OB HydraCel Bioelectrolyzer: Retrofittable device for hydrogen generation as auxiliary power onboard ships

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Synopsis

Driven by recent IMO restrictions, "green" or zero emission onboard power trains are gaining ground every day. Hydrogen as a clean fuel for naval vessels, stands to be extensively adopted if efficient technologies for onboard generation mitigate the excessive space occupied by stored hydrogen. The authors of this study have developed a land-based, retrofittable device named the OB HydraCel Bioelectrolyzer or HBE for on-site hydrogen gas generation by utilizing the chemical content of high-strength effluents. In this paper, the authors describe the present physical form, method of operation including performance parameters of the land-based HBE. The device currently treats effluents generated by the petrochemical industry and this paper demonstrates its value for naval vessels. The HBE, in its current iteration, performs its functions, by utilizing a bioelectrochemical system, for the conversion of organic and inorganic matter in wastewater streams hydrogen gas. The technology differentiates itself from other electrochemical hydrogen production technologies by using specialized microbial communities for the simultaneous treatment and recycling of the effluents. For its maritime use, the authors have projected the hydrogen generation capacity of the HBE based on onboard effluents such as bilge water, sewage, operational washes and even ballast as potential feedstock. In partnership with the Indian Navy, processes for mitigating the challenges associated with transitioning the HBE from its current land-based form to one suitable for naval vessel deployment have also been discussed. Finally, the authors discuss the future applications of this device to enable improved EEDI for current vessels based on reduced carbon emissions and easing compliance with MEPC 107(49) regulations for maritime transport as a whole.

Keywords: Hydrogen, Biorenewables, Biohydrogen, EEDI, Greenhouse gases, Energy Efficiency Design Index (EEDI), MEPC 107(49)

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1. Introduction

Earlier this year, IMO released (Joung et al 2020) a greenhouse gas (GHG) emission policy with a target to reduce their GHG emissions by 50% before 2050, with further announcements planned for 2023.

For these long term measures to take effect, zero emission power trains look to becoming a must. Two types of zero emission technologies today have reached technical maturity suited to the maritime industry and these are hydrogen powered Fuel Cells and Batteries (Thomas et al 2020). However, batteries are restricted by their size and fuel cells are restricted by the need for storing large quantities of pressurized hydrogen onboard, limiting cargo space and requiring frequent docking for refuelling (Minnehan and Pratt 2017). Yet, fossil fuel mitigating technologies like the use of hydrogen stand the best chance of minimising policy driven restrictions because of its high energy density and relatively low footprint in comparison with battery stacks.

Several studies have performed retrofit analysis (Saito 2018, Baldi, Wang and Maréchal, 2012, Souppez 2018) of commercial ships and point to the fact that practical applications of hydrogen for power plants would require frequent docking as the mass and volume available onboard to store hydrogen gas either in the form of liquid hydrogen or hydrogen gas is limited. One of the many ways by which the problems associated with frequent refuelling and hydrogen storage can be managed is by generating hydrogen gas onboard (Platzer et al. 2014, Erussard and Delafosse 2019).

One of the green methods, for hydrogen gas generation today, includes the use of bioelectrochemical systems (BES) (Ivase et al. 2020, Jung et al. 2020) for their ability to utilize electroactive microorganisms inherent to wastewaters as catalysts for releasing the nascent chemical energy in the form of hydrogen gas. BES could prove to be a game changer for military and commercial ships because it allows for hydrogen generation as supplementary fuel during the process of onboard effluent treatment.

Author's Biography

Kamar Suhail Basha is the Chief Technology Officer at Ossus Biorenewables in India. A Mechanical Engineer by background, he has previously led other renewable energy projects before developing the OB HydraCel Bioelectrolyzer for on-site hydrogen gas generation.

Sai Swaroop Sinduluri is the lead designer at Ossus Biorenewables. He has a bachelor's in mechanical engineering.

Suruchi Rao, PhD., holds a doctorate in Bioprocess Technology and leads the biology involved with the Bioelectrolyzer. She has previously worked on biomass based liquid biofuels.

 https://doi.org/10.24868/issn.2515-818X.2020.031

The authors of this paper have developed one such bio-electrochemical system, the OB HydraCel Bioelectrolyzer (HBE) that aims to retrofit onto naval vessels for onboard hydrogen gas generation by utilizing onboard effluents with high organic strength and salinity as feedstock. In its current form, the bioelectrolyzer, has been developed for the land-based application of treating highly organic petrochemical refinery effluents as detailed in the sections ahead.

The process of bioelectrochemical hydrogen generation relies on utilizing living microbes to drive the process of organic/inorganic chemical conversion to hydrogen. Selection, culturing and development of stable microbial catalysts remains one of the key innovations within the HBE. Derived directly from the source of the wastewater, these microbial catalysts are a *consortium* (Jiang *et al.* 2017), a synergistic group of different electroactive microbial species which have been specifically been developed by the authors for their capability to target chemical compounds native to the effluent, such as aromatics, phenols, inorganic salts and others for the production of electrons, which are then reduced to hydrogen gas as a pair of electrodes within the primary reactor.

The device has also been designed for minimal footprint in comparison to conventional water management/treatment solution such as oily water separators, desalination systems or conventional effluent treatment plants. These features have uniquely positioned the bioelectrolyzer as a novel solution for military and commercial vessels, which in addition to onboard hydrogen generation would also benefit from better effluent discharge capability. However, in order to become ready for vessel deployment, the device has to overcome challenges associated with marinization and appropriate naval equipment design qualifications.

Thus, the objective of this paper, is to describe the utility of the bioelectrolyzer for hydrogen gas generation as supplementary fuel for onboard powerplants. The paper details the mechanisms and performance parameters of the HBE in its current land-based use-case while evaluating the feasibility of utilizing bilge water, greywater and other effluents onboard as a feedstock to generate hydrogen gas during voyage. Further, this paper also intends to bring forth the challenges associated with marinizing the device in order to qualify its potential as a composite supplementary zero emission fuel generator and onboard effluent treatment device.

