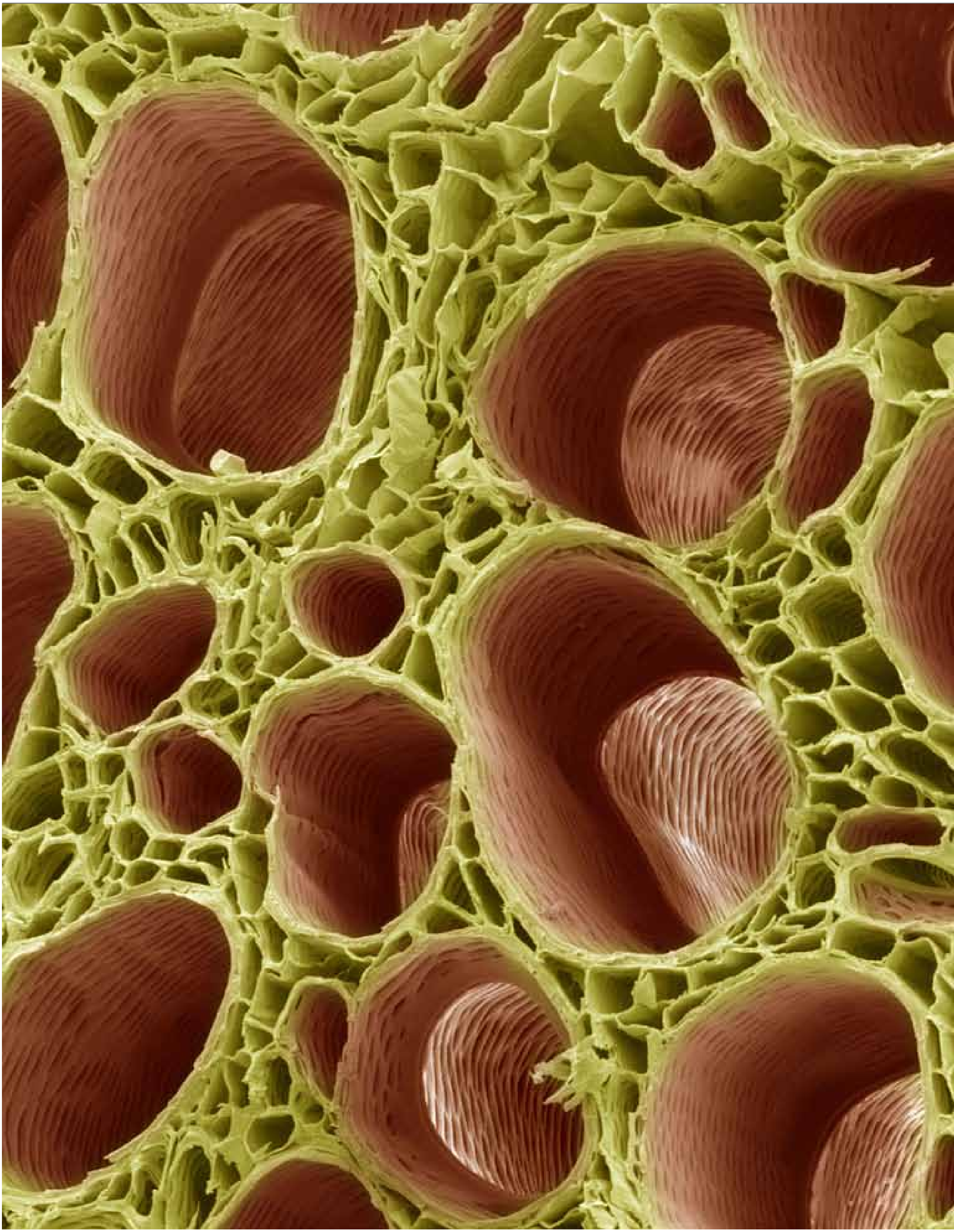


The lignin refinery

Lignin is what gives plants their rigidity but the compound is also a treasure trove of valuable basic chemicals. Wageningen researchers are gradually prising it open. Bringing a sustainable alternative to oil within reach.

