Provides

Deep Eutectic Solvents for Sustainable Paper Production

Deep Eutectic Solvents in the paper industry

TOWARDS 40% ENERGY SAVINGS
AND 80% CO_2 EMISSION REDUCTIONS

www.providespaper.eu

The pulp and paper industry has been bio-based for centuries. Technologies that are currently applied for M - ª J´´ Z³JN-1-«J-1-« J«T ³XN-ÆX³XT °J°X³ º³XJº ª X«º ÇX³X TXÆX-°XT ª -³X º|J« J NX«ºÄ³É Jz-₩ J«T |JÆX MXX« -°-1 ª ´XT XÆX³ ´ «NX A|X ;>8E.&(? N-«´-³-1Ä ª ´|-Ç´º|Jº J ³XÆ-Ä-1-«J³É N|J«zX ´ «-Ç °-´´ M XŸ 6XÇ₩ ª T °Ä° «z ºXN|«-Ä-z X´ MJ´XT -« «JºÄ³J &XX° (ÄºXN-1N ?-ÆX«º´ XJT º- J´z« `NJ«ºÉ ª -³X ´Ä´ºJ «JM X °³-NX´´ º|Jº ´ X«X³zÉć N-´ºć J«T ³X´-Ä³NXćX]XN-1ÆXŸ A|´ºXN|«-Ä-z NJ «««-ÆJ-1-« °³-TÄNX´ NX ÄÄ-´X `M³X´ Z-³ °J°X³ ª J¦ «z₩ Ç| X´ ª ÄºJ«X-Ä´É °³-TÄN «z | z|ć ²ÄJ ºÉ z« « J«T |X ª NX ÄÄ-´XZ³JN-1-«´Z-³ | z|ćÆ-ÄªX J°° NJ-1-«´Ÿ

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A|X -ÆX³J -MXN-1ÆX -Z º|X &(? N-«NX°º ´º- JN| XÆX a **40% reduction of energy use** and an **80% reduction of CO_2 emissions** in pulp and papermaking through the J°° NJ-1-« -Z &XX° (ÄºXN-1N ?-ÆX«º´ A|X &(? N-«NX°º will enable the industry to:

- -MºJ « J ³JT NJ É «XÇ₩´Ä´ºJ «JM X J«T ºXN|«-XN-«-- ª NJ É ZXJ´ M X °Ä° «z ºXN|«-Ä-zÉ MÉ Ä´ «z &(?´º-T´´-ÆX Ä z« « Z³- ª Ä z«-NX ÄÄ-´N M - ª J´´ J«T Ä´X this lignin for further processing into materials and N|X ª NJ´ Ç º| J | z| JTTXT ÆJ ÄXŶ
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ACHIEVEMENTS

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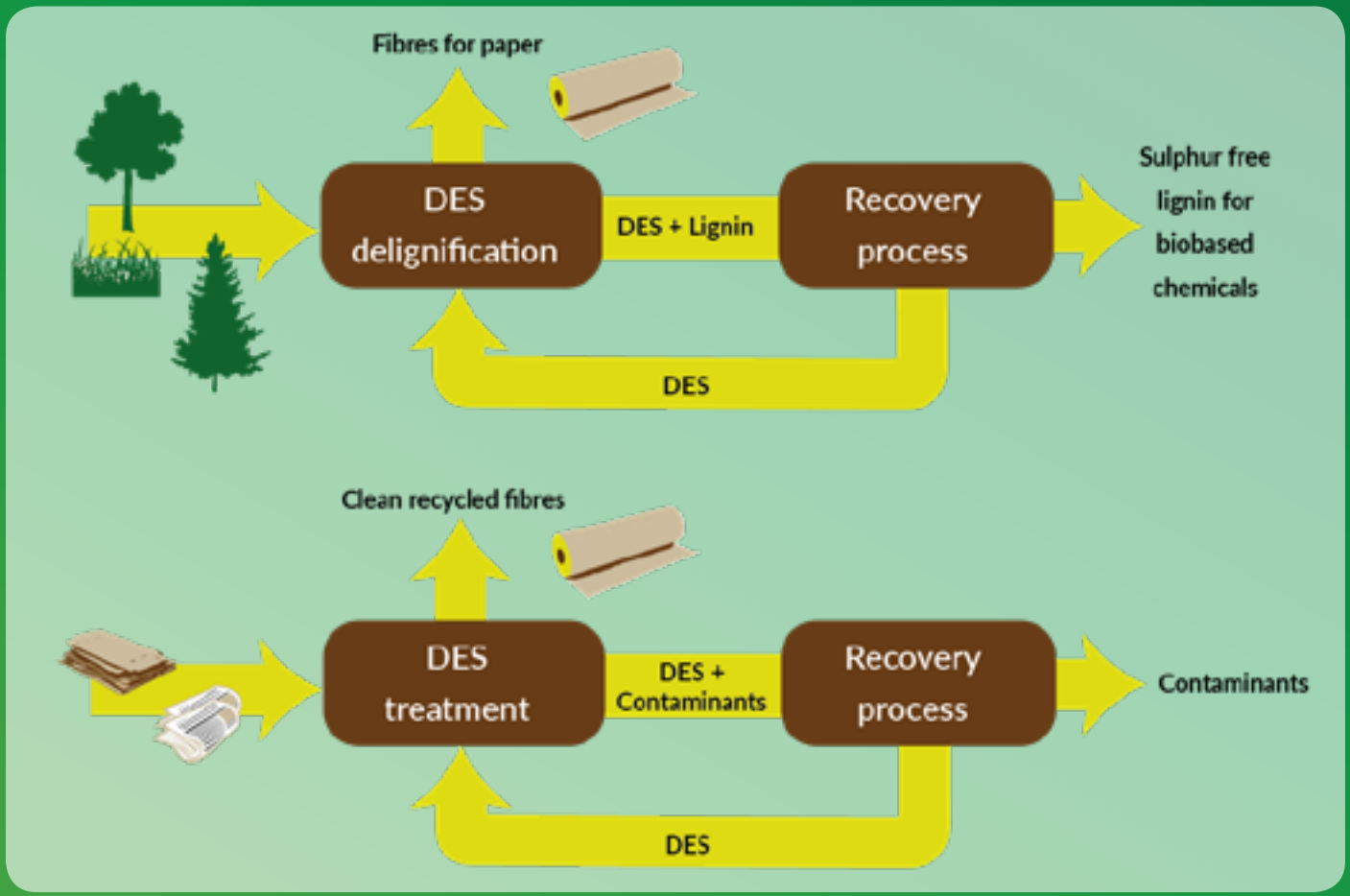

FOREWORD

Breakthroughs that revolutionise an industry do not happen overnight and cannot be realised within a year. We have had disappointments and surprises, but overall we are happy to report that we have gained interesting insights into opportunities that will enable us to make the delignification process of wood even more efficient and sustainable.