2. OB HydraCel Bioelectrolyzer for Hydrogen Generation and Effluent Treatment

OB HydraCel Bioelectrolyzer (HBE), is a microbial hardware device, which converts the organic and inorganic content of highly organic or brine laden wastewater into biohydrogen. The device is essentially a bioelectrochemical system wherein the oxidized content of wastewater is converted into electrons which are then reduced to hydrogen gas at the cathode of a pair of electrodes within the reactor, as described in the next section.

2.1 Process Overview

Bioelectrochemical systems (BES) refer to engineered systems coupling microbial oxidation of organic matter to electrochemical systems (Pant et al. 2012) for generating gaseous value-added products. The output of BES are typically one of two kinds, electrical power in an open circuit or hydrogen gas in an anoxic closed circuit.

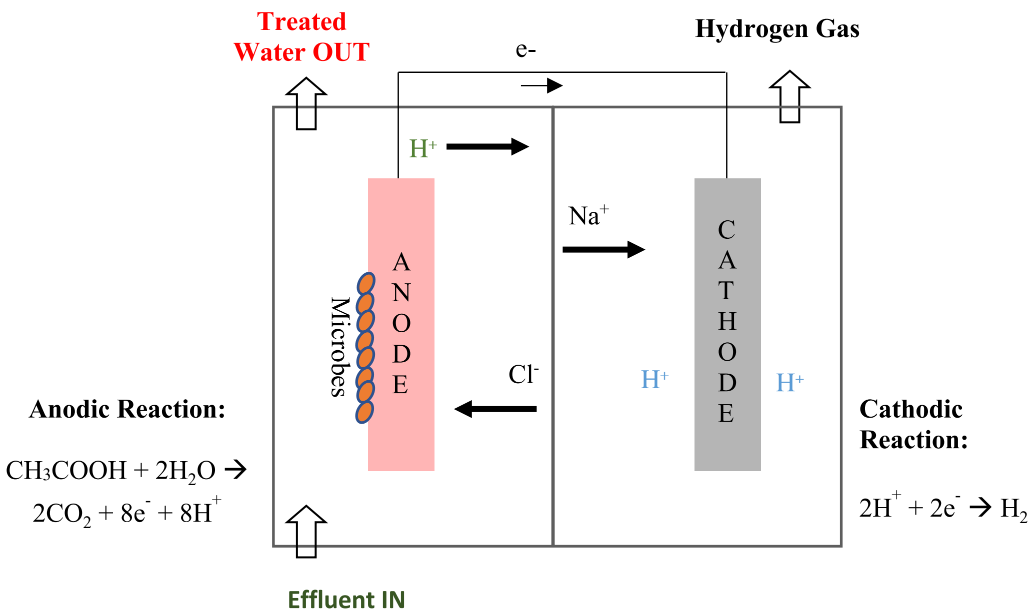

Fig 1: Chemistry of Hydrogen Generation by OB HydraCel Bioelectrolyzer

 https://doi.org/10.24868/issn.2515-818X.2020.031

The OB HydraCel Bioelectrolyzer is a closed-circuit system (Fig 1) that generates hydrogen gas in an anoxic environment using organic wastewater, sewage and industrial effluents as feedstock. In the schematic above, organic content of effluents, is represented by acetic acid (CH_3COOH) while, the inorganic content is represented by ionic groups such as (Na+ and Cl-). The oxidation of acetic acid and other organic acids results in the generation of electrons, collected via an external circuit. Oxidation of organic matter in the HBE is carried out by electroactive bacterial communities (Czerwińska-Główka and Krukiewicz 2020), which use the dilute chemical energy in wastewater to grow, donating electrons to a conductive surface (anode) during the process.

These electrons gathered by the electrode are transferred to the opposite electrode (cathode), where they are reduced to hydrogen gas by an endogenic process, which requires additional input of energy in the form of external voltage as detailed in Equation 1 and Equation 2 (Rousseau et al. 2020). As seen in Fig (1), only two electrons from microbial electrogenesis are necessary to combine with protons produced by microbial activity (shown in green in Fig. 1) (Liu *et al.* 2005) and those freely available in the effluents (shown in blue in Fig. 1) (Aiken *et al.* 2019) or to produce hydrogen gas. The cumulative redox process is supported by the exchange of inorganic ionic species such as Na^+ and Cl^- ions.

At Anode:

$$CH_3COO^- + 4H_2O \longrightarrow 2HCO_3^- + 9H^+ + 8e^- \quad \Delta G_o = +104.6\text{ kJ} \quad \text{-------} \ (1)$$

At Cathode:

$$8H^+ + 8e^- \longrightarrow 4H_2 \quad \text{--------} \ (2)$$

Positive Gibb's Free Energy requires an external input of energy in the form of external voltage (v = -0.14)

$$E_{eq} = \frac{-\Delta G_r^{o/}}{nF} = \frac{-104.6\times10^3 \text{ J/mol}-\text{acetate}}{(8e^- \text{ mol} - \text{acetate})\ (96500\text{C / mol } e^-)} = -0.14\text{V}$$

As detailed in Equation 1 and Equation 2, theoretical conversion limits, allow 12 moles of hydrogen gas to be generated from each mole of acetic acid, when at least 0.14V is suppled as external voltage.

The imposed potential difference drives electrons generated by the microorganisms as they oxidize the organic matter in the effluent. However, for a specific wastewater stream, the actual power requirement stemming from losses to electrode overpotentials vary between 0.2-1.2V. Also, the conversion efficiency of the HBE relies on the microbial catalyst extracted from the source of wastewater and consequently determines the final quantity of hydrogen. The power requirement of this process is dictated not only by the external potential difference but also by current generation which is a biological phenomenon. The current generation capacity is also linked to physical attributed of the reactor such as the volume of reactant, typical characteristics of the effluent such as its organic content, salt content, conductivity, pH along with the material and characteristics of the electrodes. The overpotentials caused by these physical parameters (Ki *et al.* 2016) affects the total input power required by the bioelectrolyzer for generating hydrogen gas. In order to describe the efficacy of the bioelectrolyzer, the next section details a pilot run of the HBE for the treatment of effluents generated by petrochemical refineries.

