TOWARDS NEGATIVE EMISSIONS THROUGH DIRECT AIR CAPTURE

Every day, the news has some mention of climate change. A flood, a forest fire, a climate summit, climate protestors,... Climate change is real and it is happening faster and faster. The world needs solutions with a real impact to tackle climate change. Carbyon is an Eindhoven-based start-up company, developing novel equipment to help solve the biggest challenge humanity has ever faced. To make use of Carbyon's USPs, advanced manufacturing techniques are needed for the production of CO_2-capturing materials. Carbyon is developing their own dedicated set-up for this, which will be explained in detail.

JASPER SIMONS

Carbyon's mission

Carbyon's founder and CEO Hans de Neve was working on novel thin-film materials for solar applications at Solliance. The idea arose to apply these materials for capturing CO_2 directly from the atmosphere (direct air capture, DAC). Some 'Friday-afternoon' experiments were done and results looked great. The principles were patented by TNO shortly after. Because TNO did not want to pursue DAC at the time, De Neve decided to spin out and found his own company, fortunately supported fully by TNO. Carbyon joined the programme of Eindhoven-based venture builder HighTechXL and made great progress in acquiring essential testing equipment and proving the fundaments of the technology in lab-based experiments (technology readiness level TRL 4).

Early 2021, Elon Musk tweeted, "Am donating \$100M towards a prize for best carbon capture technology", and engaged in a cooperation with X-prize, an independent international organisation with the goal to accelerate innovation through competition. With Musk's \$100M as the biggest prize-pot in X-prize's history, the 4-year contest started in April 2021. The challenge is to present a carbon-capture solution that can be scaled to gigaton scale. As this contest fits Carbyon perfectly, we joined right away.

The competition consists of two parts; after the first year (in April 2022) it was possible (not obligated) to participate in the 'Milestone Award' and the big final will take place in April 2025. The Milestone Award consisted of a sizeable submission on paper, comprising a description, calculations and hard evidence from lab measurements. On Earth Day 2022, we received the news that we had won one of the 15 \$1M prizes from the hundreds of submissions worldwide. To be able to compete in the final, the challenge is to capture and store 1,000 tons of CO_2 within the timespan between 1 February 2024 and 1 February 2025.

Today, the team has grown to about 20 people in house and dozens more in external cooperations with companies and academics in the region. The mission of Carbyon is to slow down, stop and eventually reverse climate change by restoring the carbon balance in the atmosphere.

AUTHOR'S NOTE

Jasper Simons studied Mechanical Engineering at Eindhoven University of Technology (TU/e) and graduated from the Constructions and Mechanisms group. He worked at CCM (now Sioux) and MI-Partners, in the field of high-tech mechatronics, and in 2020 became the CTO of Carbyon in Eindhoven (NL).

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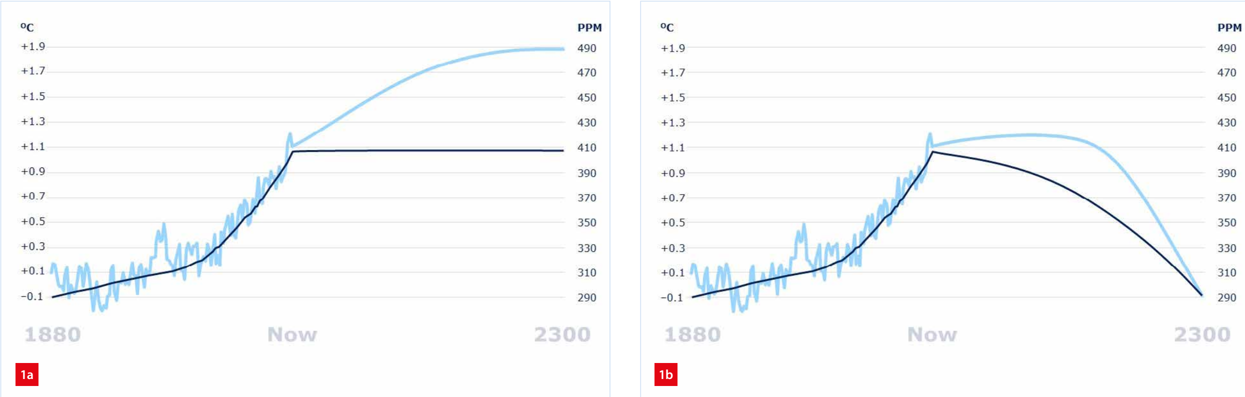
Climate change

