Hunting for Treasure among the Wood Chips

Wood waste and straw contain valuable substances for the chemical industry, and these substances are what chemists from the **Max-Planck-Institut für Kohlenforschung** in Mülheim an der Ruhr and the **Max Planck Institute for Dynamics of Complex Technical Systems** in Magdeburg want to get their hands on. The researchers are looking for ways to convert biomass into useful chemical compounds and use them as energy sources or raw materials.

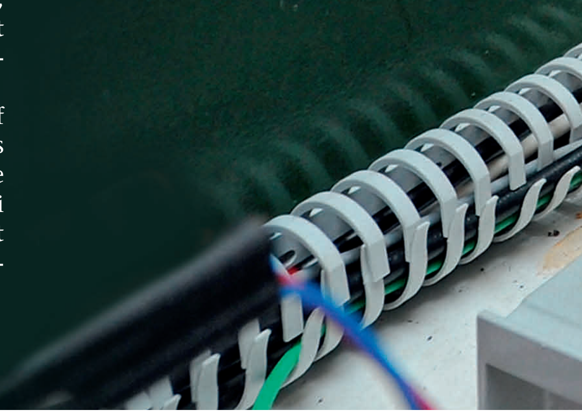
TEXT **CATARINA PIETSCHMANN**

Petroleum isn't being traded for the price of extra virgin olive oil quite yet, but we know that deposits will soon be running dry. Natural gas and coal won't last forever, either, and besides, all fossil fuels harm the climate. So it's high time to give serious thought to finding sustainable and climate-neutral energy sources.

Wind power and solar energy would be ideal for generating electricity and heat, or moving vehicles from A to B. Solar cells covering just part of the area of the Sahara would be sufficient to supply the entire world's electricity needs. Perfect! Except for one problem: Electricity can't be turned into skin cream or painkillers. It can't be molded into computer casings or plastic bottles. And aircraft can't take off with it. Electric current is nothing more than the directed movement of charge carriers. No material, not a single molecule is involved.

Petroleum, on the other hand, has a lot more to offer than its energy content. It's also a multipurpose raw material for countless items that make life easier, or simply nicer. This dark, dirty liquid, the result of millions of years of decay of dead marine organisms, is the basis for medicines, cosmetics, plastics, paints and coatings, fertilizers and plant protection products, insulation materials, detergents, and the list goes on.

"Providing an ongoing supply of energy and raw materials to industry is one of the most urgent issues we face over the next 30 years," says Ferdi Schüth. As a chemist, he's certain that there can be only two long-term re-



Only high-performance catalysts can efficiently convert biomass into basic chemicals and increase yields from fossil raw materials. Here, Mario Soorholtz (right) and Tobias Zimmermann use high-pressure reactors to test the effectiveness of catalysts developed at the Max-Planck-Institut für Kohlenforschung.