3. OB HydraCel Bioelectrolyzer as a Land Based Solution

The OB HydraCel *Bioelectrolyzer* was developed as a retrofittable device for hydrogen production on-site at effluent treatment plants or wastewater handling infrastructure and was piloted for a multinational energy company. Their existing effluent treatment process handling wastewater generated during petrochemical refining suffered from several shortcomings as detailed ahead. In this section, the authors describe the development and scaling of the OB HydraCel Bioelectrolyzer during its pilot run for on-site hydrogen gas generation and improved water treatment for petrochemical effluents.

 https://doi.org/10.24868/issn.2515-818X.2020.031

3.1 Bottlenecks in Treatment of Petrochemical Refining Effluents

This pilot was commissioned as an add-on to the existing multistage system on-site for treating a petrochemical effluent stream. The existing process had several drawbacks such as being too energy intensive, producing large volumes of secondary waste and recovering minimum quantities of water for reuse. The objective of the bioelectrolyzer was to retrofit on-site to the existing effluent handling and treatment infrastructure with minimum footprint and reduce sludge formation with concomitant hydrogen gas production.

3.2 Designer Consortium Development and estimation of hydrogen generation capacity

The first step in the process of design and operation of the HBE specific to petrochemical effluents at site involved the isolation and selection of an electroactive active community of microbes or *consortium* directly from the source of the wastewater (unpublished protocol). The selection of electroactive communities was based on their ability to convert the complex chemical content of the petrochemical effluents (listed in Table 1).

Subsequent to the extraction of relevant electroactive consortia from the effluent, the authors estimated the total potential hydrogen gas production capacity, based on the hydrocarbon content, Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) content which were used to typify the petrochemical effluent.

Chemical oxygen demand (COD) and biological oxygen demand (BOD) are indirect measurements of the dilute organic content of effluents and wastewaters (Woodard & Curran 2006) and were used to determine the total oxidizable content within the effluent. The inorganic content of the effluent was measured in the form of the Total Dissolved Solids (TDS) content (Rhoades 2018). Contribution of electrons donated by the hydrocarbon content, total other organic content (COD, BOD) and inorganic salt content (TDS), during the process of microbial electrolysis were utilized to determine the theoretical limits of hydrogen gas which could be generated by the extracted microbial catalysts based on Equation 1 and 2, described in Section 2. With respect to the inorganic salt content, their contribution is attributed to supplementing the redox process involved in microbial electrogenesis and are not directly utilized by the microbes and they are recovered in the form of a sludge at the end of the process.

The aim of projecting hydrogen production capacity was to determine the footprint of the reactor and the hydrogen gas handling equipment as detailed in section 3.3.

Table 1: Estimates of Conversion of Typical Components of Industrial Wastewater

Chemical	Chemical Groups	Maximum Electrons Produced (mol/mol)	Average % wt./wt. of H_2
Hydrocarbons	C_nH_{2n}, C_nH_{2n+2}, $C_nH_{2n+2(1-r)}$	6	55%
Organic (COD, BOD)	CH_3COO^-	4	45%
Inorganic Salts (TDS)*	M^{n+}	-	28%

*M^{n+}: Refers to Metal Ion used to represent the ionic salt content measured as Total Dissolved Solids (TDS).

Overall, 55% of COD per unit volume, was estimated to be oxidized to a combination of gases including hydrogen (48% wt/wt.) along with other products of oxidation including carbon dioxide and occasionally methane.

All efflux gases at the outlet of the systems were produced at atmospheric pressure. Depending upon the final utility of the H_2, the gas has the potential be pressurized after the purification step using a conventional compressor set-up or liquefied for higher operating pressures. The input towards compression or liquefaction of hydrogen was projected and an overall balance of energy specific to the petrochemical effluent has been described in the next section.

3.3 System Configuration

Based on the conversion ratios estimated as shown previously, the bioelectrolyzer was scaled to a prototype measuring 3.7m x 1.3m x 2m and with the capacity to treat 14.4 m^3 of effluents each day. The footprint of the device was determined based on safety considerations and the ability to vent hydrogen gas at the site. At the pilot stage, compression or liquefaction of the hydrogen for downstream conversion to power was not included.

The prototype consisted of a bioelectrolyzer loop housing a pair of electrodes developed by the authors (unpublished protocol).

 https://doi.org/10.24868/issn.2515-818X.2020.031

Electroactive bacteria embedded within a matrix and installed within tubular bioreactors, for the specific breakdown of organic matter (hydrocarbons, aromatics, polymers) and other recalcitrant material with each pass of a fixed volume of effluent (1800L/hr). As shown in Fig. 2, a pump upstream of the bioelectrolyzer was used to recirculate the effluent through the bioelectrolyzer. The process of bioelectrolysis, as described in Section 2, requires an external voltage supply to drive the endogenic reaction of oxidation of organic/inorganic content and associated reduction of electrons to hydrogen gas. During the configuration of the pilot, this external voltage was produced by converting the kinetic energy of the flowing effluent into electrical energy via the means of a turbine. This turbine was designed by the authors to generate at least 1-2kW of power based on the flow rate of the effluent being pumped upstream of the bioelectrolyzer. Additive manufacturing was used to fabricate the turbine and electronic controllers were built to supply a fixed potential difference of 0.8V between the electrodes.

The additional load on the pump was minimum and the ability to generate localized power prevented the requirement of external circuitry and wires, which would have added to the ohmic losses within the system. With repeated passes, the organic and inorganic content of the effluent was estimated (COD/TDS) until requisite clearance was achieved as measured by an online water quality sensor. Gases generated by the process were measured (weight %) via specified gas flow meters and collected via a physical disengagement process, before being vented. No hydrogen gas purification or compression was included at this stage of the process.