Luckily, by now, most people understand that climate change is real, that it is moving faster than ever, that it is caused by human behaviour and that it has devasting effects on our own environment. The CO_2 in our atmosphere allows energy from the sun to reach the earth's surface, but keeps the energy within the atmosphere. The higher the CO_2 concentration in the atmosphere becomes, the more energy is 'kept' in our atmosphere.



To stop global warming (blue) due to rising CO_2 concentrations in the atmosphere (black), CO_2 emissions have to decrease.
(a) With net-zero emissions, temperature will still rise.
(b) Negative emissions are required to bring back the global temperature to an acceptable level.

The vast amount of thermal mass in the earth's surface and atmosphere causes the response of our 'system' to be rather slow. As a result, the temperature on earth is presently not in equilibrium with the CO_2 concentration in the atmosphere. This means the following: Even if we would stop emitting CO_2 tomorrow completely, reaching true net-zero emissions worldwide, even then climate change will not stop. Because we are not at equilibrium yet, the IPCC (Intergovernmental Panel on Climate Change) concludes that climate change would continue for another three hundred years before levelling off. It is this realisation that stresses the need for negative emissions (Figure 1). This requires the removal of all the CO_2 we emitted over the past 150-200 years, cleaning up our own mess. And then, hopefully, climate change would indeed slow down, stop and even reverse...

Carbon balance

All the CO_2 we emit, comes from carbon that was already on earth in a different form. Strongly simplified, carbon occurs on earth in three 'forms':

- Biosphere: in plants and trees, in the oceans, in animals and also in our own bodies.
- Atmosphere: CO_2 gas.
- Underground: mineralised in rocks and sediments, but for the sake of this story, predominantly in the form of fossil fuels.

Many processes occur naturally that exchange carbon between these different forms. Starting from the industrial revolution, humanity started burning vast amounts of fossil fuels, taking large quantities of carbon from underground and emitting it into the atmosphere. In doing so, we strongly unbalanced the naturally occurring carbon cycles. We need to undo this by removing the CO_2 from the atmosphere again and this is exactly what Carbyon's equipment is being designed for.

What to do with all that CO_2?

The captured CO_2 can go in two directions: Carbon Capture and Utilization (CCU), and Carbon Capture and Sequestration (CCS)

CCU

There are many industries that use CO_2 as a feedstock. Examples are the chemical industry, merchant gas suppliers (such as Air Liquide or Linde gas), greenhouses (will be addressed later) and the beverage industry (e.g. Coca-Cola). An additional market that is presently still small but is expected to grow to huge proportions is the synthetic fuel market, which uses CO_2 and green hydrogen to synthesise fuels such as kerosine.

The CO_2 these markets use, often comes from fossil sources and ends up in the atmosphere sooner or later. The shortest imaginable cycle is the beverage industry. They put CO_2 in their products and after a shelf life of a couple of weeks, a consumer will drink it, burp and the CO_2 goes into the atmosphere. The same happens in greenhouses. They use CO_2 to help crops such as tomatoes grow. After a few weeks of growing, consumers eat them, burn the fuel they supply and exhale the CO_2 into the atmosphere.

In each of these industries, fossil CO_2 sources could be replaced by CO_2 captured from air. As mentioned, all of these industries have in common that the CO_2 will eventually end up back in the atmosphere, which is where it came from with DAC, making this a CO_2-neutral cycle.

CCS

Contrary to utilization (CCU), sequestration (or storage; CCS) means that CO_2 is taken out of the cycle permanently (or at least for several centuries). There are two major 'sinks' for CO_2: ironically (or beautifully) underground, or locked in building materials such as concrete. Underground storage can be done in depleted natural gas fields. There are not many sites operational yet, but scientists agree that this is a safe and sustainable way of storage and the available capacity is huge.

