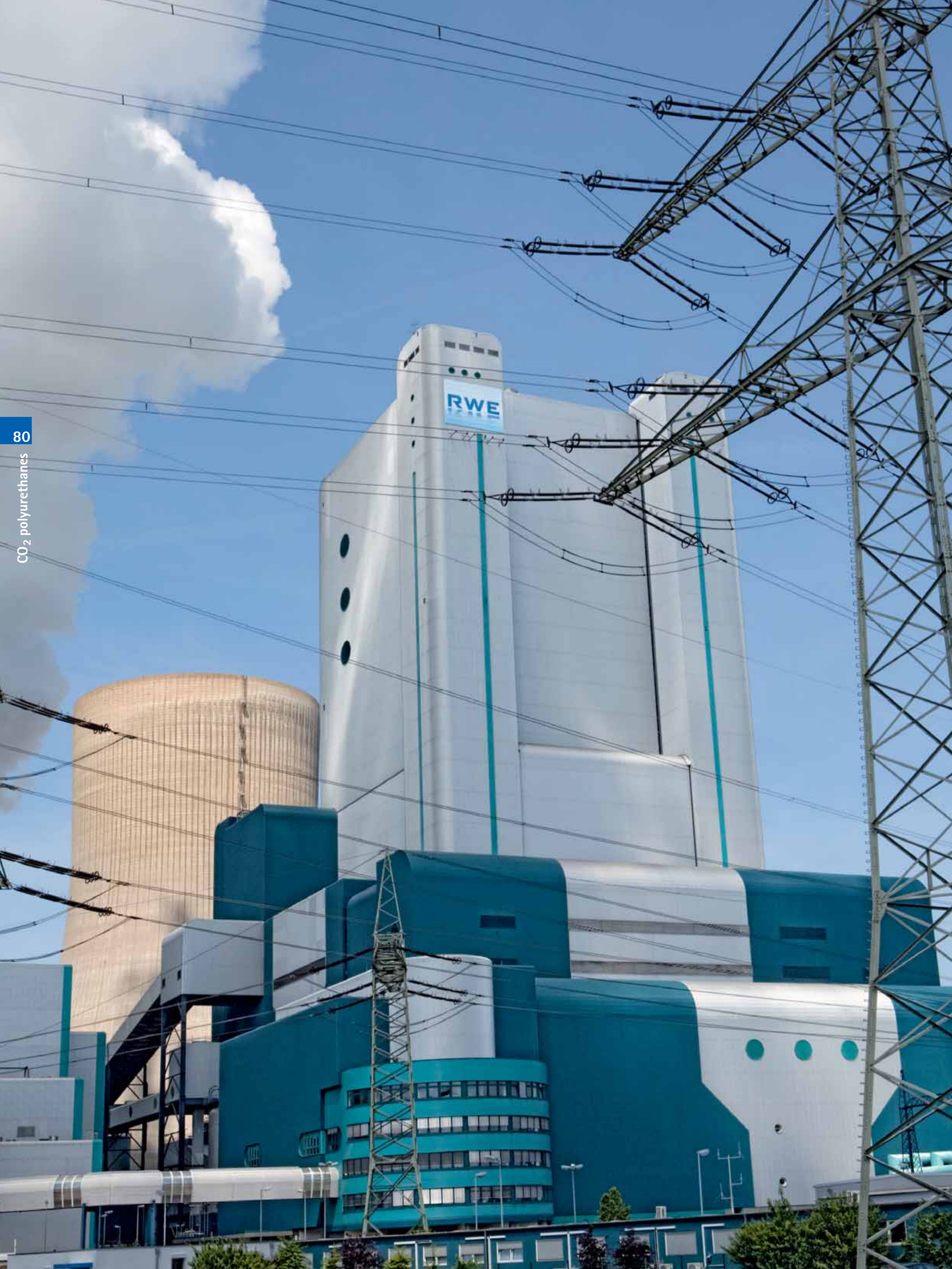

RWE

CO_2 destined to become a valuable raw material for innovative substances

Three atoms for a **clean future**

Oil is becoming increasingly scarce, and carbon dioxide an ever greater problem for the world's climate. For this reason, chemists are constantly on the lookout for new ways to replace fossil raw materials and make good use of the greenhouse gas. Together with a group of partners, Bayer researchers are making good progress in this direction, and have found a way to incorporate CO_2 into the molecular structure of polyurethanes, thus saving oil. And in future, the electricity used to manufacture these plastics could also stem from renewable sources.