TEXT RENÉ DIDDE **PHOTOGRAPHY** ANP **ILLUSTRATION** SCHWANDT

Electron microscope image. A cross-section of plant tissue with wood vessels (brown) which transport water. The thick lignin-rich walls provide structure and rigidity.

‘In the last few months we have set a world record,’ says Jacco van Haveren, a researcher at Wageningen UR Food & Biobased Research. Van Haveren and his colleagues have managed to convert 10 percent of the total amount of lignin in wood into the direct precursor of phenol, a valuable aromatic building block for the chemical industry. ‘This way, not only can we make pure bio-phenol, but also benzene. We are bringing to light useful building blocks which can provide alternatives to basic chemicals based on oil.’

The Wageningen world record may not seem very impressive, but it represents a significant breakthrough. Up to now the maximum harvest of the various aromatics from lignin barely reached 5 percent.

For years, researchers have been aware that lignin is a treasure trove of basic chemicals such as benzene, toluene and xylene (known collectively as the BTX aromatics), which are much-used raw materials. Numerous solvents and plastics could potentially be made from lignin.

This treasure trove does not give up its secrets lightly, however. The key lies in a code that is very hard to crack. Until now, lignin could only be broken down with brute force, at extremely high temperatures and producing very low yields.

The biggest success story so far comes from Norway, where the highly valuable flavouring vanilla has been extracted from lignin since 1962. ‘The yield is less than one percent, though – a pathetic three kilograms per thousand kilos of lignin. And then more than 99 percent of it is only of use for low-value applications – as a source of energy or as an additive in cement,’ says Richard Gosselink, lignin research leader at Wageningen UR. ‘We have now shown that there are milder and more subtle conversion methods which deliver a range of products with a higher yield.’

The Wageningen world record is based on a specially developed process. Lignin, dissolved in water under alkaline conditions, is exposed to a catalyst of the noble (corrosion-resistant) metal palladium at a temperature of 200 to 300 degrees Celsius. On that interface lignin is broken down into stable aromatics.

COMPLEX NETWORK

This elaborate process is necessary because the complex network of bonds in lignin are very difficult to break down. It is not surprising that lignin is such a resilient substance. Without this compound, a tree would be blown down by the first puff of wind and maize stalks would buckle under the weight of the growing cobs. If a plant only had the other two basic components – cellulose and hemicellulose – in its cell wall, the earth’s vegetation would be little more than a soup of algae. Lignin, which is sandwiched in between the cellulose and the hemicellulose in a cell wall, gives it its rigidity.

Even fungi have difficulty breaking down lignin. ‘Look how long a dead tree lies in the forest,’ says Van Haveren. ‘It is true, it starts to rot and you do see some fungi, but most species of fungus first feast on the nice digestible cellulose before they resort to the lignin. The organic breakdown goes extremely slowly.’ So Gosselink and Van Haveren are looking at an arsenal of chemical weapons. They try using acids, alkalis and catalysts to get the better of this tough substance. But even chemically, lignin can defend itself tooth and nail. ‘Exposing lignin to acids or alkalis alone often creates radicals that regenerate the broken bonds by cross-linking to other parts of the lignin. This creates a sort of unusable charcoal. We prevent that with a catalyst,’ says Van Haveren.

