Project Title: Biogas upgrade (nano-bubbles)

Reference Number: TP SFI 16/RC/3872

Recipient: Niall English

Project point of contact: Niall English (UCD), John Oliver (I-Form), Darragh Kyne / Ian Kilgallon (GNI)

Project Summary:

An integrated approach is sorely needed to treat biogas emanating from anaerobic digesters which is cost-effective, in terms of upgrade/purification to ~98% methane needed for pipeline deployment. This is a very pressing environmental and waste-management problem. At present, biogas-washing requires significant capital investment, with high operational and maintenance costs. Facile and efficient nano-bubble formation is set to disrupt gas-enrichment operations using our patented approach. In short, we achieve massive methane enrichment via selective CO_2 and H_2S take-up in water. In essence, we achieve nothing less than an integrated waste-processing vision using cutting-edge engineering-science advances, and making anaerobic digestion an economic and practical reality, that can be deployed at scale, initially developing at the small scale.

Our patented, innovative nano-bubble technology has the potential to reduce significantly the CAPEX and OPEX of this challenge. Thus, it will enable a wide range of potential anaerobic-digester users, initially at small scale, to trail and demonstrate the upgrading of biogas to technical standard ready for injection to the Grid.

In this project, we accomplished scale-up to TRL-7 for trials at UCD as well as at a digestate-processing facility (working with an industrial collaborator, Aqua-B, for commercially-oriented biogas-upgrade-device scale-up, at the 20 Nm^3/hr level for methane flow – incorporating also low-energy CO_2 capture in the form of nano-bubbles by dint of the patented approach).

Start date of project: 1 Sep 2020	**End date of project:** 31 Oct 2022 (there was further work done with Aqua-B over Summer-into-Autumn 2022)

Outputs/Outcomes for this reporting period:

1. Optimisation of Nano-Bubble <> Biogas Purification
2. Nano-Bubble Absorption Cylinder
3. Multi-Stage Carousel
4. Absorption Cylinder Regeneration
5. 20 m^3/h Fabrication, Integration & Evaluation
6. Commission, Demo & Optimisation of 20 m^3/hr biogas flow
7. Dissemination, Exploitation
8. Commercial Development
9. Project Management

Actual Outputs/Outcomes for this reporting period:

- 1. Optimisation of Nano-Bubble <> Biogas Purification – with 98.2 % CO2 in the NBs using gas-chromatography analysis

- 2. Nano-Bubble Absorption Cylinder, with delivery of 50-litre pressure vessel rated for 50 bar g, and realisation of this in smaller pressure vessel, whilst larger one is awaiting commission and demo

- 3. Design for Multi-Stage Carousel: Detailed mass-balance calculation have been carried out for a plant layout involving a cascade of these biogas-upgrade devices aligned in series, for a progressive sequence of biogas upgrade on a multiple-pass basis

- 4. Absorption Cylinder Regeneration: The emptying and refilling protocol of the pressure vessel for gas and water cycling has been completed, which allows for an option of “fed-batch” mode of operation.

- 5. 20 m^3/h Fabrication, Integration & Evaluation

This was achieved at both up to 40-45 bar g, as well as at 4 and 2 bar g pressure levels. In the first two cases, this was using both fed-batch and continuous-flow systems, respectively, on-campus, whilst in the second case, this was done closer to ambient pressure off-site at a commercial digestate facility, with the assistance of commercial partners, Aqua-B).

- 6. Commission, Demo & Optimisation of 20 m^3/hr biogas flow

This was achieved at 12-14 m^3/hr on-campus and at 20-25 m^3/hr off site (in the latter case, working with commercial collaborators, Aqua-B).

- 7. Dissemination, Exploitation

The dissemination/exploitation plan involved briefing commercial partners and prospective customers on trials, and there is interest in both digestate-processing as well as low-energy carbon-capture sectors. It is hoped to plan submission of a paper on low-energy CO_2 capture during 2023, probably in conjunction with partners to reflect some off-campus work. Naturally, should that occur, GNI will of course be acknowledged.

