ERA CoBioTech (ERA-Net Cofund on Biotechnologies)

ACHEMA2018

Kick-off session: "Biotechnology for a sustainable bioeconomy"

Project name: Environmental-friendly bioadhesives from renewable resources

Project acronym: WooBAdh

Name: Maria Teresa Moreira

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant 722361

Frankfurt am Main, 13.06.2018

Contact details

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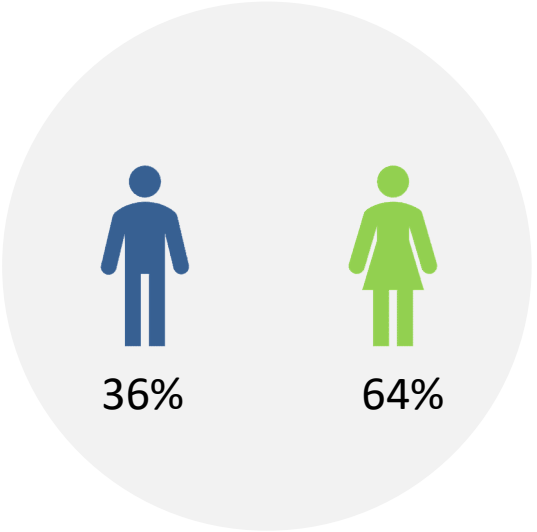
Department of Chemical Engineering
University of Santiago de Compostela

Group of Environmental Biotechnology

- 10 Professors & Ass. Professors
- 10 Post-docs
- 1 Manager, 6 Technicians (4 lab, 2 administration)
- 40-45 PhD Students



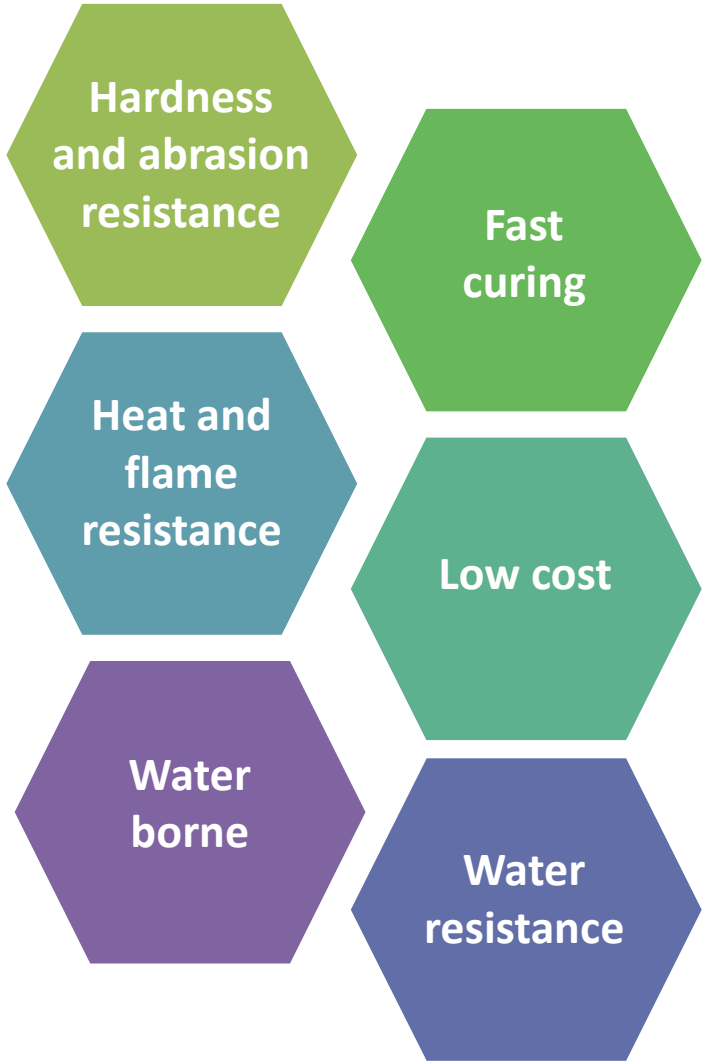
BioGroup
Group of Environmental Biotechnology

http://www.usc.es/biogrup/

Introduction

1. Wastewater to biopolymers
2. Biopolymers from renewable compounds
3. Selective VFA production from wastes
4. Integrated enzymatic process for sugar production from lignocellulosics
5. Added-value products by enzymatic transformation of natural extracts
6. Life cycle assessment (LCA) in biorefinery

Properties of formaldehyde based resins



Urea-formaldehyde (UF) resins

The most widely used thermosetting resin for wood

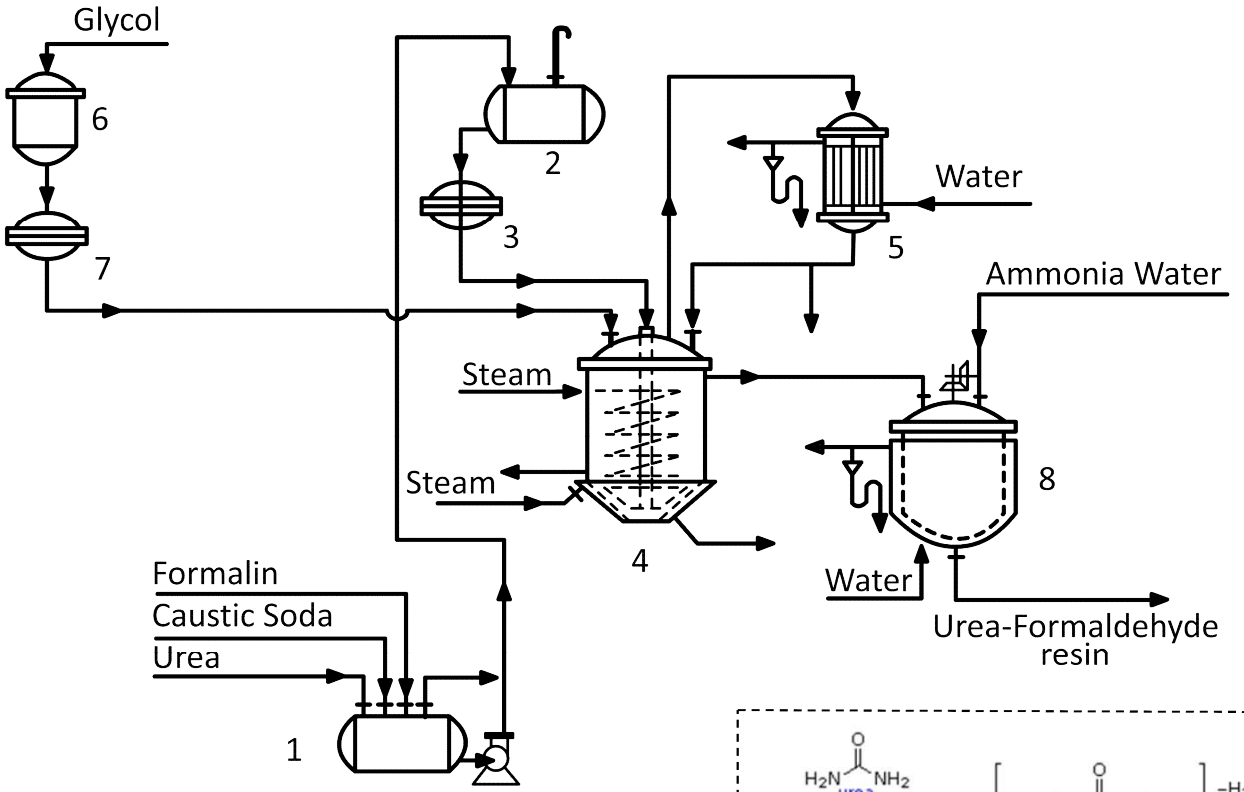
Widely used for the manufacture of interior grade plywood and particleboard

Extensively used for producing hardwood plywood for furniture and interior paneling and for furniture assembly

They are usually mixed with hardeners, fillers, and extenders to obtain formulations which cure at RT to nearly 200 °C

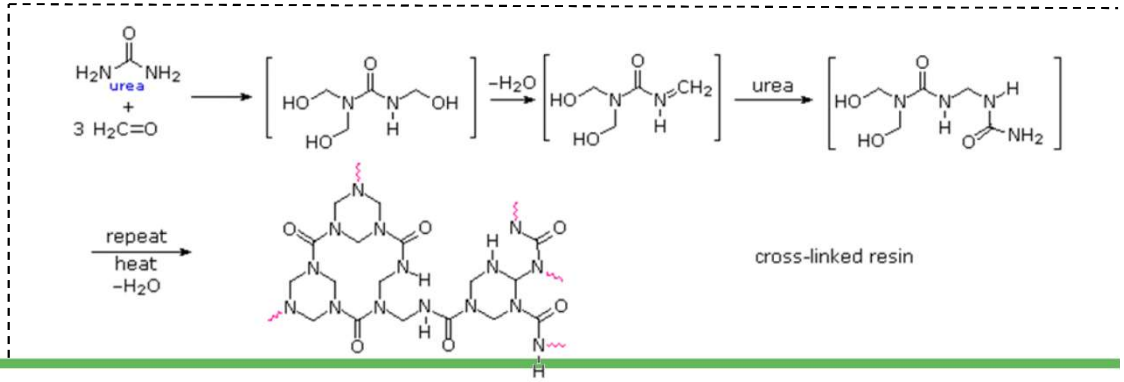
Fillers and extenders are added to the resin to control flow, viscosity and resin penetration into the wood

Production of UF resins



Non-renewable raw material Petrochemical industry !!