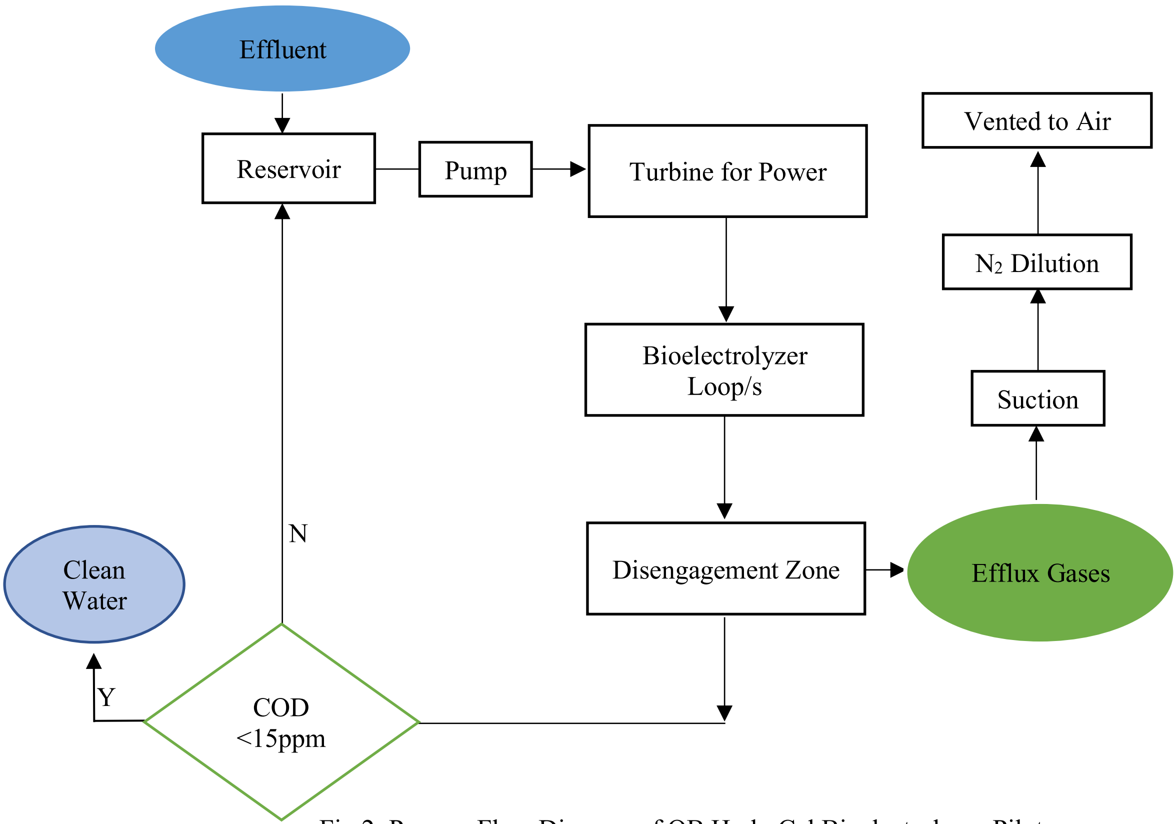

Fig 2: Process Flow Diagram of OB HydraCel Bioelectrolyzer Pilot

The prototype system, consisted of a bioelectrolyzer loop with electroactive bacteria embedded within a matrix and installed within tubular bioreactors, which specifically breakdown organic matter (hydrocarbons, aromatics, polymers) and other recalcitrant material with each pass of a fixed volume of effluent. As shown in Fig. 2, effluents were pumped into the bioelectrolyzer via a turbine, which was used as the primary source of power. After a fixed residence time, the effluent was diverted into the reservoir for recirculation until requisite COD clearance was achieved as measured by an online water quality sensor. Gases generated by the process were measured (weight %) via specified gas flow meters and collected via a physical disengagement process, before being vented.

https://doi.org/10.24868/issn.2515-818X.2020.031

The physical set-up of the pilot is shown in Fig 3., with the turbine (A), bioreactor (B) and disengagement zone and Hydrogen outlet (C) and recirculation loop (D) being the primary elements of the prototype. A pump (E) attached to the reservoir (F) helped replicate the flow of an effluent pipeline. The turbine and electrode housing are 3D printed using poly-jet technique (Khatri et al. 2020), while the bioreactors and disengagement zone were manufactured with polyvinyl chloride and acrylic, respectively. The cathode and anode (not pictured here) were made of proprietary conductive material and electroactive bacteria were immobilized onto the anode. The system was run at ambient temperature.

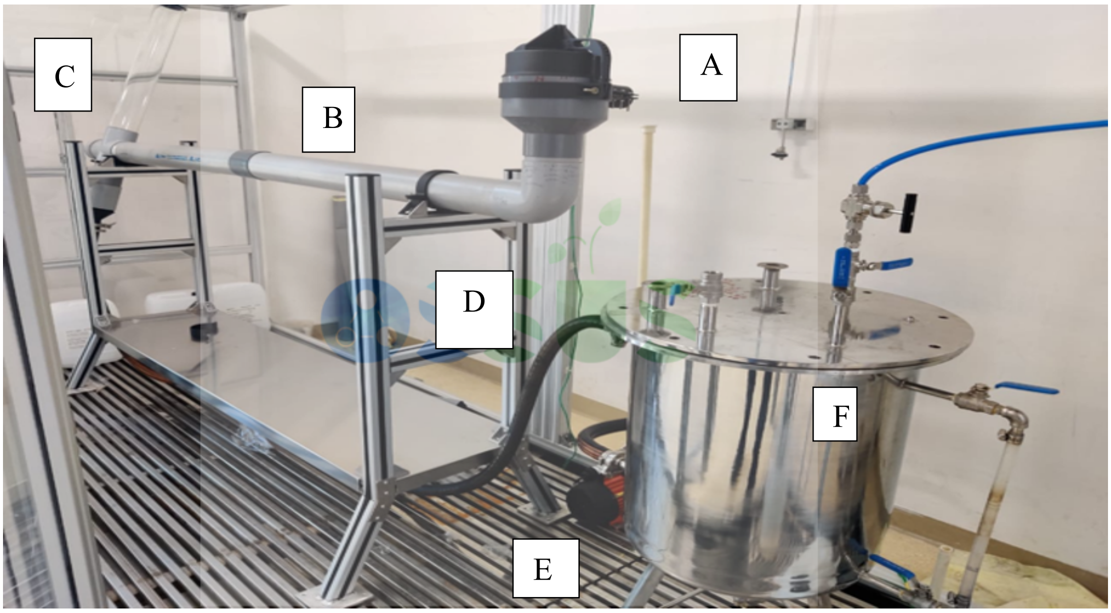

Fig 3: OB HydraCel Bioelectrolyzer Pilot On-site.

