



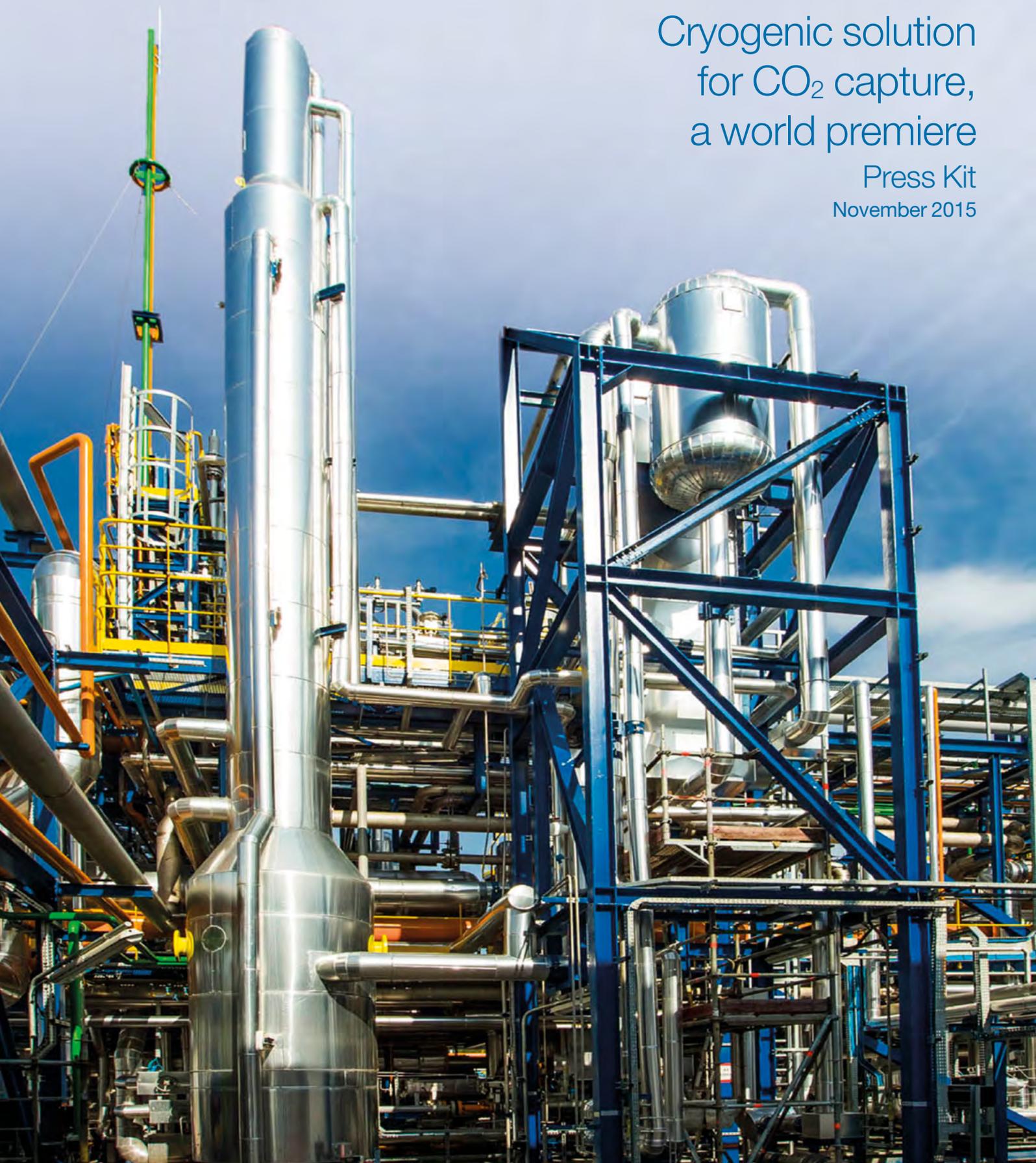
**AIR LIQUIDE**

*Creative Oxygen*

# CRYOCAP™:

Cryogenic solution  
for CO<sub>2</sub> capture,  
a world premiere

Press Kit  
November 2015



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# CRYOCAP™ – A WORLD PREMIERE DEVELOPED IN FRANCE

## A technological innovation

Cryocap™ is a technological innovation for CO<sub>2</sub> capture using a cryogenic process (involving low temperatures, around -50°C, to separate gases) that is unique in the world. Cryocap™ can be adapted to specific applications combining a variety of Air Liquide technologies: the capture of CO<sub>2</sub> produced by steel plants (Cryocap™ Steel), thermal power plants (Cryocap™ Oxy), or hydrogen production units (Cryocap™ H<sub>2</sub>).

