

Road to maritime sector decarbonization

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Abstract. Ecospray is actively working on projects for carbon capture in the marine sector, using three different technologies for removing CO₂ from exhaust gases: fuel cells, amines scrubbing and calcium hydroxide scrubbing. These different approaches can meet the requirements that are characteristic of different ship types, proposing specific solutions for each case to allow an effective retrofit and to be compliant with the limits imposed by IMO for the next years. The activity, partially carried out in collaboration with the University of Genoa, also led to the establishment of a new joint laboratory devoted to optimize fuel cell performance, while deadlines for onboard or prototypes in Ecospray laboratories are all fixed for middle 2022.

Keywords. Molten Carbonate Fuel Cells, Amines Scrubbing, Calcium Hydroxide Scrubbing

1. Introduction

Decarbonization is undoubtedly the most imperative priority in the maritime industry and, at the same time, it represents a crucial opportunity. The latest technologies, environmental awareness, sustainability and regulations are the Key drivers towards carbon neutrality.

Ecospray has mapped out its path towards decarbonization with remarkable technologies and innovative approaches to achieving the 2050 zero emission target.

In this scenario, Ecospray is promoting the development of innovative solutions based on three different technologies for removing CO₂ from the exhaust gases of the traditional engines fed by fossil fuels:

- fuel cells, for removing and concentrating CO₂
- amines scrubbing, for chemical removal of CO₂
- calcium hydroxide scrubbing, for CO₂ chemical removal and permanent carbon mineralization

Ecospray is developing Molten Carbonate Fuel Cell technology (high temperature cells operating with molten carbonate as electrolyte) as a unique solution that reduces costs and environmental impact coupling carbon capture with energy production.

In the current stage of development, with also a specific laboratory in partnership with University of Genoa, our carbon friendly fuel cells are designed to be fueled with ammonia or methane, producing energy very efficiently and acting as CO₂ concentrators too.

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Ecospray aims to achieve with this project, started in 2019 with several European partners, the first large-scale maritime implementation program of CO₂ capturing technologies.

In the amines scrubbing technology, part of the exhaust gas is extracted downstream the existing DeSO_x tower and sent to an additional reactor where an amine solution flow is recirculated in a closed loop process, absorbing the CO₂ from the gas stream. When amine flow is regenerated, CO₂ is captured and liquefied (for onboard storing).

In the last project, CaO/Ca(OH)₂ is bunkered and stored onboard as a solid bulk powder. It is mixed with water and injected directly into an auxiliary dedicated scrubber, absorbing CO₂. As a result, the environmentally safe product containing captured carbon, is discharged overboard.

Deadlines for onboard or prototypes in Ecospray laboratories are all fixed for middle 2022.

2. CO₂ removal by Molten Carbonate Fuel Cells (MCFCs)

Molten Carbonate Fuel Cells (MCFCs) have emerged as a promising CO₂ capture system, which is not only highly efficient, but also generates additional electricity [1].

The exhaust gases from the ship engines can be treated with these devices capturing up to the 90% of the CO₂ and obtaining a captured CO₂-rich stream that can be easily segregated by means of a specific purification step applied to a flow rate of an order of magnitude lower than the original flue gas [2].

The main goal of the pilot plant being designed by Ecospray is demonstrating the feasibility of the carbon capture system using MCFCs and collecting operating data. The target of the pilot plant is treating a small part of the exhaust gases of the ship engines to achieve a global removal of 20% of the CO₂ [3].

2.1. Principle of Operation

A fuel cell is an electrochemical device that directly converts the chemical energy of a fuel into electrical energy exploiting reduction and oxidation reactions in a manner that is like batteries. However, unlike batteries, fuel cells are open systems where the reactants are constantly fed to the cell and the products removed.

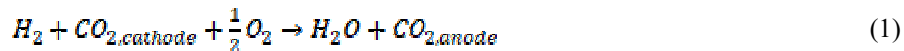
Molten Carbonate Fuel Cells (MCFCs) are high-temperature systems characterized by the use of a liquid mixture of alkali metal carbonate as electrolyte. For this reason, MCFCs operate in a limited temperature range (580°C-700°C) to ensure that the electrolyte is in its liquid state and to limit its losses due to high electrolyte volatility induced by high temperatures.