Alternatively, CO_2 can be mineralized in certain rock formations, such as olivine and basalt. For example, the captured CO_2 can be dissolved in water and pumped into underground porous basalt layers where the CO_2 mineralises and stays there forever. This mineralisation can also be done above ground (sometimes called enhanced weathering). The resulting minerals can be used as a replacement for cement, storing the CO_2 inside concrete from which it will also never be released, not even if the concrete is later demolished. This solution really cuts both ways as it reduces cement production, which is a huge emitter of CO_2, and it sequesters CO_2 from the atmosphere.

Summary

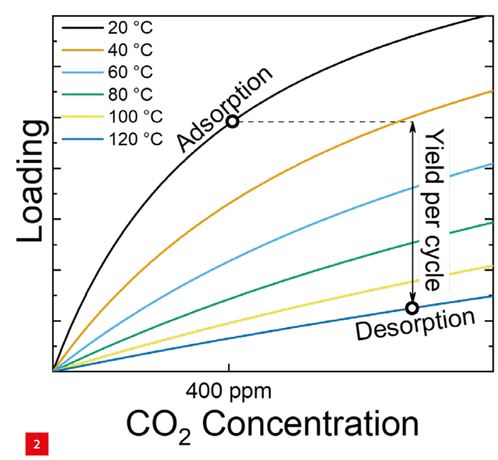
Although CCU applications are 'only' net zero, they actually support Carbyon's mission. To get to net negative emissions worldwide, we first need to get to net zero. This means reducing the use of all fossil fuels as quickly as possible and replacing the old-fashioned processes with renewable processes based on CO_2 from air. On top of that, we need to ramp up as much CCS as we can. The negative emissions we create there will first serve to compensate hard-to-abate CO_2 emissions (such as commercial aviation, which cannot easily be electrified). As emissions are reduced and CCS is scaled up, actual net negative emissions will be achieved as well.

Direct Air Capture

Recently, the concentration of CO_2 in the atmosphere has exceeded 420 ppm, which is 150% of the 280 ppm before the industrial revolution, but even then, 99.958% of the atmosphere is not CO_2... Removing CO_2 from the atmosphere is therefore like finding a needle in a haystack over and over again; only one in every 2,500 molecules is CO_2. Hence, we need a way to specifically target the CO_2 and let everything else pass. This is achieved by a thermal- and pressure-swing chemisorption process.

There are two main groups of chemicals that can capture CO_2 molecules by forming a covalent bond; amines and carbonates. These chemicals cannot be used as stand-alone materials, so they have to be coated onto a carrier structure. The combination of the carrier structure and the active chemicals is called the sorbent, which is exposed to the air at ambient pressure and temperature. CO_2 molecules will hit the surface and some of them will stick to it (forming the aforementioned covalent bond). This is called adsorption and it is an exothermic reaction, which results in a relatively stable bond.

Adsorption and desorption are continuously taking place side-by-side. The net amount of CO_2 on the sorbent is influenced by temperature and partial CO_2 pressure. Higher temperature results in more desorption, so less CO_2 on the sorbent, and vice versa, and higher partial pressure of CO_2 results in more adsorption, so more CO_2 on the sorbent and vice versa. The influence of temperature is stronger in our case. The relation between CO_2 loading on the sorbent, temperature and partial CO_2 pressure is described by isotherms (Figure 2).



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Isotherms showing the relation between CO_2 loading on the sorbent, temperature and partial CO_2 pressure.

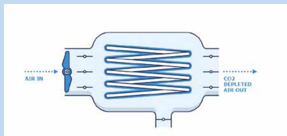
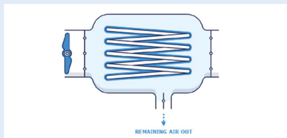
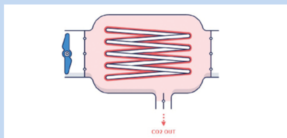
After a certain adsorption time, the sorbent reaches sufficient loading to be desorbed. Because the sorbent is heated, the equilibrium shifts towards desorption and the CO_2 is released again. As mentioned, adsorption takes place under atmospheric conditions, but obviously, desorption cannot. The CO_2 would be released back into the atmosphere then, making the entire process useless. Ad- and desorption phases therefore have to be separated in place (spatial) or in time (temporal). Carbyon has chosen the latter, which results in a batch process where ad- and desorption are separate steps, carried out sequentially. The resulting machine and process layout is presented in Table 1. Upon completion of the desorption step, the vessel is vented to atmospheric pressure again and the cycle can start over.

