Magic Coal from the Steam Cooker

Proof that basic research is by no means confined to ivory towers, but can indeed be useful in solving burning issues of practical relevance, has been provided by **Markus Antonietti,** *Director at the* **Max Planck Institute of Colloids and Interfaces** *in Potsdam. He has developed a process with which biomass can easily be converted into valuable raw materials.*

Producing the "magic coal" releases energy. An explosion in the lab on the roof of the Max Planck Institute of Colloids and Interfaces proved this very impressively.

Photos: Norbert Michalke

Institute Director Markus Antonietti pulverizes a tiny crumb of coal on his palm and inhales with obvious pleasure: "Mmmm, I like this smell!" A newly developed men's cologne? No, but rather, perhaps, the beginning of a new era in the energy industry. In Antonietti's vision, carbon takes center stage – just as it already does in the real world: the fossil fuels that we extract from the ground at a rate of billions of tons each year keep the economy running, form the basis for power generation and serve as a raw material for the chemicals industry. But the flip side is that practically all recovery methods ultimately produce carbon dioxide (CO_2). It makes up 80 weight percent of the world's entire industrial exhaust. This means nothing more and nothing less than that we are converting our fossil deposits into gas and scattering them into the atmosphere at an alarming pace. The biosphere can bind only about a third of them globally. The results have since become known: the greenhouse effect, global warming and climate change.

Markus Antonietti wants to put an end to this, and he beats nature at its own game: he invented an extremely simple method that could revolutionize the industrial carbon cycle, as it uses the world's enormous biomass stores to produce coal, humus or oil – directly and without any of the complicated process steps that are commonly used in biomass utilization today. At the same time, this process also releases energy. The Potsdam-based chemist works with pure waste: straw, wood, wet grass, damp leaves.

In Antonietti's scenario, everything that pollutes the countryside today, everything that farmers plow under to get rid of and everything that gardening enthusiasts toss onto the compost heap or into the biowaste container becomes valuable raw material. By way of coal, it can be used to obtain gasoline, diesel fuel or key chemicals, or it can be transformed into topsoil and even used in fuel cells to obtain energy directly. No additional carbon dioxide is created in the process – in fact, large quantities are actually pulled out of the atmosphere and bound.

Is this utopian? A sophistry of an academic crackpot? No. Chemist Markus Antonietti takes a very fundamental approach to the subject. For example, he first looked at the energy landscape of various carbon compounds: "Ultimately, biomass consists of sugar building blocks that contain a lot of energy. Using a chemical process to break them down into carbon and water doesn't require any further energy to be added, but rather, it actually releases additional energy." Nature showed us how it's done: over the course of millennia, coal, petroleum and natural gas were created from dead plants – in other words, biomass – deep within the Earth's layers. We all learn this in school. "But no one had previously given much thought to how it really happens," Antonietti muses.

The Liberty to Ask Trivial Questions

His in-depth literature research yielded many speculations and truisms – there is frequent mention of

Hydrothermal carbonization in a pressure container turns biomass, such as orange peels, into extremely fine powdered coal (left). On the right is the inventor of the method, institute Director Markus Antonietti, with his colleague Anna Fischer.

the "carbonization process," but no one had yet advanced to the core of the issue, namely, how this actually takes place. Antonietti had the courage to do just that. "Today I take the liberty to ask such questions," says the 46-year-old chemist, "even at the risk of being considered a crackpot. I would rather put my reputation at stake than not come closer to the truth." In the case of coal, his very first attempt met with success. The researcher not only found out how coal forms but, quite incidentally, he even discovered a process that could well change the world.

Of course, the general public is basically aware how important a sustainable energy supply is for the future of our society. What is far less known, however, is that there is still a lot of research to do; and it is not just about process technology and process control, or boosting output and efficiency. No, even today, it is still about very fundamental problems that can be solved only through basic research – and that thus number among the traditional domains of the Max Planck Society.

To address this, in 2004, five Max Planck Directors joined to form the ENERCHEM research network, a "project company for nanochemical concepts for sustainable energy supply." The projects range from improved catalytic methods for generating hydrogen to work on imitating photosynthesis and storing hydrogen in novel media (MAXPLANCKRESEARCH 2/2005, page 14 ff.).

