complex system of reactions taking place in the methanation reactors

The methanation carbon monoxide and hydrogen reaction orders were assessed experimentally over a range of temperatures up to 470°C and fitted to an empirical power law model. This supported the proposition that such a relationship is suitable for modelling the kinetics of methanation over the chosen catalyst using selected gas compositions and temperature range.

Taking all of these into account, it was possible to produce a model for the reaction network, as reported in Table 1 below.
<table>
<thead>
<tr>
<th>Reaction name</th>
<th>Activation energy</th>
<th>Pre-exponential factor</th>
<th>Reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Ea [kJ/mol]} )</td>
<td>( A )</td>
<td>( a )</td>
</tr>
<tr>
<td>R1 ( r_{CH4} )</td>
<td>95.8</td>
<td>4.33E+10</td>
<td>alpha</td>
</tr>
<tr>
<td>R2 ( r_{WGS} )</td>
<td>57.9</td>
<td>2.26E+07</td>
<td>0.57</td>
</tr>
<tr>
<td>R4 ( r_{SMR} )</td>
<td>193.5</td>
<td>1.12E+18</td>
<td>-</td>
</tr>
<tr>
<td>R5 ( r_{WGS} )</td>
<td>165.6</td>
<td>1.64E+14</td>
<td>-</td>
</tr>
</tbody>
</table>

**Appendix A** Sheaf of lines equation

**Appendix B** (with pressure CO and \( \text{H}_2 \) in barg: temperature in Celsius)

**Appendix C** CO (\( \text{alpha} \))

**Appendix D** alpha = \( [1.38 \times 10^{-3} + 1.07 \times 10^{-6} \times (760 \times \text{pH}_2 - 100)] \times T + [-0.576 - 5.55 \times 10^{-5} \times (750 \times \text{pH}_2 - 100)] \)

**Appendix E** \( \text{H}_2 \) (\( \text{beta} \))

**Appendix F** beta = \( [-1.59 \times 10^{-3} + 1.85 \times 10^{-6} \times (760 \times \text{pCO} - 20)] \times T + [1.117 + 1.82 \times 10^{-3} \times (750 \times \text{pCO} - 20)] \)

**Table 1 – Reactions network model**

Based on this modelling, methane production was predicted for a single reactor using the 8% Nickel-Alumina catalyst referenced in the foregoing and assessed against experimental data. As shown in **Figure 11**, this provides good agreement, with these reaction characteristics subsequently used and validated in Aspen simulations of demonstration plant operation. This work has formed part of a peer-reviewed academic journal paper submission.
6.0 Establishment of Operating Conditions and Initial Testing

Extensive experimental work was undertaken in conjunction with the modelling to establish the appropriate process operating conditions.

6.1 Shift Conditions

Offline tests were undertaken which supported the process modelling. This confirmed that for the high temperature iron oxide (Fe$_3$O$_4$) pelletised material, 335°C is a suitable operating temperature, at which the carbon monoxide level would be reduced from typical inlet levels of 30-35% vol. to 12-14% vol with corresponding increase in hydrogen.

6.2 Methanation Conditions

In order to select a suitable catalyst for the Demonstration Plant, further testing was undertaken using the range of catalysts of different nickel concentrations and both high and low active surfaces. Experimental runs were performed, seeking to determine the necessary catalyst loading and configuration, the design operating conditions, and the effect of gas space velocity and the various gas compositions on catalyst performance. Together this data, along with the new process model, was used to determine appropriate reactor design, catalyst configuration and operating conditions for the Demonstration Plant. A range of important insights were gained through this work, specifically:

- 8%Ni-Al$_2$O$_3$ can be successfully used as the bulk catalyst in the first methanator of the BioSNG plant. The catalysed reaction lights off at 330°C.
- 12%Ni-Al$_2$O$_3$ can be successfully used as the bulk catalyst in the second methanator of the BioSNG plant. The catalysed reaction lights off at 330°C.
- 22% Ni-Ca-Al$_2$O$_3$ shows potential for use in a final methanator, where very high carbon monoxide
conversion and methane selectivity are required.

- Initial operation of fresh catalyst always gives rise to rapid conversion and a sudden increase in reactor temperature with consequent partial catalyst deactivation. Thereafter the process is stable and controllable.
- The use of diluent, particularly at start-up, assists with process management.
- An annular catalyst configuration, especially in the first two methanation stages, aids in reaction control and exotherm mitigation without allowing significant levels of gas bypass.

Based on this work and in light of early work on the Demonstration Plant, the methanation catalyst configuration was developed to increase activity through the system to maximise methane production and control the reaction exotherm. The first reactor configuration is shown in Figure 12. The second reactor is based on a similar configuration, albeit a more active catalyst. The third reactor is configured as a conventional single packed bed.

![Figure 12 - First methanation reactor configuration](image)

6.3 Demonstration Plant Start-up and Early Testing

In order to deliver a safe and experimentally well-managed programme, a progressive approach was taken to operational testing, through the initial use of bottled gases to provide well characterised and controlled gas compositions and by testing each element of the system.

Initial testing activities related to preparation of the demonstration facility, including purging of the gas store to ensure safe, oxygen-free operation and operation of the process gas heaters. Testing with bottled gas demonstrated that each worked according to design and also allowed process heat losses to be ascertained. The losses associated with the piping between the larger heater and the methanators, as well
as the losses from the reactor vessels to the structure, were found to be significant. This issue and methods to address this are discussed separately below.

Early testing of the water gas shift demonstrated successful operation. From the experimental results it was possible to derive a figure for the exotherm of the reaction which was calculated as 39.3kJ/mol. This was in good agreement with the value of 41.1kJ/mol found in the literature and consistent with the modelling work.