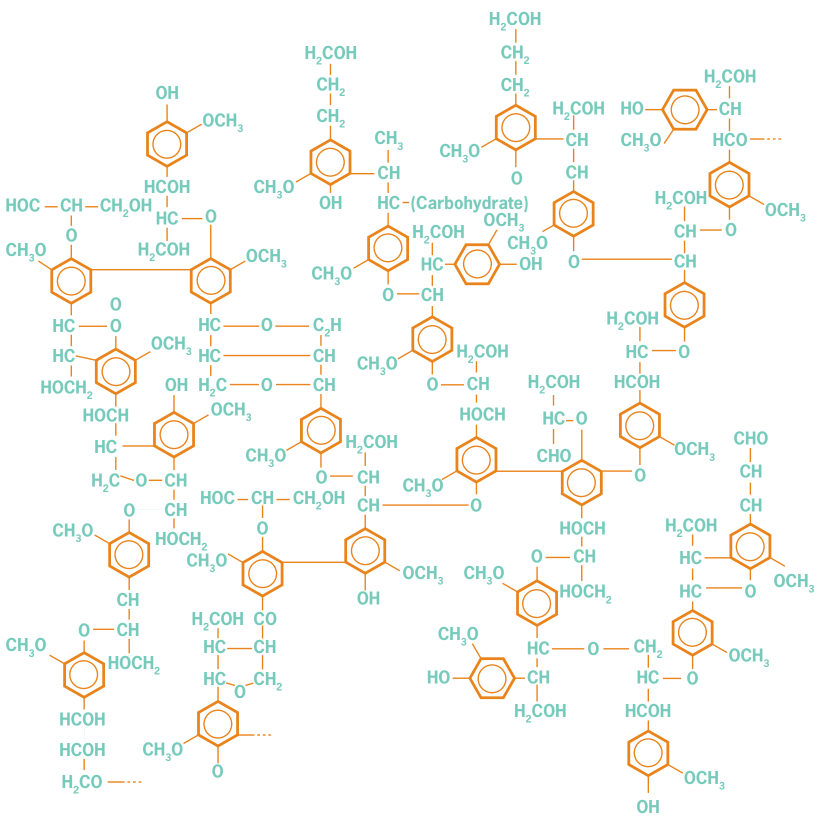
HYDRA

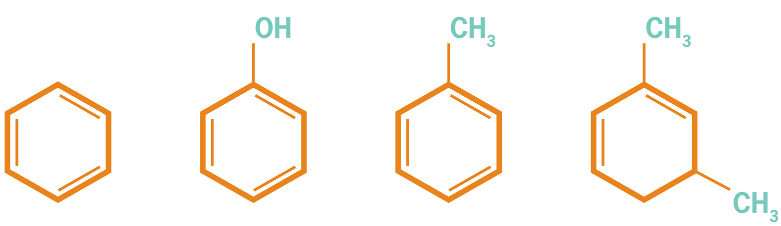
In order to slay this hydra, the Wageningen UR scientists took the initiative three >

> ‘We extract the most valuable aromatics and the rest can still be burned’

LIGNIN

Lignin polymers form a complex network of bonds that is almost impossible to break open. They are a treasure trove of valuable basic chemicals such as benzene, phenol, toluene and xylene.





benzene phenol toluene xylene

JACCO VAN HAVEREN,
programme leader at biobased chemicals Wageningen UR

'We are bringing useful building blocks to light which can provide alternatives to basic chemicals based on oil'

