Compliance & Regulation | Amine | Latest R&D news

Road to 2050

The Carbon Capture Technical Journal

Unveiling the decarbonization solutions for the shipping industry to approach the challenges of 2030 and 2050.

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ECOSPRAY
technologies for the planet

MEPC 78 Outcome

In June 2022, a series of MEPC 78 sessions were held in order to approve and adopt amendments to the current regulatory framework on – among other things – reducing GHG emissions with a focus on the technical guidelines for the EEXI, CII and SEEMP, revising the IMO GHG strategy, mid- and long-term measures to reduce GHG emissions, on-board CO_2 capture, and lifecycle GHG/carbon intensity for marine fuels. The reductions in GHG emissions as planned by IMO (designed to enable the target of full decarbonization to be achieved by 2050) is the most challenging task for the maritime industry. The following elements must be highlighted:

Use of Biofuels

Biofuels are derived from biomass sources, such as plant or algae material or animal waste. The most promising biofuels in marine applications are bio-LNG and methanol. Biofuels are considered to be carbon neutral because the amount of carbon dioxide (CO_2) generated during combustion has been directly or indirectly absorbed from the atmosphere during the growing phase. Of course, the carbon footprint depends of the fuel in question is dependent on the feedstock and the production pathway, considering all the emissions caused directly by the supply chain and by energy and materials used in the supply chain. The Committee approved a new Unified Interpretation of MARPOL Annex VI and the NOx Technical Code 2008 to provide clarity on the use of biofuels on board ships, and the possible implications for NOx emissions.
However, the most important implication is that related to the reduction of GHG emissions and the evaluation of draft guidelines proposed by an intersessional working group (ISWG) on lifecycle GHG/carbon intensity for marine fuels.

Lifecycle GHG/carbon intensity for marine fuel

MEPC 78 considered the report presented by the ISWG-GHG and divided the proposal into two groups: the first of these focused on the life cycle assessment (LCA) guidelines as a means for fuel evaluation, while the other highlighted the importance of the "tank to wake" emissions in conjunction with the CII requirements, as currently, there is no mechanism to credit biofuel in the calculation of CO_2 emissions. MEPC confirmed the intention to focus on the whole "well to wake" process, and that LCA guidelines should be technical and provide a neutral tool for the maritime sector, i.e., they should not prejudice the future development of GHG reduction measures or their application as part of existing GHG reduction measures.

On-board CO_2 capture

MEPC 78 also introduced the discussion on provisions for considering on-board CO_2 capture in the calculation of EEDI, EEXI and CII, and several delegations pointed out that the IMO should contribute to raising awareness in order to improve the collective understanding of this issue, including by inviting the industry to participate and promoting technological initiatives regarding the development of onboard CO_2 capture technologies. However, the general understanding is that the technical side of things is still not sufficiently mature, and significant R&D efforts are still needed to advance the Technology Readiness Level (TRL) of this technology. Despite this, given the interest in further consideration of the concept of onboard CO_2 capture, the MEPC 78 invited interested Member States and international organizations to submit further information and concrete proposals to future sessions.

Ecospray's contribution

In light of the invitation of the MEPC 78 delegations and IMO to industry to study, develop and test effective onboard carbon capture technologies, Ecospray is actively providing its own contribution by promoting greater dissemination of information and defining criteria for the consideration of the aforementioned technologies in the calculation methodologies of the current ship's EEXI and CII, as well as by making proposals through recognized organizations and/or Administrations. At the same time, Ecospray is involved in discussions with international bodies on the use of bio-fuels and related lifecycle assessments with a view to achieving an overall reduction in GHG emissions.

Amine-based carbon capture

As is currently the subject of extensive discussion, methods to mitigate the effects of global warming have focused on carbon capture technologies. To facilitate ship owners' eventual transition to renewable fuels and sources of energy, solutions for CO_2 capture are needed in the short term.
Post-combustion chemical absorption is one of the most promising alternatives nowadays and amine-based scrubbers are among the most proven and mature.

Amine

A chemical review

Amines are nitrogen-containing organic compounds deriving, either in principle or in practice, from ammonia (NH_3). The two main chemical species that are used in the process of decarbonization are secondary and tertiary amines. Secondary amine compounds can react readily with CO_2 due to the need of nitrogen to become more stable by losing electrons and, in doing so, attack and bond to CO_2.
Tertiary amines, meanwhile, react in a slightly different way, catalyzing the formation of a hydrogen carbonate ion (HCO_3^-) by reaction with water in the solution (a hydrolysis reaction).