The bad boy among greenhouse gases is now destined to serve as a useful raw material in the plastics industry – in the interests of sustainable management. Chemists are aiming to use some of the CO_2 produced by power plants to produce innovative new materials. By doing this, they will not only pave the way for the beneficial use of carbon dioxide, they will also reduce the chemical industry's dependence on crude oil. After all, the liquid that lubricates the global economy is becoming increasingly scarce and ever more expensive, which is why scientists around the world are constantly seeking alternatives to replace the fossil raw material – either completely or in part.

One material for which this makes particularly good sense is a widely used plastic, polyurethane – PU for short. CO_2 can be incorporated into the polyols that serve as raw materials for the production of PU. This plastic is used for a very wide range of products in our daily lives, and is regarded as particularly sustainable. When used for insulating buildings against heat and cold, for example, it saves around 70 times more energy than is used to produce it. PU not only insulates buildings, it also keeps the refrigerator cold, makes car seats comfortable and gives the soles of running shoes the necessary springiness.

Worldwide, around 13 million metric tons of polyurethanes are processed every year, and the trend is rising. And, as with many other plastics, the components that go to make up the polyurethanes are obtained from crude oil.

Plastics for climate protection: PU much in demand around the world

This fossil resource is the main supplier of the central element carbon, on which all organic chemistry is based. But it now seems that a new, virtually inexhaustible resource has opened up: thanks to recent research successes, it will also be possible in future to use CO_2 to economically integrate carbon into polyurethane. Nature itself demonstrates how useful the molecule is: during the process known as photosynthesis,

Raw material supplier: from the flue gas produced by coal-fired power plants like this one in Niederaussem (photo left), climate-harmful CO_2 is to be channeled off and put to good use. Material experts like Dr. Christoph Gürtler (photo right) and his team from Bayer MaterialScience want to use the treated and liquefied climate gas as a raw material for the production of plastics. For example, the carbon dioxide could then be used as a basis for mattresses and heat insulation products.

Photos: Michael Rennertz (3), Bernhard Moll (1), Jutta Jelinski (1)/Bayer AG, Falkenstein/Bildagentur online (1), Mandy von Charmier (1), RWE AG (1)

Partners: Dr. Jörg Hoffmann and Maria-Theresa Gleixner (photo above, left to right) from Bayer MaterialScience are working on the production of catalysts for CO_2-based polyols. Dr. Aurel Wolf (photo right) from Bayer Technology Services is working on a project to encourage inert carbon dioxide molecules to become more reactive.

plants – with the help of water and sunlight – turn CO_2 into the carbohydrates that serve as a source of energy.

But although it may sound obvious, the process is very difficult indeed to transfer to the chemical industry because the CO_2 molecule is chemically very stable and hardly reacts at all with other substances. "Anyone who wants to use carbon dioxide as a raw material first has to drive out its chemical inertness," explains Dr. Aurel Wolf, a chemist at Bayer Technology Services. The carbon atom and the two oxygen atoms are bonded together particularly tightly in CO_2, "which makes it very difficult to integrate this inert molecule into plastics," says Wolf.

To give the carbon dioxide a helping hand, a catalyst is needed. This is a kind of chemical marriage broker that induces two substances to join together more easily. Since the late 1960s, scientists all over the world have been searching for the right catalyst, but for many years without any significant success. The use of CO_2 for plastics production was simply not viable.

Zinc-based catalyst triggered the breakthrough

But a few years ago, a Bayer research team discovered catalysts that allow the efficient use of carbon dioxide, and around 200 of them were put to the test. The scientists repeatedly linked up CO_2 with propylene oxide – an oil-based feedstock for polyurethane – every time with a different catalyst. They investigated how a catalyst behaves under different testing conditions. The researchers additionally simulated the chemical reaction on the computer in order to understand what was really happening.

