# Carbon dioxide: feedstock to the chemical industry

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**Abstract** Currently, the chemical industry uses high-purity carbon dioxide streams available from fossil feedstock-based hydrogen production. Major application is the synthesis of urea which in turn is used as a fertilizer and for the production of urea formaldehyde and melamine formaldehyde glues and resins. The use of carbon dioxide as a chemical feedstock (CCU: carbon dioxide capture and utilization) is part of a strategically important concept which can lead in the long term by combination with renewable energy-based hydrogen production to safeguard our raw material base. Due to the limited volume potential, it will not be the solution to ambitious climate protection targets, but will supplement CCS (carbon dioxide capture and storage). If sufficient renewable energy for hydrogen production is available, also the production of fuels can be considered which compared to the chemical use offers at least a tenfold volume potential.

**Keywords** **Carbon dioxide capture and utilization (CCU), $CO_2$, feedstock for the chemical industry, methanol, polycarbonates, storage of excess renewable power.**

**Résumé** **Le dioxyde de carbone : une matière première pour l'industrie chimique**
Des flux de $CO_2$, de grande pureté, issus de la production d'hydrogène à partir de matières fossiles, sont actuellement utilisés dans l'industrie chimique. La première grande application concerne la synthèse de l'urée, qui est utilisée comme engrais, ainsi que dans la production de résines et de colles base d'urée-formaldéhyde et mélamine-formaldéhyde. L'utilisation de $CO_2$ comme matière première chimique (CUC : capture et utilisation du dioxyde de carbone) fait partie d'un concept stratégiquement important qui, combiné à une production d'énergie renouvelable à base de dihydrogène, peut mener à long terme à la sauvegarde des matières premières de base. En raison du volume potentiel limité, le recours au $CO_2$ ne sera pas la solution aux ambitieux objectifs fixés en matière de protection climatique, mais son utilisation complètera le principe de la capture et du stockage du dioxyde de carbone (CSC). S'il y a suffisamment d'énergie renouvelable disponible pour la production d'hydrogène, la production de carburants peut également être envisagée. Comparée à une utilisation de composés chimiques usuels, elle offre un volume potentiel au moins dix fois supérieur.

**Mots-clés** **Capture et utilisation du dioxyde de carbone (CUC), $CO_2$, matière première pour l'industrie chimique, méthanol, polycarbonates, stockage de l'excès des énergies renouvelables.**

Although carbon dioxide is present in our atmosphere only in trace amount of about 0.04%, it is of great importance to our global carbon cycle which is governed by geologic and biologic processes [1]. The fossil carbon we currently use to support our standard of living has been formed from carbon dioxide over geological periods (many hundreds of millions of years) by biosynthesis and use of sunlight. At the same time we release by our activities in a very short period giant amounts of carbon dioxide into the atmosphere.

The man-made carbon dioxide emissions by use of fossil fuels were estimated in 2009 to about 29 Gigatons per year [2]. Because of the contribution to the climate warming, a bundle of measures is discussed currently to cut emissions, among them: CCS* (carbon dioxide capture and storage), the large-scale separation of carbon dioxide from exhaust gases in combination with underground storage. This requires a new infrastructure to be established, including pipeline networks to transport carbon dioxide to the storage sites. In addition, long-term underground storage of carbon dioxide is not a fully developed technology. Due to the high costs and the uncertain acceptance of CCS in the general public, it has been proposed to use carbon dioxide as a feedstock to the chemical industry [3-6]. In addition, CCU* (carbon dioxide capture and utilization) could replace other carbon feedstocks such as petroleum.

## Available sources of carbon dioxide

The biggest single contribution to the carbon dioxide emissions (41%) is related to electricity and heat generation, followed by the transport sector (23%), and industry (20%) – production of steel and cement, oil refining, production of chemicals (*figure 1*). Due to the required infrastructure, the separation of carbon dioxide from exhaust gases is limited to stationary sources. The separation is burdened by consumption of energy, solvents and investment costs, and the lower is the concentration of carbon dioxide in a gas mixture the higher are the costs. Depending on the intended use, impurities such as sulfur compounds have to be removed from the recovered carbon dioxide.

