CENTS: A Research Network for the Sustainable Transport Community

# Circular Economy Network+ in Transportation Systems


British Geological Survey

University of Cambridge

Cranfield University

University of Surrey

WMG
The University of Warwick

UKRI
Engineering and Physical Sciences Research Council


# **CENTS Feasibility Funding Case Study:**
# Wastewater derived ammonia: contaminant to carbon free transportation fuel

## Executive summary

This project set out to practically demonstrate direct utilisation of $NH_3$ derived from wastewater as an alternative transportation fuel and understand if a vacuum distillation-based process currently developed at CU could produce an ammonia rich fuel suitable for energy generation in a DAFC. This was experimentally achieved through recovering ammonia from real wastewater obtained from a sewage treatment works (Cotton Valley, Anglian Water, UK) and testing its performance in a DAFC using new equipment set-up at CU. Through comparisons of synthetic and real solutions, design criteria for obtaining an improved ammonia fuel were identified.

This project has demonstrated the recovery of a purified aqueous ammonia fuel from wastewater and its utilisation for electrical energy generation in a direct ammonia fuel cell (DAFC) suitable for transportation applications. This has been the first practical demonstration of this process with the fuel cell exhibiting an open circuit voltage (OCV) of ~0.2V and power density ~0.005 mW $cm^{-2}$ when fed with ammonia distillate from real wastewater. Practical demonstration of this linkage between vacuum distillation and a direct ammonia fuel cell has identified key characteristics of the recovered ammonia fuel to further optimise for improved electrical energy generation. This includes increasing concentration of the recovered distillate, with fuel cell power density improving almost tenfold through an increase in ammonia concentration to 5M. Additionally, trace organic contaminants contributed to a reduction in solution pH and adsorbed to the anion exchange membrane of the fuel cell, reducing power output by around half, indicating that upstream intervention is required for their removal (e.g. granular activated carbon) to achieve an improved process energy efficiency. The project has however established the feasibility of producing a new sustainable transport fuel from wastewater and provides a fundamental understanding to build upon for process scale up.


## Project Team

**Chris Davey (PI)**

Chris' current research activities include investigating a number of membrane-based processes for: water recovery from concentrated blackwater, resource recovery and electrochemical energy generation. His research interest lies at the water-energy nexus aiming to develop new technologies and processes to achieve decarbonisation of energy systems and energy positive water treatment.

**Ewan McAdam (Co-I)**

Prof. McAdam's research focusses on the development of hybrid technologies for the water sector that enable selective separations, chemical transformations and gas-liquid mass transfer to realise opportunities in process intensification, energy production or resource recovery.

**Ben Luqmani**

Chemical Engineer with a first-class degree from the University of Bath. Ben is leading the design build and operation of a laboratory scale thermal ammonia recovery unit used to produce $NH_3$ products from wastewater.

**Nigel Janes**

Mr Janes' expertise includes overseeing the installation and commissioning of novel water treatment technologies for industrial scale testing.

**Rob Evans**

Over 15 years working in IP management and commercialisation. He leads on management of the patent portfolio and IP exploitation for Cranfield University. He has successfully commercialised over 50 technologies, through eight spin out companies and over 40 licence agreements.


**Industry Partners**

**Severn Trent Water**

Mr Peter Vale, Innovation Lead Sever

**Northumbrian Water**

Mr Andrew Moore, Commercial manager

**Anglian Water**

Dr Adam Brookes, Lead Technical Innovation Manager


## Project Rationale

This is the first project to demonstrate the intrinsic value of ammonia in wastewater as a transportation fuel through practically realising recovery of a purified ammonia product and applying it for direct electrical energy generation. The study therefore establishes the feasibility for production of a new sustainable transportation fuel from wastewater and provides fundamental understanding of a new technological innovation to unlock the available energetic potential of ammonia in wastewater.