After numerous attempts, the research team finally made the breakthrough. A special zinc-based catalyst triggered the desired reaction. Further developments went very quickly and a short time afterwards the step was taken from the laboratory to practical implementation. For this, five partners cooperated in the "Dream Production" project, supported by public funds. Apart from Bayer Technology Services, these were Bayer MaterialScience, the utilities company RWE Power, RWTH Aachen University and the CAT Catalytic Center, a research institution likewise located in Aachen and operated jointly by Aachen University and Bayer.

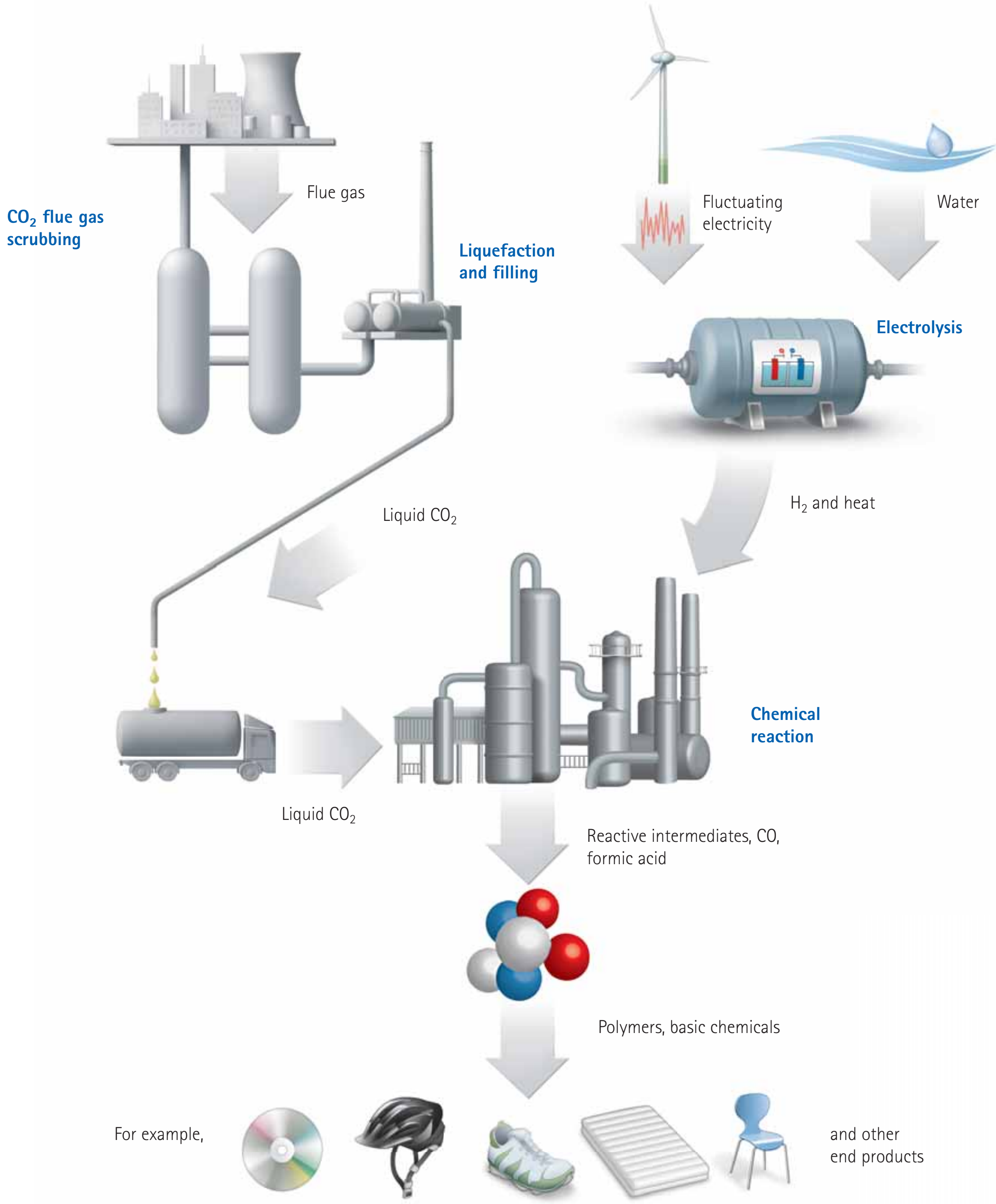
In February 2011, the researchers at Bayer in Leverkusen started up a pilot plant in which CO_2 from an RWE power plant in Niederaussem near Cologne was combined with propylene oxide for the first time on a large scale. The result is a light-colored viscous substance: polyol, one of the two building blocks needed to produce polyurethane. The plant was designed and built by Bayer Technology Services and is operated by Bayer MaterialScience. The subgroup also produces the CO_2-based test products. The researchers at the CAT Catalytic Center examine the carbon dioxide from the power plant to ensure, for example, that it is compatible with the catalyst.