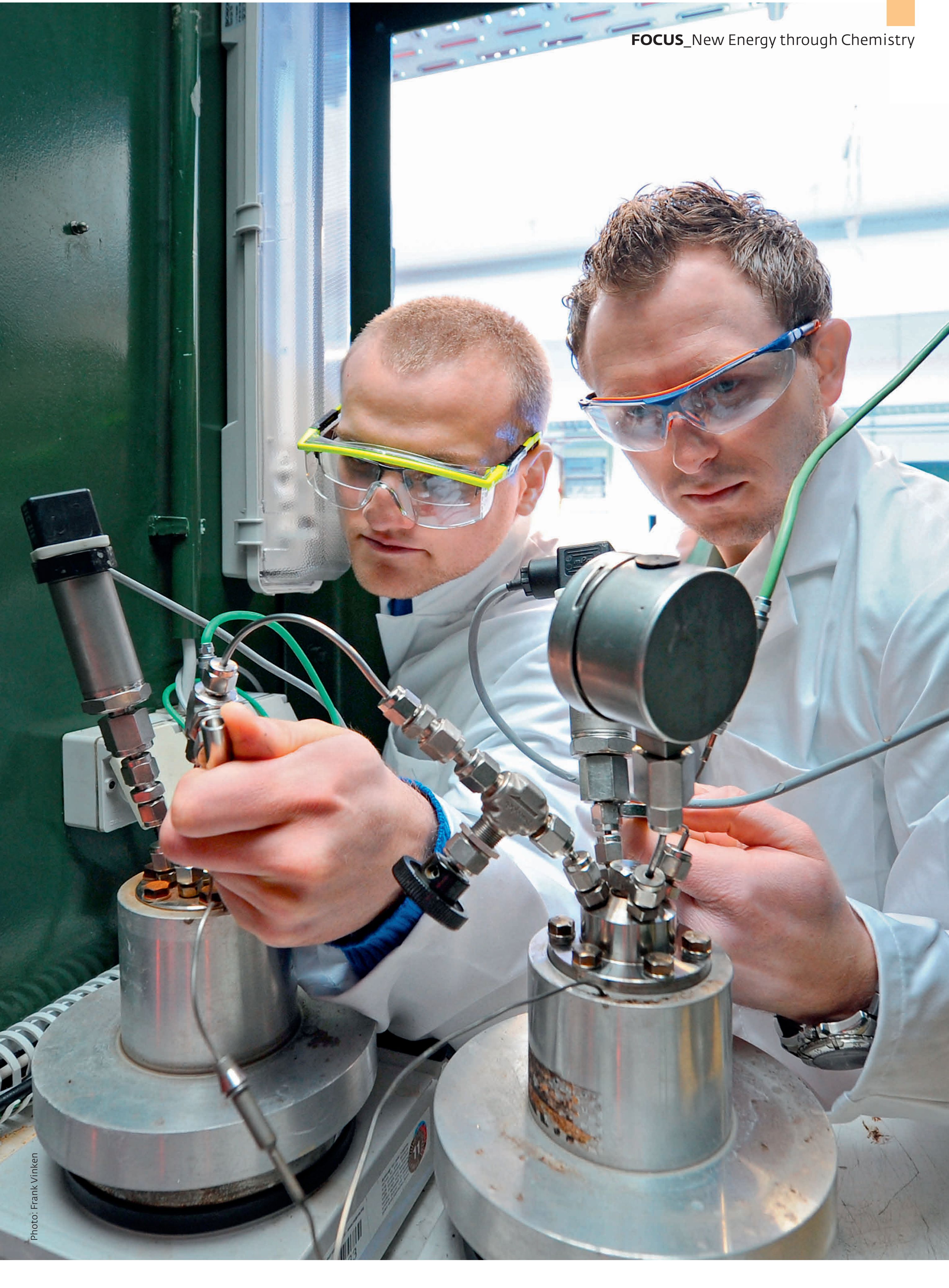


Photo: Frank Vinken

left: Wood in the pressure cooker: Udo Richter closes the lid of a pressure vessel, which chemists refer to as an "autoclave". Inside, wood is boiled with an ethanol-water mixture at around 170 degrees Celsius to dissolve the lignin out of the wood. The cellulose is left behind.

right: Fine chips of wood are poured into the autoclave (1). The resultant cellulose is a white solid and is dissolved in an ionic liquid (2). The powdered catalyst, which breaks it down into short sugars, can then easily be filtered out (3).

placements. "Biomass, which would allow us to benefit from some of the natural world's synthetic capability. And C1 building blocks." Biomass, too, could be broken down into these tiny molecules that contain a single carbon atom. Schüth is in charge of the Heterogeneous Catalysis department at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr. His team is looking for ways to make efficient use of biomass.

The Earth has no shortage of renewable raw materials. Second-generation bioethanol is no longer produced from plants containing starch or sugar, the cultivation of which competes with food production, but instead from wood waste and straw. Both of these could, however, also be chemically converted into industrial raw materials. Just that proportion of plant waste that is indigestible for humans would probably be enough to meet demand for chemical production.

Put that way, it sounds simple, but it isn't. This is because the chemical composition of biomass is utterly different from that of petroleum. The latter is a mixture of somewhat uninspiring long-chain, cyclic and aromatic hydrocarbons. It consists almost entirely of carbon and hydrogen. Biomass, in contrast, contains substantially more complex molecules. The main constituents are sugars that are linked together to form starch or cellulose chains, and these have a considerable oxygen content.

Photo: Frank Vinken

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Biomass can indeed be converted into carbon monoxide and hydrogen, or "synthesis gas," from which hydrocarbons and other classes of molecules can then gradually be synthesized. But what a waste of nature's synthesis skills, which have been refined over millions of years! Targeted disassembly into the building blocks that industry requires would be much subtler ... and more elegant. As Schüth emphasizes, "The past century has seen the development of selective functionalization reactions." By this, he means that chemists can systematically oxidize molecules, for instance to form alcohols or acids. "The task we face now is how to create an entirely new kind of chemistry, focusing on defunctionalization." The aim now is, for example, to take sugar molecules that have numerous hydroxyl groups and remove some or all of the alcohol functions. A paradigm shift is under way – exciting times for chemists.