## Key Findings

1) Electrical energy generation has been demonstrated from a concentrated ammonia product derived from real wastewater which could be applied as transportation fuel. Initial studies have produced a distillate with ammonia concentration of ~1M producing an OCV ~0.2V and power density of ~0.005 mW $cm^{-2}$ when applied in a DAFC.

2) The impact of organic contaminants reduced the pH, OCV and power density of the ammonia distillate compared to a synthetic ammonia solution of equivalent concentration. Increasing purity and concentration through simple engineered approaches (e.g. fixed carbon beds) could enhance energy generation, conversion efficiency and overall ammonia abatement of the DAFC.


## Background

In recent years, significant investment within the water industry has supported the generation of renewable fuels through schemes utilising either biomethane produced via anaerobic digestion or hydrogen generated from electric hydropower. This project set out to define an entirely new sustainable source of transport fuel available within the water sector through demonstrating the potential to utilise ammonia recovered from wastewater. As a contaminant of environmental concern, it is estimated between 0.72 and 1.9TWh per year of energy is required to treat the ammonia present in UK wastewater through biological oxidation (a major fraction of the estimated 2.3TWh per year required for all wastewater treatment). Alternatively, this ammonia has ~1TWh per annum of chemical potential as a liquid fuel. To exploit this, novel technologies for its recovery and utilisation are required in addition to understanding the synergistic linkage between these processes. Thermal recovery of ammonia from wastewater being developed by CU is advantageous as waste heat can be utilised for selective ammonia separation permitting >95 % recovery. However, the carry-over of trace contaminants such as VOCs has potential to poison emerging fuel cell technologies, detrimentally affecting energy efficiency, therefore requiring a holistic understanding of contaminant chemistry and implications.

## Results

Vacuum distillation (Figure 1a) was used to recover a purified, concentrated ammonia distillate from the return liquor of an anaerobic digester operated at Cotton Valley Sewage Treatment Works (Anglian Water). The recovered ammonia distillate (Figure 1b) had a high ammonia concentration (~ 1M $NH_3$) and pH (~ 10.5) suitable for use in a direct ammonia fuel cell (Table 1).

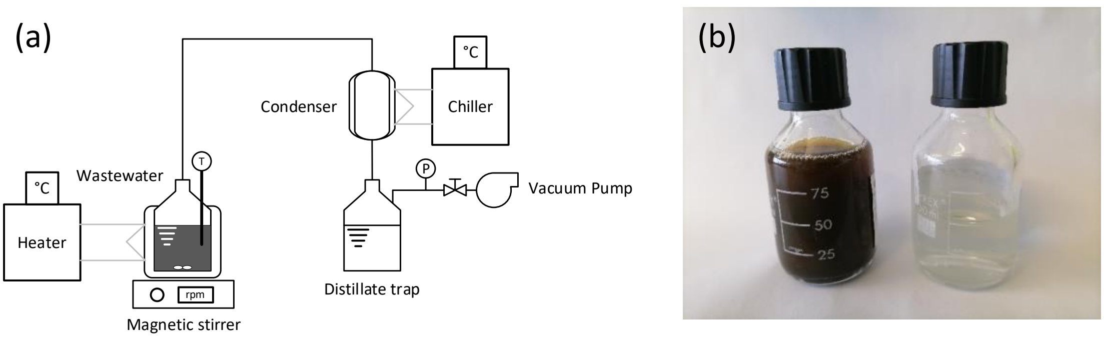


Figure 1. (a) Schematic of the experimental set-up of the vacuum distillation system used to recover ammonia distillate and (b) image of the wastewater and the recovered distillate.

Although the chemical oxygen demand (COD) indicated the organic content in the distillate was low (~1/20$^{th}$ of the initial wastewater), the solution had a significantly higher conductivity and marginally lower pH than for an equivalent concentration of pure ammonium hydroxide solution (Table 1). This has been attributed to the presence of contaminant VOCs such as carboxylic acids, alcohols and siloxanes, with aromatic or unsaturated hydrocarbons confirmed through a reduced $UV_{254nm}$ transmittance (29.6%) compared to synthetic ammonia solution (100%, Table 1). Further detailed GCMS analysis is in progress by an external company (Lucideon, UK) identifying the exact chemical speciation of this fraction carried over into the distillate.