Target for 2015: industrial application of the technology

The partners' big aim is to start implementing the technology in 2015. The first commercial product the chemists are looking at is a mattress based on CO_2. Not only could its interior well be more sustainable than before, it could also have other useful properties.

But the process is also very interesting for one of the partners, RWE. As an operator of gas and coal-fired power plants, the company is looking for ways of reducing its CO_2 emissions and finding alternatives for its use. Accordingly, RWE has great hopes for the incorporation of CO_2 in plastics. At the Niederaussem site, the carbon dioxide is first separated from the flue gas, liquefied,

CO2RRECT – From wind turbine to polymer



CO_2 can be converted into useful chemical building blocks. In the CO2RRECT project, the carbon dioxide originates from the RWE lignite-fired power plant in Niederaussem, which also has a flue gas scrubbing facility. The carbon dioxide is separated off, liquefied and prepared for chemical conversion. For intermediate storage of the fluctuating output of renewable energies, an electrolysis plant is operated to produce hydrogen (H_2). The generated heat is also utilized in the chemical plant, where H_2 reacts with carbon dioxide and converts the gas into intermediate products such as carbon monoxide or formic acid. In subsequent steps, these are then used to produce polymers and basic chemicals, which in turn can be deployed for the manufacture of a variety of plastics products such as polyurethanes.

Pioneers: in the pilot plant for producing plastics with carbon dioxide, Deniz Capar (photo left) checks the pipe connections. In future, excess electricity from wind power could additionally be deployed for utilization of the CO_2. One of the people working on the project is Dr. Martina Peters (photo right), CO_2 project coordinator at Bayer Technology Services.

filled into cylinders and transported to Bayer in Leverkusen.

"Naturally the quantities of carbon dioxide we need for polyurethane synthesis are small compared with the amount of carbon dioxide generated by a power plant," says Dr. Christoph Gürtler from Bayer MaterialScience, who heads the project. Nevertheless, every gram of carbon atom in the polymer stemming from carbon dioxide is one gram less from oil. For the chemical industry, the quantities really are quite significant.

But before the CO_2 really can be used on a large scale and before the chemist's dream can come true, two fundamental questions still need to be clarified: is the new process really better overall than the existing processes for polyol production, and will CO_2 really be saved at the end of it all? Independent researchers from RWTH Aachen University are in the process of finding the answers. At the Institute of Technical Thermodynamics, a detailed study is being made of the individual steps in the technology. As part of an eco-efficiency analysis, the scientists compare the entire new value chain with the existing processes. It is an extremely complex analysis, which will take some time to complete.

Climate protection with nano-foam

Polyurethanes (PU) make a contribution to climate protection even when they are petrochemical-based: researchers at Bayer MaterialScience are working on the development of polyurethane nano-foams, which in a few years could significantly improve heat insulation. The scientists use so-called micro-emulsions that are processed under special conditions into rigid polyurethane foams. The aim is to produce rigid foams with pore diameters of less than 150 nanometers. Because of their good heat insulating performance, nano-foams would, for example, significantly reduce the electricity consumption of refrigerators and thus help to cut CO_2 emissions (see also research *21, "Well insulated and mobile: combating climate change").*

Wind supplies green electricity for chemical processes

But the initial results have already provided encouragement for the project partners: "Our calculations to date indicate that the new process needs less energy over the lifecycle, and thus also emits less CO_2," says Professor André Bardow, who holds the Chair of Technical Thermodynamics at RWTH Aachen University. "This would mean that the process makes more ecological sense than the existing processes. Furthermore, the lower energy consumption should also mean that it is more economically efficient," adds Bardow.