It's no accident that research for the post-petroleum era is being carried out in the middle of a former coal-mining region. The Kaiser-Wilhelm-Institut für Kohlenforschung, founded back in 1912 and the predecessor of the present Max Planck institute, laid the foundations. Driven by increasing levels of motorization, Franz Fischer and Hans Tropsch developed a large-scale industrial coal liquefaction process here in 1925. In this process, coal was first converted to synthesis gas, the carbon monoxide-hydrogen mixture mentioned above, by partial oxidation at over 1,000 degrees Celsius and gasification with water vapor. In a second reaction, involving catalysis at elevated pressure and temperatures of between 160 and 350 degrees Celsius, liquid hydrocarbons were formed. These are suitable as diesel fuel or a primary material for the chemicals industry.

SALT CAN BE USED TO TURN WOOD INTO SUGAR

This *Fischer-Tropsch synthesis* was of huge significance in the darkest period of Germany's history. Under the Third Reich, motor fuel was classed as "essential to the war effort." By 1945, nine large-scale industrial plants had been built in the former German Reich with a total capacity of 600,000 tons per year to produce synthetic diesel from domestic coal. Production was carried out, in part, with forced labor and in concentration camp outposts.

Due to the unbeatably low price of oil, coal liquefaction was suspended in West Germany after World War II, but saw a first renaissance during the 1970s oil crisis. The great strength of the "Fischer-Tropsch" process is that it can make use of virtually any carbon source, making it highly topical once again. But now the desired feedstock is wood rather than coal. However, Ferdi Schüth and his team also want to use this renewable raw material in an entirely different way.

The main constituent of wood is cellulose, which consists of chains of hundreds to 10,000 glucose molecules. If the bonds between them are broken, the sugar can be fermented into bioethanol. But if this is to be achieved, cellulose must first be dissolved. This is a problem because this biopolymer is virtually insoluble in anything, because the sugar chains are additionally linked together with countless hydrogen bridges.

"In 2002, it was discovered that cellulose is soluble in ionic liquids," explains Roberto Rinaldi, winner of the Sofia Kovalevskaya Prize awarded by the Alexander von Humboldt Foundation, and independent group leader at the Mülheim-based institute. These are salts whose cations consist of organic molecules. Due to their larger molecular radii, they exhibit only weak cohesion compared with common salt. Accordingly, ionic liquids melt at temperatures as low as less than 100 degrees Celsius, while table salt doesn't become liquid until it reaches 860 degrees. Once dissolved, cellulose needs an acid as a catalyst in order to snap the bonds between the individual sugar molecules. But how can the salt be removed again? Rinaldi had the clever idea of using an acidic ion exchanger instead of sulfuric acid. Being a granular resin, it can simply be filtered out after the reaction. So, as crazy as it might sound, salt can indeed be used to turn wood into sugar. But price is a vital con-

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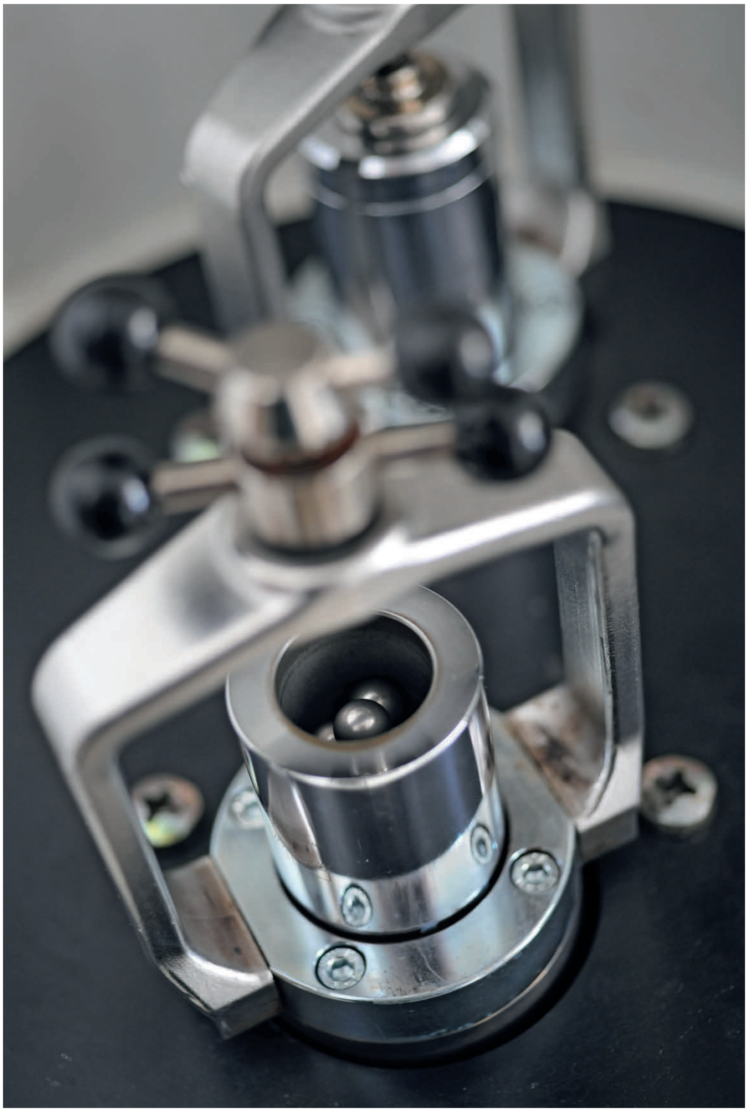