Early work on the methanator system established that it was necessary to refine the reactor configuration as described above as well as to use a pre-reduced catalyst. This was in part due to the heat losses experienced in the system, but also due to higher reduction temperatures required in practice for the selected catalysts, together making in-situ reduction difficult to accomplish.

Following the changes to the reactor configuration and actions to mitigate heat losses, the first stage methanator was tested using diluted bottled gases. Methane was successfully produced at rates varying from 18kWth to 62kWth, exceeding the original design capacity for all three reactors of 50 kWth rate3. Methane yield across the test varied between 10 and 52%, with selectivity ranging from 42.6 to 81.5% as feedstock concentrations were changed. The exotherm was assessed to be 182kJ/mol, lower than reported figures for CO methanation (206 kJ/mol) and higher than that for CO2 methanation (165 kJ/mol). This is further confirmation that the reaction set is more complex than simple CO-methanation, with CO2-methanation and (reverse) water gas shift also relevant.

Early operational work on the PSA demonstrated largely complete automation, albeit with minor adjustments to the vacuum pump and cycle times that had to be made during continuous operation which was subsequently addressed, with typical pressure cycles shown in Figure 13 below. Successful removal of CO2 from a bottled gas CO2/CH4 mixture was demonstrated.

During this initial testing phase, satisfactory operation of each individual plant element was achieved, with experimental results in line with theoretical models, therefore providing a platform for more detailed testing including integrated operation.

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3 Enhanced performance is due to the higher-than-anticipated heat losses from the reactor, which enable operation at closer to isothermal conditions. This allows the reaction to be driven further towards completion before thermal equilibrium is reached.
6.3.1 Heat Loss

As noted above, during the work, significant heat losses were encountered, both due to the small scale and flexible nature of the plant, but also due to the higher operating temperatures of the finally selected catalysts. Substantial process alterations were necessary to overcome the associated issues. These alterations included installation of trace heating beneath the insulation on key pipework and increasing mass flow through the system by increasing inlet pressure of gas and some plant rerouting. This delivered an increase of 50°C at the inlet of the first methanation reactor, to 330°C.

As outlined above, changes to reactor configuration including the use of pre-reduced catalysts and using a layer of high-activity catalyst in first two methanator vessels, enabled activation at a lower inlet gas temperature and increased temperature through the reactor. Together these changes achieved successful methane production. However, it is noted that the requirement for increase in mass flow compared with the initial design exceeded the physically available quantity of steam for the water gas shift for this plant. This reduced the H₂:CO ratio in the pre-methanation syngas.

In order to achieve integrated operation, the following further changes were introduced: increased levels of insulation and trace heating, the use of thermal blocks in the pipework, insulating heating blankets at the base of reactor units and vessel preheating using inert gas passed through process heaters.

It is important to consider whether similar heat loss issues are likely to be encountered on commercial-scale plants. For heat loss between vessels, both the surface area of the pipes and the quantity of interconnecting pipework are important, and also their relationship to the quantity of gas being transported. Demonstration plants are inherently small scale; therefore pipework has a substantially higher surface area per unit of gas transported, increasing heat loss. Because future plants will be at larger scale, with lower surface areas per unit of gas transported, it is expected that heat loss from future plants will be less problematic. This view is supported by experience from chemical plants worldwide.

In the Demonstration Plant there are significant lengths of interconnecting pipework, primarily because as an experimental facility it was deliberately designed to be flexible. Therefore, much heat is lost to other areas of the plant via conduction. Again, at larger scale, the ratio of gas flow to interconnecting pipework will be more favourable and the process will be designed for a single duty not experimentation, so it is expected that heat losses will not present such a problem. In addition, thermal breaks were not included between reactors and the building frame they are mounted on; reactors in commercial plants will be suspended on three or four pins rather than mounted directly to floor.

Experience on this plant has shown the importance of 3D CAD modelling to optimise layouts and assist in minimising pipe lengths; this learning will translate to the design of commercial plants.

As part of the development of the first commercial plant, extensive discussions have been held with the provider of the shift and methanation process element, Amec Foster Wheeler, and assurances have been received that the process has been optimised and insulated such that this will not be an issue.
7.0 Integrated Operation and Detailed Methanation Testing

Having proven the operation of individual components of the BioSNG Demonstration Plant, integrated operation of methanation and refinement was achieved, both from bottled gas feedstock and waste-derived syngas. During this work, the core process modelling was validated. The potential effect of sulphur and other contaminants on the catalysts was tested. Extensive further assessment was undertaken to further understand the operational envelope of the process including effect of temperature, pressure, the role of diluents particularly steam, reactant concentration and further validation of catalyst configuration. The technical and operational learning from this work underpins development of the first commercial facility.

7.1 Syngas Production

Prepared municipal waste was sourced from Swindon Borough Council’s Waterside Materials Recovery Facility. This was supplied in floc form, in a density range of 150–250 kg/m$^3$ and particle size between 10 and 25mm, with a typical composition as shown in Table 2 below.