Table 1. Solution characteristics of the wastewater, recovered distillate and synthetic ammonia solutions.

| **Parameter** | **Solution** | | | |
|---|---|---|---|---|
| | *Wastewater centrate* | *Wastewater ammonia distillate* | *1M $NH_3$* | *1M $NH_3$ + 1M KOH* |
| $NH_3$ (g $L^{-1}$) | 2.010 ± 0.010 | 17.3 | 17.03 | 17.03 |
| pH | 8.0 ± 0.01 | 10.5 | 11.83 | 14.43 |
| Conductivity (mS $cm^{-1}$) | 14.6 ± 0.1 | 26.2 ± 0.14 | 1.2 ± 0.0078 | 186 ± 0.22 |
| $UV_{254nm}$ (%T) | 58.3* | 29.6 | 100 | 100 |
| Total COD (mg $L^{-1}$) | 5773 ± 598 | 248 ± 1.0 | - | - |
| Soluble COD (mg $L^{-1}$) | 2791 ± 534 | 243 ± 5.0 | - | - |
| Total Solids (mg $L^{-1}$) | 4900 ± 265 | - | - | - |
| Total Suspended Solids (mg $L^{-1}$) | 273 ± 64 | - | - | - |
| Total inorganic carbon (as C) (mg $L^{-1}$) | 1659 ± 7 | - | - | - |
| Alkalinity (as $CaCO_3$) (mg $L^{-1}$) | 6875 ± 569 | - | - | - |

*Measured at 1/10 dilution.*

When applied within a DAFC, both the ammonia distillate and wastewater exhibited a reduced open circuit voltage (OCV) and power density when compared to synthetic ammonium hydroxide solutions of equivalent concentration (Figure 2).