A simple route to sugar: A ball mill grinds wood chips with sulfuric acid. Cellulose can also be broken down in this way without using a costly ionic liquid. This creates oligosaccharides that are easy to process.

sideration here. “If we are to make the process cost effective, we can afford to lose virtually none of the ionic liquid in each cycle. This is because, in a continuous process and on a large scale, losing even just one milligram per kilo of sugar is costlier than the alternative grown in a field.” One kilo of beet sugar costs 20 euro cents.

But Rinaldi has another alternative to hand. “Using a ball mill, wood chips mixed with dilute sulfuric acid can be ground down into minuscule particles: oligosaccharides that are just three to six sugars long and dissolve in water.” Brute force combined with acid catalysis – sometimes the best solutions are quite simple.

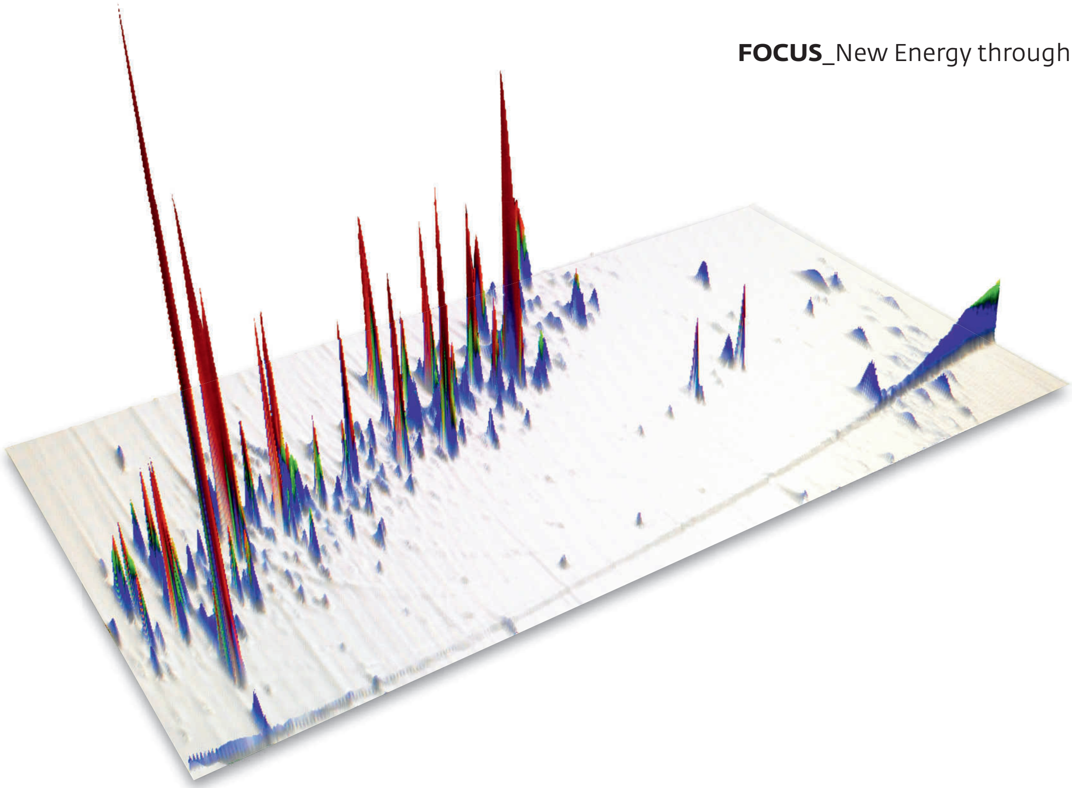
But there is more to plant biomass than just polysaccharides; there is also lignin. A resinous, disordered network of polymerized aromatics, this substance accounts for 20 to 30 percent of the solids content. It penetrates the cellulose fibers, acting as a kind of support stocking for plant tissue. Its building blocks are highly crosslinked by chemical bonds. Some researchers even believe that a tree’s lignin is a single giant molecule.