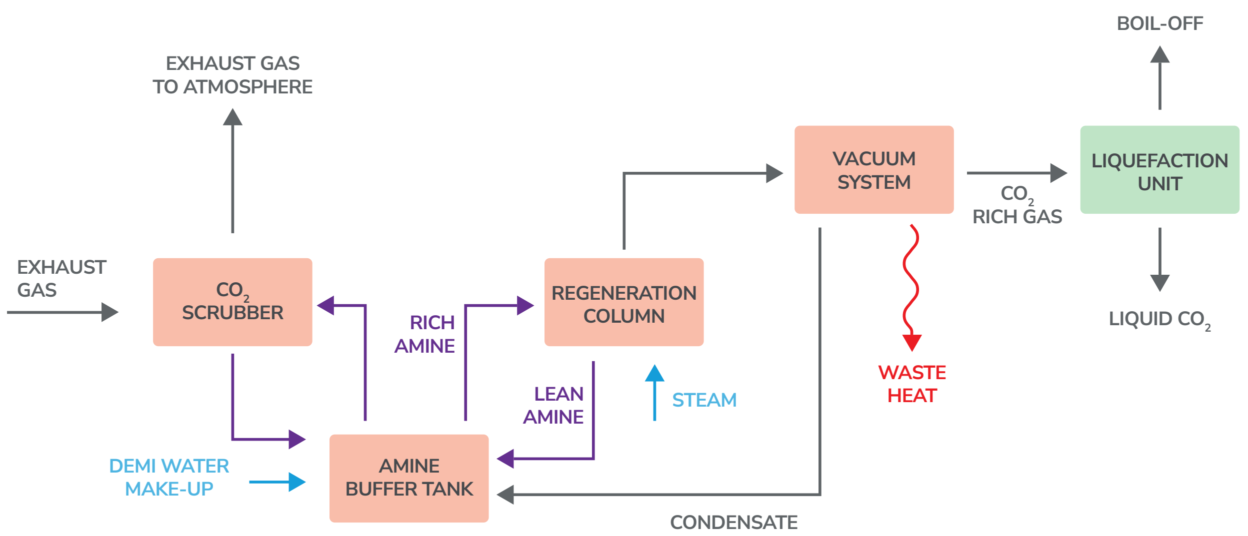
Chemical research has revealed that mixes of tertiary and secondary amines react more favorably and that a blend of these combines the high reaction rate exhibited by the secondary amine with the lower activation energies associated with tertiary amines.

$$CO_2 + NR_3 + H_2O \leftrightarrow HNR_3^+ + HCO_3^-$$

Overall reaction for a tertiary amine. R represents carbon bonded to other species.

The technology explained

The amine liquid solution is used as reagent in the CO_2-scrubber to reversibly absorb carbon dioxide from the exhaust gas. CO_2-rich amine solution is subsequently regenerated by means of the combined action of vacuum and heat in a dedicated stage of the plant and then re-used in the main scrubber. In a full-scale plant, the desorbed CO_2 is liquefied and temporarily stored on board in cryogenic tanks before disposal in port.