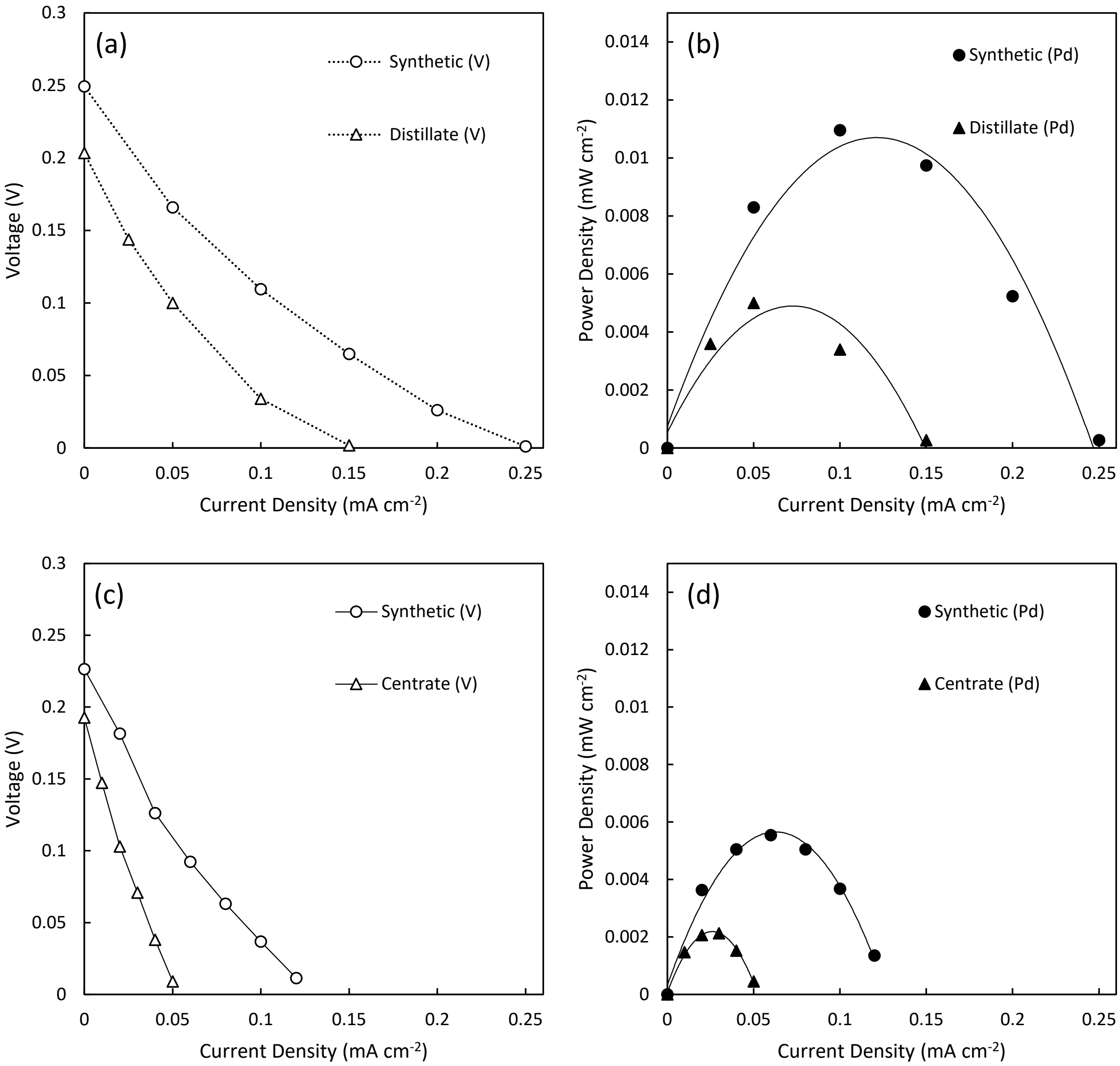


Figure 2. Performance of the direct ammonia fuel cell with either synthetic or wastewater derived ammonia solution at equivalent ammonia concentrations. (a,c) Polarisation curves and (b,d) power density.

Solution pH had a critical impact on fuel cell performance (Figure 3a), partly accountable for the reduced performance of the ammonia distillate. However, enhanced performance of wastewater at pH 8 compared to synthetic ammonia (Figure 2d, Figure 3a) indicates oxidation of organics within the wastewater when present at higher concentrations. Alkaline fuel cells with the same Pt catalysts have been demonstrated for methanol, urea and glycerol potentially present within the wastewater, contributing to enhanced power density but would reduce long term performance. FTIR analysis of the anion exchange membrane post-use indicated absorbances typical of alcohols and carbonyl bonds prevalent in wastewater VOCs.