<table>
<thead>
<tr>
<th>RDF (as received)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description:</td>
</tr>
<tr>
<td><strong>Proximate analysis, % (w/w)</strong></td>
</tr>
<tr>
<td>Fixed carbon</td>
</tr>
<tr>
<td>Volatile matter</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td><strong>Ultimate analysis, % (w/w)</strong></td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>GCV, MJ/kg (dry basis)</td>
</tr>
</tbody>
</table>

*Table 2 - Refuse derived fuel composition*

A number of Gasplasma® runs were undertaken to provide sufficient syngas for the testing programme. The pilot gasification facility has been in operation since 2008 and these tests were reasonably typical with cold gas conversion efficiencies of 78.4% on an LHV basis. Commercial scale operation with associated lower heat losses have previously been established to be in excess of 83%. The existing gas processing train
operated normally, with evidence of successful operation of the newly installed COS hydrolysis unit. The stored gas composition is shown in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stored syngas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>35.77 vol.%</td>
</tr>
<tr>
<td>CO</td>
<td>33.20 vol.%</td>
</tr>
<tr>
<td>CO₂</td>
<td>23.54 vol.%</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.67 vol.%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.89 vol.%</td>
</tr>
<tr>
<td>Other</td>
<td>4.90 vol.%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00 vol.%</td>
</tr>
<tr>
<td>Trace contaminants</td>
<td></td>
</tr>
<tr>
<td>H₂S + COS</td>
<td>&lt; 50 ppmv</td>
</tr>
<tr>
<td>Organic sulphur</td>
<td>&lt; 30 ppmv</td>
</tr>
<tr>
<td>Tars (+C6)</td>
<td>&lt; 18 μg/m³</td>
</tr>
<tr>
<td>Acetylene</td>
<td>&lt; 40 ppmv</td>
</tr>
<tr>
<td>Energy Analysis</td>
<td></td>
</tr>
<tr>
<td>Net Calorific Value</td>
<td>8.75 MJ/kg</td>
</tr>
</tbody>
</table>

Table 3 - Stored syngas composition

On this facility, a nitrogen carrier gas was used to preheat the downstream system to operational temperatures. It also allowed progressive introduction of reactants over the catalyst during first use to assist process control of the exotherms. On a commercial facility carbon dioxide would be used for this function in order to avoid nitrogen ingress and, as discussed below, moreover to provide enhanced process control compared with nitrogen.

7.2 Water Gas Shift

The aim of the water gas shift reaction is to produce an outlet gas with an H₂:CO ratio optimised for methanation. The facility uses a high temperature Fe₃O₄ shift catalyst in pellet form. Sustained operation was achieved on both bottled gas and waste derived syngas. The average exotherm measured during the trial of 42.5kJ/mol was in line with literature values. Typical compositional values at the exit of the shift are shown in Table 4.
### Table 4 - Post water gas shift gas composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Composition</th>
<th>High Temperature Shift Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>vol.%</td>
<td>41.79</td>
</tr>
<tr>
<td>CO</td>
<td>vol.%</td>
<td>16.57</td>
</tr>
<tr>
<td>CO₂</td>
<td>vol.%</td>
<td>31.47</td>
</tr>
<tr>
<td>CH₄</td>
<td>vol.%</td>
<td>1.09</td>
</tr>
<tr>
<td>H₂O</td>
<td>vol.%</td>
<td>4.96</td>
</tr>
<tr>
<td>Other</td>
<td>vol.%</td>
<td>4.12</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>vol.%</td>
<td>100.00</td>
</tr>
<tr>
<td><strong>Trace Contaminants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S + COS</td>
<td>ppmv</td>
<td>-</td>
</tr>
<tr>
<td>Organic sulphur</td>
<td>ppmv</td>
<td>-</td>
</tr>
<tr>
<td>Tars (+C6)</td>
<td>µg/m³</td>
<td>n.a.</td>
</tr>
<tr>
<td>Acetylene</td>
<td>ppmv</td>
<td>n.a.</td>
</tr>
<tr>
<td><strong>Energy Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Calorific Value</td>
<td>MJ/kg</td>
<td>7.28</td>
</tr>
</tbody>
</table>

#### 7.3 Methanation Process

Early work on the first methanator was used to validate the process model. Post-shift syngas was introduced to the first reactor at 1barg. During steady state operation, methane was produced at rates between 12 and 26kWth and at concentrations of 9-12% in volume (when normalised for nitrogen content), equating to 30-33% CO conversion.
Figure 14 - Measured gas composition on first stage syngas methanation using 8%Ni/Al₂O₃ catalyst. Inlet-Outlet temperatures: 360-493°C. Values normalised for diluent N₂ content.

This is slightly lower than the equilibrium value of conversion but compares favourably with the 22kWₚₖ predicted by the process model, as shown in Table 5. This slightly enhanced performance may be due to system thermal losses that permit the reaction to be carried out at lower than adiabatic temperature increases.

<table>
<thead>
<tr>
<th>Quality Parameter</th>
<th>Model</th>
<th>Demonstration Plant*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ vol.%</td>
<td>23.53</td>
<td>(21.1) #</td>
</tr>
<tr>
<td>CO vol.%</td>
<td>14.18</td>
<td>12.82</td>
</tr>
<tr>
<td>CO₂ vol.%</td>
<td>31.35</td>
<td>29.8</td>
</tr>
<tr>
<td>CH₄ vol.%</td>
<td>9.98</td>
<td>11.1</td>
</tr>
<tr>
<td>H₂O vol.%</td>
<td>16.3</td>
<td>19.5</td>
</tr>
<tr>
<td>N₂ (from syngas) vol.%</td>
<td>4.66</td>
<td>(5.68) #</td>
</tr>
<tr>
<td>TOTAL vol.%</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Energy Analysis

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>Demonstration Plant*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Calorific Value</td>
<td>7.05</td>
<td>7.34</td>
</tr>
</tbody>
</table>

* Values normalised for nitrogen dilution. # Calculated

Table 5 - Gas composition after methanation in the first reactor

There is good comparison between the model prediction and Demonstration Plant results, with the predicted values deviating from the experimental results within the range of 5–10%. Differences are considered to be due to syngas flow uncertainties and thermal losses within the system rather than from
the predictive model. Higher margins of errors were found for N₂ and H₂O, mainly related to the limitations of steam injection system compositional measurement techniques.