LIGNIN – A TREASURE TROVE FOR THE CHEMICALS INDUSTRY

For each liter of bioethanol produced, three kilos of lignin are obtained. “What should we do with it? Break it down into synthesis gas?” Rinaldi shakes his head. “No, we’re trying to come up with something better to do with it.” Its aromatic constituents make it a treasure trove for the chemical industry. This is because these particular hydrocarbons have uses in the production of drugs, polymers and dyes, among other things. Lignin is the only natural source for them. And, globally, around 30 billion tons are formed from scratch each year. That’s quite some potential!

Lignin is easily isolated: wood is converted into fine chips and then boiled under pressure with 50 percent alcohol. Once the solvent is removed, lignin is left behind as a viscous brown mass. If this is heated to 250 to 300 degrees Celsius, it breaks down into its component parts. “But when we do that, it’s virtually an explosion in a pharmacy,” chuckles Ferdi Schüth. Roberto Rinaldi nods in agreement. “That’s right, hundreds of products are obtained, each of them in tiny quantities.” Even using sophisticated methods, the mixture can be separated only to a certain extent. “But the real nightmare is that it immediately repolymerizes!”

Photos: Frank Vinken (2)



"An explosion in a pharmacy": Cleaving lignin releases countless substances. A gas chromatograph, combined with a mass spectrometer, provides an individual signal for each of them. The height of a signal indicates the quantity in which a compound is obtained.

The Brazilian is phlegmatic, viewing it as a personal challenge. In nature, fungal enzymes break lignin down, but only very, very slowly. Rinaldi is looking for catalysts that can do the job faster and, at the same time, deactivate all those sites on the building blocks where the molecules can reattach themselves to one another. Instead of lignin, he is carrying out tests cleaving small aromatic compounds such as diphenyl ether with nickel. He has found that the efficiency of the reaction varies depending on the solvent used. This is a first small step on the long path to making use of lignin.

Like coal liquefaction, the development of catalysts is permanently associated with this Mülheim-based institute. It was here that the second director, Karl Ziegler, developed organometallic catalysts for manufacturing plastics. In 1953, he filed a patent for a process with which *ethylene* is catalytically linked to form *polyethylene*. Building on this foundation, his Italian colleague Giulio Natta then created *polypropylene* in a similar manner. In 1963, the pair shared the Nobel Prize for Chemistry. Today, *Ziegler catalysts* are used worldwide to produce more than 70 million tons of plastics annually.

Wolfgang Schmidt is also working on catalysts for biomass conversion – specifically on catalysts that convert synthesis gas, a mixture of carbon monoxide and hydrogen, obtained from plant waste into small, useful basic chemicals. Working together with the Fraunhofer Institute for Environmental, Safety and Energy Technology (UMSICHT) in Oberhausen, he is developing a continuous process for producing dimethyl ether (DME). This gaseous compound has many different uses, for instance as an alternative motor fuel, liquefied gas or a diesel additive.

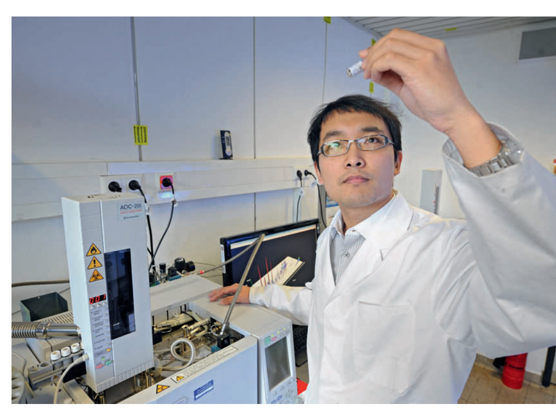
WANTED: ONE CATALYST FOR TWO REACTIONS

DME is formed in two stages: first, methanol is produced from synthesis gas, and then one molecule of water is eliminated with an acidic catalyst between two alcohols. Two-stage processes are somewhat inconvenient, especially if the intention is to use them for the continuous conversion of large quantities. "What's more, the two reactions proceed at different pressures. And different catalysts are required," says Schmidt, describing the problem. The search is on for a single catalyst that can carry out both reactions.