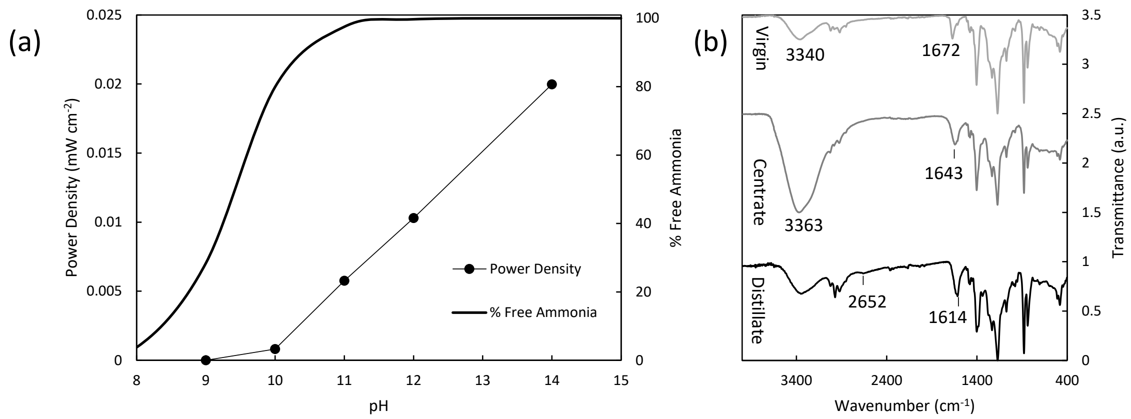


Figure 3. (a) Effect of solution pH on fuel cell performance and (b) FTIR analysis of fuel cell anion exchange membranes.

Further characterisation of the DAFC identified potential opportunities to further optimise the power production from ammonia distillate (Figure 4). Increased ammonia concentration from 1M to 5M could have a significant impact on power generation, achievable through a second distillation stage. Additionally, potassium hydroxide further enhanced fuel cell performance. There is therefore a requirement to further optimise the fuel cell process design to achieve increased energy efficiency whilst simultaneously realising high levels of ammonia abatement.