1- Mix tank
2- Condensate tank
3- Screen filters
4- Reactor
5- Shell and tuve cooler
6- Glycol weight measurer
7- Screen filters
8- Stabilizer



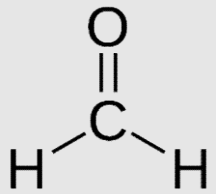
Source:
https://petrochemicalprocesses.weebly.com/

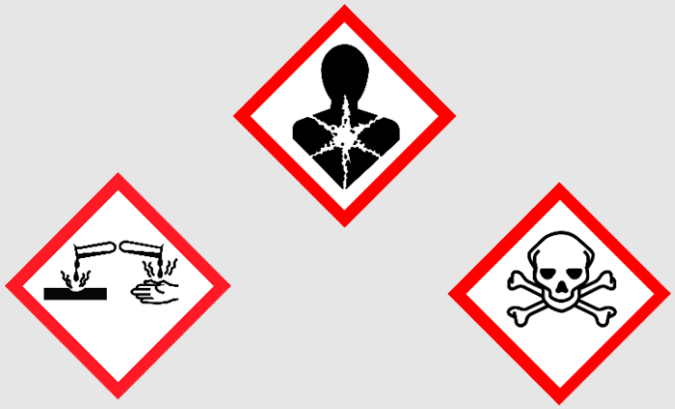
Substance Identification

EC/List no.: 200-001-8

CAS no.: 50-00-0

Mol. Formula: CH2O





European Chemicals Agency (ECHA)

EC 1272/2008
EU 605/2014

Carcinogenic category B1
Mutagen category 2

Formaldehyde and formaldehyde releasers - Strategy for future work (ECHA 11/Jan/2018)

EU will restrict the placing on the market of formaldehyde and included formaldehyde releasers in mixtures with the respective concentration limits

The regulation will be adopted in *the first quarter 2018* and the restriction on formaldehyde and some releasers for their placing on the market for supply to the general public will apply from the date of entry into force of the regulation.

Alternatives to UF resins

1. Modified UF-resins with scavenger additives, such as melamine, to reduce the rate of emissions of formaldehyde
2. Alternate formaldehyde resins, such as phenol formaldehyde, which cure at the factory during manufacture and have much lower formaldehyde emissions in use than UF
3. Alternate fossil fuel-based binders containing no added formaldehyde, such as methylene diphenyl diisocyanate (MDI)
4. Alternate binders based on renewable resource materials (Bioadhesives)

Why change to bioadhesives?

Reduce VOCs (formaldehyde) emissions

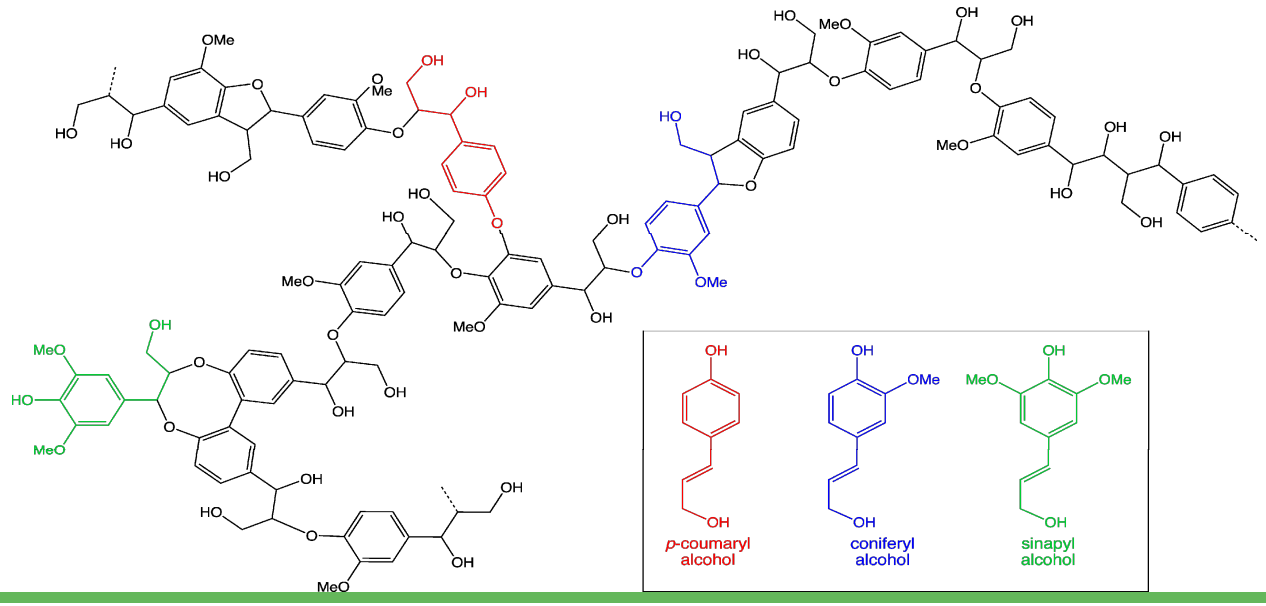
VOC FREE

Sustainability of raw materials and final products (petroleum independence)

RECYCLED

Raw Materials

- By-product from the cellulose pulping process
- Great availability, low value
- Very heterogeneous structure, quality & reactivity
- Depending on the process:
  - Sulfur containing lignin (Kraft lignin)
  - Non-sulfur biorefinery lignin (Organosolv lignin)



Raw Materials

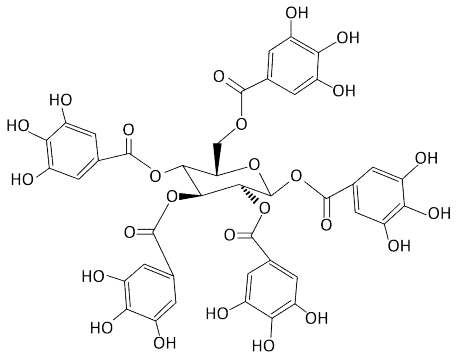
Tannins

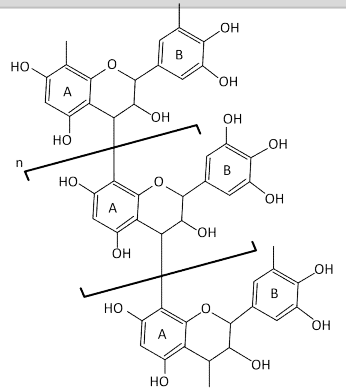
Condensed tannin

- Made of hydroxylated C-15 flavonoids
- Its structure leads to fast curing rates and high viscosity of bioadhesives

Hydrolysable tannin

- Polymeric esters of carboxylic acids and sugars
- Readily soluble in water and easily hydrolyzed

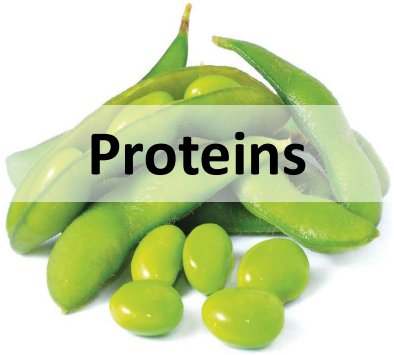




Industrial applications (Inks, Textile dyes)

Extracted from different **LCB** (*Schinopsis sp., Castanea sp., Mimosa sp.)*

Raw Materials



- **Soybean**
- **Wheat gluten**: widely available as by-product from bioethanol production

Soybean protein

Advantages

- ☑ Inexpensive
- ☑ Easy to handle
- ☑ Low pressing temperature
- ☑ Can bond wood with high moisture content

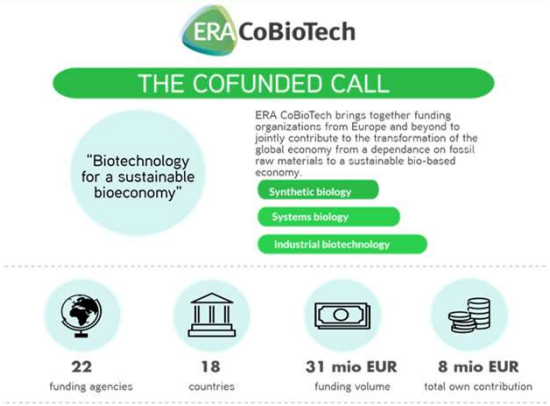
Disadvantages

- ☒ High viscosity
- ☒ Short pot life
- ☒ Relative low strength
- ☒ Sensitive to biological degradation
- ☒ Low water tolerance
- ☒ Low pressing temperature

The WooBAdh project

Project aim

The **WooBAdh** project aims to study the feasibility of replacing formaldehyde in wood adhesives by natural components derived from wood or other vegetable matter