Cryocap™ has resulted in the filing of several patents and illustrates the Air Liquide group's innovation. Its installation in Port-Jérôme, Normandy, France, at the largest steam

methane reforming hydrogen production unit operated by Air Liquide in France represents the first industrial deployment of the Cryocap™ H<sub>2</sub> technology.

Because Cryocap™ is located at the heart of the hydrogen production process – i.e. where the emissions are the most highly concentrated – it optimizes CO<sub>2</sub> capture compared with conventional solutions, in particular the chemical process known as amine scrubbing capture. **Today, Cryocap™ is the only technique that enables the reduction of the CO<sub>2</sub> released during the production of hydrogen while also increasing this hydrogen production.**

## Towards the decarbonized production of hydrogen

The most common process for producing hydrogen is based on steam methane reforming, which involves a chemical reaction between natural gas, mostly composed of methane, and steam, which produces hydrogen and also releases CO<sub>2</sub>.

Cryocap™H<sub>2</sub> enables to capture a large portion of the CO<sub>2</sub> that is released (from 60% to 90 %<sup>[1]</sup>). It can be then liquefied and purified to be finally used to meet the CO<sub>2</sub> needs of local industrial markets (agri-food, water treatment, etc.).

This solution represents an important step toward the ultimate goal of producing decarbonized hydrogen.

## An ambitious project conducted with the support of local and national government agencies



Cryocap™ represents an investment for Air Liquide of around 30 million euros, decided in 2012. It also benefited from public financial support of close to 9 million euros, provided jointly by the Haute Normandie region, the community of Caux Vallée de Seine communes, and ADEME (French Environment and Energy Management Agency) through the Programme d'Investissement d'Avenir, a government program for investment for the future.

Air Liquide has chosen to invest in France. France constitutes a solid industrial base for the Group and also hosts one of its main

research centers and one of its engineering centers. This geographic proximity of operations, researchers, and designers has allowed for fluid, optimal management of the project. Within France, Air Liquide has a strong ecosystem of innovation that involves 2,000 people and includes an R&D center, hubs of expertise, a laboratory for new ideas, the i-Lab, and ALIAD, the Group's venture capital arm in innovative technology startups. In 2014, **two-thirds of Air Liquide's spending on innovation was done in France** and additional investments of close to 100 million euros were decided to accelerate the pace of innovation in France.



[1] If hydrogen is used as an energy source in the SMR oven to replace natural gas



## CRYOCAP™ H<sub>2</sub> TECHNOLOGY

The Air Liquide site in Port-Jérôme:  
the Group's largest hydrogen production unit in France

The Port-Jérôme site, located in Notre-Dame-de-Gravenchon in Normandy, is the largest SMR (Steam Methane Reforming) hydrogen production unit operated by Air Liquide in France.