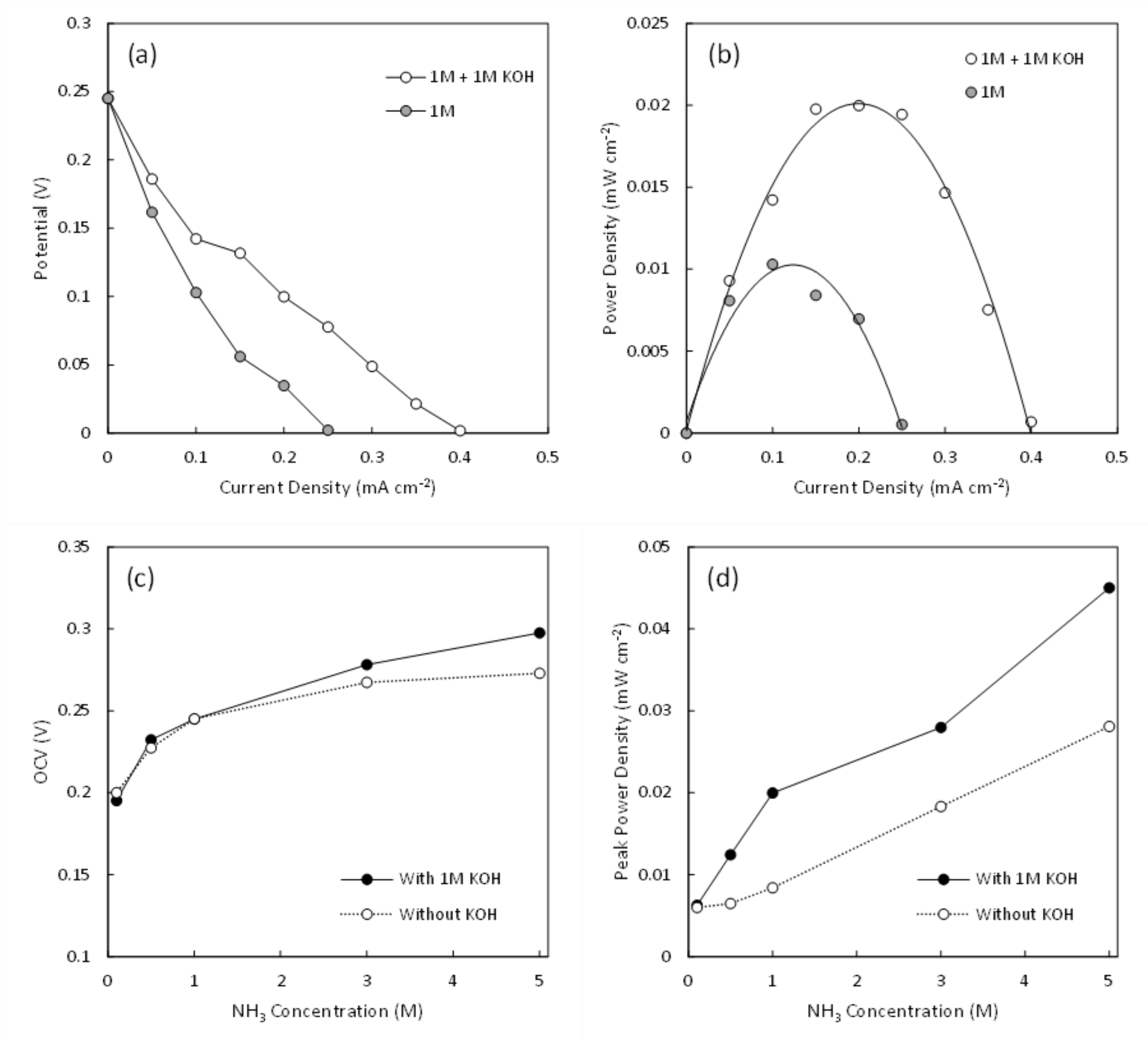


Figure 4. Performance of the direct ammonia fuel cell with synthetic solutions of ammonia or ammonia with 1M potassium hydroxide (a) polarisation curves, (b) power density, (c) open circuit voltage and (d) peak power density.

## Impact

The value of recovering ammonia from wastewater is becoming increasingly recognised within the water sector. Realising the removal and energy generation from the entire ammonia fraction within wastewater in the UK could offset 0.28 $MtCO_2$ per year through reducing the aeration requirement for biological oxidation. Additional value arises from the sustainable energy generated as well as the reduction in $N_2O$ emissions. This would provide a huge contribution to the UK's clean growth strategy within the water sector, delivering significant economic and environmental benefit. In addition, with the widespread uptake of anaerobic digestion for treatment of food waste and agricultural waste streams there is an increasing number of ammonia rich liquid streams requiring novel treatment technologies in order to meet consent in line with the European Water Framework Directive. The link between ammonia in wastewater and its potential use for energy generation demonstrated in this project will impact future research direction and potentially have wide impact on future investment if demonstration at scale can be realised. Routes towards achieving energy generation from wastewater ammonia are currently being developed for testing at demonstration scale and this study advances understanding of its exploitation for energy generation.

## Next Steps

The current outputs from this project are:

- A research article 'Demonstration of ammonia recovery from wastewater and its use as a fuel for direct electrical energy generation' is in preparation targeting the journal – *Water research* (IF: 9.13).

- A follow-on proposal has been submitted for scaling up the recovery of ammonia from wastewater and comparing its use for direct electrical energy generation such as this work, or transformation to hydrogen (EPSRC WIRE CDT).


## Testimonials

From the Early Career Researcher(s)

*"The opportunity to lead this feasibility study has provided me with a wealth of experience and allowed me the chance to develop my skills in directing a research project. I have enjoyed the challenge of proposing and delivering the research in this project as well as practicing a number of other project management skills such as budgeting, organising experimental timelines and coordinating activities. Although the current COVID-19 pandemic has posed additional challenges to the project around delivering the practical research, it has provided me with a wealth of experience in how to deal with project disruptions. Additionally, the experience I have gained from this project has provided me with the confidence to apply for other funding opportunities such as an early career fellowship and inspired me to explore additional funding opportunities for realising my research vision. In particular, the experience and learnings from this project in the application of ammonia fuel cells has unlocked a number of research directions that I am intending to explore recovering energy from wastewater.*

*I have also enjoyed being a part of and involved in the CENTs network. The workshops have been engaging and been a great opportunity to network and gain an understanding of the wider area of research for the circular economy related to transportation systems. In particular, when hosting a discussion session in the CENTs conference in January I found the training conducted by Christine Bell on conducting this in a virtual environment particularly useful and it has provided me with experience and a number of techniques to apply in future. Particularly useful with the increased use of virtual environments during the past year!"* Chris Davey