The chemists are thus producing small test quantities of nanostructured catalyst mixtures based on copper, zinc oxide and a solid acid component, and analyzing them using the latest methods. Then they test them head to head in a computer-controlled test plant in the historic development facilities. Fraunhofer engineers are in charge of process engineering aspects and are building a pilot plant in Oberhausen. The feedstock is wood chips, a starting material that is still very much uncharted territory for the industrial production of chemicals.

The DME project is a sign of things to come for the chemical industry, with process engineering also having to be rethought. "When you use renewable raw materials, you have to deal

Xingiu Wang takes a look at a sample before analyzing it in the combined gas chromatograph/mass spectrometer.



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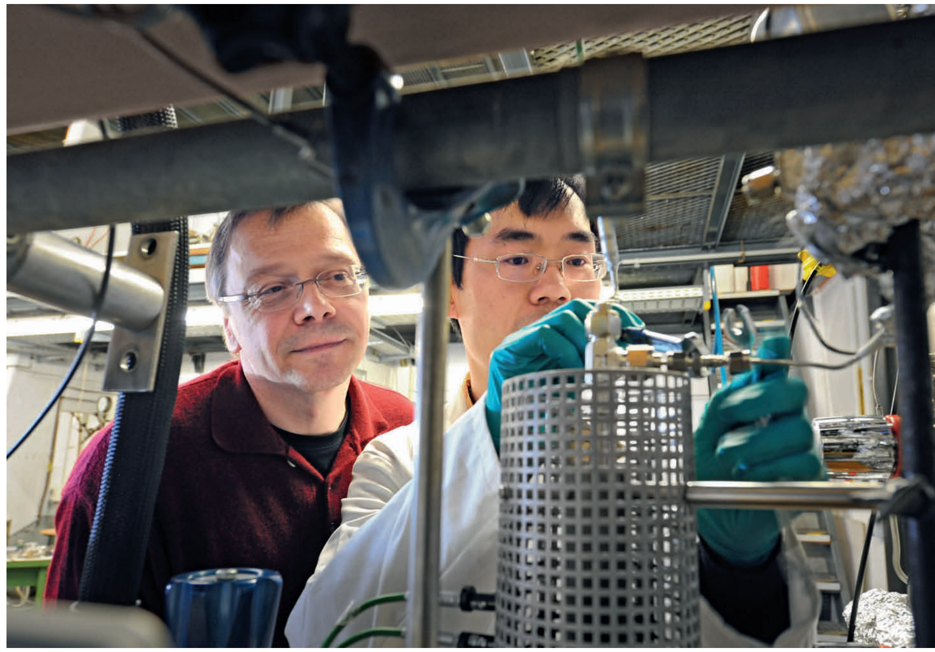


Testing catalysts: Wolfgang Schmidt and Heqing Jiang fill a laboratory reactor with synthesis gas, a gas mixture obtainable from biomass. They are testing how efficiently catalysts can convert the gas into dimethyl ether.

with long-chain molecules. If they are to be functionalized as platform chemicals, it will have to be possible to carry out chemical reactions selectively in liquid multiphase systems," explains Kai Sundmacher from the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg. In the InPROMT collaborative research center, his team is jointly developing novel process technologies with colleagues from TU Berlin, TU Dortmund, and the University of Magdeburg. Olefins obtained from biomass are mainly oily liquids. Homogeneous catalysis is the only way to bring them into effective contact with the catalyst, which means that the catalyst must be soluble. Unlike in heterogeneous catalysis, in which, for instance, synthesis gas reacts to a solid catalyst, a homogeneous catalyst requires troublesome separation after the reaction.

One solution to this problem could be switchable solvent systems. At present, the researchers are pursuing two paths in parallel: one approach provides solubilizing surfactants, which are added to an oil-water mixture or "multiphase system." (The homogeneous catalyst is in the water.) "Within a specific temperature window, reverse microemulsions, consisting of nanometer-sized water droplets, spontaneously form in the olefin, and are stabilized by the surfactant. Because the interface between the phases is now enormous, the rate of reaction increases by several orders of magnitude." After a temperature change, the liquids separate out again and the catalyst is largely left behind in the water. They are thus searching for the ideal surfactant and optimum temperature-switching conditions for the desired chemical reaction.