Carbon dioxide is formed in numerous fermentation processes, such as in ethanol synthesis by fermentation.

## Glossary

*The terms followed by an asterisk* in the article are defined below.*

***ABS***: acrylonitrile-butadiene-styrene copolymer, shock resistant, used *e.g.* for housings of electric appliances.
***Bisphenol A***: 2,2-bis-(4-hydroxyphenyl)-propane, used for the synthesis of polycarbonates and epoxy resins.
***CCS***: carbon dioxide capture and storage, requires separation of carbon dioxide form exhaust gases from *e.g.* fossil fuel based power plants, pipeline transport and subterranean or subsea storage.
***CCU***: carbon dioxide capture and utilization as a carbon feedstock in the chemical industry.
***DMC***: dimethyl carbonate, solvent, used in non-aqueous electrolytes for *e.g.* Li-ion batteries as well as in paints and coating, and reactive intermediate *e.g.* in the synthesis of polycarbonates.
***DME***: dimethyl ether, used as propellant gas, substitute for liquid gas (LPG) for heating purposes, potential use as a diesel fuel.
***Fischer-Tropsch products***: mixture of essentially linear olefins and paraffins made by catalytic conversion of synthesis gas, named after the German researchers Franz Fischer and Hans Tropsch.
***GTL process***: gas-to-liquid process, conversion of natural gas into liquid hydrocarbons (see ***Fischer-Tropsch products***).
***MF resins***: water resistant resins from melamin and formaldehyde, used in kitchenware, plastic laminate and overlay materials, in laminate flooring and as glues in wood construction.
***MTBE***: methyl-*tert*-butyl ether, made from isobutene and methanol, octane booster for gasoline.
***Sabatier process***: catalytic conversion of carbon dioxide and hydrogen into methane (synthetic natural gas), named after Paul Sabatier, French Nobel laureate.
***Synthesis gas*** (or ***syngas***): mixture of carbon monoxide and hydrogen (molar ratio typically 1:2) produced from natural gas, petroleum residues or coal, can also be made from biomass or other carbon sources.
***TDI***: mixture of 2,4- and 2,6-toluene-di-isocyanate, used for production of polyurethanes by conversion with polyols.
***UF resins***: resins from urea and formaldehyde, used in chipboards and MDF (medium density fibre) boards and as glues in wood construction.
***Zeolite***: crystalline alumosilicate with porous structure, used as an acidic heterogeneous catalyst.

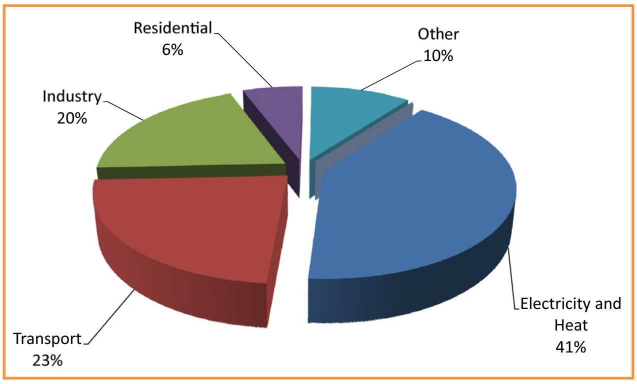



Figure 1 - **Anthropogenic carbon dioxide emissions from fossil fuels** [2].

Therefore, the production of bioethanol from sugar cane in Brasil or from corn in the US can be an important source. Some large-volume production processes in the chemical industry are associated with very pure carbon dioxide side-streams. Examples are the hydrogen production from natural gas or coal for ammonia synthesis and oxidation processes like the production of ethylene oxide. The carbon dioxide used today as a feedstock in the chemical industry originates almost exclusively from these processes and considerable excess amounts are available which are currently blown off.