The main structure of an MCFC is constituted of an electrolyte sandwiched between two electrodes: an anode for the oxidation and a cathode for the reduction.

In the specific case of MCFCs, the anode material is a porous Ni-based alloy (typically with Al or Cr), the cathode material is a porous lithiated NiO, and the electrolyte consists of an eutectic mixture of alkali carbonates of which Li₂/K₂CO₃ and Li₂/Na₂CO₃ are the most common. Moreover, MCFCs need a ceramic matrix usually made of LiAlO₂ to support and keep the electrodes and electrolytes (using capillary forces) in place.

The main reaction that provides energy is the formation of H₂O from reduction of O₂ and oxidation of H₂. However, in the specific case of MCFCs, CO₂ serves as an additional reactant with O₂ to form, at the cathode, the carbonate ion (CO₃²⁻) that function as the anion carrier through the electrolyte and matrix. It is this very fact that makes MCFCs suitable for carbon capture.

The total MCFC reaction is the following:



This is not a single step but is composed of two main half-reactions that occur at the anode and cathode side respectively.

At the anode side, H₂ reacts with CO₃²⁻ from the electrolyte to form CO₂ and H₂O and release electrons according to the following oxidation reaction:



At the cathode side, O₂ reduces thanks to the electrons coming from the anode and, by reaction with CO₂ forms CO₃²⁻ closing the circuit



From the previous equations it can be deduced that MCFCs enable the transfer of CO₂ from a flue gas containing CO₂ is fed to the cathode side to a stream (anode exhaust) in a mixture composed by CO₂ and water, with the addition of some unreacted fuels, mainly hydrogen.

As a function of the final CO₂ disposal and the industrial integration context, CO₂ contained in the anodic off-gases can be further differently utilized or sequestered.

Similarly, different application contexts affect the choice of the H₂ production process, which can exploit renewable sources as well as natural gas, syngas and other fuels.

In maritime applications the Ecospray proposed solution foresees that CO₂ is liquefied and then stored for further usage, while H₂ is obtained by onboard ammonia or LNG conversion.

2.2. Process Description of the Pilot Plant

MCFC material properties, manufacturing processes as well as system integration are under study in collaboration with the University of Genoa. In particular, a jointed laboratory has been established and is going to be inaugurated in these days.

In parallel with this basic research activity, a pilot plant will be installed in Alzano Scrivia (Italy). Here a diesel engine with a size of 80 kW is present with the possibility to vary its load or to add air to obtain different compositions of the exhaust gas. Such a gas can be fed to a water scrubber to reduce the SO_x content and then a part of this, controlled by acting on the speed of a fan, can be used as oxidant at the cathode side of MCFC stacked cells. Before entering the stack, such exhausts are preheated through a heat exchanger cross flow to achieve 580°C.

For the anodic side, H₂ is the fuel required by the main reaction and it is produced directly by an electrolyser. The generated hydrogen is mixed with nitrogen, stored in

cylinders, in order to test different compositions of the inlet gas at MCFC anode side. As for the cathodic side, before entering in the stack, the gas is preheated through a heat exchanger.

The reactions described above take place within the stack and the performance of the stack is constantly measured. Specifically, the capture efficiency is measured through gas analyzers, i.e., the quantity of CO₂ that passes from the cathode compartment to the anode compartment and the quantity of reacted hydrogen is also measured.

Furthermore, the electric power produced by the cell is constantly measured as a function of the electric current inside the MCFC stack.

After reactions in the cell stack, the anode outlet is cool down using chilled water scrubber condenser where vapor is condensed.

The part of the non-condensed current, which has reached the temperature of about 20 °C and is mainly composed of CO₂, N₂ and unreacted H₂, is sent to a burner. The same burner is also fed by the gaseous stream leaving the cathode side and by any additional air and methane to obtain a good combustion of the gas (the goal is to obtain a temperature equal to 680 °C).

The resulting gas will be used to heat the cathode feed current in the cross-flow heat exchanger and then will vent to atmosphere.

The tests that will be conducted on the pilot plant will have as final objective an overall CO₂ reduction of 20% considering both the capture rate of the treated gas fraction and the electrical power produced, which replacing efficiently the energy of the auxiliary engines reduce the production of CO₂.