- 8. Commercial Development

This has been accomplished with commercial partners Aqua-B during June-October 2022, which is a UCD spin-out company, chaired by Prof. Niall English, for nano-bubbles commercialisation.

- 9. Project Management

This has been performed adeptly throughout this project by Prof. Niall English, together with a non-cost extension into Summer 2022, so that Aqua-B could do some commercially-oriented off-site testing at TRL-7/8, reaching the 20 Nm3/hr level and beyond – showing commercial feasibility at low, near-ambient pressure (of the order of 1.5-2 bar g).

Did the project run on schedule? Yes, although there was a no-cost extension into Summer/early-Autumn 2022 to allow for Aqua-B to assist in some off-site TRL-7/8 trials with digestate (with thanks to Dr. James McGreer)

Explanation for deviation from schedule, if applicable:

Although at the time of the last update report, from 6 Dec. 2021, there were not so many delays during 2020-21 up to that time, despite COVID-19 (owing to Prof. English’s project-management skills, and early intervention in anticipation of COVID), the post-COVID relaxation of rules during Spring-into-Summer 2022 was far slower than anticipated. This necessitated a

prolongation of on-campus trials for longer than anticipated, and delayed the much-desired move off-campus (with compliance with rigorous health-and-safety measures also taking time). Owing to depletion of grant funds for having to stay on-campus longer than desired, and in the spirit of academic-industrial collaboration, AquaB generously offered to provide (i.e., donate) some larger-scale equipment fabrication, commissioning and testing for off-site trials over Summer/early-Autumn 2022 (June to October 2022). This allowed this GNI/I-Form project to reach its TRL-7 ambition – arguably going further to TRL-8 (and 25 Nm3/hr) as part of Aqua-B commercial beta-trialling (pre-TRL-9) operations. Further TRL-8/9 operations are to take place in Nov.-Dec. 2022 in Dhahran, Saudi Arabia – at Saudi Aramco R&D HQ – ahead of planned commercial deployment in 2023-24 for low-energy carbon capture for important Aramco operations (with further details withheld due to commercial-confidentiality agreements). Prof. English will be travelling to Dhahran over Winter 2022-23 on multiple occasions, getting his NB generators working in large-scale trials (exactly as he has in many places in the USA and Europe) – to deploy the prime in his Irish gas-engineering technology as Head of Aqua-B.
Lessons learned/challenges to date: • Thinking of 'Project Clover' and the RGFI, projected-NPV analysis, vis-a-vis lifetime total-cost-of-ownership have shown that substantial savings in both capital- and running-cost categories can be realised. • At TRL-8 operation at 1.5-2 bar g pressure, the energy cost (including water/gas pumping) was found to be around 0.037 kWhr per Nm3 in single-pass mode (95.7% methane purity, with 1.1% slippage), rising to 0.06 kWhr per Nm3 for 1.4% slippage and 97.5% purity. This argues for single-pass deployment, with very low CAPEX and OPEX, and this can then be passed to much longer-life Purec-Wartsila membranes – which much smaller membrane size. • The removal of most H_2S by this nanobubble-enhanced "water-washing" (much better than Greenlane) is another helpful feature to prolonging the life of much smaller membranes, i.e., it reduces corrosion.

Total Project Cost: € 156 k	**Innovation Fund Awarded: € 105 k**
Co-funding source: i-Form	**Co-funding amount: € 51 k**

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Gas Innovation Fund - Project Status Final Report

See overleaf for a more comprehensive report

Additional final project reporting on biogas upgrade via NB formation

The evolution in scale of the TRL-climbing project is shown below. In Fig. 1, we have the initial lab deployment, at TRL-3.