## Present use of carbon dioxide

Compared to the carbon dioxide emissions, less than 0.1% is used as an industrial gas or for chemical syntheses. Of it the use as an ***industrial gas*** was estimated in 2002 to about 20 million tons. Important applications are the tertiary oil production, the beverage industry and the use as a cleaning agent or as an extractant.

As a ***chemical raw material***, carbon dioxide serves primarily for the synthesis of ***urea*** by conversion with ammonia. About 107 million tons were used worldwide for this application in 2008 (*figure 2*). The majority of urea is used as a nitrogen fertilizer in agriculture. Besides, urea is used for condensation resins with formaldehyde, partially *via* the intermediate of ***melamine*** which in itself shows a rich chemistry. The ***urea formaldehyde resins*** (UF resins*) are used at a large scale for the production of chipboards and as glues in the furniture and wood construction industry. The ***melamine formaldehyde resins*** (MF resins*) show excellent mechanical properties along with a high water resistance and are used because of their food compatibility also for kitchenware. Foamed melamine formaldehyde resin is an insulating material with impressive qualities. It is very light weight, has excellent thermal and sound insulation properties, and is heat and fire-resistant. Hence, its varied applications depend on these qualities: in the aerospace industry, in the car industry or in public buildings such as metro stations.

About two million tons of carbon dioxide are used per year for the production of methanol from synthesis gas* (mixtures of CO and hydrogen) to balance an excess of hydrogen. ***Methanol*** is used as a fuel component as well as a precursor



**Thirst-quencher and life style beverage: global mineral water consumption continues to grow.**
It takes approximately 1.3 million metric tons of $CO_2$ a year to quell Europe's craving for mineral water and other sparkling beverages. At BASF's site in Ludwigshafen, $CO_2$ is obtained as a by-product of ammonia manufacturing. The plant has the capacity to produce 320,000 metric tons of $CO_2$ a year, approximately half of which is used to carbonize beverages.

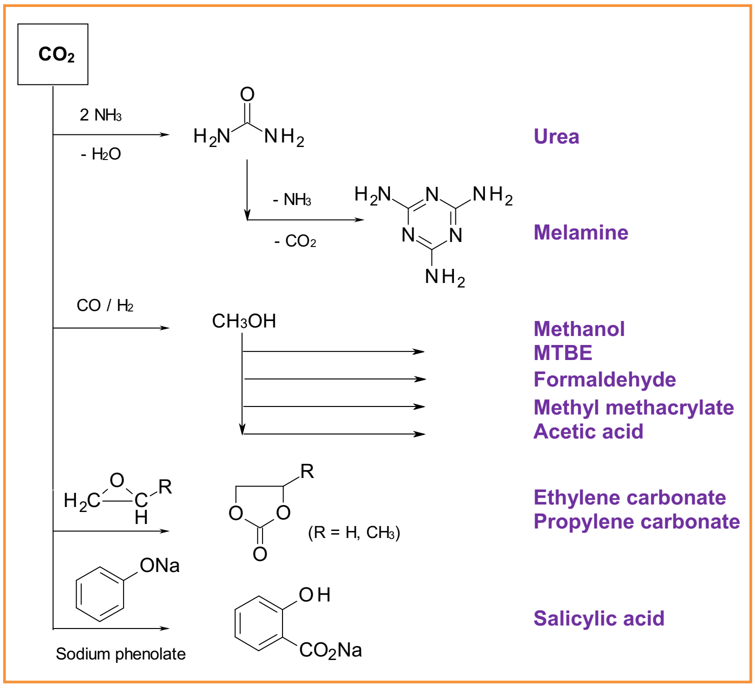
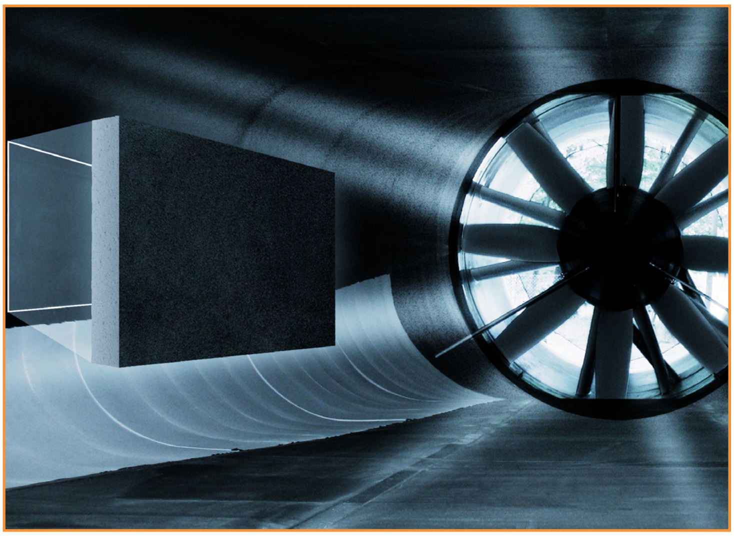