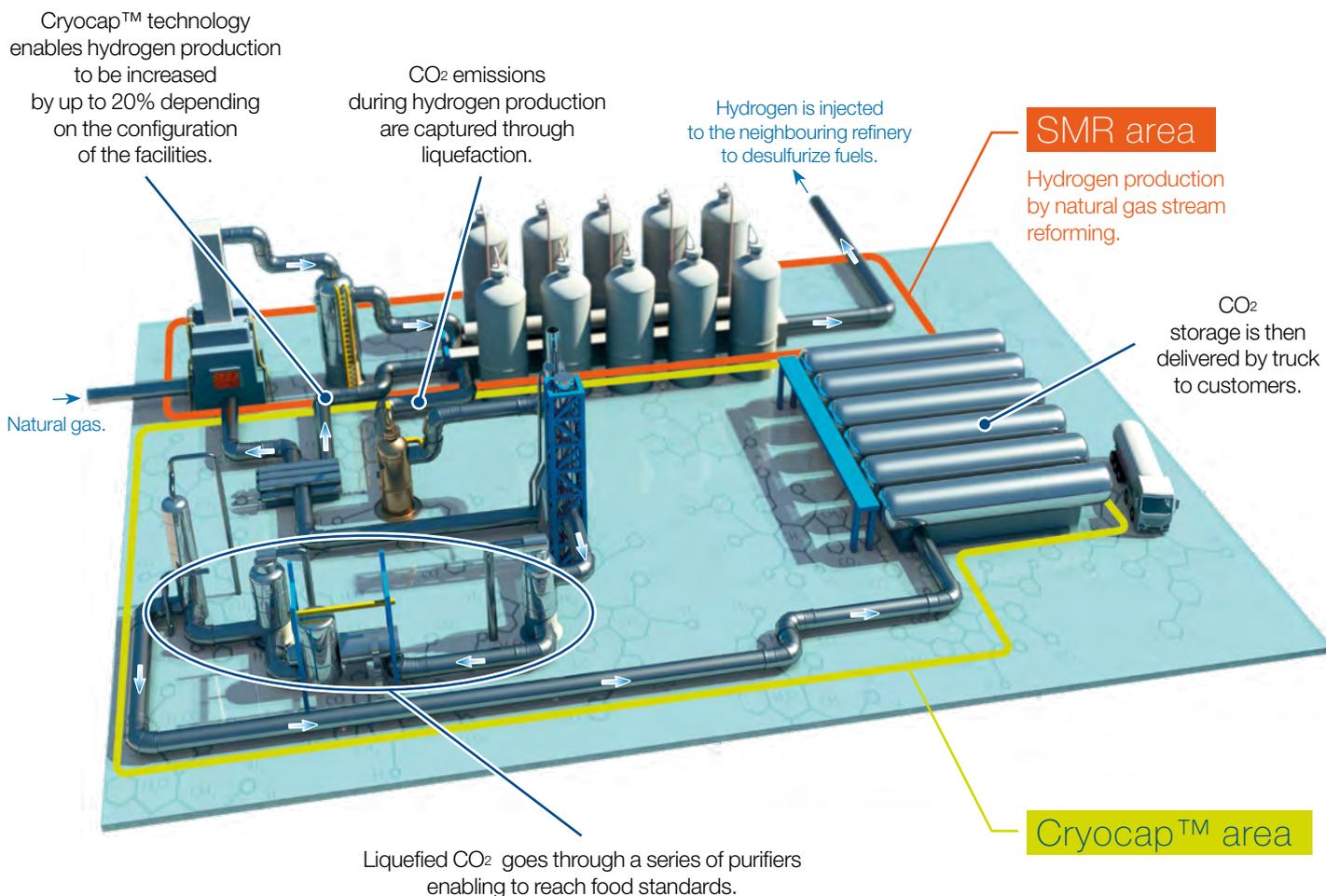
The process of desulfurizing fuels (which is notably required under European legislation) requires large quantities of hydrogen. For this reason, in 2002 the ExxonMobil group

signed a long-term contract with Air Liquide for the supply of around 50,000 Nm<sup>3</sup>/h of hydrogen for its Esso refinery, in Port-Jérôme. At that time, Air Liquide invested 60 million euros in an SMR hydrogen production unit adjacent to the facility of its customer. Operated by the teams of Air Liquide France Industrie, this unit has been supplying the Esso refinery with the hydrogen it needs 24/7 since 2005.

# CRYOCAP™ H<sub>2</sub> – HOW DOES IT WORK?

- 1- The reaction between natural gas – essentially composed of methane (CH<sub>4</sub>) – and steam (H<sub>2</sub>O) requires high temperatures and occurs in a furnace. When it emerges from the reforming oven, the synthesis gas (called syngas) that is obtained, composed mainly of hydrogen (H<sub>2</sub>) and carbon monoxide (CO), is collected.
- 2- This syngas then undergoes a catalytic reaction called “shift” that produces a gas mixture that is mainly composed of hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>).
- 3- The gas mixture is then treated in a PSA<sup>[2]</sup> to produce pure hydrogen ready to be injected into the pipeline to supply the refinery. A waste gas which contents CO<sub>2</sub> in high concentration and some hydrogen is also produced by the PSA.
- 4- This is where Cryocap™ H<sub>2</sub> comes in to treat this waste gas and separate the CO<sub>2</sub> from the additional hydrogen. Then the CO<sub>2</sub> is purified to achieve food grade standard.
- 5- The CO<sub>2</sub> is stored in its liquid form and later used to meet the need for continuous supply in certain industrial applications (for carbonating sparkling beverages, for freezing, for agricultural uses, etc.).

