PANORAMA
2016
a look at ...

Chemical recycling of CO_2

The ongoing rise of atmospheric carbon dioxide concentration is a major environmental and societal concern. Among the potential solutions for reducing carbon emissions in the energy sector, the chemical recycling of CO_2 has received considerable attention. Conversion of carbon dioxide into other recoverable substances offers the benefit of reducing the carbon footprint of newly developed products and of shifting away from the use of fossil resources. Various methods to create a wide range of products are currently being studied.

Carbon dioxide is one of the principal man-made greenhouse gases, responsible for climate change. Today, many players are seeking ways to reduce the impact of greenhouse gases on the climate, including recycling these gases through chemical conversion. However, on a global scale, only 12% of total emissions might be chemically recycled in practice (Fig. 1). Thus, recycling of CO_2 can help to lower emissions, but is not a comprehensive solution to the fight against the greenhouse effect.

Its benefit lies primarily in the conversion of a relatively inexpensive and abundant carbon-based raw material, used to develop products that already have a market – or even new products – which offer an improved carbon balance.

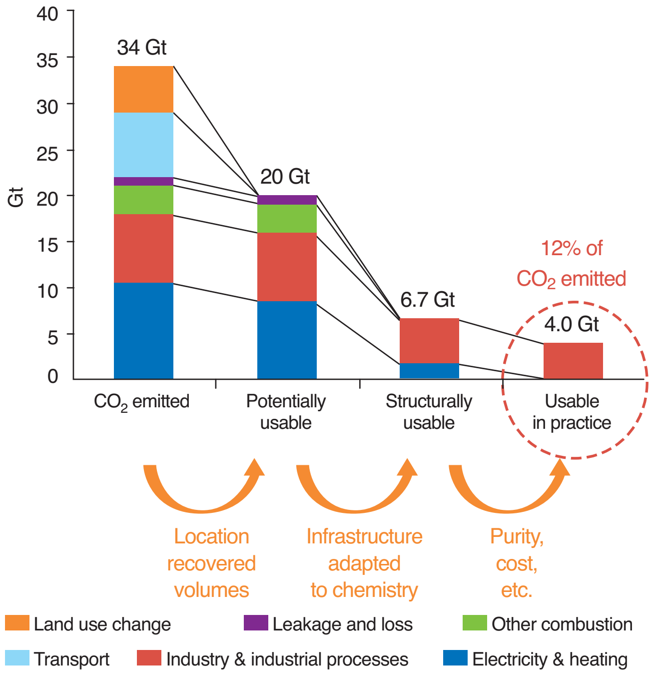
The roll-out of CO_2 recycling methods depends on economic conditions and the existing and foreseeable market, as well as the regulatory environment and any incentives that may be implemented. Because most of these methods are currently in the pilot or demonstration phase, financing support or incentives ("blending requirements", CO_2 mechanism, etc.) are necessary to their development.

Recycling of CO_2

Carbon dioxide has long been used for its physical properties, without any chemical conversion:

- for enhanced oil recovery (EOR);
- in various industries (to produce carbonated drinks, as supercritical CO_2 or refrigerants, etc.) for applications that generally require gas in almost-pure form.

Fig. 1 – CO_2 useable in chemistry



Source: IFPEN

Likewise, biological recycling of CO_2 through micro-algae cultivation is already at a commercial stage for certain applications, including the production of high value-added molecules for use in the cosmetics and pharmaceutical industries.

Chemical recycling of CO_2 is also used on an industrial scale to produce uric acid and salicylic acid.

ifp Energies nouvelles

Chemical recycling of CO_2

A number of other possible methods are currently being explored. Each has their unique characteristics and lead to products intended for the energy sector (for use as fuel) or the chemical sector (Fig. 2). These possibilities include (Tab. 1) organic synthesis, mineralization (or carbonatation, including concrete curing, a hardening of concrete using CO_2 which gives it specific characteristics), direct and indirect hydrogenation, reforming (dry), electrolysis at ambient temperature (also known as electrocatalysis), photoelectrocatalysis and thermochemistry.