Carbyon's USP

Carbyon is not the only entity pursuing DAC and most of our fellow climate-change-fighters use very similar processes: temperature (and pressure) swing of amines or carbonates. Carbyon's USP is speed. For any DAC process, one of the biggest challenges is mass transport; how do the CO_2 molecules from the bulk airflow find their way to a 'binding site' on the sorbent?

The biggest difference here is illustrated in Figure 3, showing a generic cross-section of a carrier material, which is porous to enlarge the surface area and available volume for the sorbent. The left image shows how most competitors coat their carriers; the pores are completely filled up with sorbent. This results in a high mass percentage of the active chemicals, which is good for the capturing capacity. But all gas-to-solid interactions can only take place on the surface area of the coated carrier structure, resulting in rapid saturation of the outer layer. To reach the deeper binding sites, the already adsorbed CO_2 molecules have to 'move over' to free up binding sites on the surface again. This 'moving over'

Table 1
Carbyon's machine and process layout.

The sorbent is structured in high-aspect ratio panels; the panels are placed in a filter-like configuration, resulting in a high surface area for airflow through thepanels.	
The panels are placed inside a reactor-vessel with large openings allowing high flow rates of ambient air at a low pressure drop. The air is blown through with a fan.	
After adsorption is finished, the fan is shut down and the large valves are closed, enclosing the panels. A vacuum pump is used to remove the remaining ambient air between the panels.	
In parallel, the panels are heated up. Both the high temperature as well as the low pressure ensure rapid desorption. The CO_2 is also transported out of the vessel by the vacuum pump.	

happens based on solid-state diffusion, which is a rather slow process.

On the right, Carbyon's sorbent is shown schematically. The difference is that the pores are not fully filled up, but rather a thin layer of active chemicals is 'coated' on the walls of each pore. This results in a sorbent with 'only' surface area and no volume. All binding sites can be reached by gas-phase rather than solid-state diffusion, which is three to five orders of magnitude faster. Yes, the transition from a '3D sorbent' to a '2D sorbent' results in a lower capacity, but this can be made up for by using materials with a very large internal surface area. Carbyon uses activated carbon materials with ~1,000-3,000 m²/g, due to the presence of many tiny pore structures with nanometer-scale diameters (typically between 0.5 and 5 nm). The challenge then becomes: how to 'paint' the walls of nanometer-scale pores without clogging them?

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Schematic of the adsorption process: the '3D sorbent' of competitors (left) versus Carbyon's '2D sorbent'.

Introduction into ALD

To the initiated, pursuing a thin, conformal, self-limiting coating screams for Atomic Layer Deposition (ALD).
For those who are new to ALD, some introduction might be needed. ALD and the closely related Molecular Layer Deposition (MLD) are special cases of chemical vapour deposition (CVD). In classic (temporal) ALD, a substrate is placed inside a vacuum reactor. The reactor is evacuated to ~0.1 mbar or (much) lower pressure. Then, a controlled amount of a gas-phase chemical is dispensed into the reactor; this 'precursor' contains a specific atom, or group or atoms, that is to be deposited. The remaining atoms present in the molecule act as a sacrificial scaffold that is used to protect and transport this atom to the substrate.

The molecules of this precursor are designed such that they can attach to the surface exactly once, making the reaction self-limiting. This means that – in theory – a perfect monolayer of these molecules is formed on the surface after sufficient waiting time and assuming sufficient amounts of molecules are dispensed in the first place.
After this, the remaining precursor, and any byproducts from the reaction between the precursor and the surface, are evacuated from the reactor using the vacuum system. Then the second chemical, typically called the 'co-reactant', is dispensed. It reacts with the precursor on the surface, forming the desired coating. If the precursor and the co-reactant were dispensed into the reactor simultaneously, the self-limiting nature of the ALD process would be lost and uncontrolled, and CVD-like growth would take place on the surface and potentially even in the gas phase.