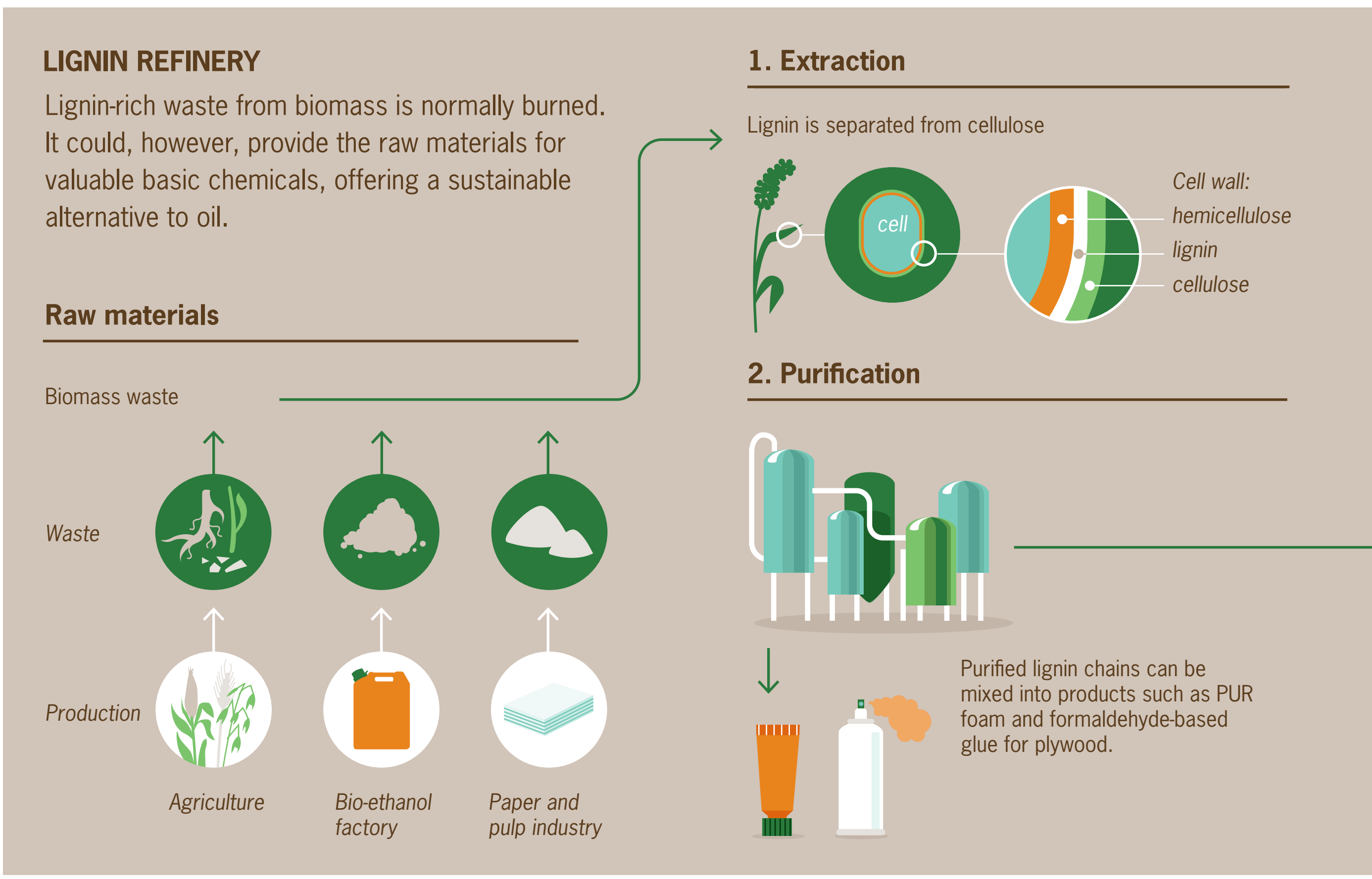
RICHARD GOSSELINK,
Lignin research leader Wageningen UR

'We want to convert lignin into aromatic building blocks as well as use it for other applications'

years ago to form the Lignin Platform in order to bring together all the existing knowledge about lignin. Wageningen UR collaborates in this with institutes including Utrecht University, the University of Amsterdam and the Technical University of Eindhoven. ‘Big chemical firms such as DSM and DuPont are collaborating on the platform as well,’ says Van Haveren. With funding from European research grants and from the Top Consortium for Knowledge and Innovation Biobased Economy, the various lines of research started within the platform are being implemented by consortia of companies and research institutes.

POTENTIAL

There is massive potential. The kaleidoscope of potential biobased applications not only includes aromatic basic chemicals such as phenol, benzene and xylene; it is also possible that the poor yields of extremely pricey vanilla could be improved, and that other aromas and flavourings could be extracted which could find a ready market in the food and cosmetic industries.
Besides breaking lignin down into components, there are also more straightforward method of largely separating lignin from the celluloses. ‘Then we get reasonably pure lignin, which we want to use for other applications besides converting them into aromatic building blocks, says Gosselink. ‘With its long chains, lignin can be used directly in PUR foam – up to a proportion of 30 percent – and even up to 70 percent in