In the future, the pilot plant could be improved by inserting the CO₂ purification section through different purification solutions (condensation, cryogenic unit, membrane, oxidation, absorption, ...) can be adopted as a function of the specific integration context and the target imposed by the final CO₂ disposal.

3. CO₂ Removal by scrubbing with amines

Amine solutions are able to reversibly absorb carbon dioxide, thus exhaust gases can be washed with these solutions in order to reduce the amount of CO₂ emitted. CO₂-rich amine solution is subsequently regenerated by mean of combined action of vacuum and heat, releasing gaseous CO₂ that, in a full-scale plant, should be liquified and stored.

The purpose of the pilot plant being designed by Ecospray is demonstrating the feasibility of the absorption/desorption process and collecting operating data, so the CO₂ is released in the atmosphere at the end of the regeneration. The target of the pilot plant is achieving a removal of 20% of the CO₂ content of the exhaust gas. An absorbent solution based on methyl diethanolamine (MDEA) and piperazine has been selected after analysis of literature and commercial availability.

3.1. Principle of Operation

Ideally, the absorbent for CO₂ separation processes should have the following properties:

- high absorption and desorption rate
- high loading capacity in terms of $\text{mol}_{\text{CO}_2}/\text{mol}_{\text{solvent}}$

- low energy requirement for regeneration
- non-corrosive behavior
- low tendency to degradation in the operating conditions
- low volatility and good stability
- be harmless and non-toxic.

Monoethanolamine (MEA) is a widely used absorbent for CO₂ because of its high removal efficiency and low molecular weight that allows for smaller recirculation rates in the scrubber. Primary alkanolamines like MEA and secondary alkanolamines react with CO₂ forming a stable compound, i.e. a carbamate ion, according to the reactions:



Tertiary amines like MDEA cannot react directly with carbon dioxide because they do not have the N-H bond required to form the carbamate. MDEA can be used in solution with piperazine that acts as a promoter, quickly forming carbamates with CO₂. Compared to MEA, MDEA has a higher loading capacity because one mole of CO₂ reacts with one mole of MDEA according to the reaction:



while two moles of primary and secondary amines are required per mole of CO₂. Moreover, MDEA is less corrosive and requires less energy for its regeneration, even though CO₂ removal efficiency of MEA in pilot plant tests was shown to be considerably higher. Other advantages of MDEA are a lower vapor pressure (meaning lower losses of solvent during operation) and a better overall performance shown in membrane vacuum regeneration studies. The main challenge of the conventional amine-based process is its high energy penalty for absorbents regeneration. In addition, thermal regeneration occurs at high temperatures which could result in problems such as thermal degradation and loss of absorbents.

Wang et al. [4] observed that membrane vacuum regeneration has the potential to reduce the energy requirement for CO₂ desorption, by introducing a low-temperature regeneration concept, and conducted extensive testing on this technology.

Yan et al. [5] experimented on reduced thickness of the solvent film combined with vacuum and concluded that this regeneration technology has better performance than heating method if the layer thickness is below 1 mm.

3.2. Process Description of the Pilot Plant

The pilot plant will be installed on a bulk carrier ship and will be connected downstream the existing Exhaust Gas Cleaning System. Exhaust gas is fed to the amine scrubber by an exhaust gas fan. The gas is withdrawn downstream the DeSO_x scrubber, hence its SO_x content is usually below 20 mg/Nm³ and the temperature is in the range 25÷50°C. Exhaust gas flow rate is controlled by acting on the speed of the fan.

Exhaust gas enters the scrubber below the lowest tray and flows counter-current to the amine solution. Amine solution fills the bottom of the scrubber that acts as a buffer

tank. A recirculation pump, takes the solution from the scrubber bottom and feeds it to the top tray. A bag filter collects fine impurities that could be carried over by the solution. Exhaust gas leaves the scrubber from the top after passing through a demister.

A side stream of amine solution is withdrawn from the bottom of the scrubber by the stripper feed pump and is sent to regeneration in the stripping column. Once filtered, this stream is heated close to its boiling point by an electric heater and then enters the stripping column through a spray nozzle.

The amine solution flows downward the stripping column that is kept under vacuum and gets in contact with the vapour phase composed of stripped CO₂ and steam. At the bottom of the column, steam is injected in order to enhance the desorption of CO₂ from the solution acting as a sweep gas. Steam is produced by an electrical steam generator.