Table 1

Examples of products created through CO_2 recycling

	Products
Organic synthesis	Polycarbonates
Mineralization	Inorganic carbonates, specialty concretes
Direct hydrogenation	Methanol
Indirect hydrogenation	Methanol, fuels
Reforming	Methanol, fuels
Electrolysis	Formic acid, methanol, fuels
Photoelectrocatalysis	Formic acid, methanol, fuels
Thermochemistry	Methanol, fuels

Source : IFPEN

Each method has certain benefits and drawbacks. Each one's appeal will clearly differ depending on the objectives pursued and the parameters with the highest priority. These parameters can be economic (market size, product price), techno-economic (technological maturity, process efficiency) or environmental (recyclable CO_2, CO_2 footprint compared with conventional methods, need for external energy).

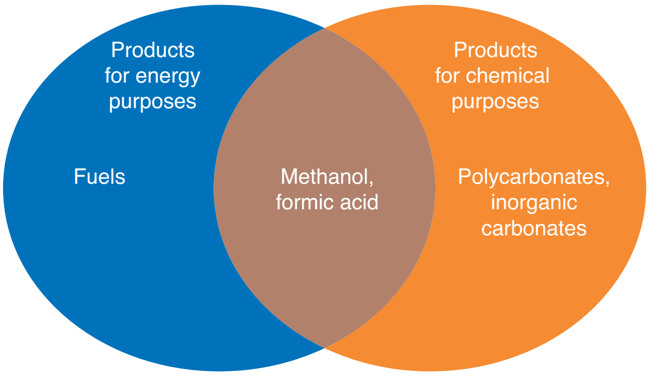
Choice of process driven by the market for finished products

The interest of a chemical recovery pathway is, above all, measured based on the product or the targeted use (chemicals, energy) (Fig. 2). We distinguish products:

- with a high unit price but generally low market volume (ex: fine chemicals);
- with a low unit price but a significant market size (ex: fuels);

both of which cannot be achieved simultaneously.

Fig. 2 – Intended use of products created from CO_2 recycling processes



Source: IFPEN

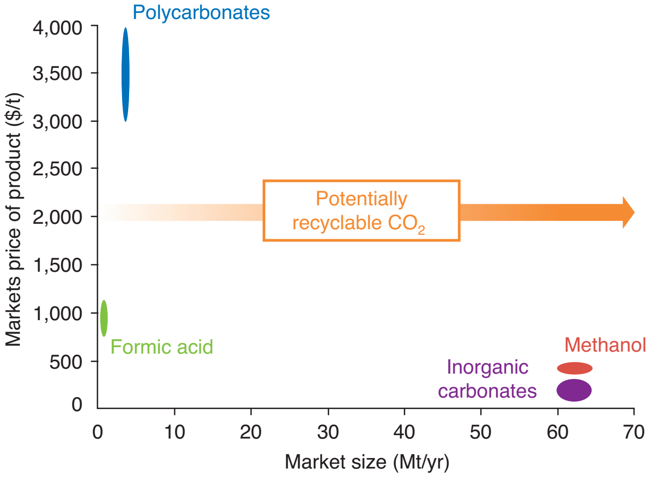
Products for chemical purposes, a broad range of possibilities

In the case of a chemical application within the "high market price" category, we find products created from organic synthesis and, to a lesser degree, formic acid. Generally speaking, these products are intended for small to medium markets, or even niche markets. Organic synthesis (aside from uric acid, an already mature process) thus gives rise to high-priced products including, in the most interesting case, polycarbonates ($3,000-4,000/t with a market of approximately 4 Mt/yr) and polyurethanes (a market exceeding 10 Mt/yr for production of insulation foam and elastomers in particular). Likewise, formic acid has a relatively small market volume (around 700 kt/yr) but with significant unit prices of around $1,000/t. It is mainly used for preservation during the silage fermentation process and in the leather and tanning industry (Fig. 3).

On the contrary, products created from mineralization as well as methanol fall within the "low unit value/high volume" group. Inorganic carbonates (specifically calcium and sodium) are sold at low prices ($100 to 300/t) but are intended for larger markets, in excess of 60 Mt/yr (specifically in the paper, glass and plastics industries, depending on the product). Concrete curing, a mineralization process, is a specific case used for specialty concretes, but whose potential market share is difficult to grasp. Methanol is sold at between $400 and 500/t and is also intended for a market that exceeds 60 Mt/yr, of which approximately one-third is dedicated to adhesives *via* formaldehyde.