This work also confirmed that the 8%Ni/Al₂O₃ is well suited for the first reactor providing process control without product recycle loops or in-vessel heat extraction systems. Up to 44% of total methanation can occur over such a catalyst, with the stream CO₂ and steam content providing a form of ballast to mitigate the methanation exotherm in the process stream. A higher activity catalyst can be used to methanate higher levels of CO in the subsequent two stages which operate at lower temperatures, with correspondingly higher CH₄ levels in the outlet. Operation of the three reactor vessel system has been modelled as shown below in Figure 15.

![Figure 15 - Average gas composition at main stages of the process](image)

*Figure 15 - Average gas composition at main stages of the process*

HT Shift (outlet temperature: 353 °C), MTH-1 (outlet temperature: 498°C), MTH-2 (outlet temperature: 412°C), MTH-3 (outlet temperature: 310 °C).

Subsequent work into highly active catalyst designed to achieve high outturn CO conversions for use in a final methanation reactor supported these findings.

The high degree of correlation between model predictions, lab scale tests and Demonstration Plant results for the first stage methanation investigated in this study gives confidence that the same power law model can be used to predict the outputs of the second and third methanators, based on appropriate kinetic parameters for higher nickel content and activity of the catalyst. Furthermore, the results show that the catalysts were performing as expected when using a waste-derived syngas when compared to models derived from work using high purity bottled gases.

Extensive trials were undertaken on the Demonstration Plant incorporating integrated operation. Over the trials, methane outputs of greater than 50kWₑ were routinely produced from the first reactor and between 80-140kWₑ for the combined first and second reactor system which were found to perform as expected. Methane concentrations from the second reactor of between 18-21% were achieved, in line with the equilibrium value from the steam to carbon ratio.
Operating at high throughputs was found to be necessary in order to address the heat loss issue and allow fully integrated operation. Throughputs were well in excess of the plant design capacity (51kWth total). However, at this level of throughput the plant was unable to deliver sufficient steam, even using an auxiliary boiler, for the water gas shift to deliver the required H₂:CO ratio. At peak flow this reduced to a ratio below 2.5:1 compared with the equilibrium requirements of 3:1 and a ratio of 4:1 which the extensive offline work in this programme identified as preferred. As a consequence, whilst CH₄ levels of around 21% were achieved and H₂ levels were down to 2% at exit from the second reactor, the CO remained at around 18%.

From this it is clear that the artificial constraining of the shift reduced the level of reaction and therefore exotherm in the second methanator. Combined with the previously described heat losses, this meant that the third methanator was not at sufficient temperature for the 12% Ni/Al₂O₃ catalyst to be active. Both of these limiting factors are fully understood and readily overcome on a commercial plant by reactor heat management and careful selection of catalyst activity to match specific reactor operating conditions.

Notwithstanding some of the practical issues experienced, the plant achieved levels of methane production at nearly three times the design capacity. Successful operation was achieved on waste derived syngas and the high degree of correlation between model predictions, lab scale tests and Demonstration Plant results provides a sound basis for the design and performance of a commercial plant.

### 7.4 Integrated Operation of the PSA

Integrated operation of the PSA was achieved on waste derived syngas operating through the methanation train. As with bottled gases, CO₂ removal efficiencies of over 99% were achieved, with evidence of ability to remove a proportion of H₂, N₂ and CO. This is presented in more detail in Section 8.0 Gas Refining.

### 7.5 Assessment of Catalyst Degradation on Waste Derived Syngas

A key element of this work was to establish that the syngas from waste resources was of sufficient quality for catalyst operation. This was achieved both through operational testing and post operational catalyst microscopy.

A single methanator stage was operated on a continuous basis using waste derived syngas as shown below in Figure 17. This demonstrated, once stabilised, consistent catalyst activity over the period with CO
conversion of 59%\(^4\) with some CO\(_2\) methanation also observed. There was no appreciable reduction in activity. The temperature profile through the reactor was also consistent, supporting the conclusion that there was no catalyst degradation.

By way of a control, the same configuration was operated with the addition of hydrogen sulphide (H\(_2\)S) dosing at 100ppm. Methane production dropped to 0.5% within one hour and fifteen minutes after testing had commenced as shown in Figure 18. This demonstrated that, as expected, sulphur poisoning causes swift deactivation of the catalyst, providing confidence that the gas quality achieved from waste derived syngas in this process was of sufficient quality for sustained methanation.

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\(^4\) Brief gaps in production are due to the need to drain water from the impinger vessel.
Fresh catalyst as well as used catalyst from waste syngas operation was assessed using a variety of microscopy techniques. The morphology of the fresh Ni/Al₂O₃ catalyst was determined by Scanning Electron Microscopy (SEM). The sample exhibited a reef-type morphology, with presence of nanosheets, spinels and clusters. The leaf-like nanosheet structure and large pore volume provides large channels to allow the diffusion of reactants and products, improving the activity of the catalyst, and the large surface area promotes the dispersion of supported nickel, leading to high activity and stability. In addition, compositional assessment was undertaken using Back-Scattered Electron views and Energy-Dispersive X-ray spectroscopy (EDX) was used to provide qualitative and quantitative assessment of composition, particularly nickel dispersion. Similar assessment of the used catalyst was also undertaken.
In both cases the catalyst exhibited well-dispersed Nickel with 12% concentrations consistent with the catalyst specification. Importantly, from the EDX analysis, no Sulphur, Chlorine or Phosphorus was detected above the error threshold (+-1%). There was evidence of some limited carbon deposition on the used catalyst. This was a phenomenon expected from operational gas analysis and found to be controllable through appropriate levels of steam through the reactor.

7.6 Establishment of Operational Envelope & Optimisation

A combination of offline and Demonstration Plant tests were undertaken to understand the operational envelope, inform process optimisation and to assist the design on the first commercial facility.