These good results are the outcome of a big effort and hard work on the part of the many partners in the PROVIDES project. The project has united the sector behind the idea that breakthroughs are necessary and can only be realised by a continuous and joint approach.

We thank the whole PROVIDES team for their commitment to this project and for working so well together.

Heiner Grussenmeyer – Industrial Coordinator
Annita Westenbroek – Operational Coordinator

October 2018

>XTÄN «z -Ä³ $8ĭ Z- -°°³ «° ´ N³ÄN J§Ÿ A|X °J°X³ «TÄ´°³É «XXT´ °- JN° ZJ´° °- ³XJN| °´ z-J§´ -« ˧ ª XŸ
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of the pulp and paper industry as the most sustainable circular and bio-based industry.

This project received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No. 668970 and was co-funded by TKI E&I with the supplementary grant 'TKI-Toeslag' for Topconsortia for Knowledge and Innovation (TKI's) of the Ministry of Economic Affairs and Climate Policy.

BBI

Horizon 2020
European Union Funding
for Research & Innovation

Bio-based Industries
Consortium

TKI ENERGIE EN INDUSTRIE
Topsector Energie

DES CLUSTER INITIATIVE

CEPI 2050 ROADMAP: 80% CO_2 EMISSION REDUCTION AND 50% MORE VALUE

In November 2011, CEPI[1] launched the Forest Fibre Industry 2050 Roadmap[2] for a low-carbon economy. This roadmap represents the vision for the sector in the next 35 years. It investigates how to achieve an 80% reduction of CO_2 emissions and at the same time create 50% more value. The roadmap concluded that breakthrough technologies would be needed to achieve the targets.

TWO TEAM PROJECT: BREAKTHROUGH TECHNOLOGIES

In 2012, CEPI set up the 'Two Team Project' to identify breakthrough technology concepts that would give the industry the required dynamic for a successful future in Europe. The winning Deep Eutectic Solvents concept was described as a truly ground-breaking discovery. It has the potential to completely revolutionise the pulping process, opening the way to produce pulp with minimal energy, emissions and residues. It can also be used to recover cellulose from waste and dissolve inks and contaminants in paper for recycling.

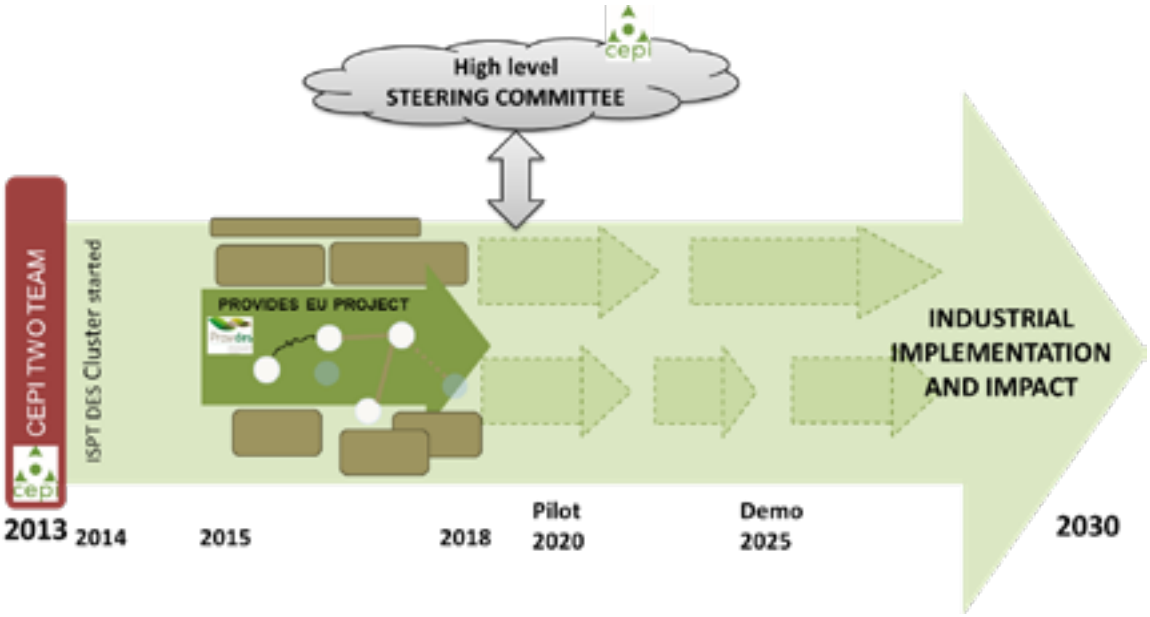
DES CLUSTER PARTICIPANTS, APRIL 2018

BIRTH OF THE ISPT DES CLUSTER

As a result, the European pulp and paper industry came together to start a joint research initiative to further research and elaborate on the DES concept. The Institute for Sustainable Process Technology (ISPT), which had introduced the idea in the Two Team Project, was asked to coordinate the initiative. This is how the ISPT cluster 'Deep Eutectic Solvents in Papermaking' was founded in April 2014.

In 2015, the DES cluster successfully acquired a BBI subsidy within the framework of the European Joint Technology Initiative 'Bio-based Industries' (BBI JU) to enhance the research activities. The objectives of this BBI project, which is called **PROVIDES**, are perfectly in line with the priorities defined in the forest-based sector value chain by the pulp and paper industry, aiming at a reduction of 80% in fossil-based CO_2 emissions, combined with a 50% increase in added value by 2050.