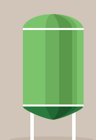
phenol formaldehyde, familiar from glue. These percentages could perhaps be raised even higher and there may be other applications,' adds Gosselink. One of the ideas the researchers are targeting is to use lignin as a substitute for bitumen and asphalt. 'Ultimately we want to develop a lignin refinery': this is how Jacco van Haveren expresses the ambitions. 'In order to extract a range of products from lignin, comparable to the way oil refineries extract a broad spectrum of products from oil.' >

'There is no competition with food production'

3. Refinery

Biological

The enzymes laccase and peroxidase break down the lignin chains



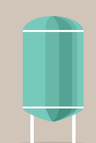
→ smaller fragments of lignin chains

Chemical

200-250 °C

Pressure

Treatment with acids and alkalis, dissolving in water / solvents, exposure to a catalyst

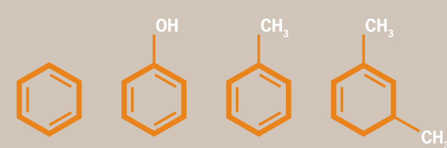


→ range of useful basic chemicals

Formerly, the only way to break down lignin was by brute force: subjecting it to high pressure or temperatures, with only meagre yields as a result.

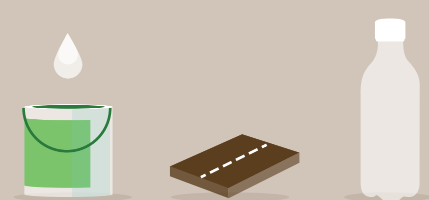
A new process only requiring low temperatures and pressure produces higher and more varied yields.

4. Useful chemicals



benzene *phenol* *toluene* *xylene*

Chemicals can provide a sustainable alternative to oil and are used in:



Solvents

Additives for fuel and asphalt

Additives for plastics such as polycarbonate and PET

In this respect, the researchers are in line with the typically Wageningen philosophy that thinks in terms of cascading and valorization. 'We focus primarily on the most valuable products, what is left is for the next useful application, and it is quite possible that there will be a third application as well. And you can always use whatever is left over then for fuel,' says Van Haveren, summing it up. 'We are not only interested in energy, like many American researchers, but target both energy and chemistry.'

PRUNING WOOD

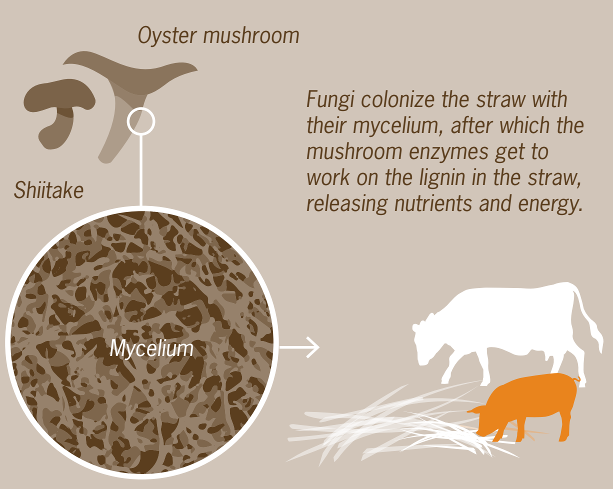
There is no shortage of sources: the world harbours enormous reservoirs of lignin. Van Haveren and Gosselink estimate that 20 to 25 percent of all plant biomass on the earth consists of lignin, and another 200 billion tons is added every year free of charge. A big potential source is all the

> 'Ultimately we want to develop a lignin refinery'

OYSTER MUSHROOM MAKES STRAW MORE NOURISHING

Two billion tons of straw are produced globally each year. For lack of juicy grass or hay, in many countries straw is fed to ruminants such as cows, goats and sheep. It is not very digestible. 'Lignin in the straw stalks affects the availability of the cellulose and hemicellulose for animals,' says John Cone of the Animal Nutrition chair group at Wageningen University. With a view to improving on this, the chair group is conducting trials with white rot fungi from edible mushrooms which are harmless for animals, such as shiitake and oyster mushrooms. 'They colonize the straw with their mycelium, after which the fungal enzymes attack the straw. By stopping the process just before new fungi grow out of the mycelium we get straw that is digestible for ruminants and full of cellulose,' explains Cone. The mixture of straw and fungi is dried and milled, and is then suitable for use in animal feed. Field trials still have to take place. The idea is that thanks to this treatment of straw ruminants in developing countries will give more milk and meat.'