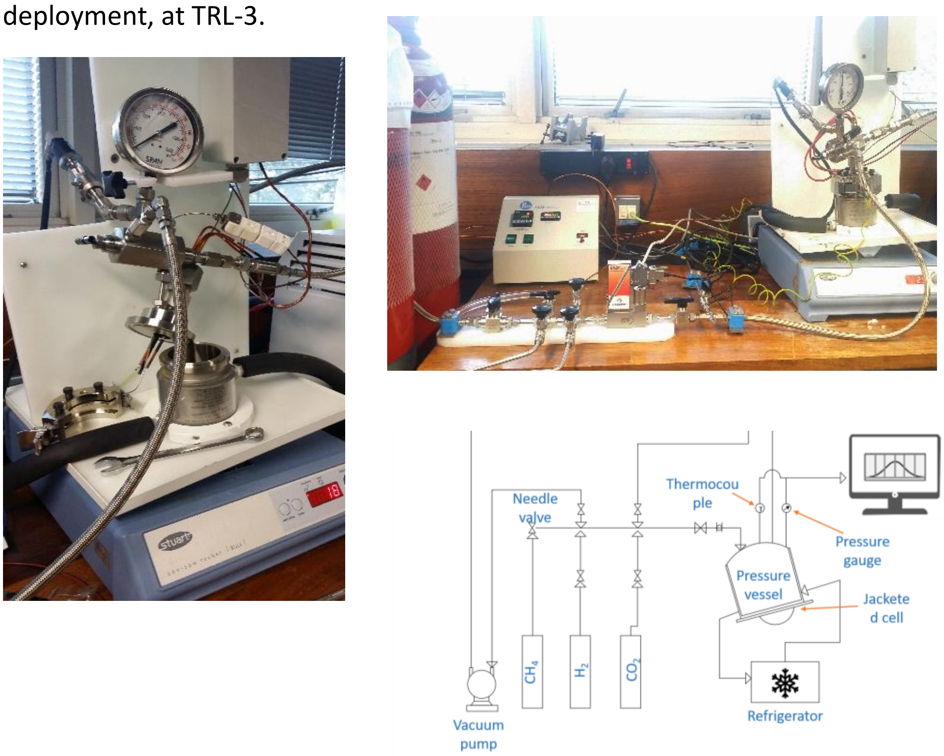

Fig. 1. Initial lab deployment for NB generation at TRL-3, with biogas upgrade. This 300 cc vessel, with an embedded NB-generator electrode therein, led to 97.5%-purity biogas upgrade as a batch process, at 40-150 bar g, although this would be less economically scalable for mass deployment.

In Fig. 2, we show the larger, 50-litre pressure vessel, designed for up to 45-50-bar operation (BS-5500, with tan-and-torispherical sections 100%-radiography-flush welded), in which we performed fed-batch upgrade, which was delayed by on-campus commissioning, aggravated by the COVID situation:

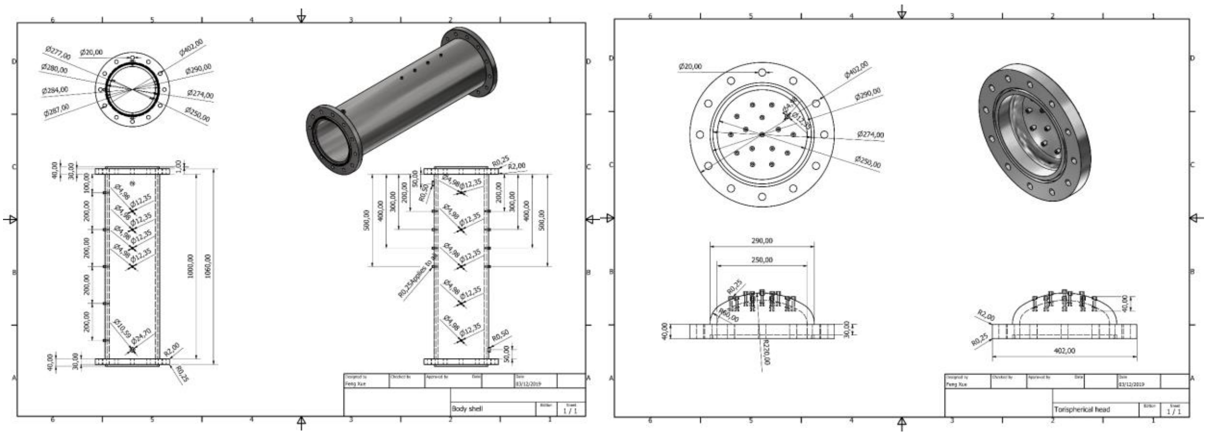

Fig. 2: Larger, 50-litre pressure vessel, designed for up to 45-50-bar operation, with fed-batch upgrade achieving up to 6 Nm^3/hr at 0.11 $kWhr/Nm^3$ at circa 15-18 bar g.