Antonietti's work with coal also fits into this organizational framework. "ENERCHEM offers the ideal environment for this," he emphasizes, "we are well positioned within the organization and have all the competence we need to evaluate our ideas." That is beneficial for everyone involved, in terms of patent rights, statutes, and even communications: "All of the partners have the same cultural background, even if we are very different personally. This way, we know that the signals we transmit are received as intended."

Creative Collaboration Creates Impetus

All ideas, inventions and problems are intensively discussed among the colleagues, considered by experts and critically tested. This applies equally to Joachim Maier's innovative battery concepts in Stuttgart and to Ferdi Schüth's improved hydrogen storage in Mülheim, to Klaus Müllen's nanotechnological electrode concepts in Mainz and to Robert Schlögl's new methanol catalysts in Berlin. So the carbon vision of the Potsdam-based institute Director is not the only result of the high-caliber collaboration. Key impulses for future energy concepts can be expected from this group of Max Planck scientists in the years to come.

Back to Markus Antonietti. His solution is impressively simple: put biomass and water into a pressure container, add a couple of bits of catalyst and heat it all up to180 degrees Celsius in the absence of air. After 12 hours, allow the mixture to cool, open the "steam cooker" and you have a black broth. "Our analyses showed that these are extremely finely distributed spherical coal particles in water," explains Magda Titirici, who has since conducted hundreds of these experiments. For the experiment, their Director, Antonietti, plundered his garden and brought in oak foliage, pine needles, bits of wood and pinecones. That is why some of the newly formed coal crumbs still contain fragrant resins and smell pungent and spicy.

Biomass is already being used today, but in other ways – for example in the form of biodiesel obtained from vegetable and animal fats. However, the facts immediately show that it can do no more than fill a niche: mankind currently consumes 4 billion tons of petroleum each year, while global production of fats is just 120 million tons. This would be sufficient to supply all cars in Germany with biodiesel, but then the world would have nothing left to eat.

So valuable products such as fats must be avoided, and preference given instead to cheap waste. Of course we can simply burn it, but that provides little energy, because biomass is usually wet and must first be dried. Furthermore, burning it releases carbon dioxide. Another method that is used today is fermentation of biomass, which produces ethanol and, likewise, CO_2. "However, alcoholic fermentation has an estimated real efficiency of 3 to 5 percent of the primary energy stored in the plants," says Antonietti. "And afterwards, the alcohol still has to be separated from the water. It takes 30 cubic meters of beer to get one cubic meter of pure alcohol. That's not a good solution for fuels."

Furthermore, converting biomass into biogas is not optimal from an energy standpoint. "What we use as an energy source is really a byproduct of microbial metabolism," says the chemist, "and half of the carbon is released again as CO_2." This leaves pyrolysis. This method carbonizes the biomass by heating it to extremely high temperatures in the absence of air. However, this requires that the vegetable material be dry, otherwise the energetics of the process are not worth it.