By repeating the cycles mentioned above, multiple layers can be built up, accurately controlling the thickness of the coating. Alternatively, it is also possible to apply multiple pulses of theprecursor before ever dispensing any co-reactant. This so-called multi-pulse strategy is sometimes needed to ensure full coating of larger surface areas.
ALD is presently typically used in the semiconductor industry, display technology, and solar. TNO has done a lot of technology development on this topic in the past and presently, two Eindhoven-based companies (SALD, formerly SoLayTech, and Spark Nano, formerly SALDTech) develop ALD equipment industrially.
One can imagine that this technique can be quite suitable for coating the carrier materials to create Carbyon's sorbents. This is indeed the case and in close cooperation with the group of Professor Adriana Creator (Applied Physics, TU/e), a multitude of samples have been produced, inspected and tested. This joint research effort quickly ran into some limitations of the existing equipment, however.
In most present-day use-cases of ALD/MLD, depositions are done on silicon wafers or other fairly flat materials. These materials have a specific surface area of ~1 m²

internal surface area for every ‘real’ m² of surface area. Coating a monolayer on such a flat surface therefore also results in ~10^{-9} m³ and ~10^{-6} kg deposition amounts per m² of substrate. Carbyon’s carrier materials have much higher specific surface areas of ~100.000-200.000 m²/m², resulting in deposition amounts that are also that much higher.

Aladdin

Operating at the low pressures described above for these large surface areas results in processing times of days or even weeks, even for very small samples quantities. To overcome these productivity issues, several orders of magnitude of improvement are needed. This cannot be achieved by minor process modifications, but requires an entirely new set-up.

Carbyon decided to develop – in cooperation with the TU/e and supported by several suppliers and SALD – their own ALD set-up: Atomic Layer Deposition Device Innovation Necessity (Aladdin). The major differences with existing equipment are:

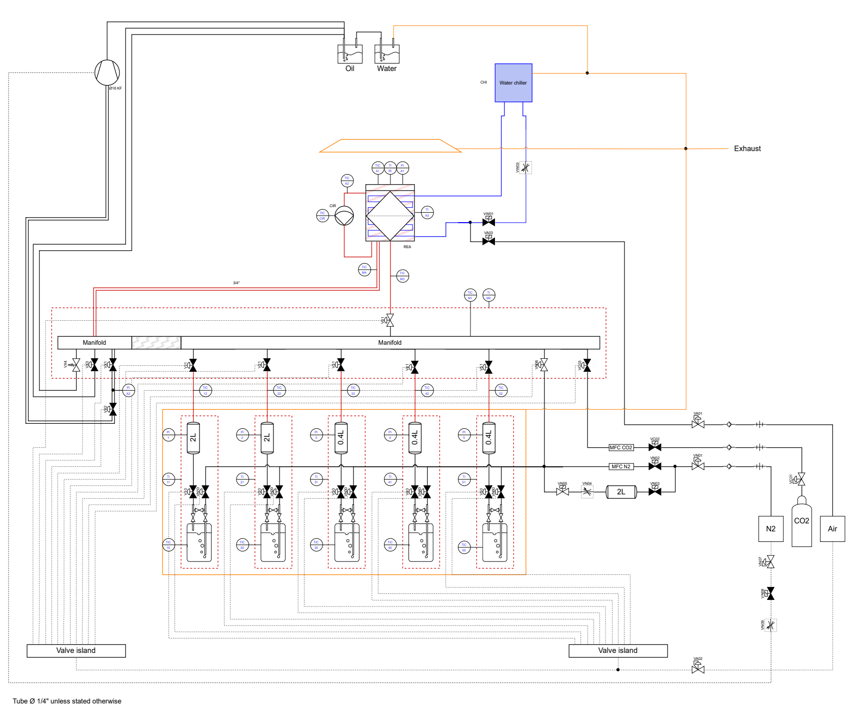
- Instead of operating at ~0.1 mbar or lower, much larger vapour pressures of the precursors are used. The target is 250 mbar.
- Similar to the adsorption process, mass transport of the precursor is also a determining factor. The byproducts mentioned above also need to be removed from the carrier at the same time. Both are achieved by recirculating the gas inside the reactor through the carrier material.