Nevertheless, some of these products also have applications in the energy sector. This is the case for methanol and formic acid (Fig. 2).

Fig. 3 – Market sizes and prices for products with primarily chemical applications



Sources: IFPEN, IHS chemical

Energy products, potential awaiting development

The main products intended to be used as fuel are hydrocarbons, which result from indirect hydrogenation and reforming.

Some of the products listed above may also have direct or indirect energy applications such as methanol and formic acid.

They are no longer limited only to their current market, but could potentially capture a share of the fuel market. This represents a much higher volume, particularly for formic acid. These products' versatility could be a major asset when choosing a recycling method.

Methanol is already used as an intermediate product for the production of MTBE (Methyl Tert-Butyl Ether) and FAME (Fatty Acid Methyl Esters), products which are incorporated as supplements in gasoline and diesel respectively. Evolving regulations could lead to increasing use of biodiesel (including FAME) or even pure methanol in internal combustion engine vehicles, thereby increasing the size of the product's worldwide market.

Formic acid also has characteristics that allow it to be used for energy, though this is not yet effective:

- either through conversion to methanol, an operation whose efficiency has recently shown substantial improvement, rising from 2% to 50% thanks to the use of a new catalyst that is more effective and less costly than the one used to date (developed at the Laboratoire de chimie moléculaire et catalyse pour l'énergie (LCMCE[1]));
- or used to store hydrogen that can later be converted into electricity. Though production on an industrial scale has not yet been achieved, work is ongoing to develop stand-alone generators. Economic constraints must still be resolved, but the mere possibility of storing hydrogen in a liquid compound – formic acid – has generated enthusiasm.

Formic acid could therefore have a presence in larger markets, following the example of methanol, of which 10% of production is already used for fuel, a figure which is growing by around 7.5%/yr.

And CO_2?

The quantity of CO_2 recycled (processed) through various methods is directly tied to the end-product market. Thus, the larger the market, the greater the possibility of carbon dioxide recycling. In the case of products for energy purposes, the markets, and therefore the quantity of recyclable CO_2, have tremendous potential.

Particular attention must nonetheless be given to the environmental impact of each process. It is not enough to consider only the CO_2 which enters the process. It is also important to analyze the overall lifecycle of the product generated from carbon dioxide, and to compare it to the product generated through conventional processes. It is essential that the unconventional process offers greater GHG (greenhouse gas) reductions than the second, with the difference between them expressed in terms of displaced CO_2.

If the products resulting from CO_2 recycling have economic and environmental characteristics that influence the choice of the technological pathway, the processes used during chemical conversion are also decisive.

Recycling processes, conditions for choice and success

The willingness to move toward a recycling method depends on the techno-economic and environmental parameters of the processes applied. These processes are at various developmental stages, have specific technical requirements, and collide with economic bottlenecks and specific environmental constraints.

Varying degrees of progress

The eight major recycling methods listed above (Tab. 1), are not all at the same stage of development. Although some processes are almost ready for commercial use, others are only in the initial phases and must contend with a number of challenges. All of these pathways,

---

(1) LCMCE is a laboratory of NIMBE (Nanoscience and innovation for materials, biomedicine and energy), a CEA-CNRS joint research unit

whether new or mature, face a range of technological, economic and environmental obstacles that must be addressed, all of which are frequently interconnected. For the newest ones, the elimination of these numerous, sometimes persistent barriers will take time, blurring the outlook for their industrial development (Fig. 4).

Recycling processes can be grouped into three categories according to maturity:

- CO_2 recycling processes in the demonstration phase, which should be ready for commercial use within the short term (less than five years for organic synthesis, mineralization and direct hydrogenation);
- those in the pilot phase, ready for production in five to ten years (indirect hydrogenation, dry reforming);
- procedures still in the research or early pilot phase, with production at least 10 to 15 years away (electrocatalysis, photoelectrocatalysis, thermochemistry).