3.4 Operation

Initially, the system was purged with nitrogen to create an anoxic environment. After the elimination of any dissolved or gaseous oxygen from within the system, the effluent was recirculated into the reactor. As described previously, the bioelectrolyzer generates localized power via an attached turbine and the power generated was transmitted to the electrodes in the bioreactor to levy a potential difference of 0.8V for chemical oxidation at anode and electron reduction to hydrogen gas at cathode. The total power input in terms of the total volume of hydrogen gas generation has been described in section 3.6.

The tubular design of the HBE's bioreactor eliminated the need for a holding tank and the wastewater was treated continuously as it flowed through the bioreactor. Unlike other systems that require scaling up to handle larger volumes, the modular design of the bioelectrolyzer allowed for scale out without hampering other unit operations within the system.

The gas generated was dissolved within the effluent and to disengage this dissolved hydrogen from the effluent a physical process was used in the disengagement zone which doubled as a gas outlet as well. The disengaged efflux gases were diluted with nitrogen before being vented to atmosphere, since the site did not have any immediate plans of closed capture and utilization of the hydrogen during operations.

3.5 Final Water Quality and Hydrogen Production Rate from Pilot Run

The final output characteristics of the effluent after the completed pilot run have been detailed in Table 2. However, due to commitments involving protection of effluent data, instead of detailing individual organic and inorganic load of the effluent, three primary characteristics have been employed including Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and the pH to showcase efficiency of the process. With a fixed residence time, the pilot run demonstrated that with the specified input, at least 91m^3/day of hydrogen gas could be generated and 14.1 m^3 of demineralized water returned at the end of the process.

https://doi.org/10.24868/issn.2515-818X.2020.031

Table 2: Input/Output Characteristics of the Pilot Study

Characteristics	INPUT	OUTPUT
COD	11988 mg/L	50 mg/L
pH	6	7
TDS	280 mg/L	0 mg/L

Water quality expected at the end of the process has a conductivity of 1-80 µS/cm and was categorized as demineralized water which can be reused as boiler feed, in cooling towers or for steam applications (Knudsen 2001). The microbial catalysts resulted in 99.5% reduction in organic content and generated 7.6 kg/day of hydrogen with the potential for dilution of flare stacks at petrochemical refineries, pending technoeconomic validation.

3.6 Balance of Energy

The HBE was able to generate 91m^3 of hydrogen gas per day utilizing the organic and inorganic content of the petrochemical effluent stream. The process of generating this hydrogen was based on electroactive microbial communities, which utilize an external supply of voltage (0.8V) to oxidize the chemical content of the effluent and transfer electrons to an external electron acceptor (anode) subsequently reduced by combining with protons to generate hydrogen gas at the cathode. The power requirement for the generation of hydrogen gas was dependent on the input voltage, current generated by microorganisms at the anode, ohmic loses and overpotentials as detailed in section 2.1.

For the pilot run described in this section, the energy balance of the HBE has been detailed in Fig. 4. The primary source of the input power was generated from the flow of the effluent as it was being pumped into the bioelectrolyzer. The pump upstream of the bioelectrolyzer was a 0.3kW centrifugal pump and at a flow rate of 30 L/min, the turbine generator produced 0.225 kW power to the electrodes within the bioreactor with an efficiency of 75% by virtue of its design. The applied electrode potential was able to facilitate breakdown of organic content, desalinate water and generate hydrogen at atmospheric pressure consuming 0.12 kW/kg of hydrogen.

In terms of the lifecycle of the produced hydrogen, the pilot did not include any compression or liquification steps as the hydrogen generated was vented to the atmosphere at site. In a real-world scenario however, liquification of hydrogen results in the most energy dense form of hydrogen at 2.3 kWh/kg and requires approximately 10 kWh/kg of energy (DOE Hydrogen and Fuel Cells Program Record 9013: Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs 2009).

This liquefied hydrogen has the potential to be converted to power using a fuel cell, such as a PEMFC, with a 53% efficiency (Minnehan and Pratt 2017). The hydrogen production capacity of the pilot thus has the potential to provide 130 kWh per day, resulting in a net positive power output of approximately 53kW/day.

3.7 Safety Measures

Hydrogen gas is collected in the headspace of disengagement zone as well as the reservoir as water is recirculated through the system. Due to the flammable nature of hydrogen, certain checks are put in place to mitigate the risk of explosion or fire, along with ancillary checks as listed below:

a. To ensure risks from microorganisms (pathogenicity, biodiversity) are reduced, only well characterized, biosafety level 1 (IGF Code 2020) microbes from the effluents were utilized as catalysts.
b. The setup was placed within a secondary enclosure to contain any possible hydrogen leak.
c. Hydrogen detectors up to 5% LEL or Lower Explosive Limit (Ho, Karri and Madsen 2009) were installed at site and within the enclosure.
d. The captured hydrogen was diluted with nitrogen before venting out to the exhaust to ensure that final concentration of hydrogen in the efflux gas stream is less than 5.5 mol%.