Figure 2 - **Present use of $CO_2$ in the chemical industry.**





**Melamine-formaldehyde foam Basotect® as sound insulation in wind tunnel at the University of Stuttgart.**
The Institute of Aerodynamics and Gas Dynamics at the University of Stuttgart (Germany) can now test components for acoustic emissions. This is possible because sound-absorbing molded parts made of Basotect®, the melamine resin foam from BASF, have been installed in the institute's laminar wind tunnel (the photo shows a model). Absorption panels of different thicknesses could be made to fit snugly against the conical walls of the wind tunnel. The Basotect® panels are lined with a thin, black polyurethane skin that protects them from dirt and moisture.

primarily for the production of formaldehyde, methyl-*tertiary*-butylether (MTBE*, octane booster for gasoline), acetic acid and methyl methacrylate, the monomer for Perspex®.

Besides there are further chemical processes based on carbon dioxide, although with clearly lower volumes: the synthesis of cyclic carbonates like ***ethylene or propylene carbonate*** by reaction with ethylene or propylene epoxide (about 0.04 million tons per year) as well as the production of ***salicylic acid*** by conversion with sodium phenolate (about 0.025 million tons per year). Salicylic acid is the precursor for the fever-lowering pain killer aspirin.

## Can the chemical use of carbon dioxide contribute to climate protection?

To evaluate a possible contribution to the climate protection from the raw material use of carbon dioxide as a carbon source for fuels and chemical products, the following aspects must be considered:

– On the one hand, carbon dioxide is the energetic end product from combustion processes. For instance, to convert (reduce) carbon dioxide to fuels, more energy has to be used for reasons of thermodynamics, than available from their combustion. The material use of carbon dioxide is therefore only reasonable if the energy required for this process is supplied from regenerative or at least carbon dioxide neutral sources. If these conditions cannot be fulfilled, the material use of carbon dioxide leads in balance to an ***increase*** of the carbon dioxide emissions.

– On the other hand, the question of the quantitative proportions has to be considered. Even taking into account the high volume production processes for polyolefins and other chemical base products, the use of carbon dioxide as chemical feedstock could lower the worldwide emissions by only less than 1% under ideal conditions. The potential would increase by one magnitude if fuels for mobile uses could be produced. However, the corresponding very large amounts of *e.g.* hydrogen produced by means of regenerative energy have to be available at the same production site.

Instead of hydrogen, other reducing agents such as methane or carbon may be used to reduce carbon dioxide to carbon monoxide or its downstream products like methanol or hydrocarbons (Fischer-Tropsch products*). Another strategy for overcoming the energy hurdle is to convert carbon dioxide through reaction with high-energy compounds like alkene oxides to cyclic or polymeric alkene carbonates.

However, it has to be noted that even if all these technologies are used at full scale, their contribution to climate protection will be insignificant due to the sheer amount of the running emissions.