Lignins

Tannins

Chemical modification

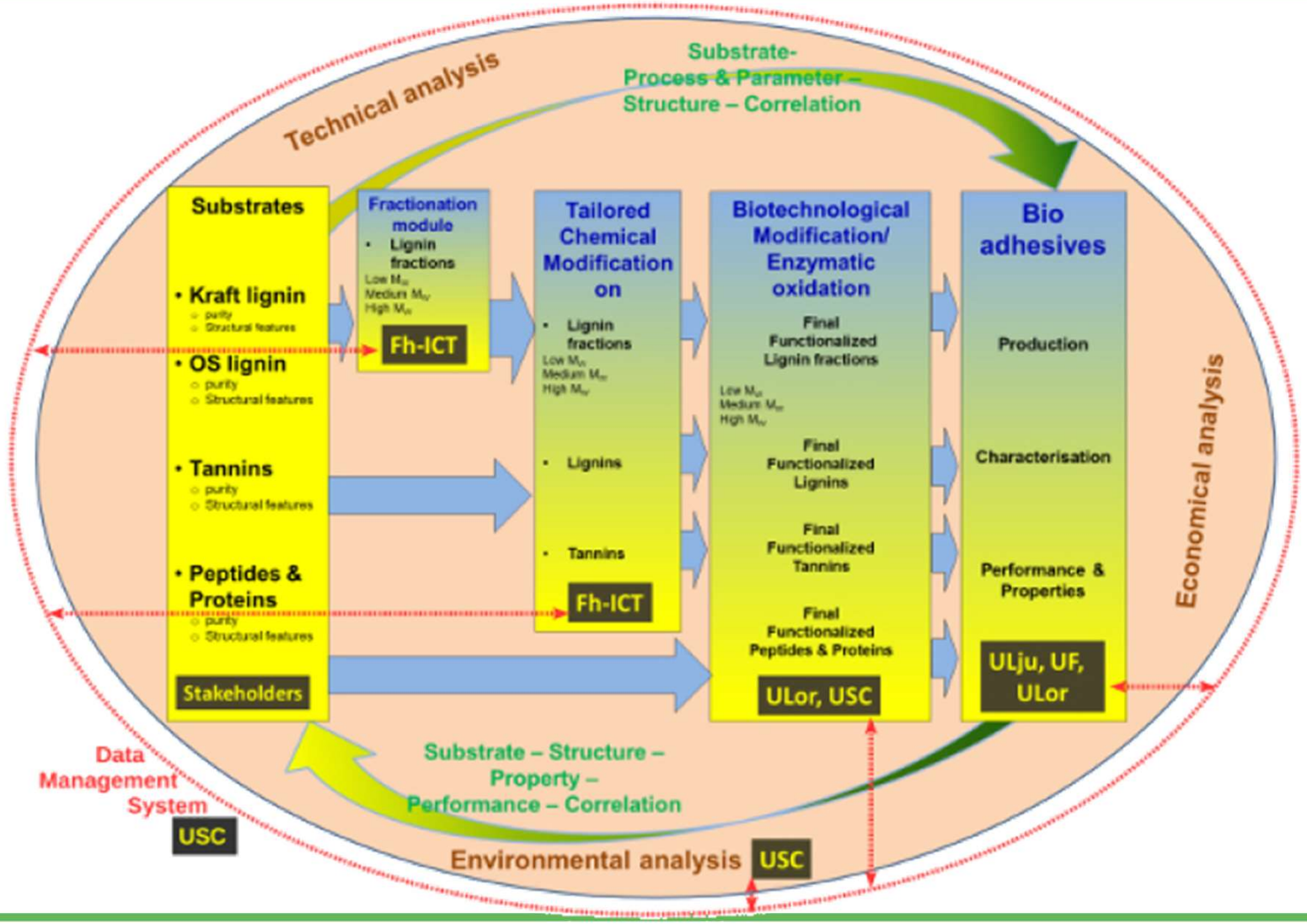
Biotechnological modification

Bioadhesive formulation

Bio-based adhesives in MDF panels

- Reduced VOCs emission
- Renewable raw materials

Project aim


Technical analysis
Substrate-
Process & Parameter –
Structure – Correlation
Substrates
• Kraft lignin
purity
Structural features
• OS lignin
purity
Structural features
• Tannins
purity
Structural features
• Peptides & Proteins
purity
Structural features
Stakeholders
Fractionation module
• Lignin fractions
Low Mw
Medium Mw
High Mw
Fh-ICT
Tailored Chemical Modification
• Lignin fractions
Low Mw
Medium Mw
High Mw
• Lignins
• Tannins
Fh-ICT
Biotechnological Modification/ Enzymatic oxidation
Final Functionalized Lignin fractions
Low Mw
Medium Mw
High Mw
Final Functionalized Lignins
Final Functionalized Tannins
Final Functionalized Peptides & Proteins
ULor, USC
Bio adhesives
Production
Characterisation
Performance & Properties
ULju, UF, ULor
Economical analysis
Data Management System
USC
Substrate – Structure – Property – Performance – Correlation
Environmental analysis
USC

The Consortium

Maria Teresa Moreira (Coordinator)

- Universidade de Santiago de Compostela (Spain)

Antonio Pizzi

- Universite de Lorraine (France)

Milan Sernek

- Univerza v Ljubljana (Slovenia)

Marie Pierre Laborie

- Albert-Ludwigs-Universität Freiburg (Germany)

Detlef Schmiedl

- Fraunhofer ICT (Germany)

Other Collaborators

SILVATEAM

Tanin SEVNICA

ence ENERGÍA & CELULOSA

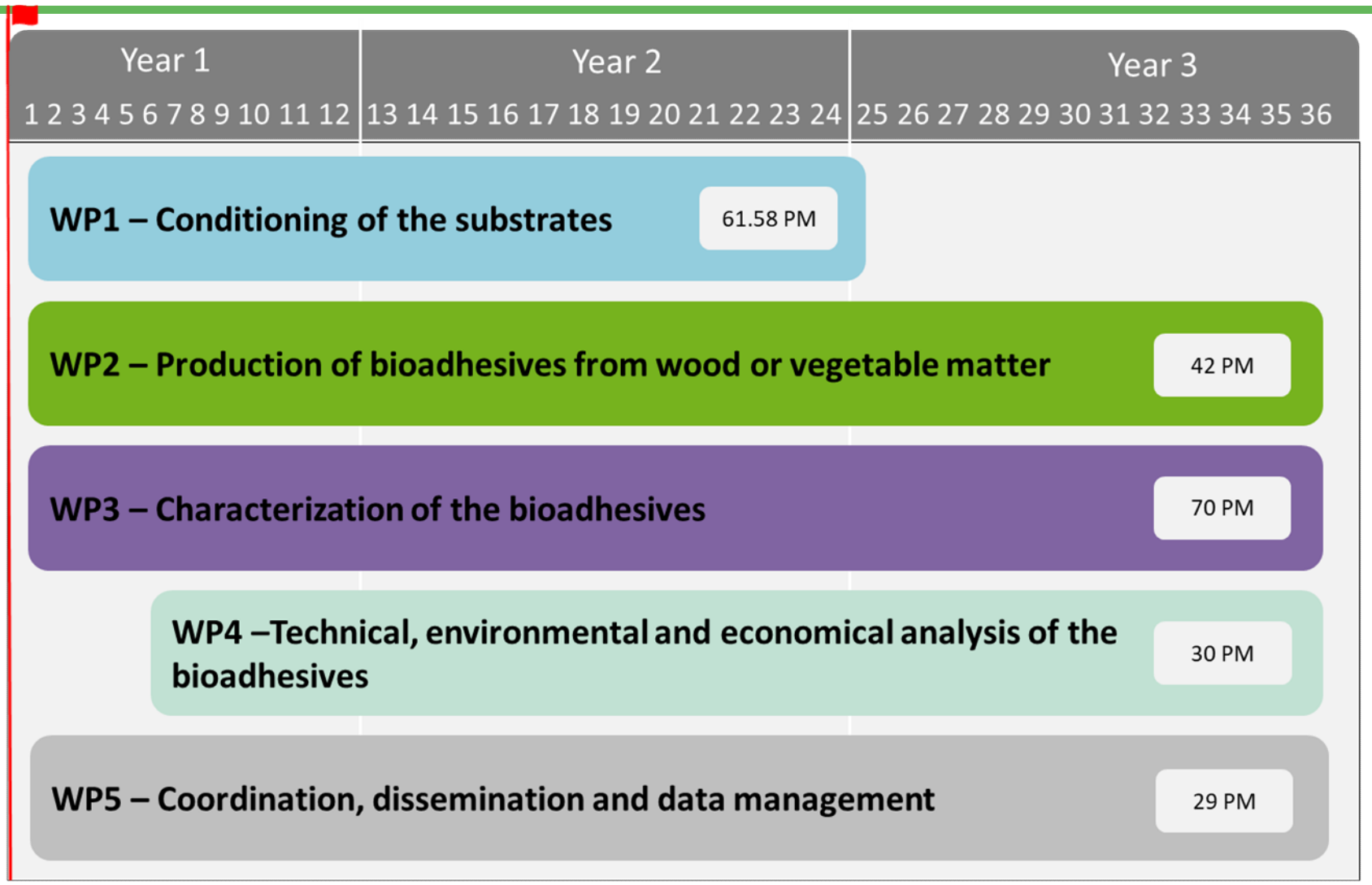
FINSA FINANCIERA MADERERA FORESA

Fraunhofer CBP

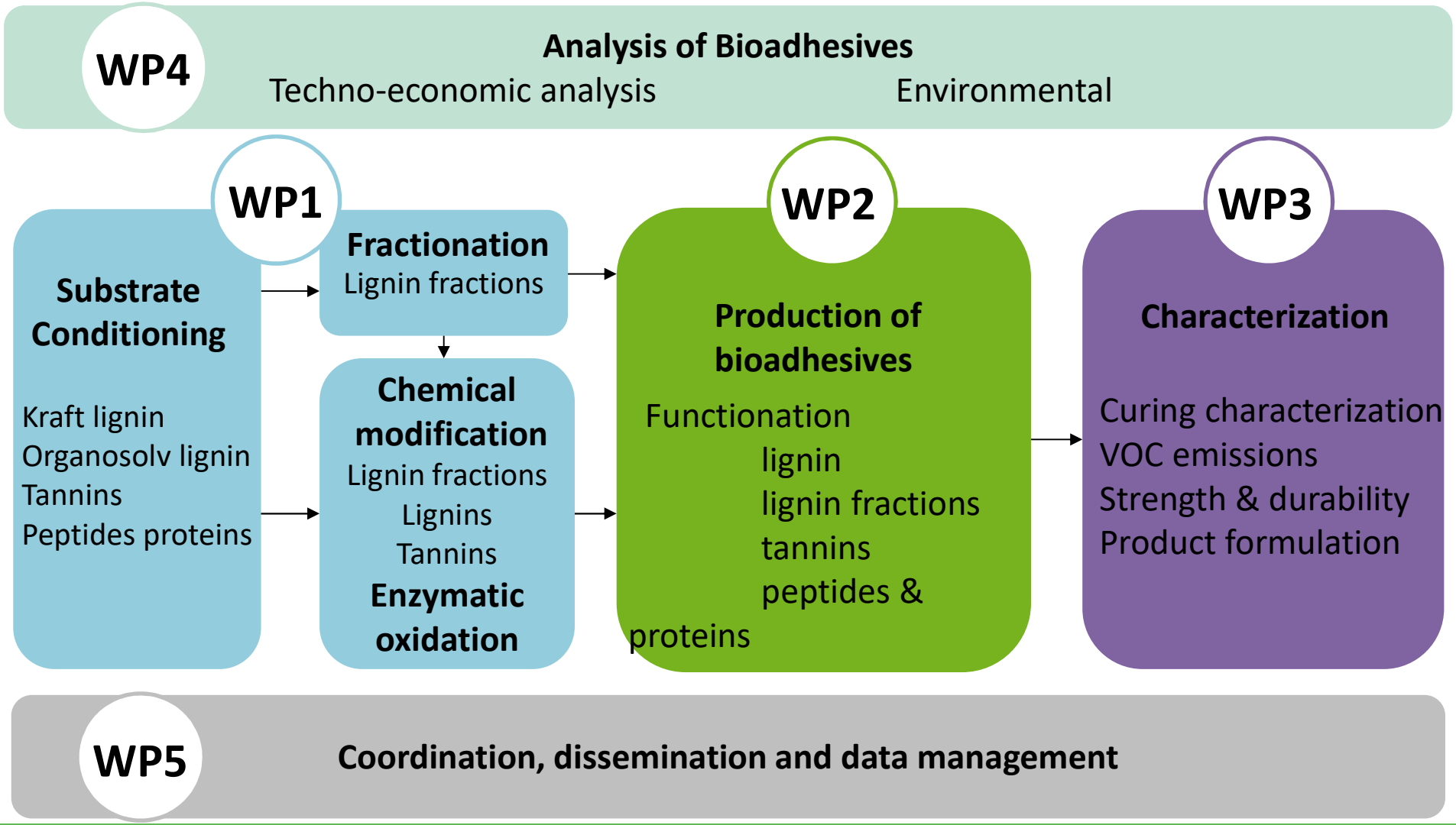
HDH HAUPTVERBAND DER DEUTSCHEN HOLZINDUSTRIE

AEP polymers

Gantt Chart of the Project



Project Overview



Work Packages

FhICT

USC

M1 **Month** M24

WP1

1.1 Tailored chemical functionalization of substances as conditioning step **FhICT**

1-24

1.2 Activation and demethylation of lignin by oxidoreductases **USC**

1-24

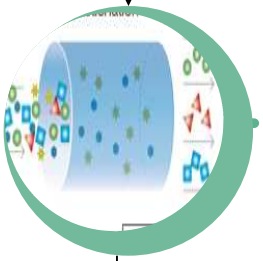
1.3 Fractionation/molecular sorting of different lignins as conditioning step **FhICT**