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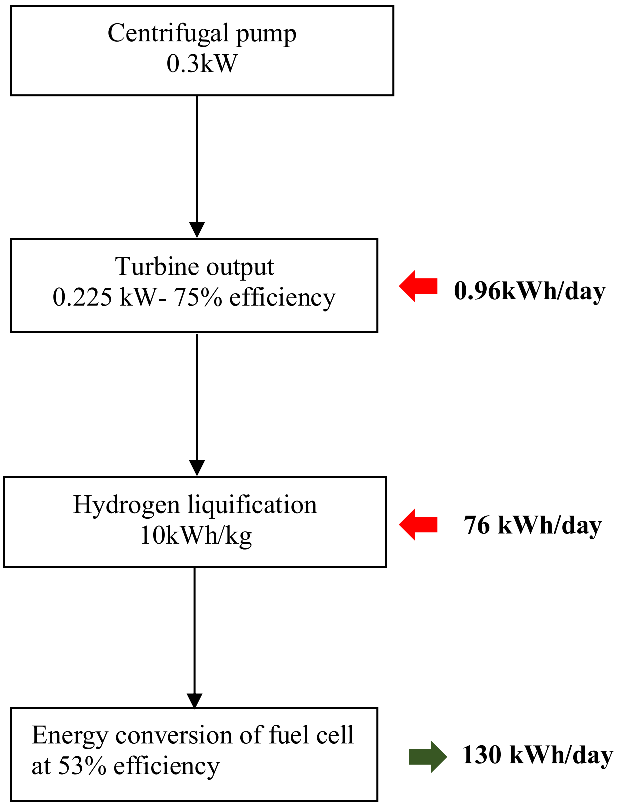

Fig 4: Balance of Energy across hydrogen production using the HBE, liquification and power generation using a Fuel Cell

4. *Process Innovations*

The process innovations developed during the pilot were captured in provisional patents covering different aspects of the microbial catalysts and reactor design as listed below;

a. PCT1; Nano-turbine for power and hydrogen generation within water-carrying piping and pipelines. This provisional patent covers the innovation involved in the design and operation of a turbine keeping in mind its installation at a pipe or pipeline carrying effluents. The designed turbine allows for localized power generation at the point of operation away from existing power lines. The turbine is able to utilize the water's kinetic energy to generate electricity albeit adding a marginal load on the pump. The term nano-turbine is intended to indicate that the quantum of power generated is restricted below 5kW. The turbine is an essential part of the bioreactor as the power generated by the turbine is used to supply the potential difference required for performing microbial electrolysis is provided by a turbine within the reactor. This patent also covers details of other sensors and actuators involved in turbine operation at site. It allows for localized power generation at the point of operation. Localized generation of power means the system does not have to rely on power lines.

b. PCT2; Consolidated biorefinery for the extraction of energy carrier, bioenergy and bioleached metals from hydrocarbon-rich wastewater. This provisional patent covers the process developed for extracting different value-added chemicals including hydrogen, methane and certain heavy metals from effluent streams. It covers the process of microbe extraction, designing microbial consortia, protection of local biodiversity and engineering microbial electrode for value generation based on individual wastewater streams.

 https://doi.org/10.24868/issn.2515-818X.2020.031

c. PCT3; Sustainable Biomaterials for Microbial Bioelectrohydrogenesis. This provisional patent protects the process of developing proprietary electrode material directly from organic wastewater for the generation of hydrogen gas.

d. PCT4; Water carrying piping and pipeline anchored nano-turbine design. A nano-turbine 3D printed with onyx composite to withstand high acidity and salinity. The turbine is anchored within the pipe to generate power from the flow of water/effluents.

5. OB HydraCel Bioelectrolyzer for Hydrogen Generation onboard Naval and Commercial vessels.

As discussed in the previous sections, the capacity for hydrogen generation using the bioelectrolyzer depends on the volume and quality of effluents apart from the withdrawn microbial catalysts.

Similar to its land-based pilot run, it is essential to understand the quality and availability of effluents generated onboard naval vessels to determine the hydrogen generation capacity of the bioelectrolyzer onboard a specific vessel. Due to a deficiency of information regarding operational discharges and effluent quality related to naval vessels, this study, drew parallels from commercial vessels to quantify the chemical content available for the bioelectrolysers as feedstock.

5.1 Effluents onboard commercial and vessels as feedstock for OB HydraCel Bioelectrolyzer

Operational discharges and wastewater generated during the operation and maintenance of ships, have many different sources (Latest News - The Management of Ship-Generated Waste On-board Ships - EMSA - European Maritime Safety Agency 2017) as shown in Table 2. Restrictions on the management and handling of shipboard effluents such as Oily Bilge Water, Sewage and Ballast water (specific to commercial vessels) stem from their oily, organic, aromatic and microbial floral content other than inherent heavy metal and salt content (Geerdink, Sebastiaan van den Hurk and Epema 2017).

Table 3: Overview of Ship-generated Wastewater and Effluents

Types of Wastewater	**Generation Rate (m^3/day)**	**Average COD (mg/L)**	**Source**	**Onboard Treatment Before Discharge**
Oily Bilge Water	0.01-19	2000-12000	Condensate mixed with Oily Discharges From Engine Room	Oily Water Separator (OWS)
Sewage	0.01-0.06 Per person	200-2000	Toilets, Crew/Passenger Numbers	Sewage Treatment Plant (STP) Inc. aerobic treatment, membrane reactors & Others
Miscellaneous				
Tank Washings	20-100	90-350	Tank Cleanings	Collected and treated in OWS
Operational Washes	0.001-0.02% of Dead Weight Tonnage	90-150	Maintenance	Collected and treated OWS/STP
Ballast Water*	30-50% of Dead Weight Tonnage	60-200	Water Intake at Port for Safe manoeuvring	Disinfection with Electrolysis, UV & Others

*Only specific to commercial vessels.