## Renewable energy storage through carbon dioxide hydrogenation

The hydrogenation of carbon dioxide is also discussed for the storage of excess renewable electric power. The reason is that wind and solar power plants lead to fluctuating power supply which is very difficult to buffer by the electrical grid. The strategy is to electrolyze water by use of excess power to generate hydrogen, which can be stored in the natural gas pipeline grid either directly or after nickel catalyzed ***conversion to methane*** (synthetic natural gas) through hydrogenation of carbon dioxide. This is the long-known ***Sabatier process****, named after the French pioneer in heterogeneous catalysis, Paul Sabatier [7]. Hydrogen storage is also possible through copper/zinc catalyzed carbon dioxide hydrogenation to ***methanol***, which can be conveniently stored as a liquid. This technology is currently developed at the pilot plant stage by Mitsui in Japan and is applied in a semi-commercial plant in Iceland based on geothermal power.

## New catalytic processes for carbon dioxide conversion

Carbon dioxide is kinetically rather inert. Hence, the activation is possible nearly exclusively with the help of suitable heterogeneous, homogeneous and biological catalysts

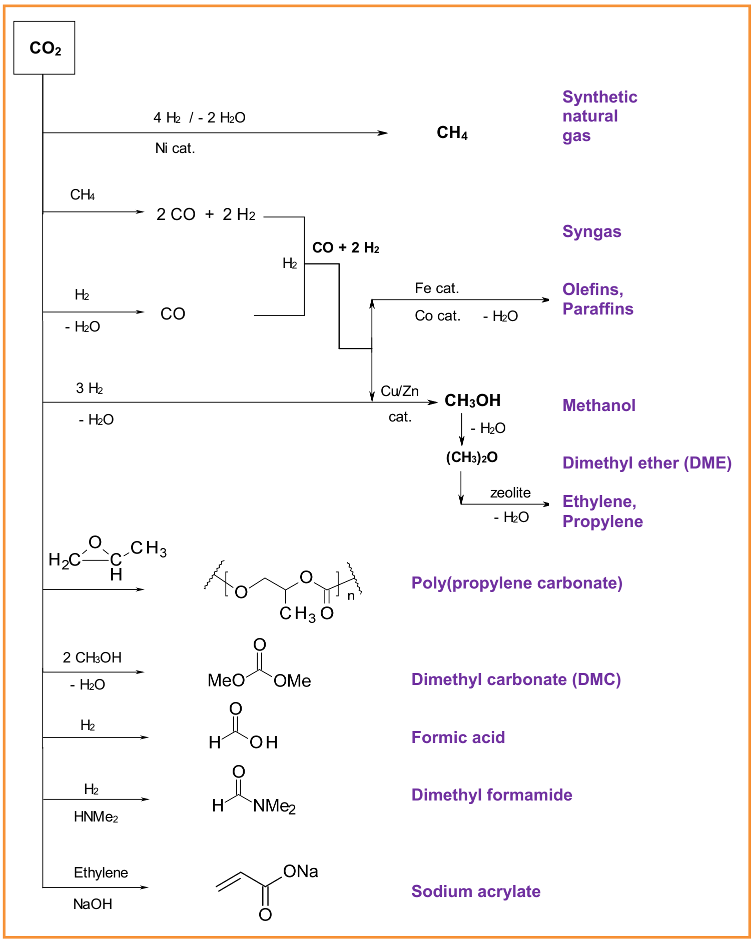



Figure 3 - **New catalytic processes for $CO_2$ conversion.**

(*figure 3*). With respect to volume, the highest potential is offered by the conversion to ***synthesis gas***, *i.e.* mixtures of carbon monoxide and hydrogen (typically at a molar ratio of 1:2), which is an extremely versatile chemical feedstock. This can be achieved by two routes: the ***dry reforming of methane with carbon dioxide*** and the ***reduction of carbon dioxide with hydrogen***.