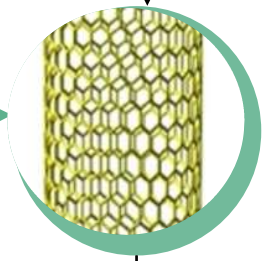
1-12

Improving the properties of bioadhesives

Evaluation of diferent **raw material** (lignin, tannins)

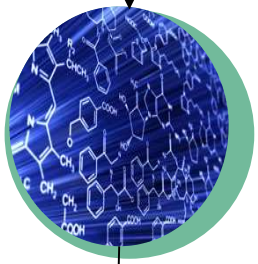
Fractionation

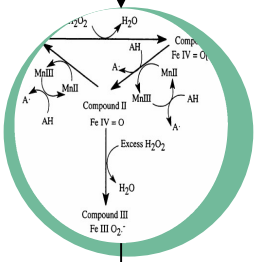




Substrate functionalization

Chemical





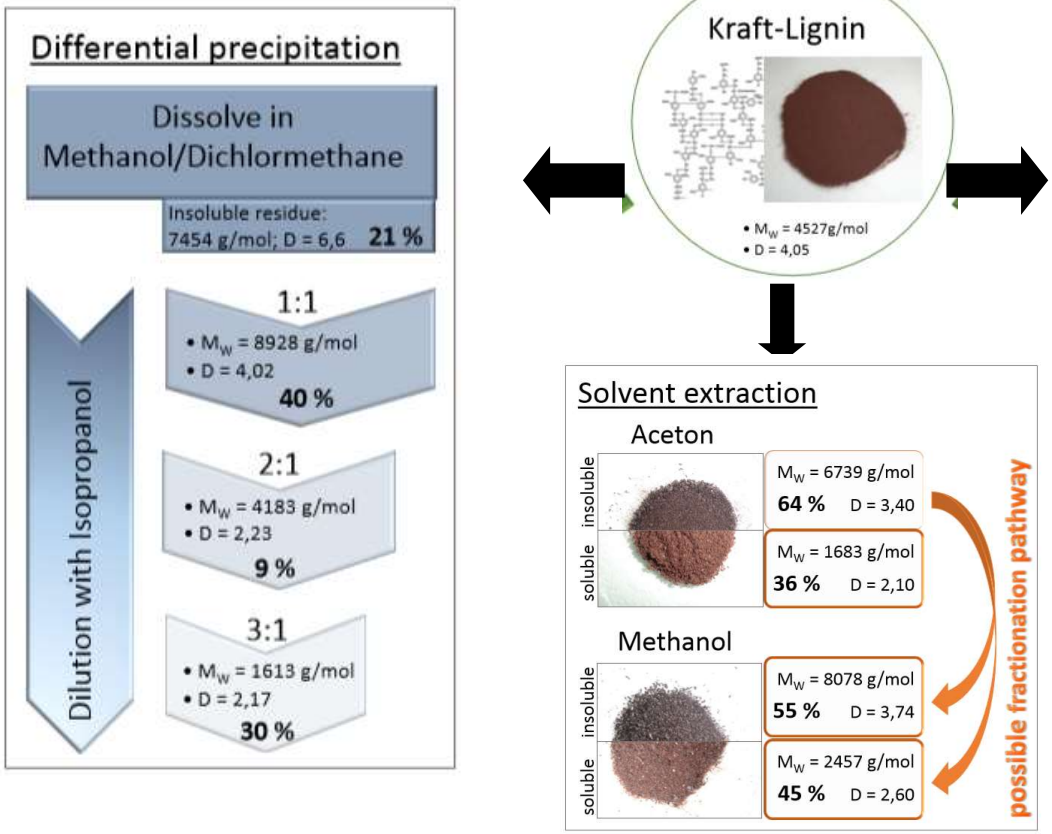
Enzymatic

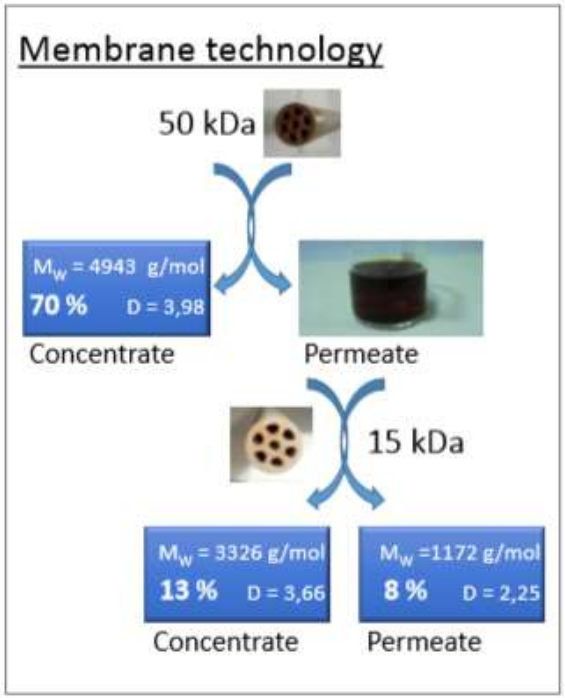
Formulation of the bioadhesives

Fractionation of lignin

Fractionation of Kraft-Lignin into low- and high-molecular weight fractions by thermal separation techniques.

- ✓ Reduce heterogeneity & polydispersity
- ✓ Increase subsequent chemical reactivity



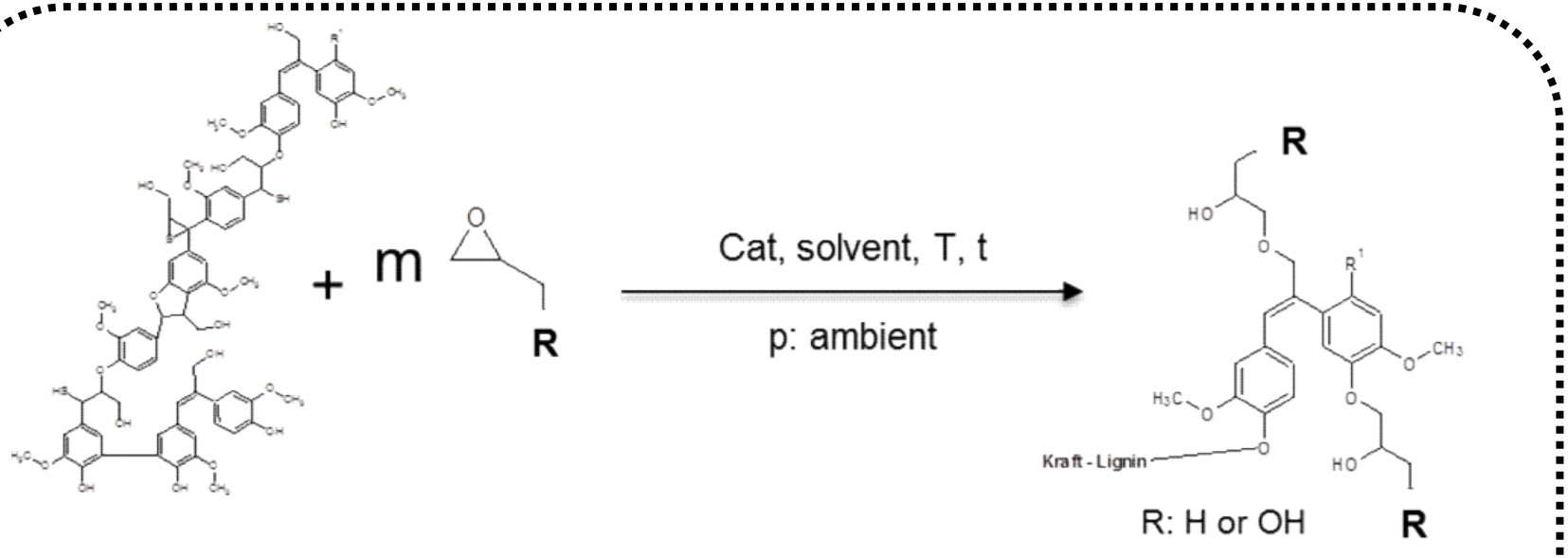


From: Rohde et al (Fraunhofer ICT)

Increasing the reactivity of substrates

Chemical functionalization

- Using epoxy molecules such as propylene oxide, 2,3-epoxy-1-propanol
- Target: Increase the number of aliphatic OH-groups