The objective of the DES cluster is to achieve industrial implementation of the technology by 2030. The BBI JU PROVIDES project and other projects running in the cluster allow us to reach this goal.



1 Confederation of European Paper Industries
2 http://www.unfoldthefuture.eu/uploads/CEPI-2050-Roadmap-to-a-low-carbon-bio-economy.pdf

THE PATH TOWARDS 2030

Deep Eutectic Solvents are a completely new class of solvents that have never been used in the pulp and paper industry or for any other biomass fractionation before. This means that many technological questions still need to be answered and gaps filled to bring this laboratory technology to the next stage. The DES cluster aims to fill these gaps and achieve the following impacts:

- >XTÄNXT °³-NX´´ X«X³zÉ «ºX«´ ºÉ MÉ Jº ƀXJ´º ŎĂ ɲ N- ª °J³XT º- º³JT ⅃-«Jƀ °Äƀ° «z °³-NX´´X´Ŷ
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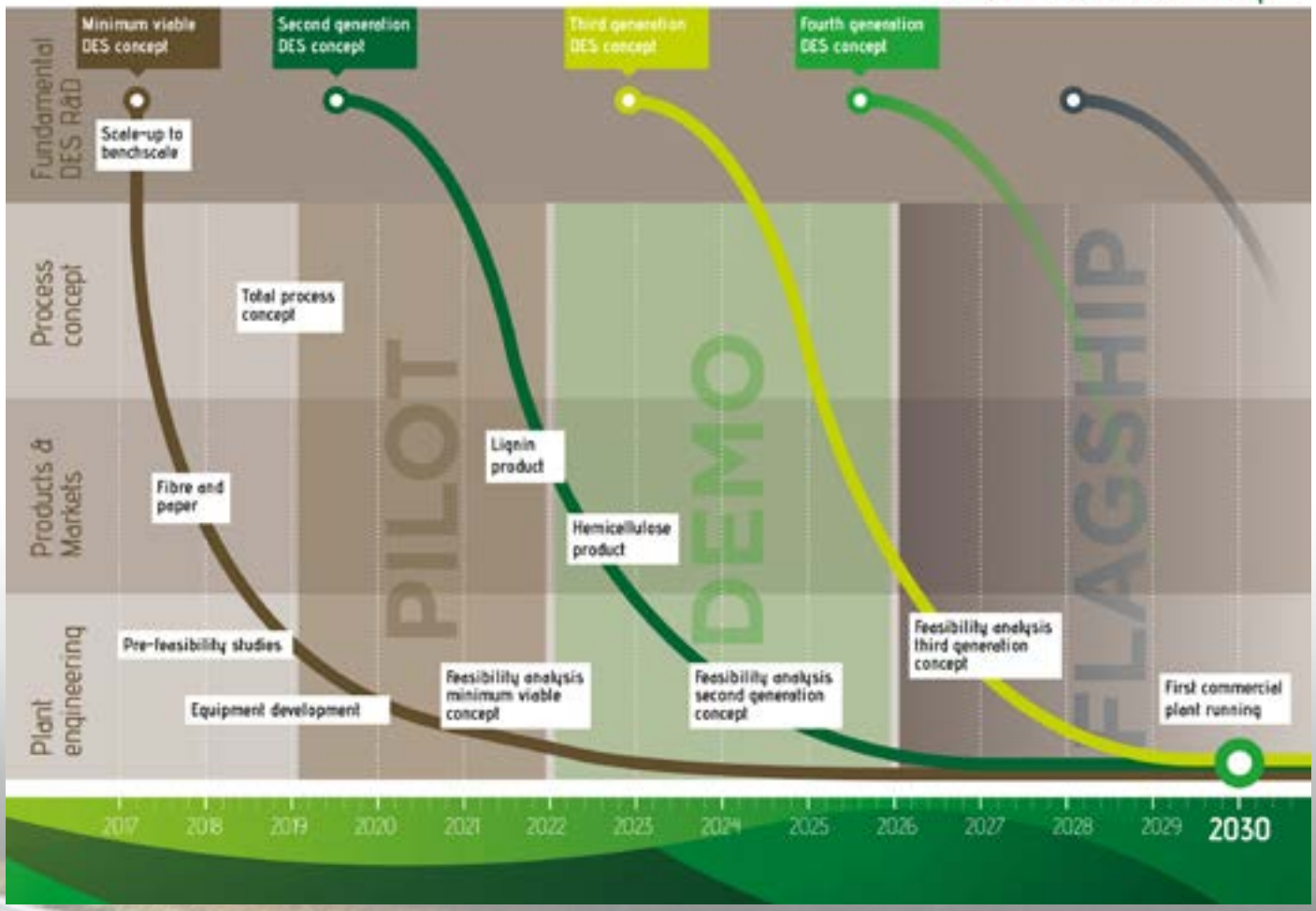
A technology roadmap was prepared, elaborating on all the parallel steps that need to be taken in the technology development in order to allow implementation in 2030.

Many development phases are taking place simultaneously. Fundamental research provides answers to questions as to 'why' DESs are effective, supporting the search for even more effective DESs and assisting application-oriented research. At the same time, the preparations for the pilot phase have been started to study the DES process at a larger scale to gain better insight into the process kinetics and physical transport required for further upscaling, using larger amounts of products for application testing, and validating production costs, climate benefits and environmental effects.

DES Roadmap


Fundamental DES R&D
Process concept
Products & Markets
Plant engineering
Minimum viable DES concept
Second generation DES concept
Third generation DES concept
Fourth generation DES concept
Scale-up to benchscale
Total process concept
Fibre and paper
Lignin product
Hemicellulose product
Pre-feasibility studies
Equipment development
Feasibility analysis minimum viable concept
Feasibility analysis second generation concept
Feasibility analysis third generation concept
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WHAT IS A DEEP EUTECTIC SOLVENT?