Regenerated amines flow from the bottom of the stripping column to a buffer tank. This tank is kept under vacuum during filling phase and, once full, it can be pressurized to atmospheric pressure. When the vessel is pressurized, an unloading pump starts and transfers the regenerated solution back to the bottom of the scrubber.

The vapour phase leaving the stripping column from the top goes to a chilled water condenser where vapour is condensed and separated. Incondensable gasses (mainly CO₂) are vented to atmosphere through a vacuum pump while condensate accumulates in a second buffer vessel. Condensate is then transferred to a storage tank onboard and should be later sent to a waste water treatment onshore.

Periodically, a minor amount of amine solution should be manually drained from the bottom of the scrubber and replaced with fresh solution. Spent amine solution should be stored onboard in a dedicated tank and sent to disposal onshore.

4. CO₂ Removal by Scrubbing with calcium hydroxide

An alternative technology to capture carbon dioxide is scrubbing the exhaust gasses with calcium hydroxide suspension in order to bind the CO₂ in the form of calcium carbonate.

4.1. Principle of Operation

The main reaction at the basis of calcium hydroxide scrubbing is the following:



A suspension of calcium hydroxide in water with a solids content ranging from 10% to 30% constitutes the so-called lime milk. Since calcium hydroxide solubility is very low (approx. 1.7 g/L at room temperature), suspensions in water are often used to increase the concentration of reactant. Calcium hydroxide reacts with CO₂ forming calcium carbonate that is only slightly soluble in water, so it will form a solid product. The suspension of calcium carbonate is harmless for the marine environment; indeed, limestone is a constituent of various marine organisms and could be discharged overboard where the big volume of seawater can dissolve it. Moreover, the discharge of an alkaline substance in the oceans can have beneficial effects for the marine environment. Indeed, purposefully increasing the alkalinity of the ocean is gaining

mounting attention for the potential to mitigate ocean acidification, a major threat for some marine ecosystems, while simultaneously removing atmospheric CO₂ [6].

Caserini et al. [6] investigated the potential for CO₂ capture by ocean liming, i.e., direct discharge of calcium hydroxide (slaked lime) in the seawater. They highlighted that local pH increase could have a detrimental impact on marine ecosystems and modelled the dispersion of lime in the wake of a ship, concluding that the complete dissolution of lime could require up to 1500 m of path. In this context, the discharge of calcium carbonate/bicarbonate instead of slaked lime could help reducing the local impact thanks to the weaker alkaline behaviour.

In order to achieve an effective reduction of CO₂ concentration in the atmosphere, the lime used for scrubbing has to be carbon neutral. Some processes to produce lime without CO₂ emissions have been proposed [7, 8]; they involve sequestration of all the produced CO₂ combined with efficient use of combined fossil or renewable energy sources.

4.2. Process Description of the Pilot Plant

The same pilot plant described above will be partially re-used for testing carbon capture with lime milk.

Exhaust gas enters the scrubber below the lowest tray and flows counter-current to the lime milk suspension. Lime milk is initially loaded in the bottom of the scrubber that acts as a buffer tank. The suspension is kept under agitation by injecting a small amount of exhaust gas through the sparger on the bottom of the column. A recirculation pump takes the suspension from the scrubber bottom and feeds it to the top tray. The bag filter is now by-passed in order to avoid quick fouling due to suspended solids. Exhaust gas leaves the scrubber from the top after passing through a demister.

A side stream of lime milk is withdrawn from the bottom of the scrubber and is sent to a bubbling vessel that acts as a second stage absorber and gives to the lime milk a long contact time with exhaust gas in order to complete the conversion of lime into limestone. Exhaust gasses are injected below the liquid level by means of a sparger. An exhaust gas blower takes a small flow of gas downstream the main fan and generates the pressure required to bubble inside the vessel. Spent lime milk leaves the vessel through a syphon and is discharged overboard. The exhaust gas exiting the bubbling vessel from the top is recycled back to the scrubber.

Fresh reagent is continuously supplied from the storage tank to the bottom of the scrubber. A dedicated dosing pump controls the flow of fresh reagent in order to keep a constant pH in the recirculation of lime milk. The storage of fresh lime milk is a removable IBC tank that can be replaced once empty. An agitator is inserted through the top opening of the tank in order to avoid sedimentation of the solids.

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