Is lignin the crude oil of the future? Maybe so, thanks to the sun and photocatalysts

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Prof. Juan Carlos Colmenares Credit: IPC PAS, Grzegorz Krzyzewski

We associate refineries with crude oil and a dense tangle of technical fittings. They may, however, change in the future, if crude oil is replaced by lignin, a product currently treated as industrial waste. The research route leading to this goal is being paved by new photocatalysts, developed by the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. They allow lignin-based model compounds to be transformed into useful chemical substances using reactions that take place under conditions that occur in nature.

Lignin is not a pretty sight—an oily, almost black sludge. In addition, it smells much worse than it looks. Inspecting lignin, especially up close and with an unblocked nose, it's hard to believe that it is being treated as a potentially important renewable source of valuable aromatic compounds for the chemical industry. Unfortunately, despite many years of attempts by teams of chemists from all over the world, we still have not managed to develop efficient methods of converting lignin. We are a step closer to cheap solar biorefineries capable of processing lignin on an industrial scale using the new photocatalysts developed at the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw, Poland, in cooperation with the Warsaw University of Technology and the University of Cordoba.

In nature, lignin is present primarily in wood, where it is responsible for wood's consistency and hardness. It is the reason why trees do not creep over the ground, but instead reach even dozens of metres up into the air. The lignin content of wood is typically from 10 to 40 percent, depending on the tree species (the species also affects the chemical composition of the lignin). In industry, lignin is produced in large quantities during the manufacture of paper, as a waste product in the wood softening process. World reserves of lignin are huge and continuing to increase. The current estimate is even 300 billion tons, so it is a raw material that is more ubiquitous than crude oil (whose reserves are approx. 230 billion tons).

"From the chemical point of view lignin is a natural polymer with a very complex three-dimensional structure, constructed of, among others, many derivative aromatic compounds including those from various phenyl alcohols. This chemical richness makes lignin a potentially very interesting raw material for the chemical industry. Unfortunately, at the same time, this is its curse, because it is very difficult to develop chemical reactions that would efficiently transform lignin into a specific, single chemical compound, readily suitable for further processing," says Prof. Juan Carlos Colmenares (IPC PAS).

The difficulty in processing lignin means that today it is an industrial waste product of minimum significance that is burdensome for the environment: only 2% of its reserves are further processed, and the resulting chemical compounds are, in any case, of relatively small added value.

The industrial transformation of lignin into valuable chemical intermediates is advancing through the development of two new photocatalysts. Their main component is titanium dioxide TiO_2, deposited on a suitably selected carrier: In one case, these are nanocomposites containing iron oxide Fe_2O_3, and in the second - zeolites (aluminosilicates), with a small addition of iron. The photocatalyst with iron oxide nanocomposites was developed in close cooperation with scientists from Spain, led by Prof. Rafael Luque.

"In order to ensure the most uniform coverage of the particles, the process of deposition of titanium dioxide on the medium is carried out in the presence of ultrasounds, according to a method developed at our Institute," says Prof. Colmenares.

In laboratory studies at the Institute, lignin with the addition of either one or other of the photocatalysts was exposed to ultraviolet light, simulating the spectrum of incoming radiation from the Sun. Both catalysts proved surprisingly effective in the transformation of the benzyl alcohol present in the structure of lignin into a benzaldehyde, a substance used, among others, in the production of dyes and in the perfume industry. In the best case, after only four hours, up to half of the original benzyl alcohol content of lignin underwent conversion. In industrial applications, the selectivity of the reaction is also important: The more selective the reaction, the less its products are polluted by unnecessary and usually difficult-to-separate additives. It turned out that a solution that had reacted with the participation of photocatalyst contained up to 90 percent of the target substance.

"In the presence of our photocatalysts, illuminated by light imitating solar radiation, the reactions took place spontaneously in lignin-based model compounds, at ordinary atmospheric pressure and at a temperature of approx. 30 degrees centigrade, thus in conditions naturally occurring in direct sunlight. This is the exact opposite of traditional refineries, which require very complicated and expensive to maintain technical infrastructure," says Prof. Colmenares.

The new photocatalysts have one more advantage: They are cheap, because they do not require expensive precious metals such as palladium, and their carriers are common materials. In addition, one of the photocatalysts has magnetic properties and thus after conversion has taken place, it can be easily recovered from the solution and reused.

The results obtained by the scientists from Warsaw and Cordoba are promising. However, they only apply to photocatalysts with model compounds. For the photocatalysts to effectively process real lignin —heterogeneous and often with a varying chemical composition—further studies and tests are required.

The work on photocatalysts involved a group of employees of the Department of Materials Science and Engineering of the Warsaw University of Technology, headed by Prof. Krzysztof Kurzyd?owski. It is there, using advanced research techniques, that a detailed determination of the physical parameters of the new photocatalysts was carried out.

More information: Juan C. Colmenares et al. Mild ultrasound-assisted synthesis of TiO2 supported on magnetic nanocomposites for selective photo-oxidation of benzyl alcohol, *Applied Catalysis B: Environmental* (2016). DOI: 10.1016/j.apcatb.2015.10.034

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