A eutectic system is a mixture of components of which the freezing point is lower than that of each of the components. The most commonly known eutectic system is salt in water: when salt is added to water, the freezing point lowers by a few degrees. The single chemical composition that solidifies at a lower temperature than any other composition made up of the same ingredients is known as the eutectic point.

TXX° XÄºXN⁻1N ´É´ºX ª ´ J ´É´ºX ª Ç º| J« Ä«Ä´ÄJ§§É ´º³-«z TXN³XJ´X « Z³XXÊ «z ºX ª °X³JºÄ³X Ç| N| NJ« MX ª -³X º|J« ăĂĂ´ $Ÿ

A Deep Eutectic Solvent (DES), also called a low-transition-temperature mixture (LTTM), is a liquid mixture of two components that shows an unusually low freezing point. The two individual components are characterised as a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). Generally, it is accepted that the self-association occurs via hydrogen bonding interactions, where it is assumed that Van der Waals forces can also play a role. The preparation of a DES consists of simply mixing the HBD(s) and HBA(s). No purification steps are needed.

NATURAL AND SUSTAINABLE

Many Deep Eutectic Solvents are nature-based, renewable, biodegradable, low-volatile and cost-effective.
A|X´X «JºÄ³J§ &(?´ J³X º|X Z-NÄ´ -Z º|X ;>8E.&(? °³-¤XNºŸ

The first DES (a mixture of urea and choline chloride) was discovered 15 years ago.[3] Originally, DESs were developed as low-melting electrolytes for electrochemical applications.[4] Only in the last few years have DESs been applied as solvents for organic reactions and separations.[5] Only five years ago, it was discovered that some natural DESs show very high lignin solubility (up to 25 wt%). It was also shown that, using DESs as extractants, lignin can be selectively removed from pine wood and wheat straw. Furthermore, upon the addition of water by precipitation, the lignin was successfully recovered from the DES. These findings have led to the idea of applying natural DESs as novel pulping solvents.

The hypothesis is that by using natural DESs we mimic what is happening in nature. In periods of water stress, plants may produce a DES from the naturally available solid material in plant cells. This means that during frost or drought, the plant produces liquids from its available solids, so that its natural metabolism can continue. It has also been proven that enzymatic processes can continue in these liquids. This also means that:

- & (?´ NJ« MX N- ª °-´XT -Z «JºÄ³J§ °³-TÄNº´ ƎJ ª TX´ŵ ´ÄzJ³´ŵ J§N- | -§´ŵ J ª «- JN T´ƏŶ
- & (?´ J³X M -TXz³JTJM§Xŵ ª ´N M§X Ç º| ÇJºX³ŵ J«T «-«ƈº-È NŶ
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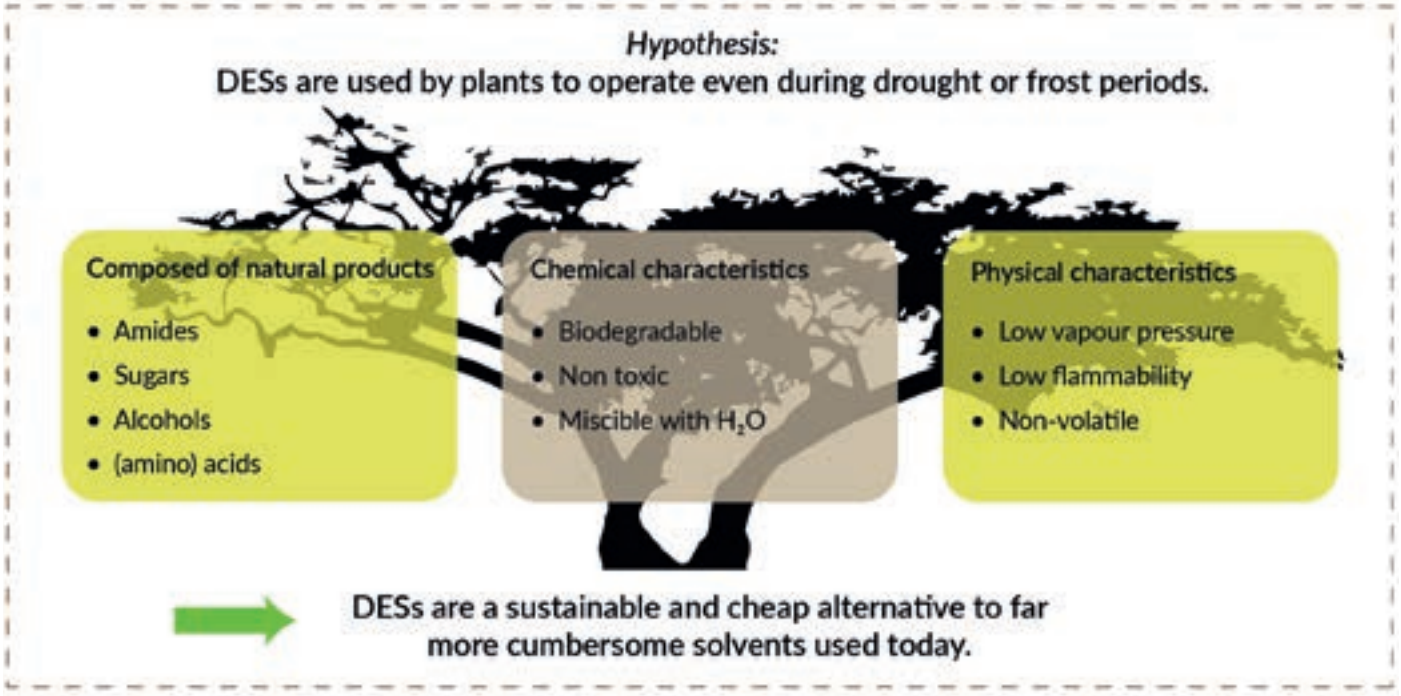
- & (?´ NJ« MX ª JTX ºJ §-³ƈª JTX Z-³ J«É J° °§ NJ-1-«Ÿ