For oily bilge water, the quality and volume generated onboard depends on several factors such as size of the ship, engine room design, preventative maintenance, and the age of the components on the ship (Cruise Ship Discharge Assessment Report Section 6: Hazardous Waste 2008). However, the study used an empirical relationship between the ship's gross tonnage, determined as a function of enclosed spaces on a ship.

 https://doi.org/10.24868/issn.2515-818X.2020.031

Other sources of wastewater range from a few cubic meters to several hundred based on day-to-day activities and the crew size, but also have the potential to contribute relevant COD onboard. The COD of these streams were estimated using an EMSA (Latest News - The Management of Ship-Generated Waste On-board Ships - EMSA - European Maritime Safety Agency 2017) report on the restrictions associated with their disposal.

These assumed values and estimations, suggest that based on a ship and the size of its crew, the total COD available per day on a naval vessel, ranges anywhere between 2440-14770 mg/L.

For estimation of ballast water volumes, the study relied on literature which suggests that cargo and container ships carry 30-50% of their dead weight tonnage (WHO 2011) in the form of ballast water.

5.2 Commercial Vessels versus Naval Vessels

The unavailability of certain streams of effluent onboard Naval vessels is acknowledged by the authors and its inclusion in the forthcoming section, is aimed only at addressing the potential of the bioelectrolyzer. It is to be noted however, that the effluent profile of naval vessels vary widely from commercial ships, most notably with the absence of ballast water as an effluent stream. Each installation of the bioelectrolyzer will thus require to be specific to the type of vessel selected for installation. Due to the efficient desalination capacity of the bioelectrolyzer, an installation on a naval vessel, can be central to enhanced IMO compliance and the hydrogen generated may be used as a supplementary green fuel for a part of the power plant or for a hybrid power plant.

Additionally, depending on the duration of voyage and time at sea, considerable volumes, ranging from a few to hundreds of tonnes, result in significant organic output per day per vessel, which stands to be recovered as hydrogen gas via the bioelectrolyzer. To project such potential, the authors extrapolated these estimates to a commercial vessel as described in the next section. Considerations regarding Naval vessels will include other streams, which could potentially replace ballast, although direct utilization of sea water for dilution of available streams onboard may also be considered.

5.3 Projections for effluents onboard Offshore Supply Vessel as a source of Hydrogen

As a preliminary estimation of total organic content and thus hydrogen capacity, onboard vessels, the authors used an equivalent in the form of a commercial offshore supply vessel. The primary objective of the OSV is to be able is to transport manpower and equipment to larger vessels at sea. The offshore supply vessel, chosen for this estimation, has a Dead Weight Tonnage (DWT) of 4654 and Gross Tonnage of 2961 (EAGLE FRONTIER (Offshore Supply Ship) Registered in Bahamas - Vessel details, Current position and Voyage information - IMO 9034767, MMSI 311000811, Call Sign C6DX7 | AIS Marine Traffic 2020). This vessel, typically traverses a route along coastal United Kingdom, delivering supplies to offshore installations in the North Sea, covering an average distance of 166 nm in each trip, at an average speed of 9.7 knots

Based on estimates calculated as described in the previous section, the daily organic loading based on daily onboard effluent production volume (Table 4), translated to 237 kg/day of organic and inorganic content can be converted to 130 kg of hydrogen gas per day with the use of the bioelectrolyzer.

Table 4: Estimation of Hydrogen Carrying Capacity of a Commercial Offshore Supply

Type of Ship	COD* of Ballast Water (kg/Unit Volume of Ballast*)	COD* of Bilge Water (kg/day)	COD* of Sewage (kg/day)	COD* of Miscellaneous (kg/day)	Total COD* (kg/day)	Hydrogen Onboard (kg/day)
Offshore Supply Vessel	236	0.4	0.67	0.019	237	130

*COD: Chemical Oxygen Demand; measurement of organic content of effluents which can be used to estimate hydrogen generation potential via the bioelectrolyzer.

Based on projected efficiencies similar to the pilot performance of the bioelectrolyzer on land (as described in Section 3), 130 kg of hydrogen per day. This would result in 2239 kWHr/day or 93.3 kW of onboard electrical power using a fuel cell at an assumed 52% conversion efficiency. Due to the high power requirements of propulsion, this power can be used to supplement auxiliary or ancillary power onboard.

The hydrogen generated by the *Bioelectrolyzer* can be used to supplement any hydrogen stored onboard if a fuel cell were to be used as the primary power plant onboard. Also, the hydrogen generated onboard, allows the

 https://doi.org/10.24868/issn.2515-818X.2020.031

recycling of 98% of all water processed, which could considerably reduce the footprint allotted to fresh water generators and sewage treatment plants, instead, making more space available for Fuel Cell and Battery utilities.

In the absence of data in public domain regarding the volumes of effluents generated onboard warships and other naval vessels, the projections here are aimed at providing a comparative view of the capacity of the bioelectrolyzer for supplementary hydrogen gas generation in combination with effluent treatment and desalination. In the next section, the authors detail their collaboration with the Indian Navy and with subsequent testing would be in a position to detail the hydrogen generation capacity of the bioelectrolyzer for naval vessels.

6. Navalization of the OB HydraCel Bioelectrolyzer

Based on the potential capacity of the bioelectrolyzer to power a naval vessel, the emphasis lies on ensuring its ability to handle conditions prevalent on board a naval vessel. In order to ensure the successful navalization of the bioelectrolyzer from a land-based solution to a retrofittable device on board a naval vessel, the authors have identified certain standards and guidelines (Military Standards MIL-STD, Military specifications MIL SPEC 2020) that the bioelectrolyzer must adhere (Table 5) to for its successful deployment and operations.