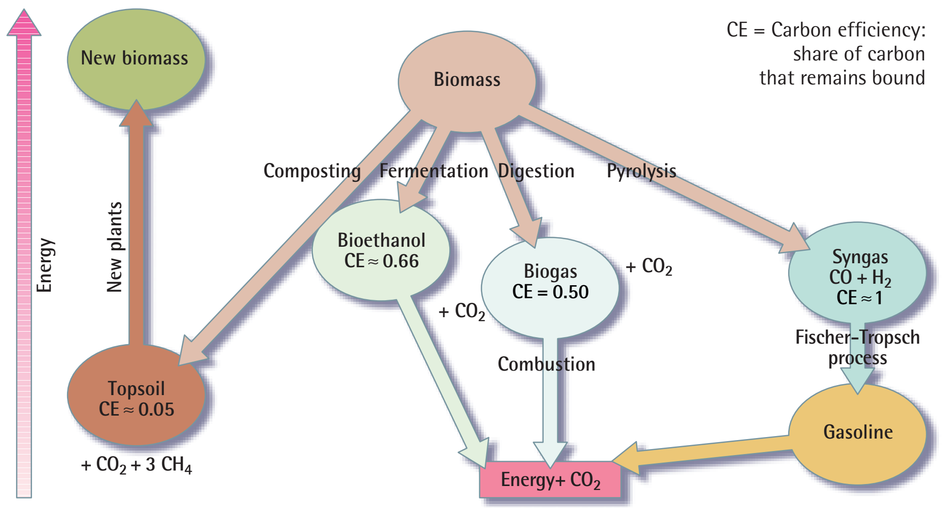
A Wonderful Gift of Nature

Antonietti's plan to use vegetable waste is much cleverer, and that is why it will rule the future: his hydrothermal carbonization completely converts biomass – even when it is wet – into carbon and water. "And that is the crux," enthuses the Max Planck Director. "No CO_2 is produced – the sole byproduct is simply water. All of the carbon contained in the material remains bound in the product. This means that our carbon efficiency is 100 percent. The carbon we put in at the beginning comes out as carbon at the end – the best solution for the carbon balance. It isn't possible to sustainably bind more carbon than that."

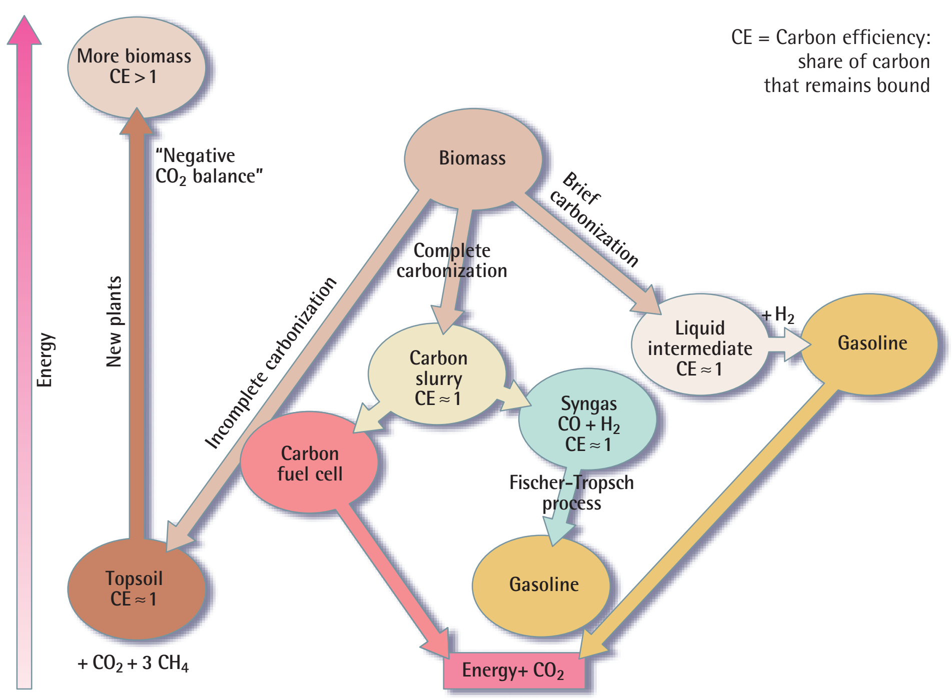
The formula makes it obvious: if you remove five water molecules from a sugar molecule, you get practically pure carbon with a couple of residual hydrogen and oxygen groups: lignite. This is made up of tiny spheres and is extremely porous, with a pore size of 8 to 20 nanometers, which is very interesting for many applications. "This is purely coincidence," says Antonietti, "we never planned it – it is a gift of nature." The carbonized pinecone still retains its original form, but it is no longer a pinecone, but rather, strictly speaking, a nanoproduct.

Nature does exactly the same thing, but very slowly. Peat takes 500 to 5,000 years to form, lignite 50,000 to 50 million years, and anthracite formed from carbon is even 150 million years old. The Potsdam-based researchers, on the other hand, can do it overnight. And their reaction is an exothermic one, meaning that heat is created spontaneously. In fact, during one of the experiments, the reaction chamber exploded because too much energy was released. "What is so ingenious about this process is its simplicity," says Markus Antonietti. But it is apparently too obvious to be included in textbooks. "Even Edgar Allan Poe knew that the best place to hide anything is in plain view." ►

Put some biomass, such as greens, into a pressure container (left), add a couple of crumbs of a catalyst and heat it all up to 180 degrees Celsius in the absence of air: 12 hours later, out comes the black powder consisting of coal nanospheres (right).