The Cryocap™ H<sub>2</sub> installation in Port-Jérôme has an annual capture capacity of **100,000 tonnes of CO<sub>2</sub>**.



[2] Pressure Swing Adsorption

# UPGRADING THE RECOVERED CO<sub>2</sub>

The concentration of CO<sub>2</sub> in atmospheric air is very low (0.04%). CO<sub>2</sub> is one of the gases sold by Air Liquide around the world. It is recovered from industrial facilities such as fertilizer or bioethanol plants, which emit it during their own processes. The market for CO<sub>2</sub> is a relatively tight one. With the Cryocap™ installation in Port-Jérôme, Air Liquide strengthens and secures its production capacities, as well as improving its ability to satisfy demand.

## The main applications of CO<sub>2</sub>

### The agri-food industry: carbonation, preservation, and refrigerated transport

In the form of snow or ice, CO<sub>2</sub> constitutes an **extremely powerful and practical source of cold** that has a variety of uses in the production and shipment of food products, for example to preserve in-flight meals served onboard airplanes at the correct temperature.

In its gaseous form, it **extends the shelf life** of certain products by replacing the air in packaging with CO<sub>2</sub>, alone or combined with nitrogen. This helps to cut down on food waste. **It is also used in sparkling beverages, for which it provides the bubbles**, as well as for beverages served in restaurants on tap.

Used in greenhouse growing, it helps to speed up the process of photosynthesis and improve crop yields.

### Other industries

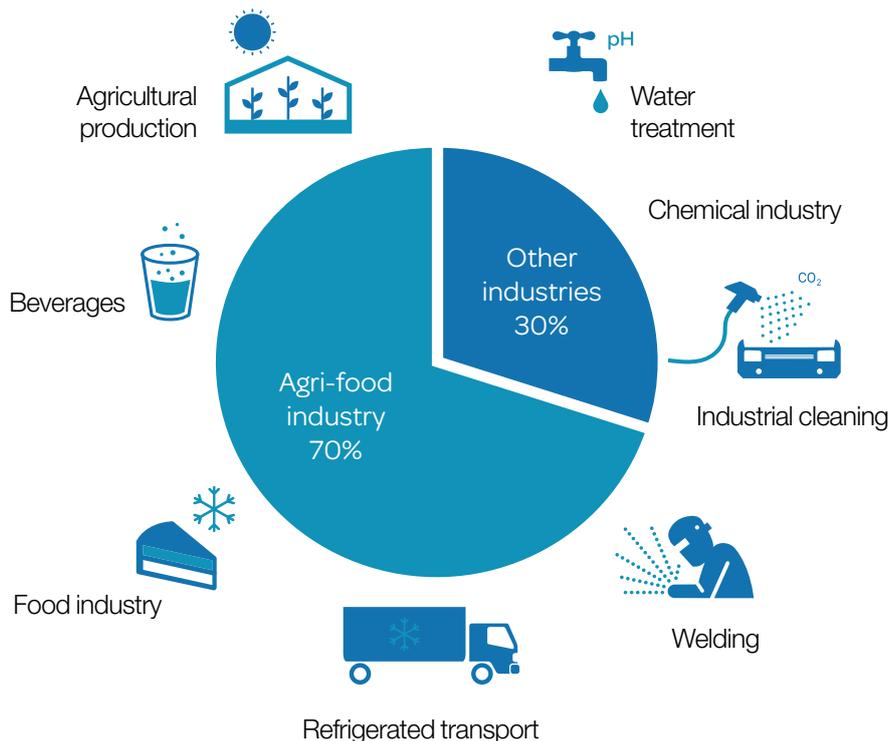
CO<sub>2</sub> is slightly acidic, which makes it suitable for use in water treatment to control pH content and neutralize effluents. It can also be used to remineralize drinking water.