The other approach uses *thermomorphic* liquids. These are mixtures of two or three solvents of differing polarity that mix together completely or divide into two parts, depending on the temperature. The challenge is to identify the ideal solvent and the perfect mixing ratio for a particular desired reaction. Researchers are simulating all these factors using computer simulations and experiments in mini-plants, or production plants on a laboratory scale.

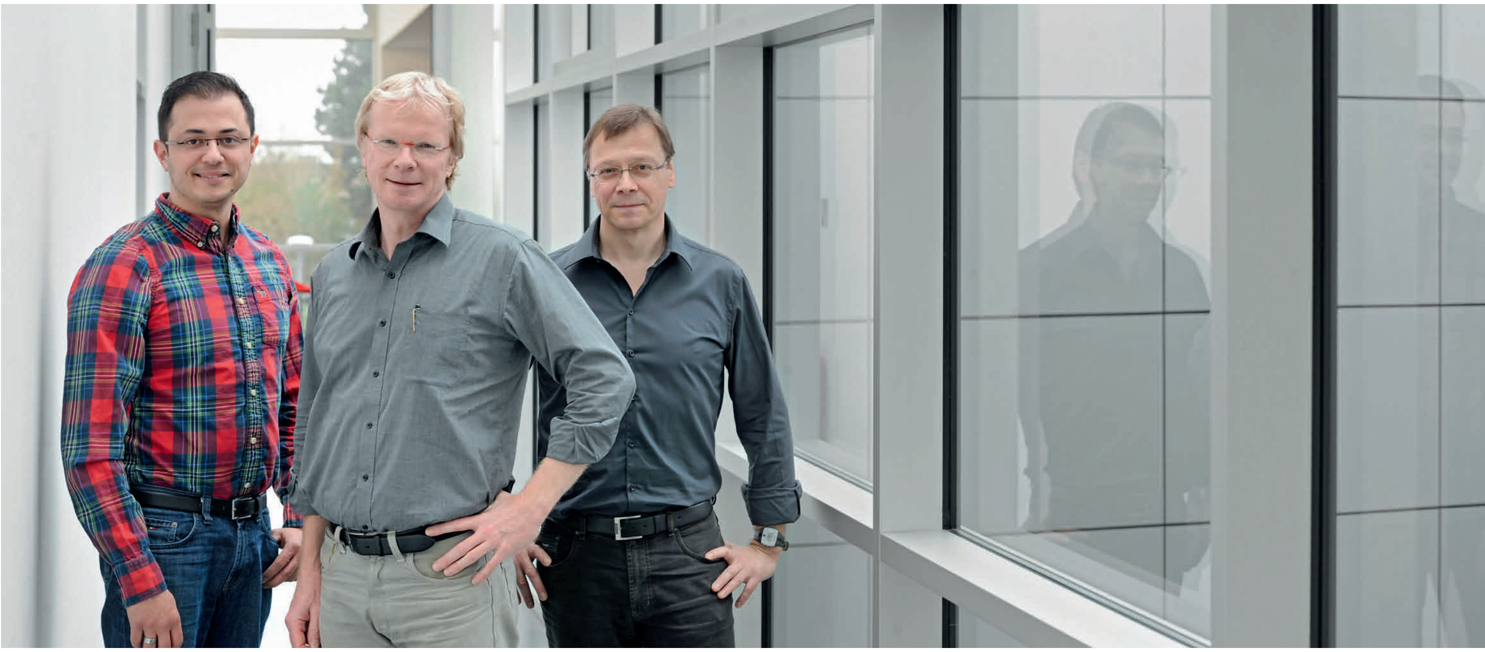
A POWDER CONVERTS METHANE TO METHANOL

Biomass might be able to replace petroleum and natural gas both as a raw material and as an energy source, but this will still take quite some time. Thus, in the meantime, it is vital to make the best possible use of fossil resources. We can't go on wasting the methane that is released from wells in petroleum production. It can be used to make synthesis gas, from which, in turn, gasoline can be obtained. "That is why giant Fischer-Tropsch plants are currently being planned or built, or are already in operation, for example in Qatar," explains Ferdi Schüth. However, the expenditure involved can't be justified in many places, for example when methane escapes only in small quantities, known as *stranded natural gas*. "It's usually simply flared off, resulting in the destruction of considerable quantities of energy sources." But simply discharging it into the environment would be worse still, because methane is 25 times more climate-damaging than carbon dioxide.