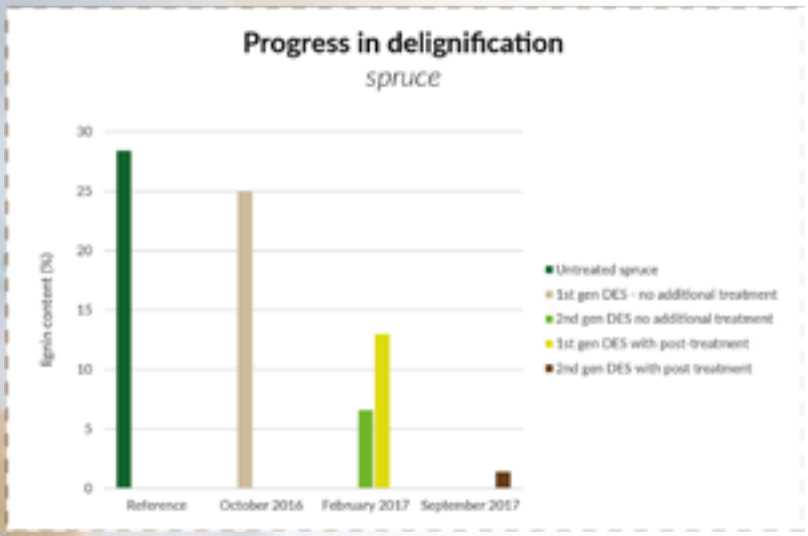
3 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, Novel Solvent Properties of Choline Chloride/Urea Mixtures, Chem. Commun. **2003**, 70-71.

4 Q. Zhang, K. De Oliveira Vigier, S. Royer and F. Jerome, Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev. **2012**, 41, 7108-7146.

5 M. Francisco, A. van den Bruinhorst and M. C. Kroon, Low-Transition-Temperature Mixtures (LTTMs): A New Generation of Designer Solvents, Angew. Chem. Int. Ed. **2013**, 52, 3074-3085.

APPLICATION OF DES IN PAPERMAKING

Application-oriented research was performed on the functionality of DES as a dissolving/separation agent for lignin, cellulose, stickies and ink.



DES DELIGNIFICATION

The main aim of the PROVIDES project was to develop radically new, sustainable and techno-economically feasible pulping technologies. This includes both an energy-efficient pulping process to separate high-quality fibres and lignin, as well as an efficient process to recover and recycle DES while maintaining its physico-chemical and dissolving properties.

So far, two potential DESs for pulping by dissolving hardwood and softwood lignin are known:

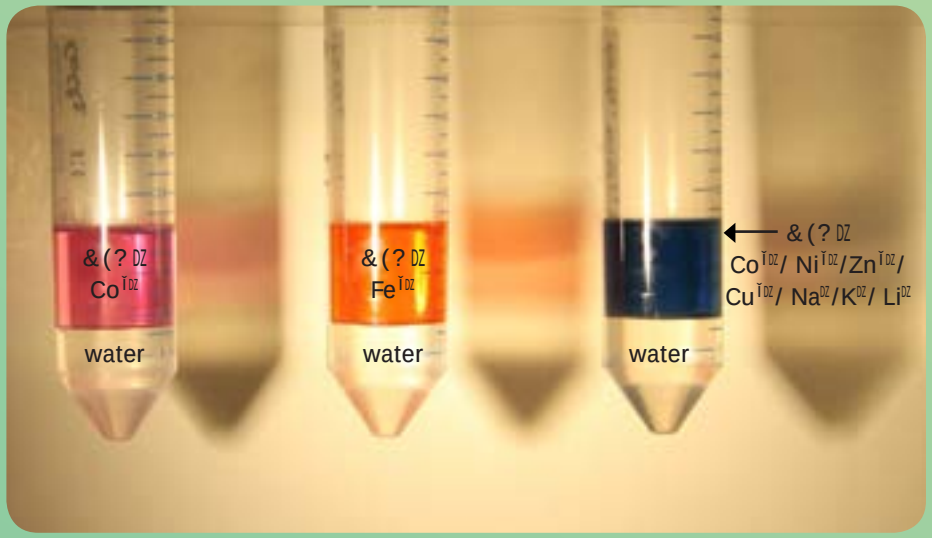
1. 2JN⊣N N Tŷ $ | -ƀ «X $ | ƀ-³ TX
ĬŸ Malic Acid: Tetraethyl Ammonium Chloride.

In the research project, temperature, pulping time, wood/DES ratio, pre- and post-treatments were optimised to improve the efficiency of the process, the extent of lignin isolation and the pulp quality.

DES RECOVERED PAPER PROCESSING

The aim was to develop DESs that were able to either dissolve and isolate contaminants from 'paper for recycling' to achieve clean fibres for recycling or dissolve cellulose to obtain pure cellulose.

For this purpose, hydrophobic DESs were developed.[6] Hydrophobic DESs do not mix with water, significantly facilitating the process of isolating components from aqueous pulp.



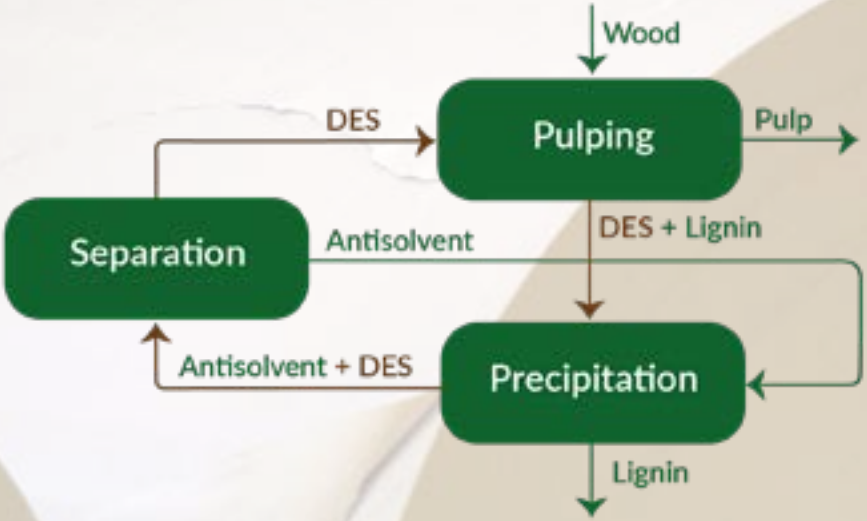
A variety of hydrophobic DESs were tested on the dissolution of specific contaminants. Hydrophobic DESs appear able to dissolve volatile fatty acids,[6] metal ions,[7] and some ink and sticky contaminants. Although the mineral oil content was halved, deinking trials did not lead to higher brightness.