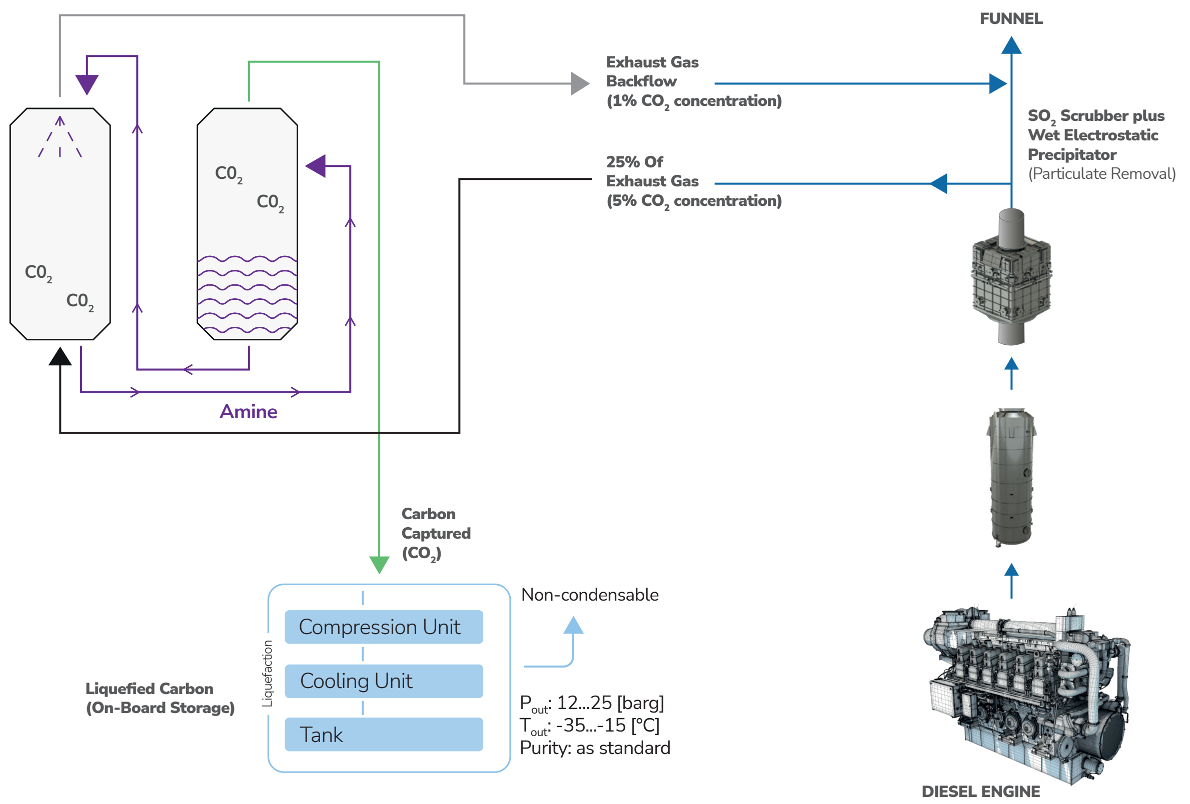


Source: Ecospray

Amine regeneration

Amine thermal regeneration represents the main operating cost associated with amine scrubbing.
The main method of regeneration currently in use in industry is heat regeneration wherein the solution of CO_2 rich amine is heated to elevated temperatures (typically 140° C to 160° C), forcing the removal of CO_2. However, this process is very energy intensive and requires additional fuel. For this reason, additional CO_2 needs to be captured, increasing the size of the plant and the OPEX cost. Moreover, this high regeneration temperature is one of the reasons for the ammine chemical degradation.
Amine degradation is the breakdown of the initial amines in the solutions into other species. Degradation not only reduces the CO_2 capturing performance, but can also be potentially dangerous, creating by-products that could cause equipment corrosion, waste disposal issues, foaming and the generation of volatile and harmful compounds.
Furthermore, degradation implies the replacement of the amine batch, in order to keep the capturing performances at a higher level of efficiency, increasing the system OPEX for the new reagent and for the disposal of the used one.
The solution that Ecospray is using is thin-film regeneration, which allows for the removal of CO_2 from the amine solution at lower temperatures thanks to the optimum combination of temperature, vacuum and low quantity of steam injection. This represents an important saving, because this heat can be recovered by the engine cooling system without burning additional fuel.

On board amine-based carbon capture application



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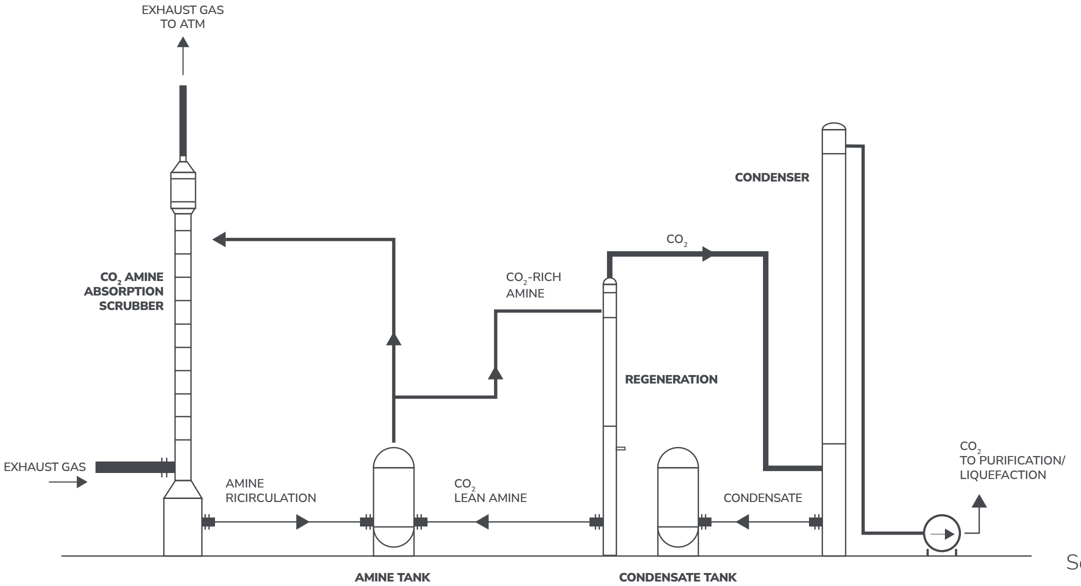