Biomass Management Today: By far the majority of biomass decomposes directly into atmospheric carbon dioxide and methane right where it forms. Only very small quantities become topsoil or otherwise turn into a carbon sink (for instance in swamps or on the ocean floor). Current biomass utilization technologies include – apart from direct burning of wood and straw – alcoholic fermentation, biogas production in digesters, and direct syngas production.



An Alternative Vision of Biomass Management: The various technologies of hydrothermal carbonization can be used to produce, with very high carbon efficiency, artificial topsoil that sustainably improves the quality of barren soil. In this way, it serves to create greater quantities of biomass (negative CO_2 balance). However, the carbon slurry that forms upon "complete carbonization" of waste matter can also be used for energy, for example in central plants for manufacturing syngas. Or – according to one vision – it can be fed into carbon fuel cells. A better understanding of the processes that take place during carbonization should also make it possible to obtain liquid fuels directly. For this, however, due to the fundamental chemical equilibria involved, hydrogen has to be added from other sources.

So what is the coal-water mixture good for? It could, of course, be burned as coal, but that would just be the easiest solution and by no means the best one. It is much better, for example, to use this fine powdered coal and water mixture to operate a new kind of fuel cell. The prototypes, which already exist today (for example at Harvard University), have an efficiency of 60 percent. It is operated with "coal slurry in water" – like that formed in hydrothermal carbonization.

To generate fuel with it, rather than electricity, the carbon-water mixture is simply heated up even more, as then an exothermic reaction creates what is known as syngas, or carbon monoxide and hydrogen. This can be used directly to produce gasoline using the tried-and-tested Fischer-Tropsch process. The biomass used has also become a very valuable source product that can be piped out or converted to gasoline. "Instead of simply letting a cubic meter of compost decompose in a corner of your garden, in the future, you could take it to a local factory and get 200 liters of gas back," says Antonietti, envisioning the practical implementation.

1,300 Liters of Biodiesel per Hectare

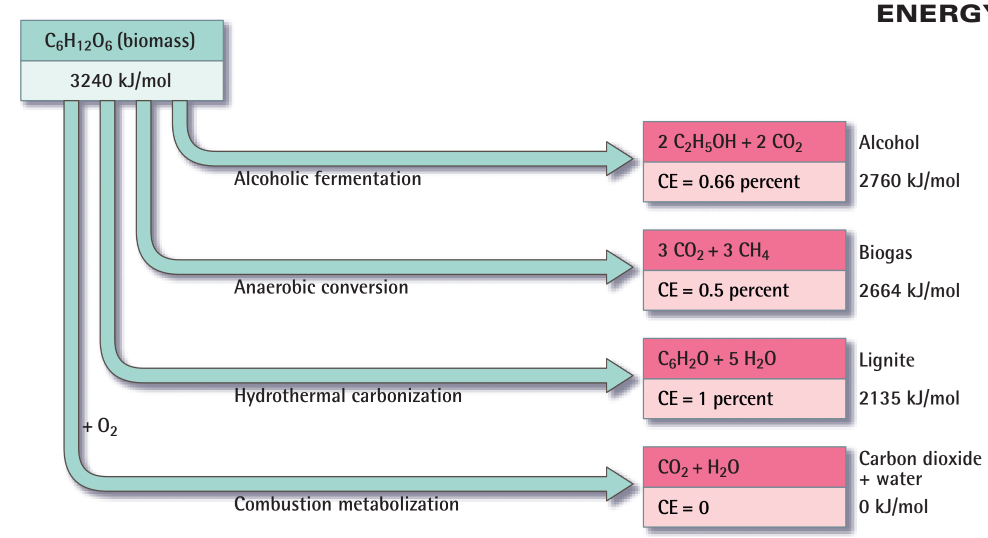
There is plenty of biomass in the world, although its potential is difficult to assess. The International Energy Agency cites various studies whose spectrum ranges from 9 to more than 360 billion kilowatt hours per year. One study by the World Energy Council even calls biomass "the potentially largest and most sustainable energy source in the world." However, experts also add that: "Both the production and the use of biomass still need to be modernized."