In addition, it can be used as a chemical reagent to extract the molecules from certain oil and gas products or even for cryogenic cleaning, because it leaves no trace or residue.

CO<sub>2</sub> is also present in the composition of certain shielding gases used in welding.

Lastly, it can be used to produce theatrical smoke and fog or for other forms of entertainment.

## CO<sub>2</sub> is used in various forms: gaseous, liquid, solid...



# CRYOCAP™ H<sub>2</sub> – TOWARDS A DECARBONIZED HYDROGEN SECTOR

Cryocap™ H<sub>2</sub> establishes a link between the traditional use of hydrogen – indispensable for producing clean fuels – and its emerging use to charge hydrogen-powered electric vehicles. In doing so, it is reinforcing the Air Liquide's leadership in technologies designed to protect the environment.

## The production of hydrogen – at the core of Air Liquide's business for 40 years

Air Liquide's hydrogen business got its start in the 1970s for the purpose of fueling space rockets and since then has grown constantly, due to environmental regulations concerning fuels as well as the growing trend toward outsourcing hydrogen production by players in the chemical and refining industries. The Group's Engineering & Construction activity, reinforced by the acquisition in 2007 of the German engineering firm Lurgi, has key hydrogen production processes.

Currently, Air Liquide produces around **13 billion m<sup>3</sup>** of hydrogen annually for the refining and petrochemical industry around the world.

## Hydrogen applications today

### Refining and chemical industries

The hydrogen sector is mainly of interest to oil and gas refineries, which use hydrogen to crack crude oil and to desulfurize hydrocarbons (around 2/3 of the Group's total annual sales by volume) in order to produce sulfur-free fuels. The sulfur dioxide that is released by combustion engines can provoke respiratory problems in human beings; in addition, it is responsible not only for the smog that hovers over many large urban areas but also for the acid rain that causes deforestation and water supply acidification. Moreover, sulfur causes a rapid deterioration in the catalytic converters of vehicles.

**In 2014, the volumes of hydrogen supplied by Air Liquide to refineries around the world were sufficient to avoid releasing approximately 935,000 tonnes of sulfur dioxide into the atmosphere**, which is close to four times the total sulfur dioxide emissions of a country like France.