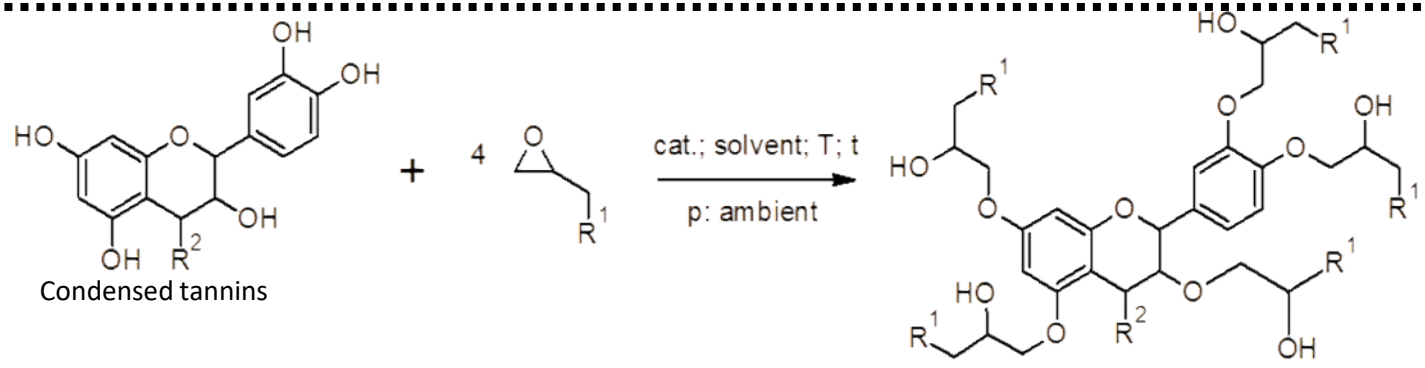


Chemical functionalization of Kraft lignin by catalyzed region-selective ring opening reaction with propylene oxide or 2,3-epoxy-1-propanol

Increasing the reactivity of substrates

Chemical functionalization

1. The catalyzed region-selective ring opening reaction takes place without side product formation
2. Use of green organic solvents and special catalysts (nucleophilic amines)
3. The reactions can be carried out at high pressure/high temperatures or as long term processes (24 h) at ambient temperature



Chemical functionalization of condensed tannins by catalyzed region-selective ring opening reactions with propylene oxide or 2,3-epoxy-1-propanol

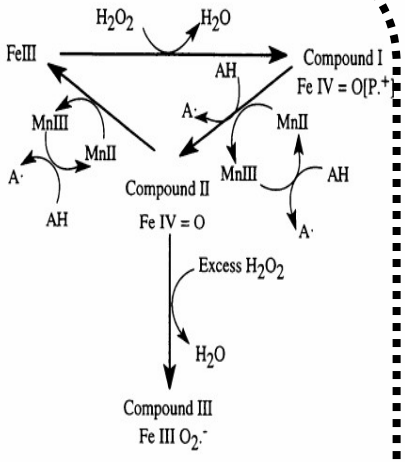
R^2: tannin
R^1: H or OH

Increasing the reactivity of lignin

Enzymatic functionalization

Abundant methyl groups in lignin makes it less reactive and reduces cross-linking

White-rot fungal enzymes



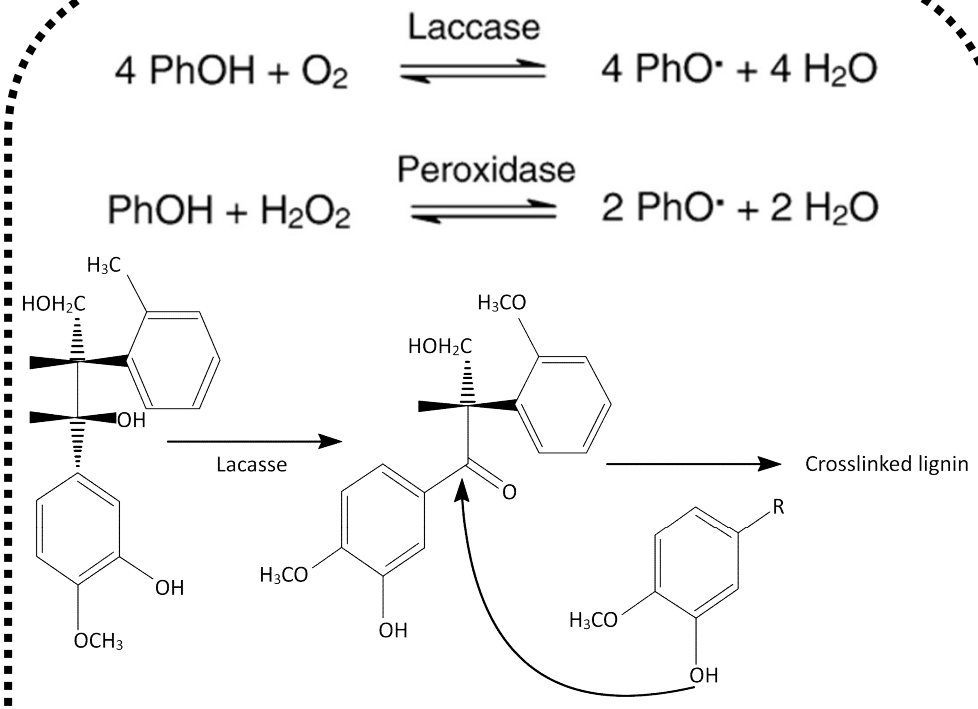
Catalytic cycle of MnP

Demethylation of lignin aromatic rings can be used to increase lignin reactivity using **oxidases** or **peroxidases**

Extracellular enzymes (Laccase (Ganoderma and Myceliophthora), MnP (Irpex) and VP (Bjerkandera)
Oxidative processes (O_2, H_2O_2)

Increasing the reactivity of lignin

Enzymatic functionalization

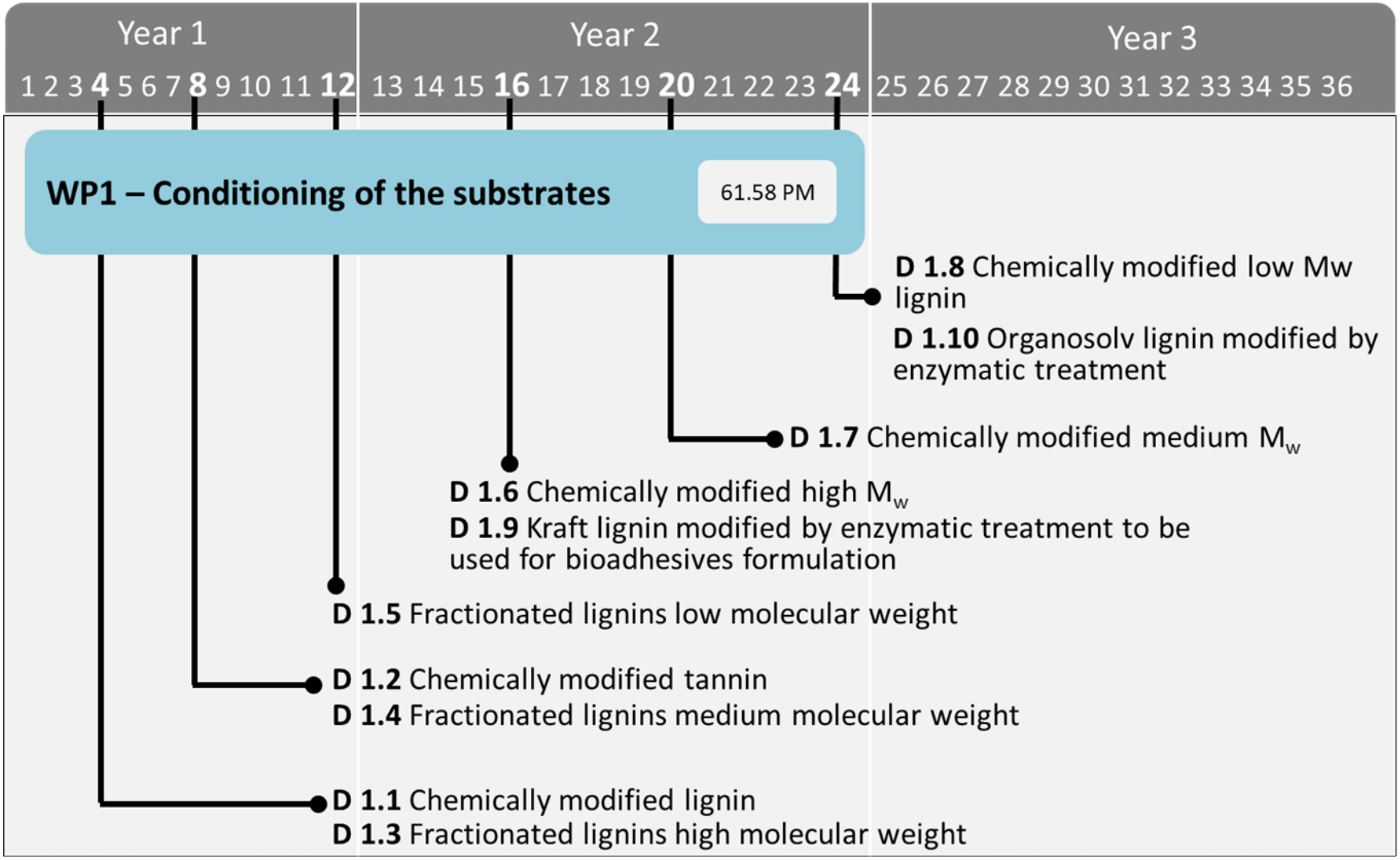


Laccase-mediated oxidation of lignin model compound and further reaction leading to lignin cross-linking

From: Steward 2008 (10.1016/j.indcrop.2007.07.008)

The enzymatic activation can release monomeric subunits from lignin, which are reactive towards other groups and/or could further polymerize

Deliverables WP1



Work Packages

ULor

UF

M1 **Month** M36

WP2

2.1 Study of different lignin sources
Ulor, UF
1-28

2.2 Study of different tannin sources
Ulor, UF
1-28

2.3 Determination of mechanisms of cross-linking, hardening reaction
Ulor, UF
12-24

2.4 Formulations of mixed lignin or lignin derived aldehyde with tannin to obtain a formaldehyde-free adhesive
ULor
18-30

2.5 Copolymerization of lignin and modified lignin with other natural compounds
UF
18-30

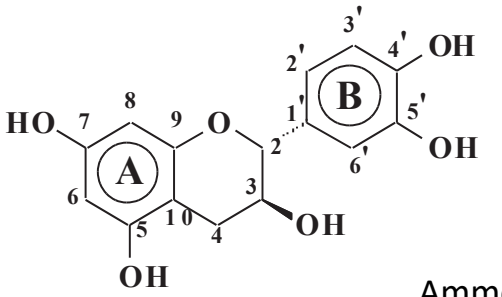
2.6 Evaluation of bonding of the new different adhesive formulations
Ulo, UF
30-36