7.6.1 Temperature

The methanation reaction is exothermic and the total stoichiometric number of moles of products is less than the number of moles of reactants. Therefore, the performance of the methanation reaction is improved as the reaction temperature decreases. Validation work was undertaken to verify the change in methane concentration at the reactor outlet as the temperature is reduced from 490°C to 370°C, shown in Figure 20 for the 12%Ni/Al2O3 catalyst. Both CO conversion and methane concentration increase, as expected for an exothermic equilibrium reaction. At low temperatures below 300°C the performance of the methanation reaction deteriorates due to limitations in the reaction kinetics.
7.6.2 Pressure

There are a number of factors for a commercial plant which determine the optimum operating pressure such as gas compression loads, vessel and pipeline size, pressure rating requirements and CO$_2$ separation technology, as well as the underlying reaction. The effect of pressure on reaction completion was assessed over a range of pressures between at 5.5 barg and 1 barg. This work confirmed that higher pressures favour methane production. This is expected according to Le Chatelier’s Principle, as CO methanation is a volume reducing reaction. Over this pressure range, conversion was increased by around 20% and CH$_4$ selectivity was also improved, with 15% less CO$_2$ being produced. However, at pressures above 10 barg, the performance of the methanation reaction deteriorates with lower selectivity towards methane due to increased reverse reaction rates and increase in carbon deposition. A further effect of increased pressure was higher CO$_2$ levels in the outlet gas.

7.6.3 The Role of Diluent

Managing and, therefore, controlling the exotherm in a once-through methanation process is critical. Over the testing period various diluents were assessed on the offline facility and the principles validated on the Demonstration Plant.

Steam provides a number of important functions in system control. According to Le Chatalier’s principle, it is expected that an increase in steam will inhibit methanation. There was some evidence from offline operation that this was the case, and operation of the Demonstration Plant demonstrated that steam attenuated the exothermic rise in temperature within the reactor. Higher levels of steam addition result in higher levels of CO$_2$ in the outlet stream, highlighting the influence of the water gas shift reaction in the system. Furthermore, steam also has a high heat capacity allowing greater removal of heat from the reactor.

Steam was found to have an important role in controlling carbon deposition. This is important as it could not only cause deactivation of the catalyst by encapsulation, but may even result in destruction of the catalyst and blocking of the reactor because of excessive growth of filamentous carbon. Trials on the offline facility demonstrated that inconsistency or absence of steam led to significant carbon deposition. However this could be effectively controlled by steam addition. Furthermore, it was demonstrated that steam carbon reforming (SCR) of carbon previously deposited on the catalyst could be achieved, providing evidence that steam could be potentially used in catalyst regeneration.
The addition of CO₂ was also found to play a role in reducing overall system temperature and inhibiting carbon monoxide conversion. An increase in quantities of steam and CO in the product gas proved the occurrence of reverse water gas shift which is thermodynamically favoured at high temperatures (> 400°C). This was established through extensive testing on the offline rig facility and the inhibiting effect validated on the Demonstration Plant. Maintaining CO₂ in the gas stream through the methanation process has a role in maintaining operational control.

It was also confirmed that N₂, even at high levels, did not significantly assist in exotherm control. As part of the offline work, N₂ and CO₂ were directly interchanged demonstrating clearly the above findings. Given the challenges that nitrogen presents with regard to downstream separation, it is not suitable for full-scale operation in any case and entrainment should be minimised.

Together this work shows that for a once-through methanation system, retention of CO₂ in the process stream through the primary methanation phase, as well as an excess of steam, is important in maintaining process control and catalyst activity. The first commercial facility will use the Vesta Methanation process, developed by Amec Foster Wheeler, which uses both of these characteristics.

### 7.6.4 Reactant Concentration

Both the selected core methanation catalysts, 8%Ni/LAS-Al₂O₃ and 12%Ni/LAS-Al₂O₃, used in the first and second reactors respectively, were tested to establish their response to the H₂:CO ratio.

The average conversion efficiency of CO for the less active catalyst (8%Ni/LAS-Al₂O₃) through the trial was 36.3%. Conversion efficiency and selectivity towards methane were found to be strongly dependent on H₂:CO ratio; at H₂:CO of 4:1, conversion was around 35%, with a 70% selectivity towards methane, whereas at H₂:CO of 3.5:1, CO conversion dropped to 28%, with a 60% selectivity towards methane. The conversion efficiency for the more active catalyst (12%Ni/LAS-Al₂O₃) was found to be similarly sensitive to H₂:CO, in this case dropping from 55% to 42% with H₂:CO dropping from 4:1 to 3.5:1 respectively.

At lower H₂:CO ratios, water produced by the methanation reaction reacts with CO in a shift reaction, producing CO₂. However, when there is a large excess of H₂ (>3), the reverse water gas shift reaction is favoured, and so, rather than CO reacting to produce more CO₂, CO₂ produces CO which can then be methanated. As a result, selectivity to methane and overall yield improve.

This work demonstrated an important sensitivity to the H₂:CO ratio with both conversion and selectivity towards methane substantially reduced with a lower H₂:CO ratio. This confirms that the lower H₂:CO ratio on the Demonstration Plant is a key cause of the residual CO, but provides confidence that under optimal conditions design levels of conversion should be achieved.

### 7.6.5 Latter stage methanation steps

Further work was performed to investigate the use of a highly active catalyst in a final methanation reactor designed to achieve high output CO conversions. This used a 22%Ni/Ca-AL₂O₃ catalyst in a bed diluted with 50% alumina for the bulk reactor and a pure catalytic layer for final conversion. This design is particularly suitable for the final methanation stage in which quasi-isothermal operation at low temperature and full CO conversion are required. Over the trial, the average CO conversion efficiency was 95% and methane selectivity close to 90%, in line with thermodynamic predictions. Outturn methane concentration averaged 32%.