Especially interesting for large-volume uses is the dry reforming process which converts carbon dioxide with methane to synthesis gas. This concept offers a possibility for the exploitation of remote natural gas fields by production of methanol or GTL* (gas-to-liquids) products. In principle also cleaned biogas could be used which consists of equimolar amounts of methane and carbon dioxide. The known catalysts for this process are insufficient, since they are based on expensive precious metals and are rapidly deactivated by coking. The production of CO by reduction by hydrogen is the reversal of the industrially applied water gas shift reaction. In contrast to the latter, it has to be applied at high temperatures in order to shift the equilibrium to high CO concentrations.

The thus generated synthesis gas can be used for the cobalt or iron catalyzed ***Fischer-Tropsch hydrocarbon synthesis*** for the production of fuels (diesel, gasoline) or of chemical base materials (olefins, paraffins). Also ***methanol*** offers potential in the fuel area. It can be used directly, or in the form of the derivatives methyl-*tert*-butyl ether (***MTBE****), dimethyl carbonate (***DMC****) and dimethyl ether (***DME****). Methanol can also be used as a general feedstock for base chemicals. Zeolite*-catalyzed dehydration yields ethylene or propylene by the ***MTO (methanol-to-olefins) process*** or alkyl aromatics by the ***MTG (methanol-to-gasoline) process***. Recently, several large-scale MTO plants started up in China, making use of cheap coal derived methanol.

A biodegradable polymer, ***poly(propylene carbonate)***, can be produced by copolymerization of carbon dioxide with propylene oxide. For this process, heterogeneous zinc or homogeneous cobalt catalysts can be used which suppress the formation of the cyclic monomer, propylene carbonate. Poly(propylene carbonate) contains about 44% of carbon dioxide by weight, is biodegradable, and can be used to the production of clear, tear-resistant and flexible sheets for food packaging and agriculture; it can replace ABS* (acrylonitrile-butadiene-styrene) copolymers as a shock-resistant material if mixed with polylactic acid, a polymer from renewable feedstocks. Also, a ***polyol for use in polyurethanes*** can be made from carbon dioxide and an excess of propylene oxide which results in a product of lower molecular weight and with a larger portion of polyether structures. The final polymer is made by conversion of the polyol with diisocyanates like TDI* (2,4-toluene-di-isocyanate) and is used for flexible and rigid foams; the carbon dioxide content by weight in the final polymer is in the range of 10 to 15%.

***Dimethyl carbonate*** substitutes increasingly the highly toxic gas phosgene in the production of polycarbonates from bisphenol A*. Today, it is produced by oxidative carbonylation of methanol or by methanolysis of ethylene carbonate. The direct synthesis from carbon dioxide and methanol is strongly disfavored unless the water produced by the esterification process is removed from the system. The substitution of phosgene would also be of interest in the synthesis of isocyanates, and



**Extrudate of poly(propylene carbonate)**, a highly transparent, tear resistant and flexible polymer made at lab scale from alternating polymerization of propylene oxide and $CO_2$.

besides dimethyl carbonate, the use of urea is investigated for this process.

The industrial chemical that is closest related to carbon dioxide is ***formic acid***. The hydrogenation of carbon dioxide is possible, for example, by homogeneous precious metal complexes under basic conditions. This leads to salt-like formates from which the formic acid has to be released by thermal splitting. This is a topic of ongoing research activities. Similarly, ***methyl and dimethyl formamides*** are accessible by hydrogenation of carbon dioxide and here the problem of the processing is easier to solve. Other interesting target products are still in the very early research stage; one example is the catalytic synthesis of ***sodium acrylate*** from ethylene, carbon dioxide, and sodium hydroxide.

Nature uses carbon dioxide by means of ***photosynthesis to produce biomass***. This process can be accelerated by raising the carbon dioxide concentration which is already exploited today in greenhouses, into which the exhaust gases of the natural gas-fired heating installations are fed. ***Green algae*** are studied at the pilot stage to convert carbon dioxide from the flue gas of power stations into biomass. The biomass separation procedures as well as transformation processes into valuable products are currently under investigation. The use of ***solar energy*** by ***artificicial photoconversion*** of carbon dioxide and by ***photocatalytic water splitting*** is currently addressed as long-term basic research topics [8].

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