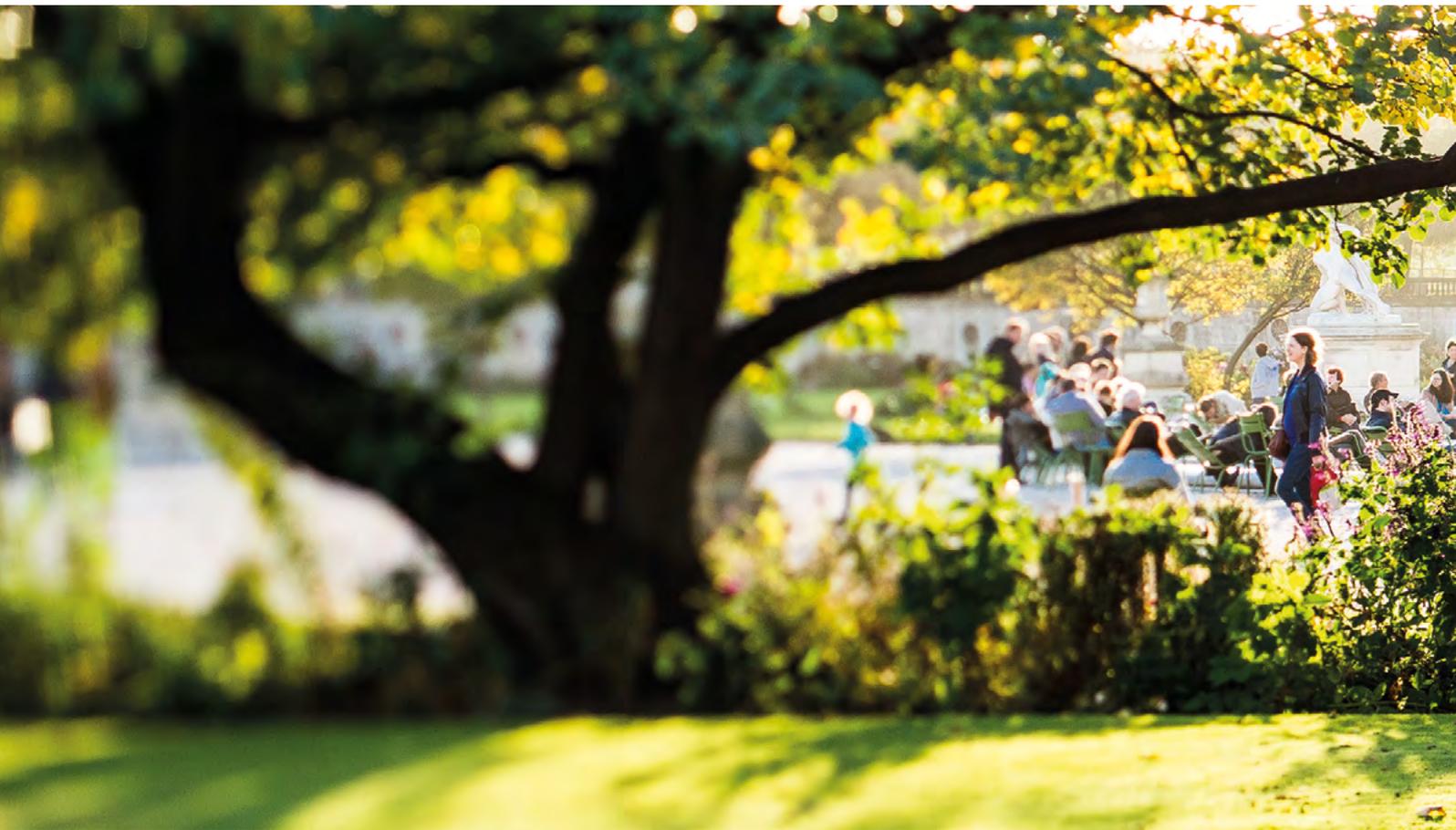
Hydrogen is also used in smaller quantities for the manufacture of numerous chemical (in the nylon, plastics, detergent and paint industries), pharmaceutical, and agri-food (hydrogenation of cooking oils, artificial sweeteners) products, as well as for the heat treatment of metals.

### Hydrogen energy

Hydrogen is a rapidly developing alternative to fossil fuels. It is used to power hydrogen fuel cells for stationary applications (relay antennas) as well as for clean mobility: forklift trucks, urban transportation vehicles, and now passenger cars.

**To date, 75 hydrogen charging stations have been designed and delivered by Air Liquide around the world.**





## AIR LIQUIDE, A PLAYER IN THE ENERGY TRANSITION

Air Liquide solutions to protect life and the environment represent more than **40% of the company's sales**. As part of its approach to corporate responsibility, the Group is constantly seeking to reduce the environmental impact of its production facilities and also to offer its customers the

most environmentally-friendly technologies and applications available. With Cryocap™, the Group is opening up new opportunities for reducing the CO<sub>2</sub> emissions released by its own production sites and those of its customers around the world.

### Contributing to lower emissions for Group customers

In addition to the CO<sub>2</sub> emissions avoided as a result of the energy performance of its production units, Air Liquide supplies numerous products and services that enable its customers to reduce their own CO<sub>2</sub> emissions and improve their environmental footprint.

Air Liquide enables its customers to produce cleaner via two principal applications:

- The desulfurization of hydrocarbons using hydrogen, which reduces the sulfur dioxide emissions (SO<sub>x</sub>) that cause acid rain and allows the catalytic converters on vehicles to function properly.
- The use of oxygen in furnace burners (glass or cement) that significantly lowers their electricity consumption. In

steelmaking, the injection of oxygen into blast furnaces reduces the consumption of coke. Air Liquide estimates that the use of the oxygen provided for these two applications alone **enables its customers to avoid CO<sub>2</sub> emissions of around 10 million tonnes a year**.