6 **Hydrophobic deep eutectic solvents as waterimmiscible extractants**, Dannie J.G.P. van Osch, Lawien F. Zubeir, Adriaan van den Bruinhorst, Marisa A.A. Rocha and Maaike C. Kroon. **Green Chem.**, 2015, **17**, 4518-4521

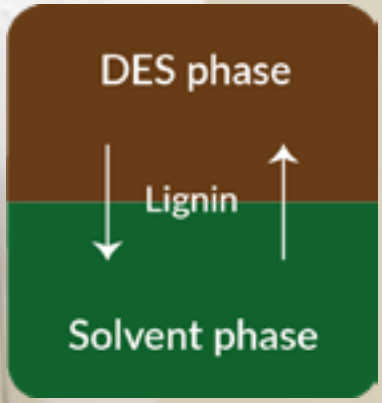
7 **Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents**, Dannie J.G.P. van Osch, Dries Parmentier, Carin Dietz, Adriaan van den Bruinhorst, Remco Tuinier and Maaike C. Kroon. **Chem. Commun.**, 2016, **52**, 11987

DESs AND COMPONENT RECOVERY

Research was also performed on efficient recovery technologies for both the DESs and the dissolved components. Although dissolved components can easily be separated from DESs by adding water as an anti-solvent, this process is not favoured, as the subsequently required water evaporation implies high energy consumption. A liquid-liquid extraction technology was therefore developed, achieving energy savings of 80% in the recovery process.



Lignin precipitation using water as anti-solvent



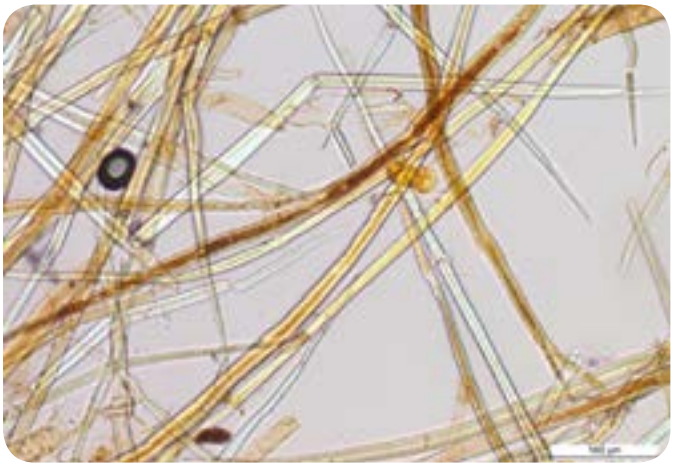
Liquid-liquid extraction using bio-based solvent with low ΔH_{vap}

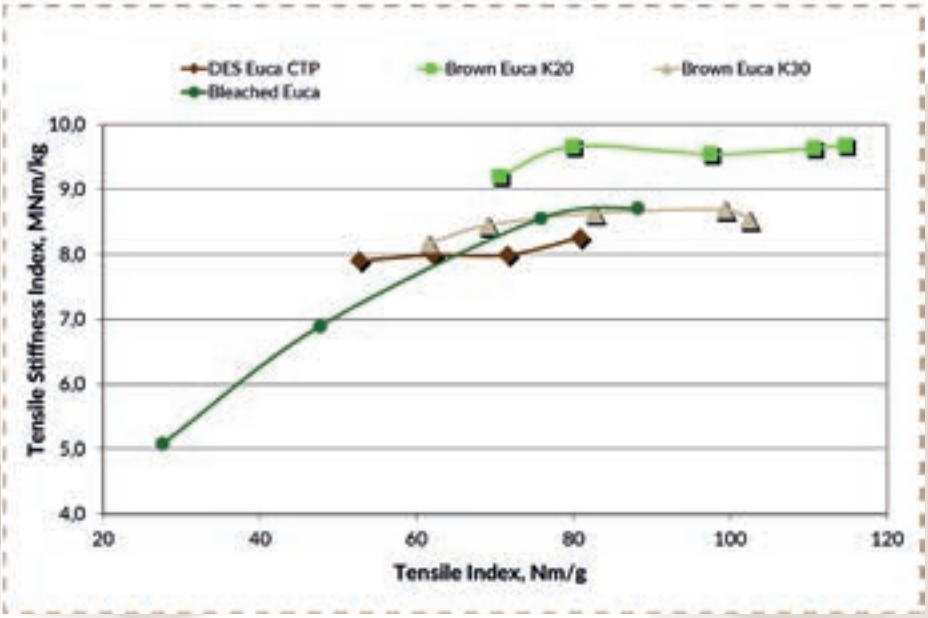
First lignin produced

PROPERTIES OF THE ISOLATED COMPONENTS

FIBRE AND PAPERMAKING PROPERTIES

Fibres obtained from the DES pulping process are well shaped and straight, with normal drainage. Paper produced from the fibres has extremely good internal bond and good tensile strength. The tear strength is still somewhat lower than regular kraft fibres.

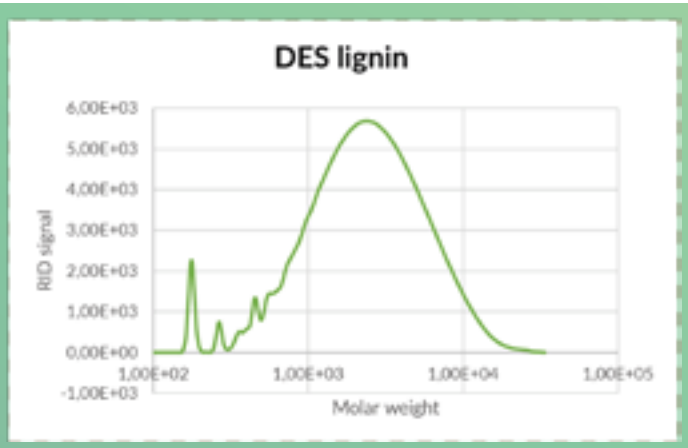




DES LIGNIN PROPERTIES

Lignin isolated by DES pulping of Eucalyptus was characterised by GPC and HSQC spectroscopy. Further characteristics of the DES-isolated lignin will be analysed and published by the ISPT DES cluster in due course.