However, this methane could be converted into something useful: methanol. "The solution could be small plants, for instance on ships, that are brought out to an oil platform to liquefy the gas on site for as long as extraction from the field continues," says Schüth. It is, in principle, possible to oxidize methane directly to yield methanol. There is a catalyst that does this efficiently, but under truly caustic conditions. The soluble Periana catalyst, an organometallic, nitrogenous platinum complex that was developed in California in 1998, works only as a homogeneous catalyst, and then only in fuming sulfuric acid. "And as a result, it's virtually unrecyclable."

But sometimes the solution comes about by chance. While Schüth was thinking about the problem, his Max Planck colleague Markus Antonietti from Potsdam-Golm mentioned a chemical structure in a paper, giving Schüth pause for thought. "Adding platinum to this would result in a solid form of the Periana catalyst" was the thought that flashed through his head. Ferdi Schüth laughs. "Ninety-eight percent of such ideas are nonsense." But in this case, it worked straightaway. When combined with platinum salts, the nitrogenous, graphite-like solid gives rise to a powder that can be used like the Periana catalyst.

Photo: Frank Vinken



How will we be able to make our economies work and brake climate change once the petroleum era is over? Roberto Rinaldi, Ferdi Schüth and Wolfgang Schmidt are developing catalysts to replace fossil raw materials, or at least make more efficient use of them.

Photo: Frank Vinken

"And now it can simply be filtered out." Since then, the team has found similar, even more efficient materials. One problem facing methane liquefaction has thus been solved, at least in the lab.

And speaking of using waste materials, isn't plastic waste a good raw material? Schüth plays this option down. "It certainly is possible, but one must ask if it makes sense to invest a lot of energy in it. A plastic bag has the same caloric value as heating oil. The thermal benefit wouldn't be the worst."

No stone is being left unturned. What impact will all this have on our energy supplies in a hundred years? "We will be harvesting solar energy efficiently," says Ferdi Schüth, "and nuclear fusion is a major hope for the future." That would leave us with more energy than we needed, thus solving several of the challenges facing a world with a population of ten billion in a single stroke. "When it comes down to it, almost everything is an energy problem: feeding the world is a distribution problem. Energy enables seawater to be turned into drinking water, and shortages of raw materials such as lithium and platinum can be overcome by reaccumulating these materials. After all, nothing on Earth is ever truly lost."

Ferdi Schüth has to laugh and says: "But my predictions are just a linear extrapolation. Suppose it were 1850 and I had to make a prediction for today's world. I would have failed miserably! I probably would have bet on faster horses and low-friction carriages." ◀

TO THE POINT

- **Raw fossil materials are finite and damage the climate; biomass could replace them as a renewable source of energy and basic chemicals.**
- **Chemists from the Max-Planck-Institut für Kohlenforschung have found catalysts that break down cellulose and lignin, the essential components of biomass, into small molecules for fuels and chemical feedstocks.**
- **Processes developed at the Max Planck Institute for Dynamics of Complex Technical Systems are enabling the chemical industry to process oily, long-chain substances using water-soluble catalysts.**

GLOSSARY

Aromatics: These compounds are named after the pleasant odor of the first members of the class to be identified. They contain a number of double bonds. These are arranged in such a way that electrons participating in the double bond are delocalized between several atoms in the molecule. This makes aromatics particularly stable.

Functional group: A characteristic structural unit of an organic molecule that determines its behavior, for instance in a reaction. When a molecule is functionalized, atoms of elements other than carbon or hydrogen, so for instance oxygen or nitrogen, are often introduced into a molecule, giving rise to, for example, acids, aldehydes or alcohols/amines.

Heterogeneous catalysis: The reactant and catalyst are present in different phases. In practice, the gaseous or liquid starting materials are usually passed over a solid catalyst in a reactor, and can then be collected at the other end. Some solid catalysts have to be added to the reaction mixture as a powder, and must therefore be filtered out after the reaction.

Homogeneous catalysis: The reactant and catalyst are present in a single phase, for example dissolved in a liquid. If it is to be possible to reuse the catalyst, which accelerates the reaction but is not consumed in the process, then the reaction mixture, which may also still contain the starting materials, must be subjected to a complex separation process.

Polymerization: The formation of long, sometimes branched chain molecules from many building blocks, usually of a single, but sometimes several, starting materials.

Hydrogen bridge bond: The electrostatic interaction between positively polarized hydrogen atoms, such as in alcohols or water, with negatively polarized atoms such as oxygen gives rise to a bond that is, however, weak compared with a bond created by a shared electron pair.