Source: Ecospray

Design

Having conducted a thorough investigation into the application of the industrial amine absorption process, Ecospray has begun the process design, as well as embarking on an in-depth study on the marinization of the technology, focusing on two crucial aspects: reducing the footprint and power consumption of the system. During the installation of more than 700 SOx scrubbers on board ships and mantaining the same performance levels, Ecospray has carried out the significantly reduction of the dimensions of the systems. In the last 10 years, the dimensions of SOx scrubbers have decreased by around 40% in cross section and 30% in height, whilst maintaining the same level of efficiency. The other aspect, related to the reduction of power consumption in amine regeneration activities, is essentially linked to the capacity for reducing the temperatures needed for the regeneration of the amines solution; as previously explained, this also serves to reduce the degradation of the amine solution with a lower quantity of fresh ammine necessary, and a smaller amount of waste to be disposed of in port.

Looking at the specific process, a typical design will envisage a stream of exhaust gas treated with amine solution in order to reduce the amount of CO_2 emitted; the balance between the quantity of exhaust gas to be treated and the specific CO_2 removal rate will be customized according to the specific requirements. After the CO_2-rich amine solution regeneration, a purification and liquefaction skid will be used to obtain the CO_2 in liquid form for onboard storage. Exhaust gas leaving the DeSOx scrubber is fed into the amine scrubber by means of an exhaust gas fan. It is necessary to remove as much SOx with desox scrubber and NOx with SCR systems as possible, to avoid degradation of the amine solution. Installation of a wet electrostatic precipitator between the DeSOx scrubber and the amine scrubber is also suggested in order to minimize carry-over of dust and SO_3 that could also add to the early degradation of the solution. Exhaust gas enters the CO_2-scrubber from below and flows counter-current to the amine solution. A recirculation pump takes the solution from the amine tank and feeds it to the top tray of the scrubber. A filter collects fine impurities that could be carried over by the solution. CO_2-reduced exhaust gas leaves the scrubber after passing through a demister. A side stream of amine solution (approx. 10% of the recirculation rate) is withdrawn from the amine tank and is sent to undergo regeneration in the stripping column. After a further filtration stage, this stream is heated to close to the operating temperature of the stripping column. The amine solution flows downward into the stripping column, which is kept under vacuum, and enters into contact with the vapor phase, composed of stripped CO_2 and steam. At the bottom of the column, steam is injected in order to enhance desorption of the CO_2 from the solution, acting as a sweep gas. Gravity enables the regenerated amines to flow to the amine tank.
The vapor phase leaving the regeneration column moves to the condensers, where water vapor is condensed and separated. Incondensable gasses (mainly CO_2) are transferred to CO_2 purification and liquefaction through a liquid-ring vacuum pump, while condensate accumulates in a dedicated tank and can be mixed with the amine solution in order to control the concentration of the scrubbing solution.

Operating conditions

ME power: 36MW
Treated Gas flow: 100.000 m^3/h
Removed CO_2: 20% (on total exhaust gas flow)
Absorbed Power: 2,6 MW

Design data

Daily CO_2 removed: 76 tons/day
Liquid CO_2 storage volume: 480 m^3
Hold-up time: 7 days

Road to 2050: where are we?

Q1-2021
MCFC: process definition for marine applications

Q2-2021
MCFC: feasibility study for different types of ships

Q3-2021
AMINE: feasibility study for amine technology and lime milk technology

Q4-2021
MCFC: electrode chemical mix, production methodologies and quality control

Q1-2022
MCFC: stack geometry, thermofluid dynamics and selection of materials

Q2-2022
AMINE: class approval for onboard installation and tests - LAB 1 Alzano

Q2-2022
MCFC: new lab for fuel cell development and testing (Genoa, Italy)

CapLab
ELECTROCHEMICAL CELLS

Q3-2022
AMINE: Pre-assembled skid ready for onboard installation & on board test and first tests of lime milk technology

Q4-2022
MCFC: CO_2 liquefaction system and treatment for onboard storage

Q4-2022
LIME MILK: start of onboard testing

Q4-2022
MCFC: marine engine exhaust gas pollution check for fuel cell compatibility (ULEV) – LAB 1 Alzano

Q1-2023
MCFC: Ultra-compact catalytic steam reforming reactor and ultra-compact heat exchangers for high temperature applications