Molar weight		*Inter-aromatic bonds (per 100 aromatic units)*	
M_n	1382	β-O-4	7.6
M_w	3224	β-β	7.9
		β-5	1.4



DES lignin GPC diagram

6Ä ª MX³ JÆX³JzX ª -ƀXNÄƀJ³ ÇX z|º 5 n ǵ ǎ ǐ Ɉ Ǐ
F X z|º JÆX³JzX ª -ƀXNÄƀJ³ ÇX z|º 5 w ǵ ǐ Ǐ Ǐ Ǒ
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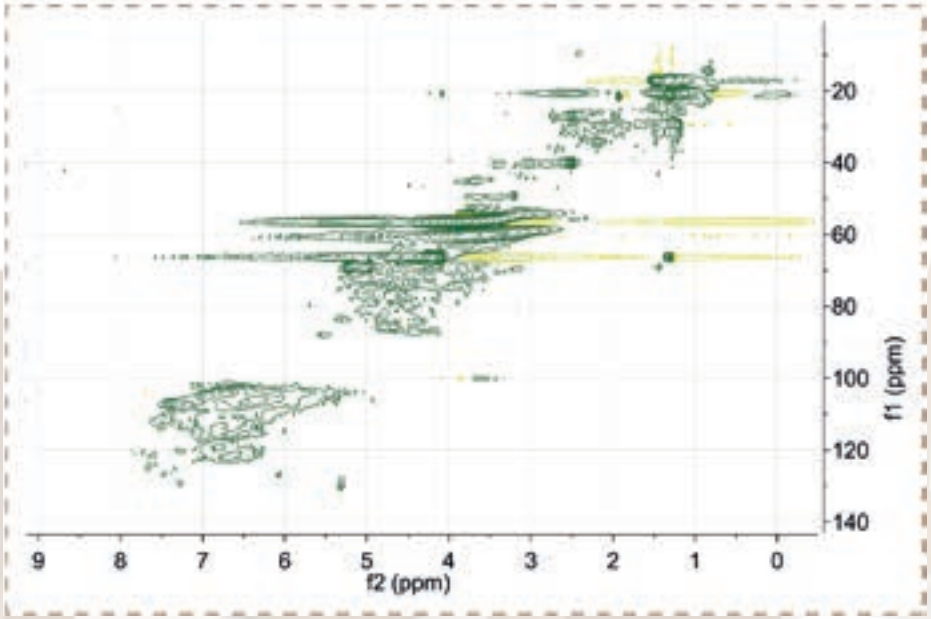