Formulation of bioadhesives

- Reaction of tannins and lignins with ammonia to change the –OH group of polyphenols by the more reactive –NH_2.
- Reaction of tannins and lignins with diamines and polyamines, yielding aldehyde-free cross-linking
- The cross-linking and hardening reaction of tannin and lignin with triethyl phosphate
- The reaction of tannins with furfuryl alcohol

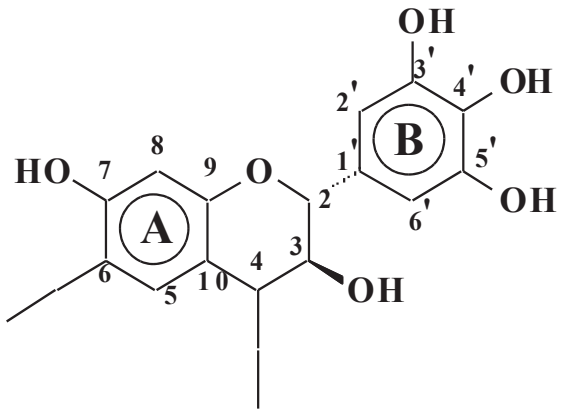
Formulation of bioadhesives

Amination of condensed tannins



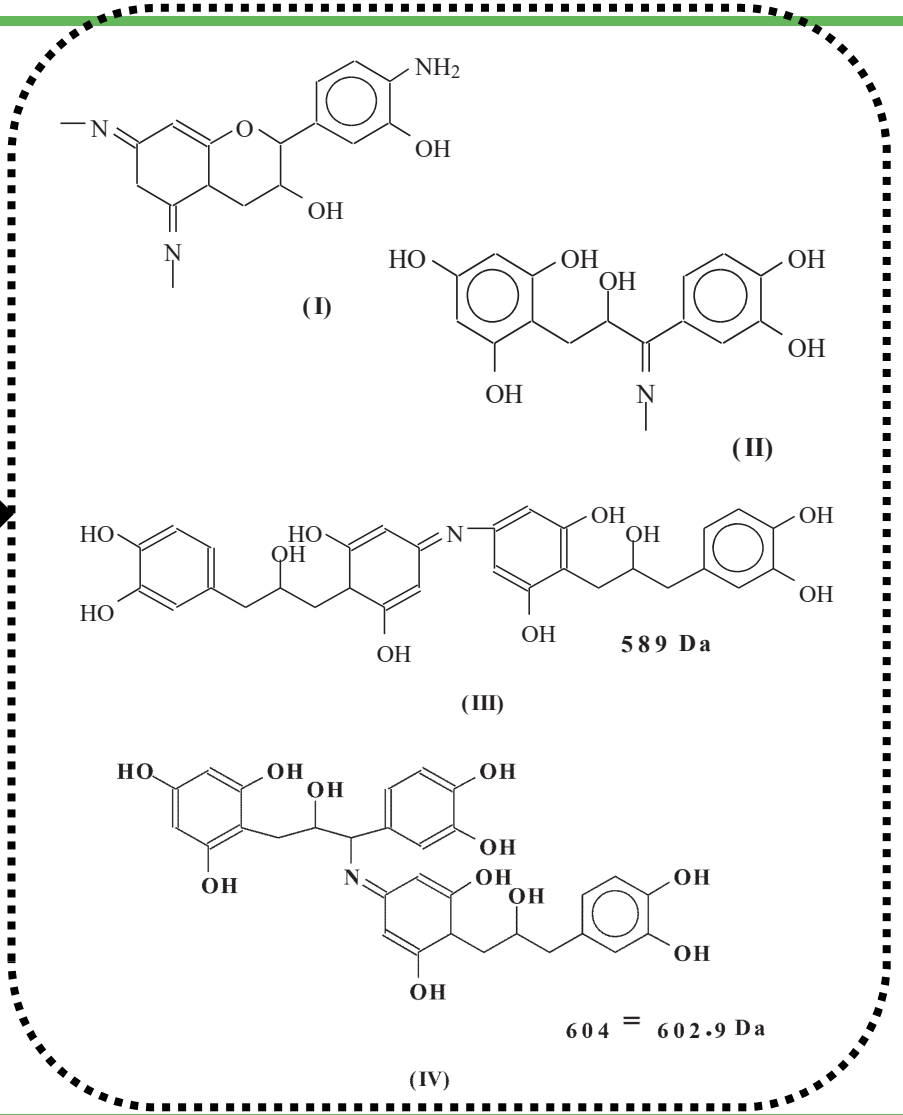
Catechin

Ammonia (28% aq.)
t = 1 h, pH = 9-12



Acacia mearnsii (mimosa), prorobinetidine

From: Braghiroli et al 2013 (10.1016/j.indcrop.2012.11.024)



Formulation of bioadhesives

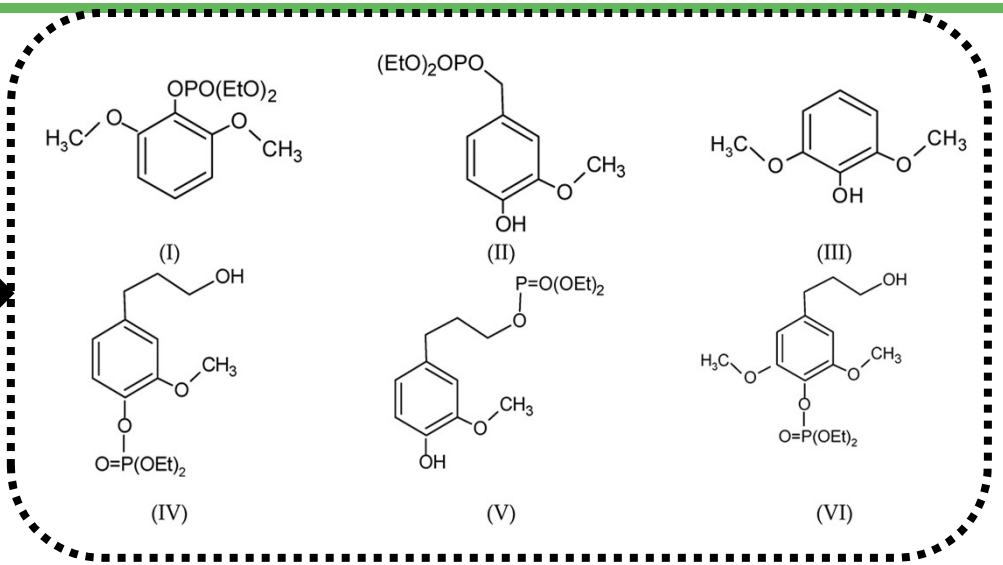
Cross-linking reaction of lignin with triethyl phosphate

Desulfurized Kraft lignin

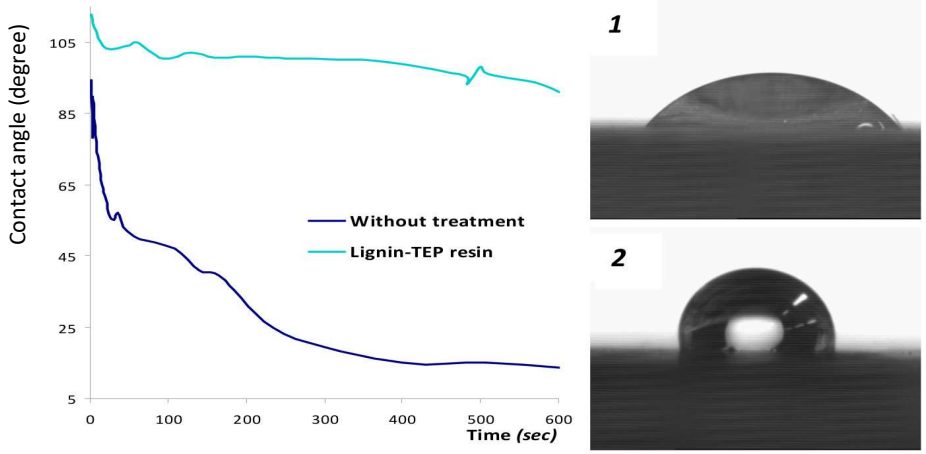
Glycerol (aliphatic chain)

Cathecol (aromatic part)

NH4OH (25%)
Triethyl phospate (TEP)
T = 90-220ºC



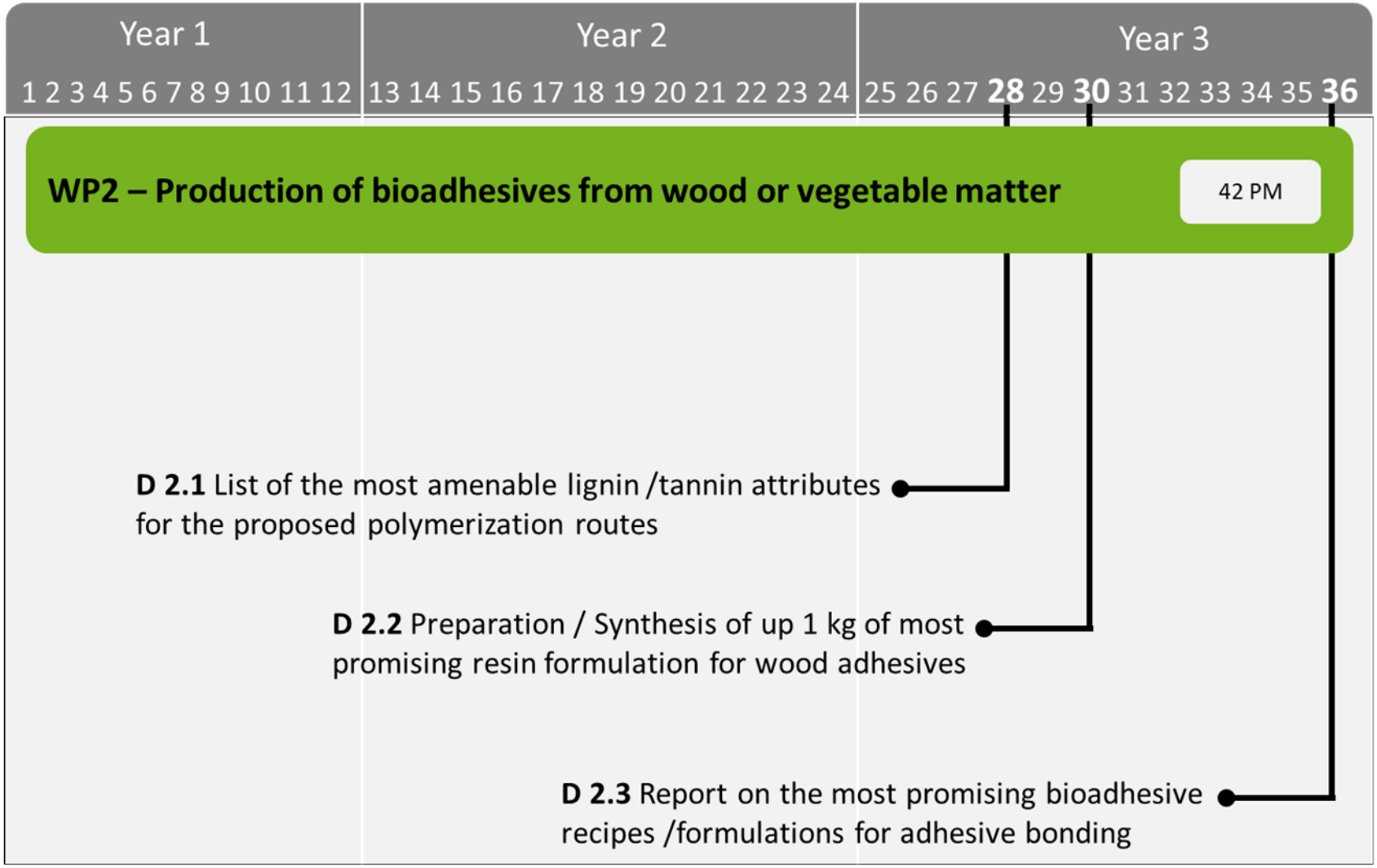
Proposed structures of some oligomers detected by MALDI-TOF for the reaction of lignin +TEP