Processes with various technical requirements

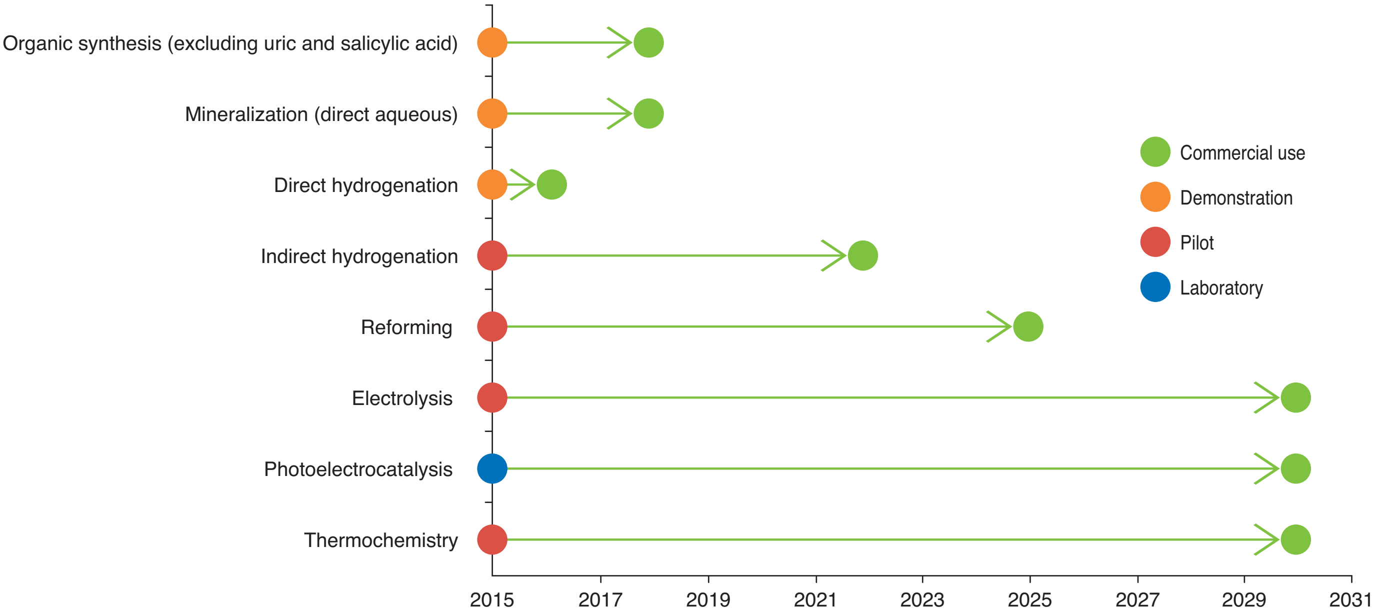
The first requirement concerns the concentration and purity of CO_2 needed for each process. One key factor is whether or not catalysts are present. Catalysts are generally very sensitive to impurities; their performance and durability can be significantly altered if the CO_2 used is insufficiently pure. Except for mineralization, all other reactions require the presence of catalysis, at least upstream (in reality, photocatalysts for photoelectrocatalysis). Mineralization is the only process that can use carbon dioxide directly from industrial flue gases, provided the end product will not be used in pharmaceuticals or food. In other cases, the CO_2 must be treated to improve its concentration and purity, which may be an economic obstacle to its industrial and commercial development.

The second area of concern relates to the energy required for CO_2 conversion. The amount of energy (often significant), its cost, its origin (inherent CO_2 content) is critical information when assessing the various processes. Certain methods have advantages in this regard, such as the use of organic synthesis for production of polycarbonates. For this method, energy is provided by one of the reagents (such as ethylene oxide) under mild operating conditions. In photoelectrocatalysis and thermochemistry, energy is primarily generated by solar power, a renewable source. On the other hand, reduction of energy consumption is a real challenge for other procedures. For example, demand for energy can be linked to grinding during the mineralization process, hydrogen production in the case of hydrogenation (direct and indirect), increasing temperatures for dry reforming, or catalyst efficiency in general, and so forth.

Finally, performance, reliability and durability are key requirements that may be new for processes such as thermochemistry or reforming (very high temperatures) and electrocatalysis (electrode and membrane) for example.

Nevertheless, some of the processes may benefit from technical advances achieved when developing other technologies, such as Fischer-Tropsch (FT) synthesis, the Reverse Water Gas Shift (RWGS) and the Syngas to Methanol process (Tab. 2).