Air Liquide also participates in several research programs in Europe and in the United States that involve the combustion with oxygen enriched air or pure oxygen, as well as technologies for capturing this gas after combustion. In fact, the combustion of pure oxygen (known as oxy-combustion) results in smoke with a high concentration of CO<sub>2</sub>, which makes its capture possible. This is one of the main technologies that could eventually reduce CO<sub>2</sub> emissions and thereby lead to a decrease in greenhouse gas emissions.



## Hydrogen energy, an alternative to fossil fuels

Faced with the energy and environmental dual challenge the Air Liquide group has been committed for nearly 20 years to the development of solutions, in particular for clean transportation based on alternative fuels, including biogas and hydrogen.

Hydrogen is one of the energy solutions being developed to address the clean transportation challenges: by combining hydrogen with the oxygen that is present in the air, the fuel cell produces electricity while releasing only water as a byproduct.

The Air Liquide group masters the entire industrial chain (production, storage, distribution and use by the final customer) of this rapidly developing sector.

Air Liquide is contributing to the development and use of hydrogen to meet the needs of the transportation sector by supporting the rollout of the charging stations needed on a global scale.

Hydrogen provides real benefits to address urban pollution: not only does a hydrogen car offer great driving comfort,

it does not release any greenhouse gases, particles nor make any noise. **Plus, it takes just five minutes to recharge it and it offers an extended driving range of 500 kilometers.**

Even when it is produced using conventional methods i.e, from natural gas, hydrogen offers a definite environmental benefit: for an equal distance covered, hydrogen electric vehicles enable to **reduce greenhouse gas emissions by 20% compared with vehicles powered by internal combustion engines.**

# BLUE HYDROGEN, AIR LIQUIDE'S COMMITMENT

With **Blue Hydrogen**, Air Liquide is moving toward a gradual decarbonization of its **hydrogen production dedicated to energy applications**.

In practical terms, Air Liquide has made a commitment to produce at least 50% of the hydrogen necessary for these applications through carbon-free processes by 2020 by combining:

- biogas reforming,
- the use of renewable energies during water electrolysis,
- the use of the technologies for the capture and upgrading of carbon emitted during the process of producing hydrogen from natural gas.

Cryocap™ in Normandy is part of this initiative.



# INNOVATION AT AIR LIQUIDE

Innovation is one of the pillars of the Group's strategy. Innovating enables Air Liquide to open up new markets, creates new growth opportunities and address the major challenges facing society.

For Air Liquide, innovation is where scientific expertise meets the entrepreneurial spirit. Air Liquide's scientific and technological expertise is represented by its Research & Development department, its Engineering & Construction business unit and its centers of expertise, as well as by structures designed to promote entrepreneurship, like the aB&T network, i-Lab, Air Liquide's laboratory for new ideas, and ALIAD, its venture capital arm.

The Group's innovation ecosystem is backed by an "open innovation" approach. Today, the Group cultivates outside collaboration around the world with customers, universities, research institutes, SMEs and start-ups.



## KEY FIGURES

**6,200** employees contributing to innovation

More than **200** industrial and academic partners

Nearly **300** patents filed every year

**€278 M** innovation expenses in 2014

**9** R&D centers worldwide

**15** engineering centers and **3** manufacturing centers worldwide

**60%** of innovation spending is dedicated to protecting life and the environment



World leader in gases, technologies and services for Industry and Health, Air Liquide is present in 80 countries with more than 50,000 employees and serves more than 2 million customers and patients. Oxygen, nitrogen and hydrogen have been at the core of the company's activities since its creation in 1902. Air Liquide's ambition is to be the leader in its industry, delivering long-term performance and acting responsibly.

Air Liquide ideas create value over the long term. At the core of the company's development are the commitment and constant inventiveness of its people.

Air Liquide anticipates the challenges of its markets, invests locally and globally, and delivers high-quality solutions to its customers and patients, and the scientific community.

The company relies on competitiveness in its operations, targeted investments in growing markets and innovation to deliver profitable growth over the long-term.

Air Liquide's revenues amounted to €15.4 billion in 2014, and its solutions that protect life and the environment represented more than 40% of sales. Air Liquide is listed on the Paris Euronext stock exchange (compartment A) and is a member of the CAC 40 and Dow Jones Euro Stoxx 50 indexes.

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