The water dynamic contact angle of the lignin-TEP-based resin-coated surface and of the untreated beech sample. The water drop shape after 60 s.

From: Basso et al 2017 (10.3390/polym9060206)

Deliverables WP2



Worck packages

ULju

ULor, UF

M1 **Month** M36

WP3

3.1 Curing characterization of the bioadhesives

ULju, UF

1-24

3.2 Strength and durability testing of new adhesives and classification according to EN standards

ULju

12-36

3.3 Technology of bonding with new adhesives

ULju, Ulor

18-30

3.4 Determination of the VOC emissions

ULor

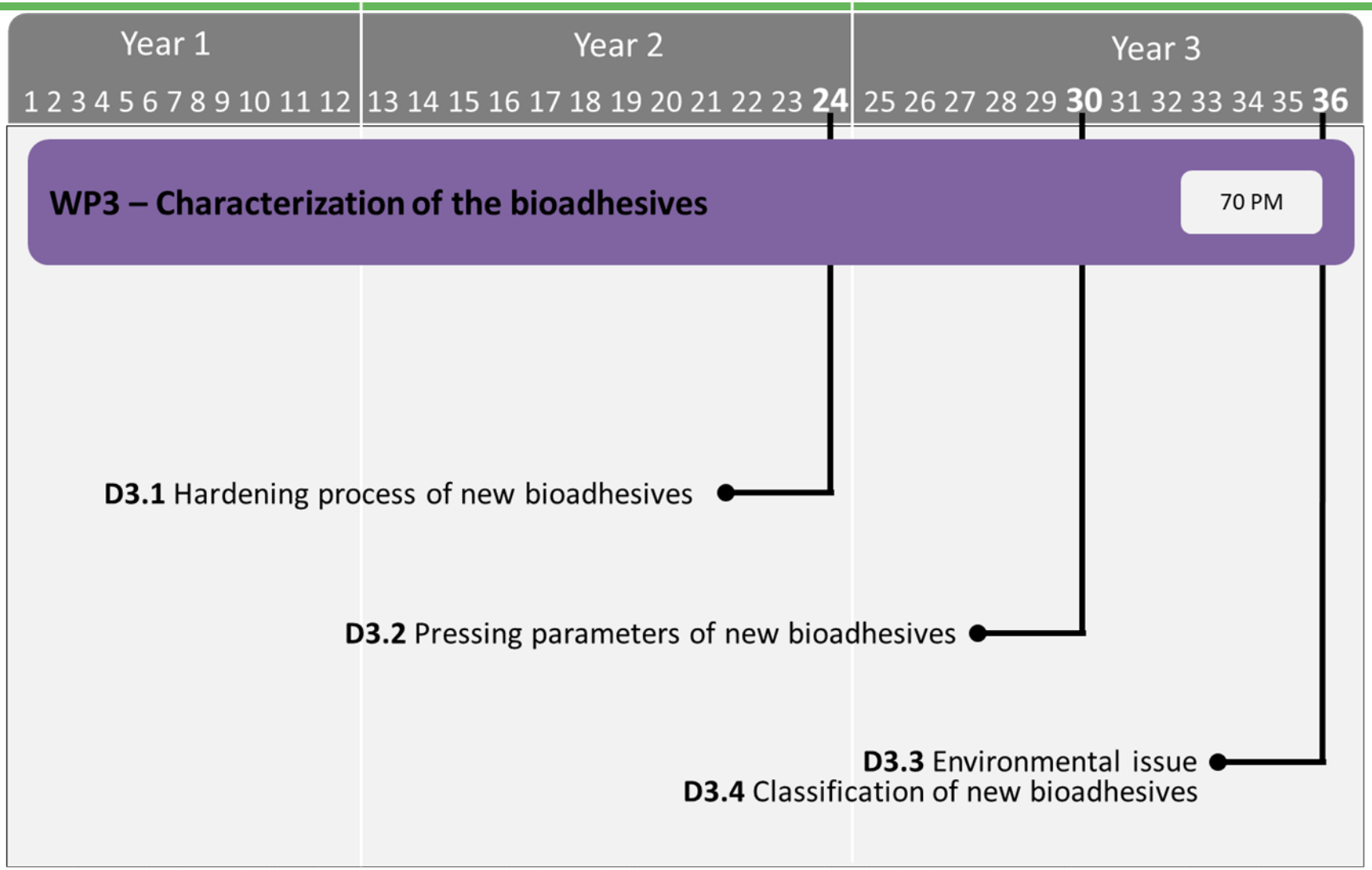
24-36

3.5 Selection of the product formulation that presents the best characteristics

Ulju, UF, ULor

18-30

Deliverables WP3



Work Packages

USC

M6 — **Month** — M36

WP4

4.1 Techno-economical evaluation — **USC**

12-24

4.2 Scope definition in LCA — **USC**

6-12

4.3 Inventory and impact assessment of WooBAdh — **USC**

12-24

4.4 Sustainability analysis — **USC**

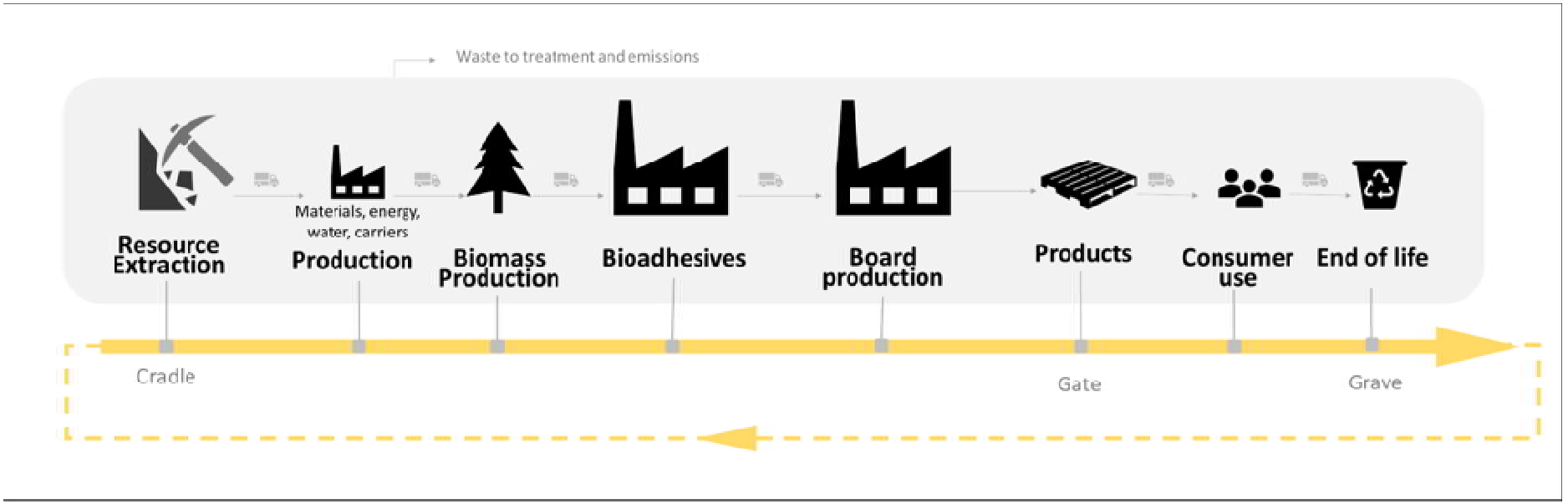
24-36

Life cycle of a product