However, science and industry are pursuing other lines, too. Another consortium headed by Bayer is working on a project to also provide, from renewable sources, the energy needed for the utilization of CO_2 as a carbon supplier. That would be a dual sustainability effect.

The problem is that the electricity output from wind and solar power fluctuates enormously according to the weather. If the wind blows particularly strongly, for example, it creates an

Basic research: to better understand the principles of CO_2 chemistry, Bayer is cooperating with scientists such as Torren Carlson from the CAT Catalytic Center in Aachen, which Bayer operates jointly with the Institute of Technical and Macromolecular Chemistry at RWTH Aachen University.

excess supply of energy that has so far not been possible to harness in optimum fashion. In most places, however, not enough storage facilities such as pumped storage plants are available to store these peak loads.

Yet the excess electricity could, for example, by stored chemically. This is the approach being pursued by the CO2RRECT initiative (CO_2-Reaction using Regenerative Energies and Catalytic Technologies) under the leadership of Bayer Technology Services. Apart from Bayer MaterialScience and RWE, it also comprises the Siemens technology group and a number of renowned scientific institutions. "Our goal is to deploy the peak loads to produce the energy source hydrogen from water by electrolysis," explains project manager Dr. Daniel Wichmann from Bayer Technology Services.

Change in the raw material base necessitates new approaches

The hydrogen can then, together with CO_2, be converted into chemical intermediates such as formic acid or carbon monoxide (CO). From CO it is then possible to produce isocyanates – the second component in polyurethane production alongside the polyols. This would complete the circle.

But that's still all a long way off. The research project launched at the end of 2010 – also funded from outside – is looking very promising, but, as things stand today, its practical realization is unlikely to happen before 2020. Nevertheless, the world needs not only more climate protection. "The general change in the raw material base for the chemical industry also calls for new approaches of this kind," says Dr. Martina Peters, CO_2 project coordinator at Bayer Technology Services.

But with CO2RRECT and Dream Production it is not only the processes that are new. The initiatives are also based on a changing approach by industry: major sectors like the chemical and energy industries are moving closer together. "We have recognized how important it is to exploit synergies," says Gürtler, summing up. "And that's precisely the right way to go about it!"

Video on the web: new process for polyurethane production at bayer.de/r012

www.research.bayer.com/co2
Further information on the subject of CO_2 as a raw material

Interview

"Raw materials from the power plant"

CO_2 as the raw material of the future: *research* talked to Dr. Johannes Heithoff, Head of Research and Development at RWE Power AG.

What requirements have to be met in power plants to enable the CO_2 to be utilized?

In the power plant itself, it is merely necessary to install a CO_2 flue gas scrubber. For this, a sufficiently large area of land is required.

What is the biggest challenge technically with the CO2RRECT project?

The development of efficient electrolysis units for hydrogen production and the development of catalysts to convert the separated CO_2 with hydrogen into hydrocarbons for storing chemical energy. The reason for this is that the electricity market will in future be dominated by the inconsistent supply of electricity from wind farms and photovoltaic units.

Will the energy suppliers in future become raw material suppliers to the chemical industry?

Yes, we as power plant operators also see ourselves as raw material suppliers to other industries. CO_2 is nowadays a waste product from the combustion of gas, oil or coal. One incentive for using the CO_2 in other processes is the avoidance of costs for emission rights. So in this way, the CO_2 becomes a useful material in exactly the same way as the gypsum produced as a by-product in the desulfurization of flue gas and the power plant ash, which is used in road building or as an additive to concrete.

What will the material flows of the future look like so that projects such as Dream Production can be built up on an industrial scale?

As a supplier of CO_2 to the chemical industry, we are at the beginning of the value chain for, let's say, plastics production. Ideally, to minimize the cost of transporting the CO_2, it should be further processed close to the power plant. Here, the additional energy requirement could then also be made available in the form of process heat and electricity directly from the power plant, which would increase the overall efficiency – for example by combined heat and power generation – even further.