Important lessons from cylinder-recharging with the fed-batch system underscored the importance of microbubble generation for optimal flow turbulence, i.e., upstream two-phase macroscopic-bubble mixing via energy-efficient eddy-vortex mixing. In other words, by generating a population of “mother” micro-bubbles in an hydrodynamically-efficient way, we can then “cannibalise” these micro- and fine-bubbles to form a much larger sub-population of “daughter” nano-bubbles. Indeed, if one wishes to understand more of the electrostriction physics for this general process, one may refer to a user-friendly 5-mniute Youtube “lecture” by Prof. English on the core of his invention at:

https://www.youtube.com/watch?v=gwvPZMvSyN8

The next on-campus effort, during 2022, as we waited to get more oout of COVID lockdown towards desired off-campus activity, aimed to operate a full flow-system at around 4 bar g, featuring more optimal upstream gas-mixing – cf. Fig. 3:

Fig. 3: “Triple-leg” system with in-pipe electrodes. We connected a raw-biogas cylinder to the upstream Venturi-system to allow for microbubble generation of the raw biogas, and subsequent in-pipe CO2 capture.

This "triple-leg" system captures most of the CO2 in each of the three pipes by the embedded NB-generating electrodes lining the interior of the pipes, and the NBs absorbing CO2 much more readily than methane, as per the patents (with simplified Youtube explanation above). This was at about 4 bar g pressure, and was about 0.8 kWhr per Nm3, with 96% methane purity and 1.5% methane slippage – not so bad at all, particularly for lower-pressure operation – not requiring pressure-vessel certification (and much lower CAPEX to boot!).

By Summer '22, we wanted to get off-site, but the project funds had run out. Not to be deterred, as lack of funds are common, Prof. English's UCD group had been collaborating with Aqua-B since Winter 2021-22 and the days of Omicron - to create a TRL-7/8 device capable of up to 250 l/min of water for single- or multiple-pass flow options. Teaming up together in a UCD-AquaB collaboration – see Fig. 4 for off-site photo at a UK digestate facility in Summer '22 commercial beta-testing.

Fig. 4: On-site installation at a UK digestate facility of large-scale unit

Both CO_2 cylinders and biogas feeds were linked to the Venturi section, and the water flow of municipal tap-water supply was initially about 80 l/min – also using digestate. The pressure in the electrostriction section was about 1.5 bar g. So, the pressure-difference "driving force" for CO_2 injection (in the form of NBs) was about 1 bar. There were three passes of 1,000 l of IBC water (including digestate) put through the unit (from and to IBCs), each time with a similar water and bioags/CO_2 flow-rate.

Earlier, high-pressure tests at about 70-80 bar g for CO_2-NB generation showed a drop in pH down to about 4.5 (measured after about two days following post-experiment exposure to atmosphere – cf. Fig. 1), owing to the higher level of solubility from Henry's Law with the high pressure of CO_2 driving this (with NBs providing for about 45-50% extra CO_2 mass). For lower-pressure generation of NBs (around 1-2 bar g) in the larger-scale continuous-flow system, the initial drop in pH was similar enough to these earlier results. It was found that the pH of the control water was 7.64, whilst that of the 1st, 2nd and 3rd pass were initially about 4.5, 4.35 and 4.3, respectively. After three weeks, these rose to 6.22, 6.11 and 6.04, respectively. After six weeks, these rose to 6.44, 6.35 and 6.13, respectively. Therefore, most of the change took place in the first 3 weeks – and more slowly between weeks 3 and 6.