Fig. 4 – Process maturity and outlook for commercial use



Sources: ENEA Consulting, RECORD, IFPEN

Table 2

External advances that benefit CO_2 recycling processes

	FT	RWGS	Syngas to Methanol
Organic synthesis			
Mineralization			
Direct hydrogenation			✘
Indirect hydrogenation	✘	✘	✘
Reforming	✘		✘
Electrolysis	Electrolysis of water to produce hydrogen		
Photoelectrocatalysis	Fuel cells, electrolysis cells		
Thermochemistry	✘		✘

Sources: IFPEN, Ademe

Economic outlook: a critical issue for emerging technologies

Economic issues of more or less high importance are directly linked to the previously mentioned technical requirements. It is clear that the newness of a process directly influences the understanding of its profitability. The processes that are poised to enter the market, such as organic synthesis, mineralization and direct hydrogenation, may be considered technically viable though not always highly competitive, unless new economic models or additional services provided by the product or process are devised. This may be the case, taking as an example the Power to Gas process for producing methane from CO_2 and H_2. This technology can also be viewed as a way to produce methane as well as to store electricity.

Conversely, little information is available on reforming, electrocatalysis, photoelectrocatalysis and thermochemistry. Because these pathways are emerging, their economic profile is more difficult to establish and is therefore less accurate. It is clear that the label "CO_2 recycling" is not enough to replace a more traditional fossil fuel-based process. These new pathways must also be more competitive. In addition, the economic validity of a CO_2 recycling method is not based on the end-product production cost alone, but also on the ability to bring the new production process to market.

Finally, all inputs, CO_2 as well as consumables such as energy and the catalyst, must be accounted for in the economic analysis. The same applies to investments in the production unit, whose profitability can be substantially hindered by depreciation, and whose total amount may slow down project launches.

Environmental impact compared with conventional methods

Some specific characteristics of the process, steming from the technical requirement, may also affect its environmental impact. Thus, electricity used to produce hydrogen during hydrogenation, or the electrochemical reduction of carbon dioxide to formic acid, has a "CO_2 content" that must be as low as possible. Likewise, the construction of mirrors for use in thermochemistry or the use of fossil resources in mineralization have an environmental impact that should be taken into account. Nevertheless, specific features of the reactions can also reduce the overall environmental impact. Certain products resulting from organic synthesis can be used instead of toxic components such as bisphenol A or phosgene.

As a general matter, then evaluating the environmental benefit of a CO_2 recycling process, it is necessary to analyze the process life cycle to the fullest possible extent and compare it with conventional methods. Development of a CO_2 recycling process may be relevant so long as its environmental impact is substantially better than conventional processes.

A preferred method?

Many industrial players around the world are interested in recycling CO_2, and are seeking to develop a process relevant to their needs. While some are looking at mineralization methods (Skyonic, Calera, etc.), others are focused on polycarbonate production (Bayer, Novomer, etc.) or the production of methanol *via* direct hydrogenation (Carbon Recycling International, Mitsui Chemicals Inc., etc.).

The wide range of stakeholders positions shows that there is no "universal" pathway to CO_2 recycling. In the end, there is no doubt that recycling will be achieved by superimposing several of these processes, as technological discoveries will eliminate the technical, economic and environmental barriers.

The challenge will be to find a relevant purpose for each approach:

- technical: balance and yield on energy and materials of these processes;
- economic: competitiveness with traditional processes, market for products and processes;
- environmental: life-cycle assessment compared with conventional methods.

Each of these aspects should be studied and taken into account as early as possible as the process is developed, and on a regular basis as new data is obtained. Support for research, especially for the most innovative and long-term processes, the development of new "multiservice" models, and implementation of regulations that favor products from "sourced CO_2" are drivers that may accelerate their development and, in some cases, may support the emergence of these processes.

Laurent Forti – laurent.forti@ifpen.fr
Florian Fosse – florian.fosse@ifpen.fr

Final draft submitted in December 2015

IFP Energies nouvelles
1 et 4, avenue de Bois-Préau
92852 Rueil-Malmaison Cedex - France
Tel.: +33 1 47 52 60 00

IFP Energies nouvelles-Lyon
Rond-point de l'échangeur de Solaize
BP 3 - 69360 Solaize - France
Tel.: +33 4 37 70 20 00

www.ifpenergiesnouvelles.com