The research is being funded by the Wageningen University Fund. 'We are one of the seven honoured Food for Thought projects that have been granted funding from private donors. We applied for 1.5 million euros and have already been given 700,000 euros.'



trees and branches coming out of forests, parks and gardens every year after pruning. The woody leftovers of maize, grains and elephant grass could contribute too, although there is something to be said for leaving some of this post-harvest biomass on the land to help maintain soil fertility. Millions of tons of lignin come out of the paper industry as waste products, too. For manufacturing paper fibres, the industry is interested in the cellulose fibres and not the lignin. For similar reasons, the production of bio-ethanol from sugar beet, sugar cane and other crops produces lignin-rich waste too. Since the emergence of the political goal of mixing more fuel from plant sources into petrol, the amount of lignin waste from bio-ethanol production has gone up. To date, this lignin is simply burned, whereas it could be put to much better use. There is another advantage as well. 'These raw materials do not compete in any way with food production in the world. You do not need to cultivate lignin specially,' says Gosselink.

He expects the first lignin refineries to be built in places where a lot of biomass is processed. 'Paper and bio-ethanol factories are obvious locations. Then we would first extract the most valuable aromatics and the rest can still be burned.' In future he thinks there will also be smaller factories at places where pruning wood and dead trees from municipal parks or the forest service are collected.

HELPED BY FUNGI

Van Haveren has great expectations of the mild chemical catalyst reactions such those used for the Wageningen 'world record for phenol'. 'We will gain a better understanding of how lignin reacts with the chemical substances we add, which will make more lignin building blocks available.'

The researchers also hope eventually to be able to combine chemical breakdown with organic breakdown using enzymes from white rot fungi. This group of fungi has a preference for lignin. 'We know that the enzymes laccase and peroxidase play a key role in this,' says Gosselink. 'In the long term we might be able to prise the treasure chest a bit wider open by combining enzymatic and chemical breakdown.'

Van Haveren: 'I expect that within three years we shall have lignin-based additives for shipping fuel which will make the engines work more efficiently and emit less soot. And we have the world record of having brought the production of phenols from lignin up to 15 to 20 percent.' ■

www.wageningenur.nl/lignin

PLATFORM TACKLES LIGNIN

The Wageningen UR Lignin Platform is a multidisciplinary expertise network of researchers from both Wageningen and other academic institution, which works closely with the business world. The aim is to do interdisciplinary research that will eventually lead to the industrial production of fuels, chemicals and materials made of lignin.

Wageningen UR Food & Biobased Research plays a key role in the platform, which is currently working on three projects.

In collaboration with ECN in Petten and with industrial partners, the LigniFAME project is exploring the potential for converting lignin into fuel additives for shipping, materials (bio-bitumen) and energy. The raw materials for this are waste products from the production of bio ethanol, prunings from town councils and harvest waste. The main focus lies on developing new catalytic processes.

In YXY fuels, chemical company Avantium is working with the paper industry on converting cellulose waste into energy conductors and chemical building blocks. Wageningen UR is contributing a patented catalytic breakdown process for depolymerizing the released lignin chains to obtain phenols.

Heat and electricity are useful by-products.

The CatchBio project is more academic. Key players in this programme are several universities (Wageningen, Utrecht, Amsterdam, Eindhoven, Groningen), which collaborate on new catalysts that are not based on noble metals and consume less energy. This is fundamental research with a strong commitment from the business world as well.

Info: www.wageningenur.nl/lignin-platform, richard.gosselink@wur.nl