The role of the Sabatier reaction was also investigated. Methanation of CO₂ proceeded with a yield of ~30%
and selectivity above 80% with the 12%Ni/LAS-Al2O3 catalyst. By replacing CO2 with CO, CO methanation was restored, with higher yield (~45%) and lower selectivity of 60-70% when compared to CO2 methanation at same conditions (although this may have been a function of the H2:CO2 ratio used). The Sabatier reaction is recognised to be important, particularly as a means to convert residual H2 at the back end of the process using highly active low temperature catalysts, as is used in the Vesta process.

The use of higher activity catalysts being used by Amec Foster Wheeler in the Vesta process for the commercial Compressed Bio-Methane plant was also investigated, with simulation of a series of methanators. In all cases, the measured compositions matched the modelled compositions, with a mixture of CO and CO2 methanation. In the first methanator, CO methanation appears to be the primary reaction. In the second methanator, it appeared that CO methanation and the waste gas shift both proceeded, but that the reverse Sabatier reaction was also influential. In the third methanator, the major reaction was the Sabatier reaction which proceeded forward but reverse CO methanation also took place.

7.6.6  Space Velocity

A number of tests were undertaken to establish the relationship between methane production and space velocity, an example of which is shown in Figure 21. The in-bed temperature was maintained at ~460°C, and space velocity was varied between 0.35 and 1.5 times the baseline. The clear correlation between residence time and conversion indicates that the catalyst conversion activity is similar across the range of space velocities. At low space velocities equilibrium is approached and further reduction gives only minimal additional methane production. This data was valuable in validating process modelling.

![Figure 21 - Methane production as Space Velocity (GHSV) is varied](image)

7.6.7  Reactor Vessel Configuration

More detailed assessment of the annular vessel configuration was carried out using the offline rig and compared with standard configuration. The results were consistent, confirming that both systems were close to equilibrium and that the annular configuration did not result in significant quantities of gas bypassing the catalyst. The temperatures observed during the run were more consistent than previously with more stable product component concentrations, indicating that the annular configuration achieves its primary aim of aiding reaction control and mitigating the exotherm. This configuration also reached optimum catalyst activity at a lower temperature, with benefits for methane yield and, it should be expected, catalyst longevity. Whilst this approach is not used in the Vesta process, it demonstrates a
potential design technique for enhancing process control if required.

7.6.8 In-situ Enrichment

Due to the differences in calorific value between natural gas generally flowing in the UK gas networks and pure methane, biomethane will not meet the minimum threshold for entry into the local gas network. As with biomethane from anaerobic digestion, this can be overcome with fossil propane addition at the point of entry. Economic and environmental advantages could be gained if alkanes such as ethane and propane could be generated as part of the BioSNG process in proportions sufficient to raise the CV of the product gas. This concept was conceived and patented prior to the commencement of this project.

Using the offline facility, this principle was tested using an iron-ruthenium catalyst in both the conventional and annular configuration reaction vessel. The objective of producing significant proportions of ethane and propane was achieved, under a variety of operational conditions.

![Figure 22 - In situ production of Ethane, Propane and Hexane](image_url)

For significant periods of operation, ethane production exceeded 10% and propane production exceeded 4%. These levels are sufficient to ensure that the product gas meets the CV requirements for network entry without the need for fossil propane addition.

As with the methanation work, the operational characteristics were investigated in more detail. It was observed that no hydrogenation reaction took place on the catalyst until the reactor temperature had exceeded 350°C and carbon had been deposited according to the Boudouard mechanism. Subsequently, hydrogenation was observed with temperatures as low as 250°C. This suggests that the reaction mechanism relies on dissociatively adsorbed carbon, rather than CO. The presence of methane in the feed gas also contributes to the production of C2/3 hydrocarbons by the hydrogen exchange reaction between methane and molecular hydrogen.

As with methanation, lower space velocity is advantageous for CO conversion and ethane and propane yields, and also reduces alkene production.

When CO2 was added to the feed, catalyst activity decreased by 60%, but no increase in water formation was observed; the catalyst does not appear to catalyse the reverse water gas shift reaction. Catalyst activity was immediately restored when CO2 addition ceased. As with methanation, maintaining partial pressure of water in the input was found to be important.

An increase in the H2:CO ratio was observed to increase the reaction rate, but dramatically decrease the selectivity to alkenes, so high H2:CO ratios favour both methane and alkane production.
A range of temperatures were trialled, and optimal selection towards alkanes was found at approximately 310°C, where 10-12% ethane and propane were consistently produced. Above 500°C, methane reforming became significant and no heavier alkanes were detectable.

In summary, this work has provided valuable evidence that it is possible to provide in-situ enrichment of the biomethane, to a level that avoids the requirement for fossil propanation. It is expected that this would be implemented either through a dedicated reactor or potentially as part of the catalyst mix in a downstream methanation reactor.
8.0 Gas Refining

There are a variety of techniques available to separate carbon dioxide from a raw biomethane or BioSNG gas stream including chemical or physical solvents as well as pressure swing adsorption (PSA). Each process has different selectivities towards CO₂ removal, with some chemical approaches being highly selective. PSA offers the prospect of also being able to separate other components, particularly H₂ and N₂ and also potentially CO, which may be beneficial as a tool for meeting gas quality specifications. This is an unusual duty and so this work has not been undertaken before.

