

Local Chemical Creation and Manufacturing Opportunities

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Abstract

A circular economy has the potential to contribute economic and environmental benefits to the water industry by extending the value of materials through reuse and waste elimination. This project identifies three high value by-product streams from which water treatment chemicals can be manufactured: including the production of CO₂ from wastewater treatment biogas, extraction of high purity electrochlorination salt from desalination brine, and the regeneration of spent activated carbon. This paper presents an investigation into the first opportunity, identifying biogas as a stream with problematic impurities which must first be removed in a pre-treatment process. The concept design recommends a hybrid setup of membrane separation and cryogenic liquefaction to perform the final separation and purification of CO₂, for the advantages of modularity, scalability and established commercial use in other industries. The second stage of this project is to assess the economic viability of these proposed solutions, such that the highest potential opportunities can be identified and further explored by Water Corporation through process modelling and potentially pilot scale implementations.

1. Introduction

Promoting a circular economy within water treatment operations has had growing interest within Water Corporation in recent years. From an environmental standpoint, the reuse of by-product streams would enable the elimination of wastes and reduce impact of operations on the environment. It also presents commercial opportunities, to create products in a less resource intensive manner and to extend the value of limited materials.

There is also significant benefit to increasing the self-sufficiency of water treatment plants to mitigate supply chain issues, especially within Australia where many water treatment chemicals are heavily dependent on overseas imports and strongly influenced by external pressures (Productivity Commission, 2021). Currently, Water Corporation relies mainly on short-term solutions to mitigate this risk, such as chemical stockpiling and contingent sourcing. Each year these solutions become decreasingly cost effective, due to impractical storage costs and safety issues with stockpiling, and expensive surcharges when entering option contracts with contingent suppliers. For example, an interruption in carbon dioxide (CO₂) supply (a critical chemical utilised in pH control of drinking water) can result in incurred surcharges of 300-600% of the original price (Water Corporation, 2019). In this way, chemical recovery from waste and by-product streams would provide a longer-term solution to this issue.

Within this project, three circular economy opportunities have been investigated:

- 1) Recovery of CO₂ of appropriate quality for use in drinking water treatment, from biogas streams sourced from anaerobic digesters on wastewater treatment plants (WWTPs).
- 2) Recovery of high purity salt for use in electrochlorination processes (used to produce disinfectant for drinking water) from desalination brine.
- 3) Regeneration of spent activated carbon that was previously utilised in odour control.

This seminar paper will focus on the first opportunity.

1.1 Industry Standard for CO₂ Recovery

CO₂ recovery has been extensively studied in the flue gas and landfill gas industries, in a field described as carbon capture and utilisation. Technologies used to achieve this separation of CO₂ include physical and chemical absorption, adsorption, membranes and cryogenic processes (Echevarria Huaman, 2015). The limitation to these studies is that there is rarely any intention of utilising the CO₂ for any purpose other than sequestration. Studies that have focussed on the removal of CO₂ from biogas (known as biogas upgrading), are mostly interested in harnessing high energy density methane (CH₄) to be used as an energy source (Mel et al., 2016), and hence these processes typically leave CO₂ in a stream mixed with all other impurities. To the best of our knowledge, there are no conventional processes and only a handful of small pilot-scale plants to manufacture CO₂ of appropriate quality from biogas.

1.2 Project Objective

This project aims to perform a preliminary technoeconomic analysis on various chemical manufacturing opportunities within Water Corporation's treatment operations. As demonstrated by a review into CO₂ separation methods, although the technologies for resource recovery have been well reported in literature, there is a gap in knowledge for how these technologies can be integrated within the water industry and adapted towards the manufacture of water treatment chemicals. Hence, this study proposes concept designs for these processes and makes assessments on their economic viability.

2. Process

The assessment process of the identified manufacturing opportunities (Figure 1) can be generally divided into the following stages:

2.1 Technological Assessment

Firstly, flow rate and composition data specific to Water Corporation sites were gathered to understand the characteristics of the by-product (feed) stream and requirements of the manufactured product. Each manufacturing opportunity then presented its own set of challenges to consider in the development of the proposed process. For example, the associated tasks for CO₂ recovery included identifying steps for impurity removal from biogas, disposal procedures for impurities and the technology for CH₄/CO₂ separation. The proposed conceptual designs were reported in the form of process flow diagrams (PFDs) (Figure 2).