In terms of dissolved CO_2 (d_CO_2), the equilibrium, Henry's-Law level is about 0.85 mg/l for water in contact with atmospheric air (at around 20 deg C – and lower still at 40-50 deg C for desert Summer temperatures – of the order of 0.5 mg/l or less). Now, given that a d_CO_2 probe does not "see" CO_2 mass in NBs directly, it does witness them indirectly via the turbulence of the "mother" micro-bubble generation in the Venturi and downstream vortex-mixing section (and subsequent development of "daughter" nano-bubbles via electrostrictive cannibalisation). This was about 115, 130 and 135 mg/l initially, for 1st, 2nd and 3rd passes, resp., and there was estimated to be another 30-60 mg/l beyond that in the form of CO2 NBs – "leaking" slowly to pass their CO_2 into the conventionally-dissolved state via Fick's Law. About 5-6 weeks later (whilst partly sealed), this had declined to ~45, 110 and 132 mg/l. So, we see that there is a larger NB mass level in the 2nd and 3rd pass, "sustaining" the d_CO_2 level higher for longer – in particular, for the 3rd pass, there was no appreciable decline in d_CO_2 level over 5-6 weeks (at about 150 times Henry's Law level). Another 2nd-pass sample was also kept fully open to atmosphere (i.e., no cap on the sample-jar lid), and after 5-6 weeks, this was ~90 mg/l instead of ~110 mg/l – showing the effect of a cap versus no-cap for slightly faster escape to atmosphere.

The energy for biogas upgrade was about 0.37 kWhr per Nm3 on a single-pass basis with up to 96% purirty and about 1.1 % methane slippage – making this an ideal, lower-cost/lower-energy preliminary-treatment option.

Dynamic light-scattering (DLS) analysis is helpful in characterising the nature of these extra 2nd- and 3rd-pass NB populations that sustain this d_CO_2 level further, for longer – possibly larger, semi-agglomerated NB bubbles, perhaps fewer in number but with larger size and different area-to-volume ratios that sustains their lifetimes yet further. We took DLS data on samples after 6-7 weeks below (see Fig. 5), and this confirms this expectation for the 2nd-versus 3rd pass.