Table 5: Standards for Navalization

Standards**	**Description**
Def stan 08-123	Requirements for design and testing equipment to meet environmental conditions
MIL-STD-167	Mechanical vibration of shipboard equipment
MIL-STD-1474E	Design criteria for standard noise limits
MIL-STD-740-2	Structure borne vibratory acceleration measurements and acceptance criteria of shipboard equipment
JS55555	Environmental test methods for electronic and electrical equipment
MIL-STD-416E	Requirements for control of electromagnetic interference characteristics of systems and equipment
IS-IEC 60529-2001	Degree of protection provided by enclosures for electrical and electronic equipment
MEPC 107(49)	IMO MARPOL resolution
IGF Code[&]	International Code of Safety for Ship Using Gases or Other Low-flashpoint Fuels
MIL-S-901	High impact shock tests
DME 463	Valves
NES 328	Desalination plants
NES 366	Desalination machinery trials and inspection
Def Stan 61-5	Electrical power supply system

** All information regarding standards were drawn from everyspec.com as cited in section 5 and references
[&] (IGF Code 2020)

In addition to the specified tests and standards. Bioelectrolyzer will have to be integrated with an appropriate monitoring and control system, providing information to the Integrated Platform Management System in the Machinery Control Room or Ship Control Centre.

7. Hydrogen Generation, Oily Water Separation and Desalination System for the Indian Navy

The Indian Navy, in its quest for indigenously developed technologies to keep up with MARPOL resolutions, selected OB HydraCel Bioelectrolyzer as a prospective solution for hydrogen generation onboard Indian naval vessels for green supplementary energy in the form of hydrogen. The bioelectrolyzer is uniquely positioned as it fulfils other secondary functions as both, oily water separator and desalination plant. The technology is currently undergoing certain tests and trials based on a set of prescribed requirements by the Indian Navy. These requirements are as listed below;

I. Vetting of design by a 3rd party such as Lloyd's Register (Manufacturing assistance and design assurance for vessels – lr.org 2020)
II. Certification and classification of equipment within the bioelectrolyzer.
III. Demonstration of unmanned operational capability with remote monitoring.

 https://doi.org/10.24868/issn.2515-818X.2020.031

IV. Closed capture of Hydrogen for power generation.

Unlike an onshore installation, the conditions onboard a sea faring vessel would be challenging due to space constraints and ship motions (Bruschi et al. 2015). With third party design vetting the final footprint along with the location of the bioelectrolyzer would not only be optimised but also aptly classified & certified. The way forward would then be to demonstrate auxiliary power production by means of fuel cells, using the hydrogen generated on board. Auxiliary power here refers to power load required on board for lighting, HVAC, communications in case of warships (Jurkiewicz et al. 2013). The intent here lies in upgrading the EEDI (Perera and Mo 2016) of the vessel by partially offsetting CO_2 emissions and improving effluent discharge quality in a vessel with an efficient and greener auxiliary power source.

8. Conclusion

This study highlights that technologies such as the *bioelectrolyzer* hold considerable promise for being focused on a waste-to-value approach for the production of carbon free source of clean energy produced directly onboard naval vessels to supplement existing power plant or hybrid power trains. The quantum of hydrogen production onboard using the HBE is inextricably linked to the quantum of onboard effluents.

Based on future assessments of the technology's life cycle within the larger maritime space, the use of selected electroactive microorganisms to tap into dilute organics in seawater and/or the high salinity as the prime feedstock, would allow bioelectrolyzer, without relying on effluents alone.

Use of microorganisms derived directly from the source of effluent, position the bioelectrolyzer as a truly green source of clean energy as well as address issues faced with a one-size-fits-all approach observed frequently in the effluent treatment frameworks.

The retrofittable design of the *bioelectrolyzer* also favours naval vessels and operators to consider retrofitting existing vessels with onboard with hydrogen generation capability, without compromising manoeuvrability or safety. The maritime industry stands to benefit from this transition and more collaborations between stakeholders will allow rapid adoption of OB HydraCel Bioelectrolyzer and help achieve IMO's goal of 50% reduction in emissions by 2050.

Acknowledgements

The technology has primary been funded by Innovations for Defence Excellence (iDEX) sponsored by the Department of Defence Production, Ministry for Defence in India and India Innovation Growth Programme 2.0 by Department of Science & Technology, Lockheed Martin and Tata Trusts. The authors would also like to thank Shell E4 program for helping with the platform and testing facilities for hydrogen generation from oily wastes. We are grateful to Mr. V.S. Surya Teja for assisting the authors to gather information related to onboard effluent characteristics.

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Glossary

Acronym	Definition
IMO	International Maritime Organisation
HBE	OB Hydracel Bioelectrolyzer
MARPOL	The International Convention for the prevention of Marine Pollution
EEDI	Energy Efficiency Design Index
GHG	Green House Gases
EMSA	European Maritime Safe
BES	Bioelectrochemical Systems
Na^+	Sodium ion
Cl^-	Chloride ion
CH_3COOH	Acetic acid
CO_2	Carbon dioxide
H_2O	Water
e^-	Electron
H^+	Hydrogen Ion
H_2	Hydrogen gas
CH_3COO^-	Dissociated Acetate Ion
HCO_3	Bicarbonate
ΔG_o	Spontaneity of Reaction Determined by Gibb's Free Energy
E_{eq}	Nernst potential
F	Farad
mol	Number of Moles
C	Coulomb
V	Volts
M^{n+}	Metal Ion, used to represent inorganic salt content of effluent.
TDS	Total dissolved Solids
BOD	Biological oxygen demand
COD	Chemical oxygen demand
Hr.	hour
µS	MicroSiemens
cm	centimetres
L	litre
g	grams
CH_4	Methane
mg	milligrams
LEL	Lower Explosive Limit
m	Meter
OWS	Oily Water Separator
STP	Sewage Treatment Plant
UV	Ultraviolet
DWT	Deadweight Tonnage
kg	kilogram
SCADA	Supervisory Control And Data Acquisition
PLC	Programmable logic controller
HVAC	Heating Ventilation and Air Conditioning
Def Stan	Defence Standard
MIL-STD	Military standards
IEC	International electrotechnical standards
DME	Directorate of Marine Engineering
NES	Naval Engineering Standards
MEPC	Marine Environmental Protection Committee
MIL SPEC	Military specifications
kW	kilowatt
kWh	Kilowatt-hour

 https://doi.org/10.24868/issn.2515-818X.2020.031