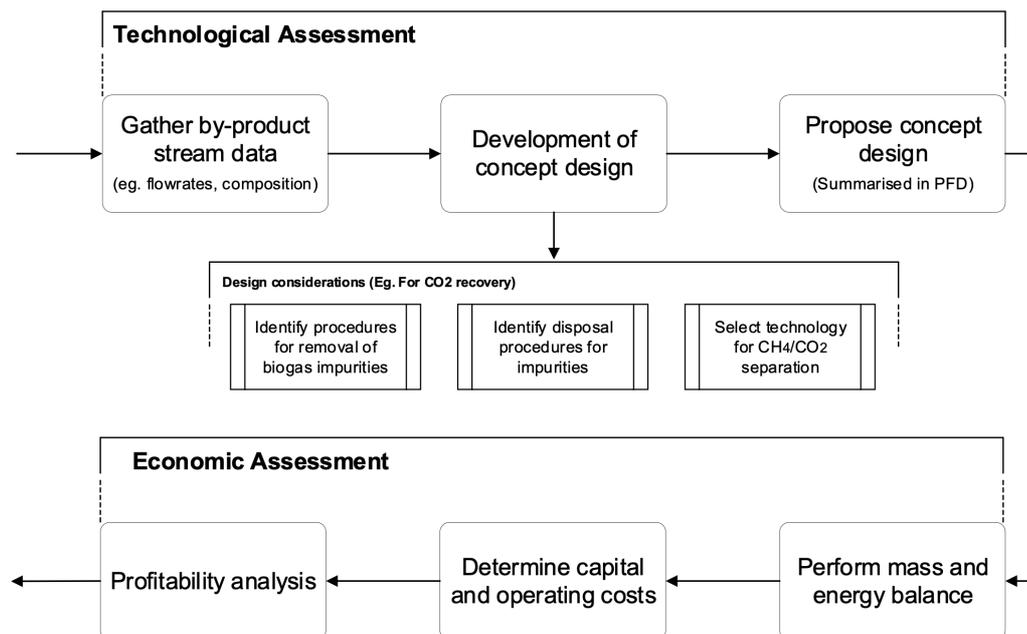


Figure 1 General approach to the techno-economic assessment.

2.2 Economic Assessment

Economic assessment for each proposed solution will be generally similar. The approach begins with performing mass and energy balances on the proposed system using data gathered in the technological assessment stage. This balance will identify product yield, quantity of material streams and the energy consumption of the process. Using this information, equipment sizing will be done to acquire the capital costs of the process. The operating costs can also be calculated from energy usage and other operational requirements. A profitability analysis will then be conducted, identifying the rate of return, net present value and other indicators to identify the overall economic viability of the process.

3. Design and Discussion

Biogas compositions typically differ between various sites and in different seasons of the year, however, the average composition generally follows the values reported in Table 1, comprising mainly of CH₄ (59.5%) and CO₂ (33.1%). The ISBT/EIGA standards specify impurity limits for CO₂ use in food and beverage production, which is a 99.9% purity with maximum limits of 50 ppm CH₄, 0.1 ppm total sulfur content, 20 ppm moisture, and 50 ppm total volatile hydrocarbons (European Industrial Gases Association, 2016). In order to achieve these conditions, the proposed conceptual design (Figure 2) comprises two main stages: 1) biogas pre-treatment, and 2) CO₂ recovery.

3.1 Biogas Pre-Treatment

The biogas pre-treatment stage comprises all processes up to the activated carbon filter and has the purpose of removing impurities that may impact the performance of the CO₂ recovery stage further downstream. This is especially relevant when using membrane and liquefaction technologies, where the presence of hydrogen sulfide (H₂S) and siloxanes can cause membrane failure (Iulianelli & Drioli, 2020), and the freezing out of water vapour can cause equipment blockages in the liquefaction stage (Yousef et al., 2018).

Component	Composition	Unit
Methane	59.5	%
Carbon Dioxide	33.1	%
Nitrogen	6.03	%
Oxygen	0.89	%
Carbon Monoxide	2	ppm(v)
Ammonia	<1	ppm(v)
Hydrogen Sulfide	2000	ppm(v)
Siloxanes	5.2	mg/Nm ³

Table 1 Average biogas composition from Water Corporation wastewater treatment plants.

Pre-treatment begins with dehydration, where the raw (water saturated) biogas passes through a water chiller, which condenses out almost all moisture and heavy organic compounds (Esposito et al., 2019). The dehydrated biogas then enters a water scrubber, which runs a biogas stream and water jet countercurrently through a packed column (Basu, Khan, Cano-Odena, Liu, & Vankelecom, 2010); this is utilised to remove solid/liquid particulates and water-soluble compounds such as H₂S and ammonia (Esposito et al., 2019). Water scrubbing is typically followed by a drying unit, which counteracts the humidity rise in biogas resulting from water evaporation in the scrubber.

Desulfurisation is then utilised to reduce the H₂S concentration in the biogas. Water Corporation WWTPs utilise bioscrubbers for biogas treatment and hence it is possible to repurpose these existing units towards a larger pre-treatment process. The bioscrubber comprises an absorption process using an alkaline sorbent, which is regenerated in a bioreactor using naturally occurring organisms to convert the absorbed sulfide into elemental sulfur (Cline, Hoksberg, Abry, & Janssen, 2003). This sulfur can be dewatered into a sulfur cake which can be used in fertiliser.

Activated carbon is then used to remove most organic impurities from the biogas, including halogenated hydrocarbons, volatile organic compounds (VOCs), terpenes and siloxanes. It is important that this stage is preceded by both desulfurisation and dehydration as the presence of H₂S and moisture can saturate the adsorbent and decrease its capacity. In this step siloxanes are also typically removed to a concentration below 0.1 mg/m³ (Shen et al., 2018).