Q1-2023
LIME MILK: completion of onboard testing

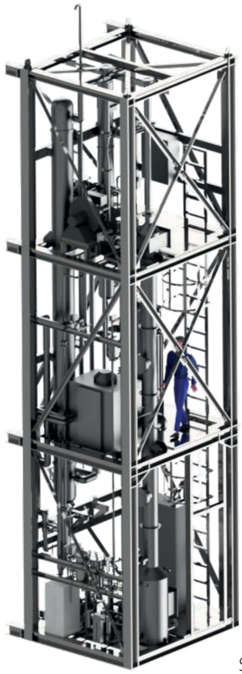
Q2-2023
MCFC: pilot system installed in LAB 1 (power: 20 kW) – lab & testing

Q2-2023
AMINE: industrialization

Q3/4-2023
MCFC: industrial pilot system installed on board (power 400 kW) – lab & testing

Amine and lime milk: the pilot plant - coming soon

As anticipated in the first issue, Ecospray is developing a range of different customized technologies to help shipowners find the right solution for decarbonization: carbon capture with fuel cells and carbon capture with amines and lime milk. On the latter two, Ecospray is developing a pilot plant that combines the two innovative technologies for CO_2 capture: namely, carbon capture with amines and carbon capture with lime. The system is built in a transportable skid; the process will be first tested at Ecospray's laboratories, with the exhaust gas coming from an 80 kW diesel generator and subsequently it will be installed on board a commercial ship in order to test and assess the results in a real environment. The skid already includes the reactors and ancillaries necessary to study and test both technologies, and once the tests are completed, a very important milestone will be established, allowing further optimization and a conscious design of real scale systems.



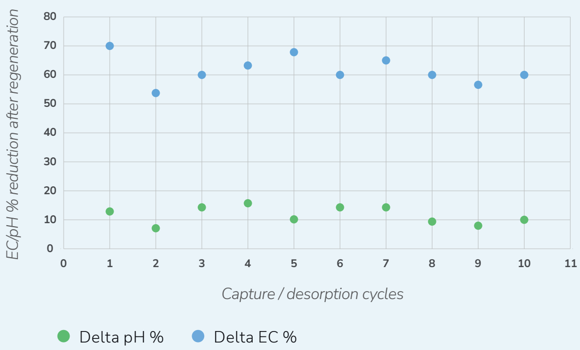
Source: Ecospray

Ecospray and Universities

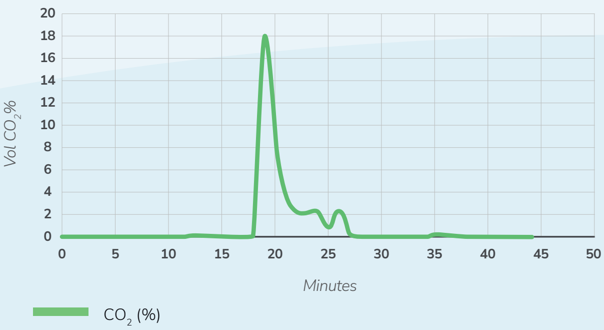
Results UNITO

The Department of Earth Science of the University of Turin is playing an important role in assisting Ecospray in the definition of the chemical parameters to be applied to the Carbon Capture industrial processes. Thanks to two new laboratories, one dedicated to amine and another to lime milk, several tests have been done for both technologies.
The amine laboratory have demonstrated the feasibility of the carbon capture process based on cyclic absorption and regeneration, with the optimum vacuum and temperature combination. Different operating conditions were tested and the functionality of the solution after several cycles was assessed: pH and electrical conductivity (EC) before and after regeneration showed good repeatability.
Determination of the correlation between pH, EC and absorbed CO_2 is ongoing. Chromatographic analyses of amine solutions after CO_2 loading and regeneration have been carried out in order to investigate undesired degradation processes. Degradation products appear to be negligible.

In the lime laboratory, different samples of CaO have been characterized by x-ray spectroscopy and SEM. Absorption tests of CO_2 in lime milk suspensions designed to investigate kinetics and mass transfer phenomena are ongoing to define the capture efficiency and the reagent utilization.



▲ Distribution of ph and electroconductivity values of the amine solutions over 10 capture/desorption cycles. The stable values mean the good absorption/desorption capabilities of the solution with negligible or absent degradation signs.



◄ Trend of CO_2 concentration in the vapor phase during regeneration. The sudden increase in concentration shows that once the correct operating conditions are reached, carbon dioxide is readily released.

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In the next issue:

"An in-depth look
at calcium hydroxide technology"

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