Another challenge is to supply the gas-phase chemicals to the reactor. This is done using ‘bubblers’; airtight stainless-steel vessels that contain a liquid or solid precursor. These vessels need to be heated to create vapour pressure of the chemicals inside. They are called bubblers because they are generally also equipped with a ‘dip-tube’; a tube that leads to the bottom of the vessel, allowing a carrier gas such as nitrogen to be dispensed into the liquid chemical. The bubbles that come up, will carry some of the chemical vapours. They can also be operated without a carrier gas; this method is called ‘vapour-drawn’. The vapour pressure is then directly related to the temperature and varies between the different chemicals.
To be able to supply the desired vapour pressure levels of ~250 mbar, temperatures up to 250 °C are required. This is far from straightforward as component availability (such as manual and pilot valves) becomes limited to only a few suppliers worldwide. Furthermore, the entire path from the bubbler up to the reactor cannot contain any cold spots as this would result in condensation of the precursors.

Figure 4 shows the piping and instrumentation diagram (P&ID) of Aladdin. In the lower middle, five identical bubblers can be seen. These contain the different precursors and co-reactants needed. Each bubbler has three manual valves to open, close and flush them. A nitrogen supply from the wall is connected to all the dip tubes to be able to use the bubbler functionality if needed. This can also be used to flush the tubes for cleaning.
Each bubbler is placed inside its own custom-built oven (Figure 5). This is the best way to heat the bubbler and the five valves on top and the vessel above uniformly. Each oven has a thermocouple on the ‘load’ (the bubbler) and on the heating element to protect against overheating. All five ovens are placed inside a cabinet with active ventilation for safety.

If the vapour would be dispensed directly into the reactor, the deposition reaction would start immediately; especially since the reactor is designed for high productivity. As mentioned before, most precursor molecules release one or more groups as byproducts when they attach to the surface. If the number of separate molecules coming off of each deposited molecule is larger than one, this means that more molecules are ‘created’ inside the reactor. This results in an increase in pressure, which is actually a really nice way to monitor the progress of the reaction. But the fact that this pressure increase starts immediately, makes it very difficult to accurately dose the amount of vapour dispensed into the reactor. Accurate flow measurement devices do not exist for 250 °C, so an alternative solution was needed.

The vessel above each bubbler is called the ‘dosing vessel’, a passive tank that acts like a ‘waiting room’ for the vapour. The volume of the tank is known accurately from calibration.



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Piping and instrumentation diagram (P&ID) of Aladdin; see text for explanation.

Combined with an accurate pressure sensor, the amount of precursor inside the dosing vessels can be calculated. When the valve between the dosing vessel and the reactor is opened, the pressure will equilibrate rapidly. The volume of the reactor and the tubing leading there, is also calibrated. Therefore, the amount of vapour dispensed into the reactor can be calculated with sufficient accuracy.