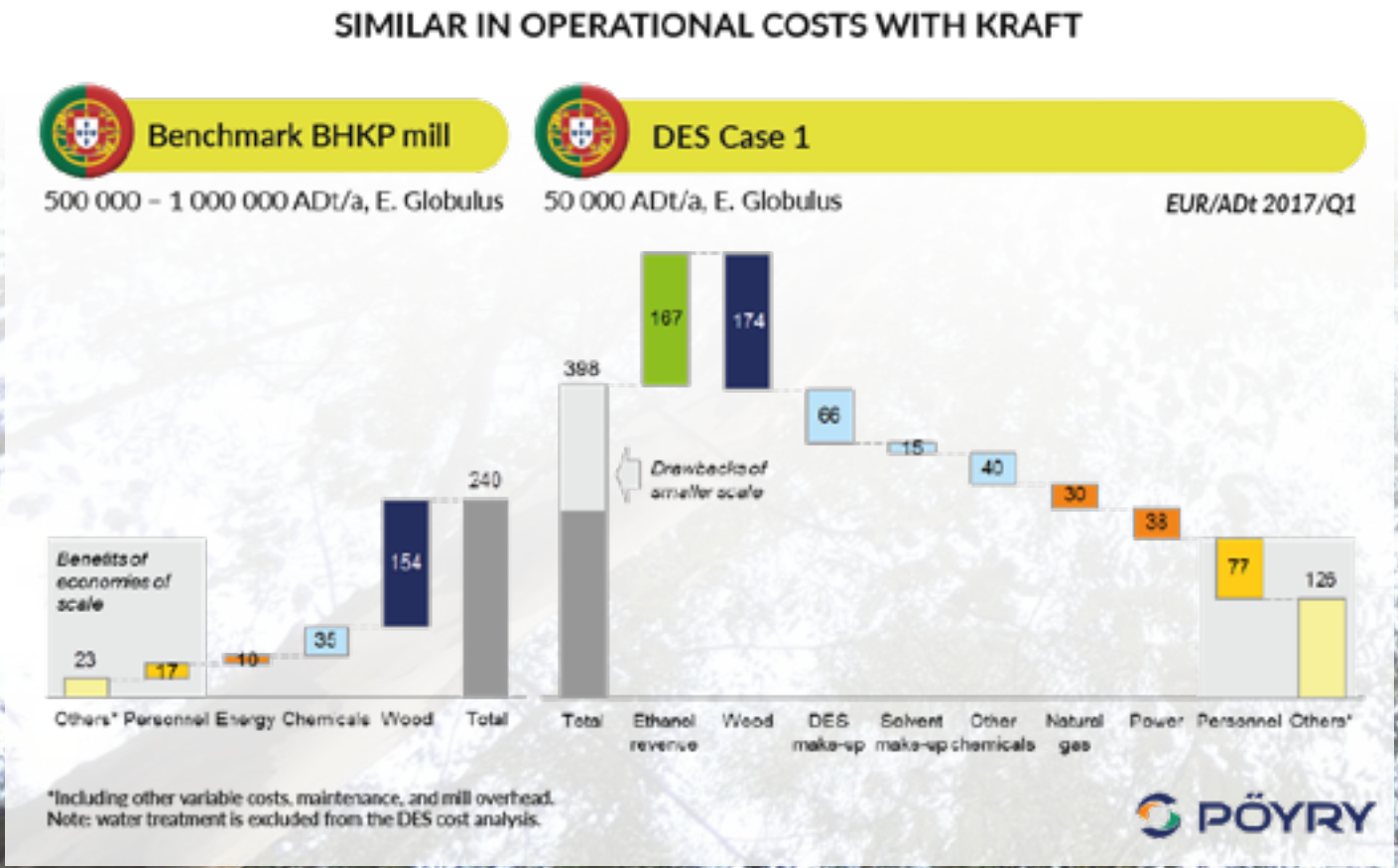
DES lignin HSQC spectrum

IMPLEMENTATION AND EXPLOITATION

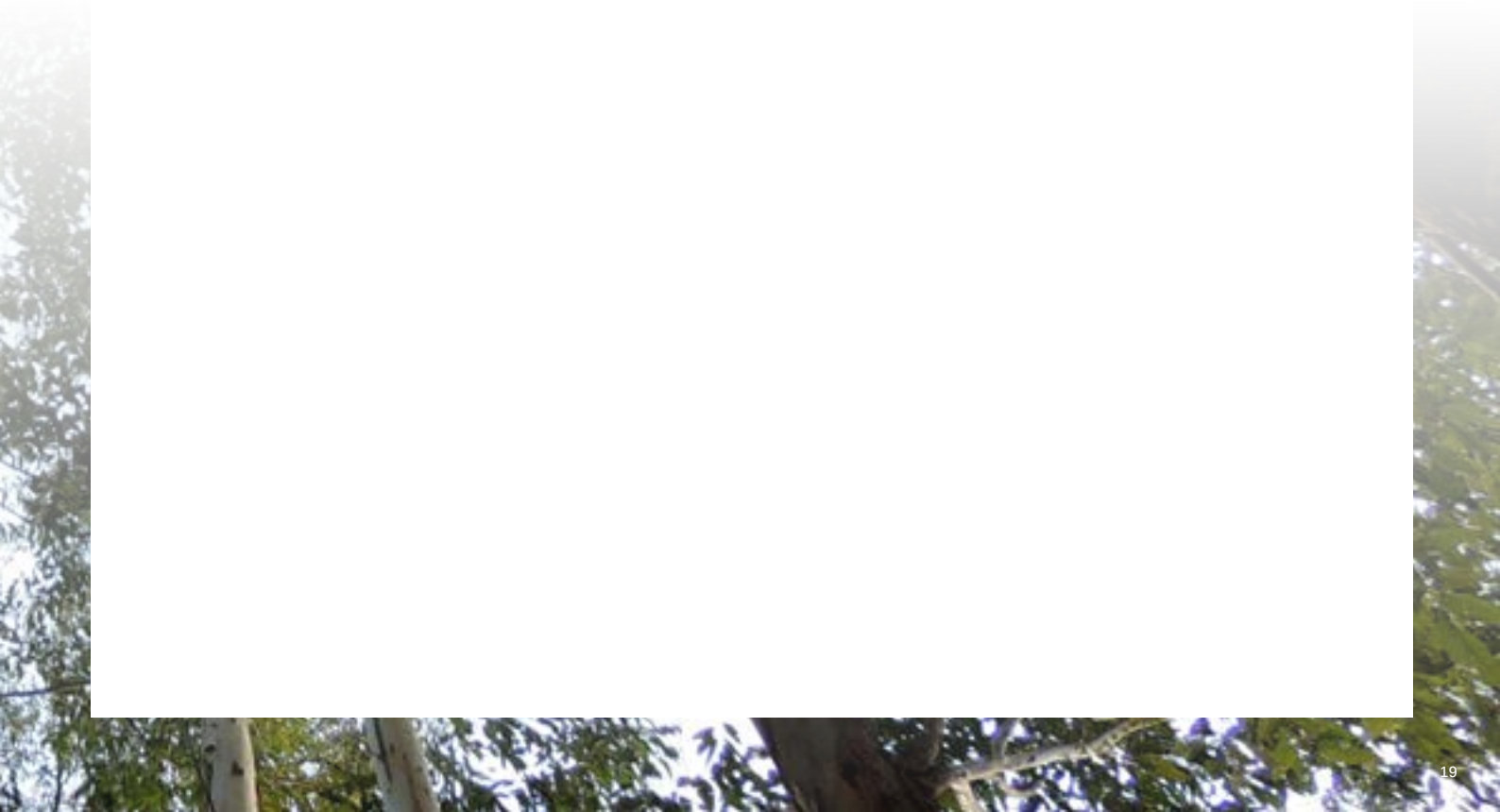
The first important steps have been made towards calculating the economic and ecological feasibility of the total process of delignification.

THE DES BUSINESS CASE

First indications show that the concept based on the laboratory findings is already cost comparable with the kraft process developed 100 years ago. Only specific investment costs as well as personnel costs are higher, as we aim for smaller mills (50,000 ton) to facilitate the first implementation of the technology and to achieve important savings from biomass logistics. Smaller capacity mills will make it possible to use raw materials produced closer to the mills, thus reducing transport needs.



REDUCTION OF CO_2 EMISSIONS

Energy savings in the pulp and paper sector are estimated to be about 40%, representing huge potential annual savings of more than 160,000 GWh in Europe. The corresponding potential CO_2 emission savings are estimated to be about 10%, which represents a reduction of more than 4 Mt of CO_2 emissions at European level.

In a broader perspective, beyond the boundaries of the current pulp and paper industry sector, the implementation of the new DES pulping processes in a biorefinery concept will produce both pulp and bio-based chemicals. When the pure lignin isolated in the DES pulping process is used to replace aromatics in the chemical industry (instead of used fir heat or electricity), much higher energy savings and CO_2 emission reductions will be achieved. Taking into account the simultaneous production of an equal tonnage of chemicals, the total energy use and CO_2 emissions of the combined system can be 90% lower than with the separate systems of pulp and fossil chemicals production.