Indeed, current usage, for example as fuel, is not particularly efficient: when biodiesel is produced from oleaginous fruit, one hectare of farmland yields about 1,300 liters of fuel, because only the seeds of the plants are used. "If fast-growing plants were cultivated there instead, such as willow wood, reeds or even just normal forest, and fuel then produced from the entire biomass through hydrothermal carbonization, 14 cubic meters of fuel could be obtained per hectare," says Antonietti. That would be 10 times the amount cited above. According to estimates of the Forschungszentrum Karlsruhe, Germany alone produces some 70 million tons of dry biomass annually from biogenic residues and waste. That would be more than enough to supply our fuel.

But it gets even better, because Antonietti's process does much more: inside the steam cooker, biomass is not abruptly converted to coal. Instead, gradual processes take place that form intermediate products that are at least as useful as the end product carbon. If we open the container after just a few minutes, we find a petroleum precursor. "Remove, for instance, three waters from the sugar molecule, rather than five," explains the researcher. This intermediate is still too reactive, but with a bit of research, he hopes to tame it to such an extent that "we can also produce oil directly from plant waste."

Another intermediate of hydrothermal carbonization is already more technically sophisticated: after the liquid phase, a pulpy solid forms inside the pressure container. It is nothing other than what we buy at the garden center as potting soil: humus. The Potsdam chemists are actually able to use their method to turn plant matter into pure topsoil with 100 percent carbon efficiency. Natural composting, on the other hand, generally produces only about 10 percent soil, while the rest escapes into the air as methane and carbon dioxide. "This is the most important process in nature in which energy volatilizes," explains Markus Antonietti.

Our predators, as it were, are microbes. When we toss something into the forest, such as straw, leaves or wood, it eventually just disappears – but the energy associated with it disappears, as well. We feel good about it because we don't see what happens, but the truth is that, when we do this, we are producing enormous amounts of carbon dioxide and methane. In Markus Antonietti's words: "Viewed this way, the forest is not just a blessing for the environment, it is also the world's biggest polluter!"



The Third Alternative: Carbohydrates such as cellulose, starch and sugar are energy storage molecules that release a lot of energy when burned. Theoretically, 15 percent of the stored energy is already lost when sugar is converted to alcohol, and two of the six carbon atoms are immediately released as CO_2 (carbon efficiency CE = 0.66). In anaerobic conversion, when producing biogas, ideally, 18 percent of the energy is lost, and half of the bound carbon is released again. However, both alcoholic fermentation and biogasification are biological processes that are not as efficient as theory predicts.

The hydrothermal carbonization method described here binds, in a chemical process, nearly 100 percent of the original carbon as coal or topsoil, retaining 66 percent of its original calorific value and the rest occurring as process heat. This third method makes sense anywhere that direct combustion isn't possible, or where the material isn't sufficiently accessible to the biological processes.

A Negative Carbon Dioxide Balance

If, however, we were to use the artificially produced topsoil to vegetate eroded areas in southern Spain or in the tropics, plant growth could be used to bind large quantities of carbon dioxide in the air, creating a negative CO_2 balance there. For years, Johannes Lehmann of Cornell University in Ithaca (USA) has been working on this method of making burned soil along the Amazon fertile again – with highly encouraging results. However, Lehmann and his colleagues have been using matter that was produced by pyrolysis.

Markus Antonietti is proud of how he and his team have achieved their successes: "We all looked at nature – we truly gave meaning to the word biomimesis. It's the old familiar trick: if someone doesn't know something on a test in school, he sits next to the smartest kid in the class and tries to learn from his approach. After all, we live in a system that has been functioning in a cycle for millions of years. We can learn a lot from its rules."

The researcher is well aware that it will take time for his ideas to catch on: "I would be pleased if people would come up and say: I want to take part. Owners of small garden centers who want to try something out and be part of this change in values. My hope is that people will see a future again, and become patrons of science or perhaps even get actively involved."

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