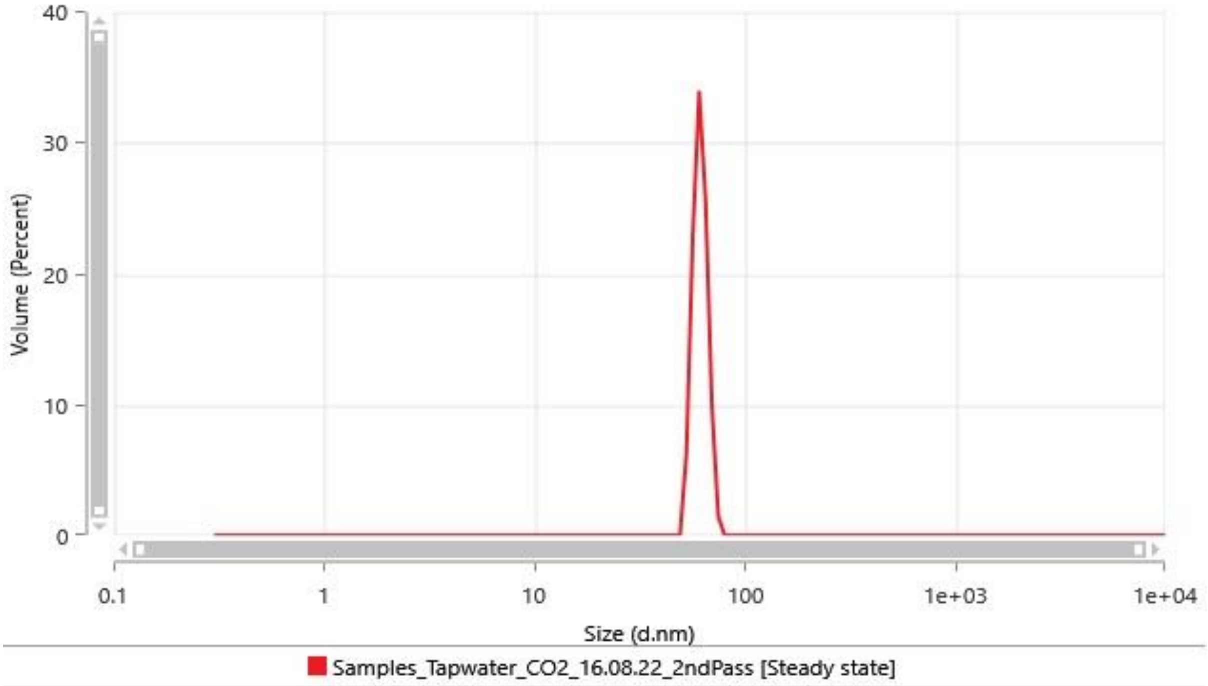

Fig. 5a: 2^{nd}-pass DLS analysis after 7 weeks, with averaged NB population of 1.6 x 10^8 per millilitre and mean diameter of ca. 60 nm

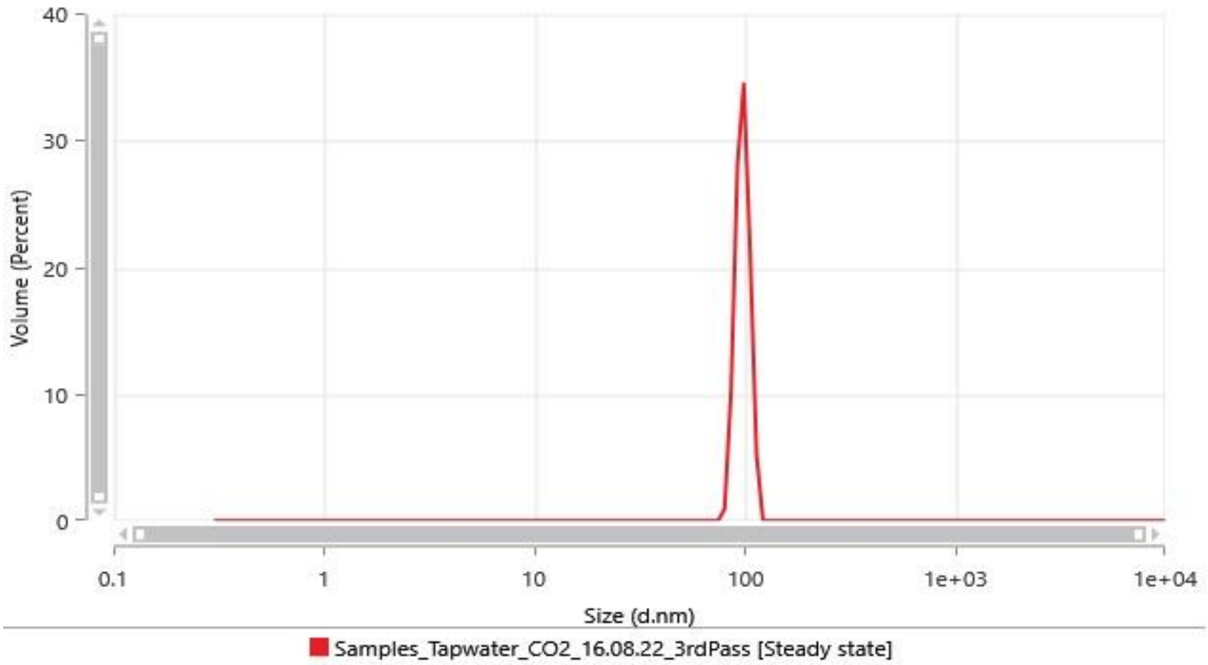

Fig. 5b: 3^{rd}-pass DLS analysis after 7 weeks, with averaged NB population of 2.6 x 10^7 per ml and mean diameter of ca. 95 nm. There is evidence of some level of NB agglomeration compared to the second pass in Fig. 2a – with partial agglomeration and consolidation of the population into longer-lasting NBs (considering the unchanged level of dissolved-CO_2 at about 130-135 mg/l afer 6 weeks, compared to a drop towards 90 or 110 mg/l for the second-pass sample if left open or capped).