8.1 PSA Assessment and Optimisation

Detailed investigations on the SNG refining plant were undertaken using both bottled gases and waste derived gases. The purpose of this work was: (a) to ascertain the ability to separate CO₂ as well as H₂, N₂ and CO; (b) to provide confidence that there were no adverse effects of operating on waste derived gas; and (c) to understand its ability to handle inevitable transients in gas composition in a gasification process. These issues were addressed and understood in the programme.

Figure 23 shows the removal efficiency of key process contaminants in the process, based on the volumes of each component removed compared with the input volume. The various runs represent a series of four baseline conditions (B1, B2, B3, Waste) and transients (T1 onwards) associated with each baseline condition. Operational settings were not adjusted under the transient conditions which covered a wide range of input variations (for example, Base 1 transients covered CO₂ +7%/-7%, H₂ +2%/-0.5%, N₂ +4%/-0.5%, CO+2%/0%, each absolute %vol).

![Figure 23](image.png)

*Figure 23 - Removal Efficiency of CO₂, H₂, N₂ and CO using the PSA system*

In all cases, the removal efficiency for CO₂ was extremely high (over 99%). This is the primary function of the PSA and was achieved very effectively and consistently.

The other primary target components for removal were N₂ and H₂. These were also removed consistently, with efficiencies of 40% (+/-0.15%) and 35% (+/-0.2%) respectively. This novel work demonstrates that the PSA is capable of removing appreciable levels of these components. However, despite this efficacy,
significant quantity of these components remains in the product stream, demonstrating that to meet gas grid quality requires upstream control of these components.

In all these cases PSA operation was extremely resilient under transient conditions and able to accommodate gas composition changes whilst maintaining gas removal levels.

CO removal efficiency was greater than for N₂ and H₂, although it was noted that CO removal was not set out as a primary objective in these tests which may explain the inconsistency in operation.

Operation on waste derived gas showed good consistency with bottled gas in terms of component removal and no signs of other adverse operational impacts. This is unsurprising given that the upstream catalysts are extremely sensitive to contamination, and so no rogue components would be expected to reach the PSA.

However, in achieving these levels of component removal, an appreciable level of methane slip was experienced, at least 20% in all cases. This is a consequence of optimisation for removal of the non-CO₂ components. Clearly, such levels of slip would not be acceptable in a commercial plant, both from environmental or economic reasons.

In summary, this work shows that a PSA is able to achieve high levels of CO₂ removal, operates effectively on waste derived gas and is able to deliver consistent separation under transient conditions. This also demonstrates that some removal of H₂, N₂ and CO can be achieved using a PSA, but significant levels of these components remain, and even at the levels tested here, there is appreciable methane slip. Therefore, the upstream process must be controlled to avoid these components which the wider works has demonstrated could be achieved on a commercial facility.

Therefore, whilst a PSA is feasible for this application, alternative separation techniques such as chemical solvents can also be used for this duty. Chemical solvents use heat to effect separation which offers the prospect of integration with the waste heat available from the methanation process. The high level of selectivity also means that the high quality CO₂ stream from such processes is suitable for industrial sales or storage without further purification.

8.2 Gas Grid Requirements

Commercial plants must comply with appropriate requirements for grid injection. The Gas Safety (Management) Regulations (GS(M)R) sets specifications that all gas injected into the UK grid must meet. All gas injected into the local grid is subject to a Network Entry Agreement (NEA), agreed between the producer and the local Gas Distribution Network (GDN). The NEA specifies criteria for the gas that are additional to those set out in GS(M)R. For waste-derived BioSNG, the gas must also meet End of Waste requirements outlined by the Environment Agency’s Biomethane from Waste Quality Protocol.

Based on the work undertaken in this programme, a commercial plant, including the appropriate grid entry unit with propane injection and odorising will be able to meet these requirements, as summarised below:

**Sulphur species:** Methanation catalysts are extremely sensitive to sulphur; these must and can be removed to ppb levels upstream for successful operation and therefore grid entry sulphur criteria will, de facto, be met.

**Hydrogen:** With sufficient reactors and using a more active catalyst for the last reactor, as used in the Vesta plant configuration, required hydrogen levels of 0.1% for GS(M)R can be achieved. However, a derogation
to introduce gas with higher levels of hydrogen, as allowed elsewhere in Europe, would simplify the plant, lowering capital and operational costs.

**Oxygen**: The presence of oxygen in the gas processing stream would present a high risk of syngas ignition and damage to active catalyst systems, and so the process will trip if oxygen levels greater than 0.1% are detected; BioSNG will meet this criterion.

**Organo halides**: Organo-halides are not expected to be present at problematic levels post-gasification and plasma treatment. Spot sampling will be used to verify this.

**Bacterial colonies**: Bacterial colony presence is not considered credible following thermal biomethane production.

**Siloxanes**: Siloxanes are not expected to be present in thermally produced biomethane.

**Other contaminants**: Appropriate filtration will remove solid contaminants present in the gas and is, in any event, required to ensure the sustained running of the methanation process. Heavy metals must be removed to limit levels to < 5ppb for the methanation process, so this criterion will be met. Olefins will be removed by hydrogenation prior to methanation. Other relevant contaminants (aromatic, poly-aromatic and poly-cyclic hydrocarbons, oxygenated species and ammonia) are not expected to be present at problematic levels, due in part to the plasma system employed. Spot sampling will be used to verify all components.

**Dewpoints**: Hydrocarbon and water dewpoint control is included as part of the process. For the commercial plant under construction, the gas will be injected at a maximum of 2barg at this pressure with a water dewpoint of -57°C with the hydrocarbon dewpoint lower still, thereby meeting the dewpoint criteria.

**Wobbe**: BioSNG, like conventional biomethane, will be enriched by propane addition. The CBM plant post-enrichment, will have a Wobbe number of 49.6MJ/m³, compliant with the entry criteria.