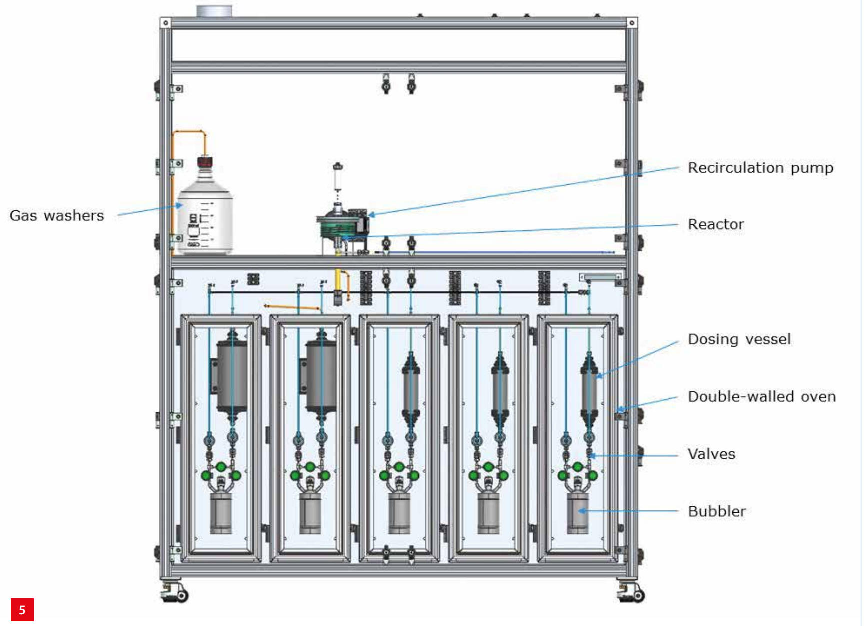
The precursors from each bubbler (always operated one at the time) enter the reactor through a manifold. The reactor is then closed off and the recirculation pump is activated. This is a membrane pump with a temperature-controlled heated head that can operate up to 250 °C. All the gases in the reactor (precursor and byproducts) are recirculated through the porous samples while the pressure is monitored. As the pressure levels off, everything can be flushed out using nitrogen and the next step can start.

Flushing is also not entirely straight-forward. Some precursors are pyrophoric (they will burn in contact with air), which is a safety concern. To solve this, all gases that come from the reactor need to pass through a gas washer. As this particular precursor reacts with the water in the air, the gas washer in this case is the water vessel shown at the top of the P&ID. By 'bubbling' the gases through this water tank, any remaining precursor that did not react inside the reactor, will react with the water in the tank in a controlled way. The reaction product will simply sink to the bottom of the tank.

If only the water gas washer were present, water vapour from this tank could diffuse into the tubing towards the reactor. In that case, the reaction product would form inside the tubes and valves, potentially clogging them. To prevent this, an additional gas washer with oil is added upstream. The precursor does not react with the oil, but the oil acts as an 'oil-lock', keeping the water vapour out of the tubes.

The reactor is heated electrically, but active cooling is also added; cooling water is pumped through channels in the reactor to cool it down in ~15 minutes instead of 2-3 hours. This allows faster changing of samples and therefore more productivity. Introducing room temperature water into a 250-°C reactor would result in steam generation and rapid pressure build-up. This is a safety concern as well, and therefore, the initial cooling from 250 °C down to ~100 °C is done with compressed air. This compressed air is also used to flush out any remaining cooling water before heating starts again, to prevent boiling water in the cooling channels.

The set-up (see Figure 5 for a partial overview) is presently being assembled by LT Technology, which designed and built multiple components of the system. After completing the mechanical assembly and the 'plumbing', the set-up will come back to Carbyon, where VHE industrial automation will install the electronics and complete field wiring. Next, ICT will come to integrate the PLC software and the Python-based user interface. After integration testing in Carbyon's labs, the set-up will be transported to the TU/e Applied Physics PMP (Plasma & Materials Processing) labs, where joint research will be conducted with Carbyon's scientists and researchers. The set-up is planned to be operational in January 2023.



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Partial overview of the Aladdin design.

Conclusions and outlook

Presently, we are at TRL 4, based on lab-scale measurements of our sorbents. In Q1 2023, our first 'integrated prototypes' will become available in our labs, bringing us to TRL 5. We call these integrated prototypes because these will be the first set-ups that include all elements of the process in a single set-up. These prototypes will have a small reactor (roughly 1% reactor volume compared to the size we envision for the commercial products) and much more diagnostics to enable us to learn a lot from these set-ups.

Parallel to product development, Carbyon's technology research group will continuously improve the sorbent to obtain higher capacity, faster kinetics and lower energy use, for which Aladdin is a key part. Development of first full-scale systems is already ongoing, in collaboration with Demcon in Best (NL). These systems will roughly have the volume of a 20-ft shipping container and can capture 100 tons of CO_2 every year; we are aiming to have the first systems operational by the end of 2023. Pilot testing will be done in all major market segments and we hope to achieve our first commercial sales by mid-2025, scaling up to gigaton deployment worldwide in the decades after that.