3.2 CO₂ Recovery

The purpose of the CO₂ recovery stage is to separate the major components of CO₂ and methane. This stage consists of a hybrid setup of membrane separation and cryogenic liquefaction.

3.2.1 Membrane Separation

Membrane separation works on the principle of separating mixture components using selective permeation through a thin porous layer (Iulianelli & Drioli, 2020), and provides several advantages over conventional technologies. Firstly, membranes have a low energy consumption and operating cost. Secondly, membrane units have a modular design which provides ease of plant scalability (Echevarria Huaman, 2015). Scalability is important in the context of retrofitting a biogas upgrading process to a plant where biogas production is expected to

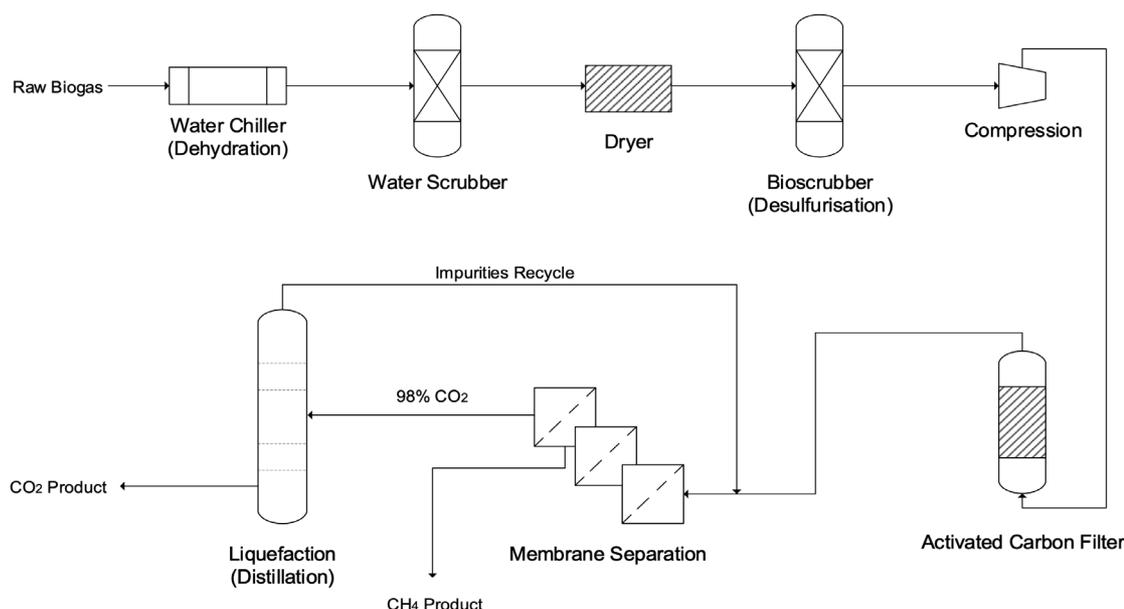


Figure 2 Proposed concept design for the manufacture of CO₂ from biogas.

increase over time. Modularity also allows for multi-stage configurations to be constructed, which can be utilised to optimise the process. The methane product stream which is of relatively high purity can also be used as an energy source.

3.2.2 Cryogenic Liquefaction

The liquefaction process is required to bring the CO₂ stream up to a purity of 99.9%. It works on the principle of separating out constituents of a mixture based on different boiling or sublimation points (Kadam & Panwar, 2017). Liquefaction has been commercially applied to the capture and production of high purity CO₂, especially in the hydrogen industry where processes such as Air Liquide's CRYOCAP have utilised partial condensation and distillation methods to recover CO₂ from the off-gas in steam methane reforming plants (Air Liquide, 2022). There are several limitations to consider with the use of cryogenic technology, with the dominant one being cost. Liquefaction processes typically require multistage compressors, heat exchangers and pumps, which can add up to a high capital cost. Maintaining high pressures and extremely low temperatures also leads to high energy usage, especially if refrigeration (which uses electricity) is employed (Song et al., 2019). However, since the proposed design utilises liquefaction as a final purification step (where the feed stream is already high in purity), energy usage should not be a major concern. Scholz et al. (2013) reports that using a *hybrid* cryogenic process reduces specific upgrading costs to below 9% of the cost that would be required for an *independent* cryogenic process.

4. Conclusions and Future Work

This paper presents the first of three circular economy opportunities, which describes a potential membrane/liquefaction hybrid system for the separation of CO₂ of appropriate quality from wastewater treatment biogas. The final stage of the project will perform a preliminary economic analysis on these conceptual processes, to identify its profitability and financial viability when integrated with existing Water Corporation operations. Future work should extend these solutions past the theoretical concept, using process modelling to identify the optimal

configurations and operating conditions to make a greater economic argument for these opportunities.

5. Acknowledgements

I would like to thank my client mentor Ron Silvestri and academic supervisor Michael Johns for providing their ongoing support and helpful advice throughout this project. I am also grateful to the team at Water Corporation who have provided inspiring insights into their work and have helped provide data and information for this project. I would finally like to appreciate Jeremy Leggoe and Kimberlie Hancock for the opportunities offered by the CEED program.

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