**Incomplete combustion factor**: BioSNG produced by the CBM plant will, post-enrichment, have an ICF of -0.5, compliant with the entry criteria.

**Soot index**: BioSNG produced by the CBM plant will, post-enrichment, have an SI of 0.52. This is compliant with the entry criteria.

**Calorific value**: The GCV of the pre-enrichment BioSNG is expected to be 36.3MJ/m³. The flow weighted average in the distribution zone will be met by addition of propane by the GEU, in common with anaerobic digestion biomethane facilities.

**Stenching/odorisation**: BioSNG injected to the grid will pass through a Grid Entry Unit including a system for odorising the gas. This is the case for all grid-connected biomethane plants.

**Pressure**: The gas will be injected to the network at the pressure agreed with the GDN, and specified in the NEA.

**Temperature**: Gas temperature will exit the BioSNG process within the required temperature range in the NEA, with a chiller used as required.
9.0 Key Technical and Operational Outcomes

The experimental and modelling work from this project has delivered significant technical and operational learning for commercial scale operation, as summarised below.

9.1 Plant design

Fundamentally the work has demonstrated that it is possible to produce methane from a waste feedstock. The Gasplasma® combination of an oxy-steam fluidised bed gasifier directly coupled to a tar-cracking plasma unit delivers a high quality raw gas with very low levels of organo-sulphur compounds. The downstream gas processing and polishing techniques have been shown to provide syngas of sufficient quality for catalyst operation, with no evidence of sulphur-induced degradation, nor other contamination or deactivation.

The fundamentals of a once-through methanation process train have been established on the demonstration facility. For the commercial plant, Amec Foster Wheeler’s Vesta process has been selected which relies on similar principles, but can be supplied with appropriate process guarantees.

For a once-through methanation process, retention of CO₂ as well as adequate partial pressure of H₂O in the process stream is important for process control. Steam in particular is found to mitigate carbon deposition in the catalyst beds. N₂ is not as effective as a diluent and is challenging to separate downstream so should be minimised at source. These findings are consistent with the Vesta process fundamentals.

The high degree of correlation between model predictions, laboratory scale tests and Demonstration Plant results across the range of scales, gives confidence in the thermodynamic and kinetic modelling and, therefore, ability to predict performance on the commercial plant. This allows rapid assessments of different scale, configuration and feedstock types. Experimental work using the catalysts that will be used in the commercial plant and internal modelling is consistent with heat and mass balances provided by Amec Foster Wheeler for the Vesta process.

The kinetic parameters assessed using the offline facility were further validated on the Demonstration Plant, providing confidence in the fundamental process understanding. The offline rig provides a highly controllable facility for establishing kinetic parameters as well as more general process operation. These can be used to validate parameters for catalysts, thereby reducing technical risk, and will also be a useful facility for trouble-shooting in the future.

Extensive work was undertaken in developing reactor geometries which provide greater levels of process control. Whilst these designs are not adopted in the Vesta process, knowledge of such approaches may be of assistance in the future.

Heat loss on the Demonstration Plant was identified as a significant issue. This was in part due to scale, as well as inherent design for experimental flexibility, which led to higher than anticipated losses. This will be addressed in commercial plant design which will also include uprated insulation (<0.03W/m.K) and electrical trace heating, with assurances secured from Amec Foster Wheeler. Further, the commercial plant will incorporate heat integration to maximise thermal efficiency.

This work demonstrated the possibility of in situ enrichment of biomethane, offering potential environmental and economic benefits compared with conventional fossil fuel propanation.

This plant provided demonstration of the efficacy of a PSA system for separation of CO₂ as well as the
potential to remove a proportion of residual H₂, N₂ and CO₂, although this was associated with appreciable CH₄ slip. Whilst a PSA is feasible for this application, alternative separation techniques, such as chemical solvents, use heat to effect separation which offers the prospect of integration with the waste heat available from the methanation process and produces a high quality CO₂ stream which would be suitable for industrial sales or storage.

### 9.2 Plant Operation

Operation of the Demonstration Plant has required development of a range of competencies within the operations team which are directly transferable to a commercial plant.

Operation of the demonstration facility was predicated on the development and risk assessment of standard operating procedures. Whilst the individual procedures may be different on a commercial plant, the skill set and fundamental approach developed is transferable.

Extensive experience was gained regarding safe catalyst handling requiring specific operational procedures. For a commercial plant specialist organisations will be used for this. Reduction of catalysts (reversion of catalyst metal oxides to their active metal forms) in-situ requires high operational temperatures; where possible pre-reduced catalysts simplify operations.

Safety assessments identified a number of control loops that required Safety Integrity Level (SIL) ratings. Whilst SIL assessments for a commercial design will be bespoke, the test and documentation competency developed by the plant operations team is directly transferable to commercial operation. The fundamentals of the safety pressure testing regime will be transferable to the commercial plant, albeit adapted to the design specifics. Detailed assessment has been made of the purge gas requirements and specific thresholds for residual O₂ content in the system. This important safety assessment and process control will be embedded in the commercial plant.

Operators were trained on the fully integrated control system for this flexible plant designed to handle the experimental work. This learning will be translated to the commercial plant which will use a Distributed Control System for which additional training will be undertaken.

The exposure of the Operators to the technology of pressurised catalytic reactors operating at high temperatures has provided opportunity for specific knowledge, language and vocabulary to be developed and to become part of the tacit knowledge skills set of the organisation.
10.0 Other BioSNG Documents

The following project documents are publicly available:

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<td>3rd December 2013</td>
<td>Final Network Innovation Competition full submission to Ofgem.</td>
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<td><strong>First Project Progress Report</strong></td>
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11.0 Contact Details

If you have any questions on the project or would like access to any project documents please contact:

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