USC

M6 **Month** M36

WP4

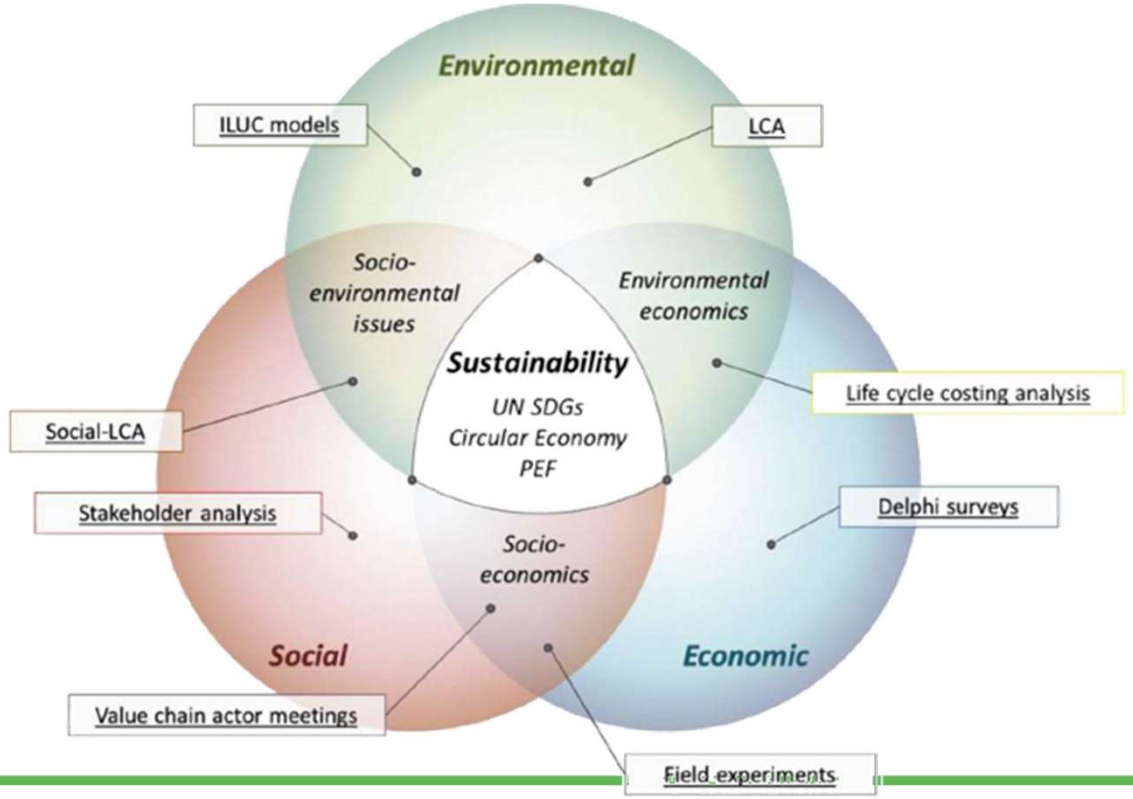


Sustainability Goals

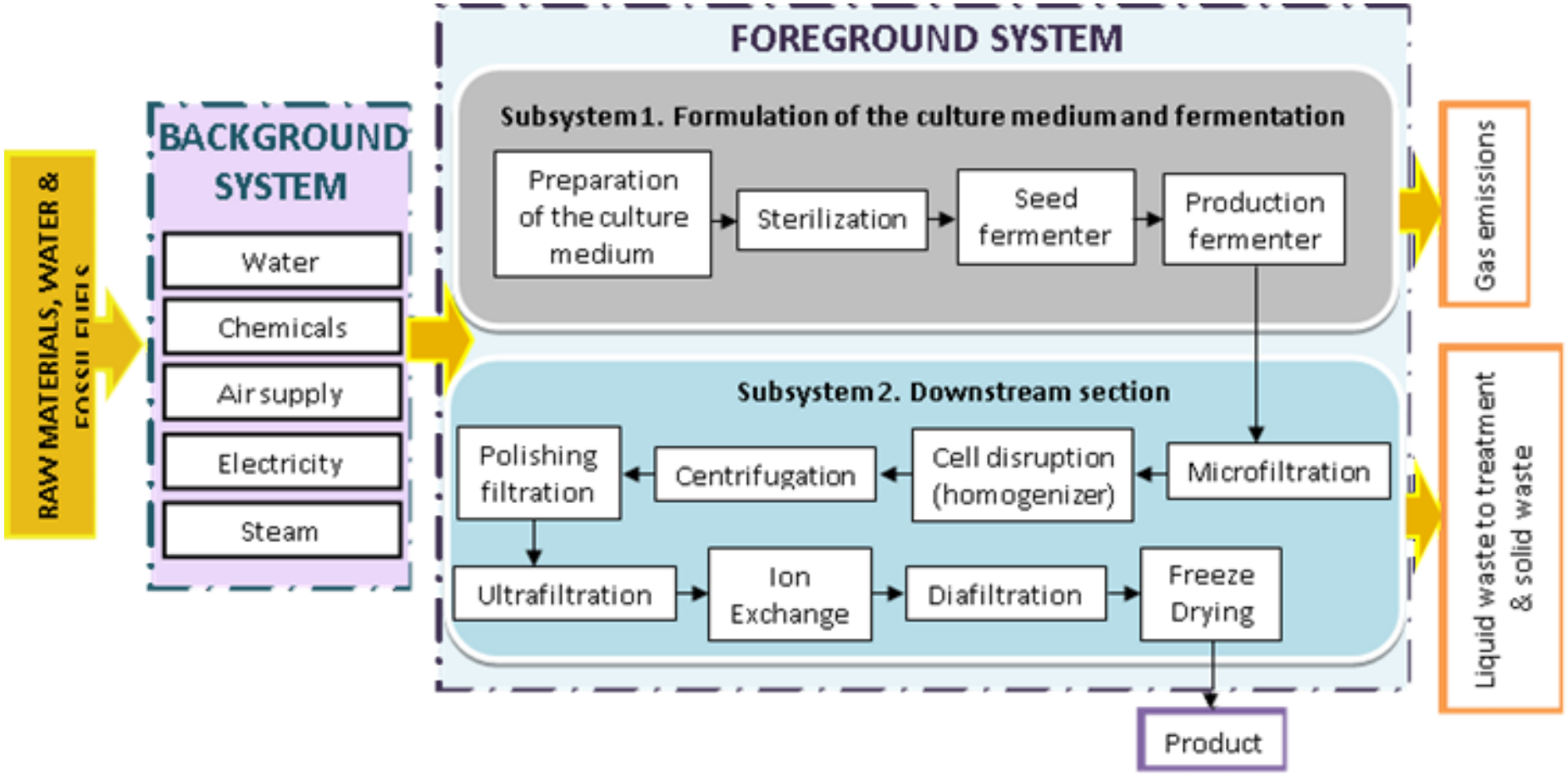
USC

M6 **Month** M36

WP4



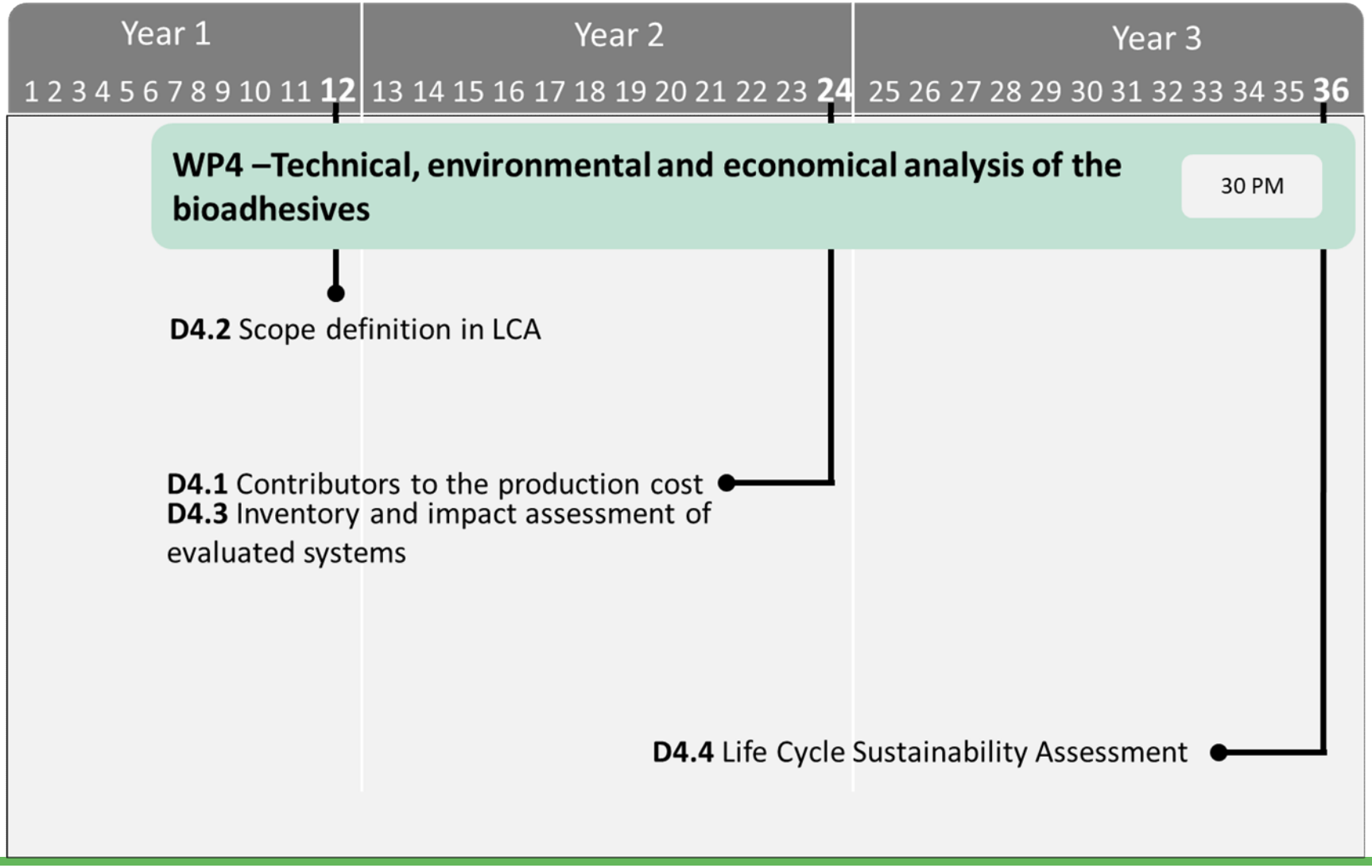
Scheme of a fermentation process



Socio-economic indicators

Stakeholder category	Subcategory	Indicator
1. Workers	Equal opportunities	Women-to-man ratio of labor force participation
	Fair salary	Women-to-man-ratio of salary (for similar work)
	Working hours	Total working hours per week
2. Consumers	Health & Safety	Fulfilled existing regulations
	Transparency	Information on the formulation, use and effects
	Benefits of the product	Value added of the product (according to its applications)
3. Society	Contribution to economic development	Importance of sector in the country
	Public commitments to sustainability issues	Performed environmental assessments (LCA, risk assessment...)

Deliverables WP4



Work Packages

USC ULor, UF, Ulju, FhICT

M1 **Month** M36

WP5

5.1 Project management & coordination — USC, all

1-36

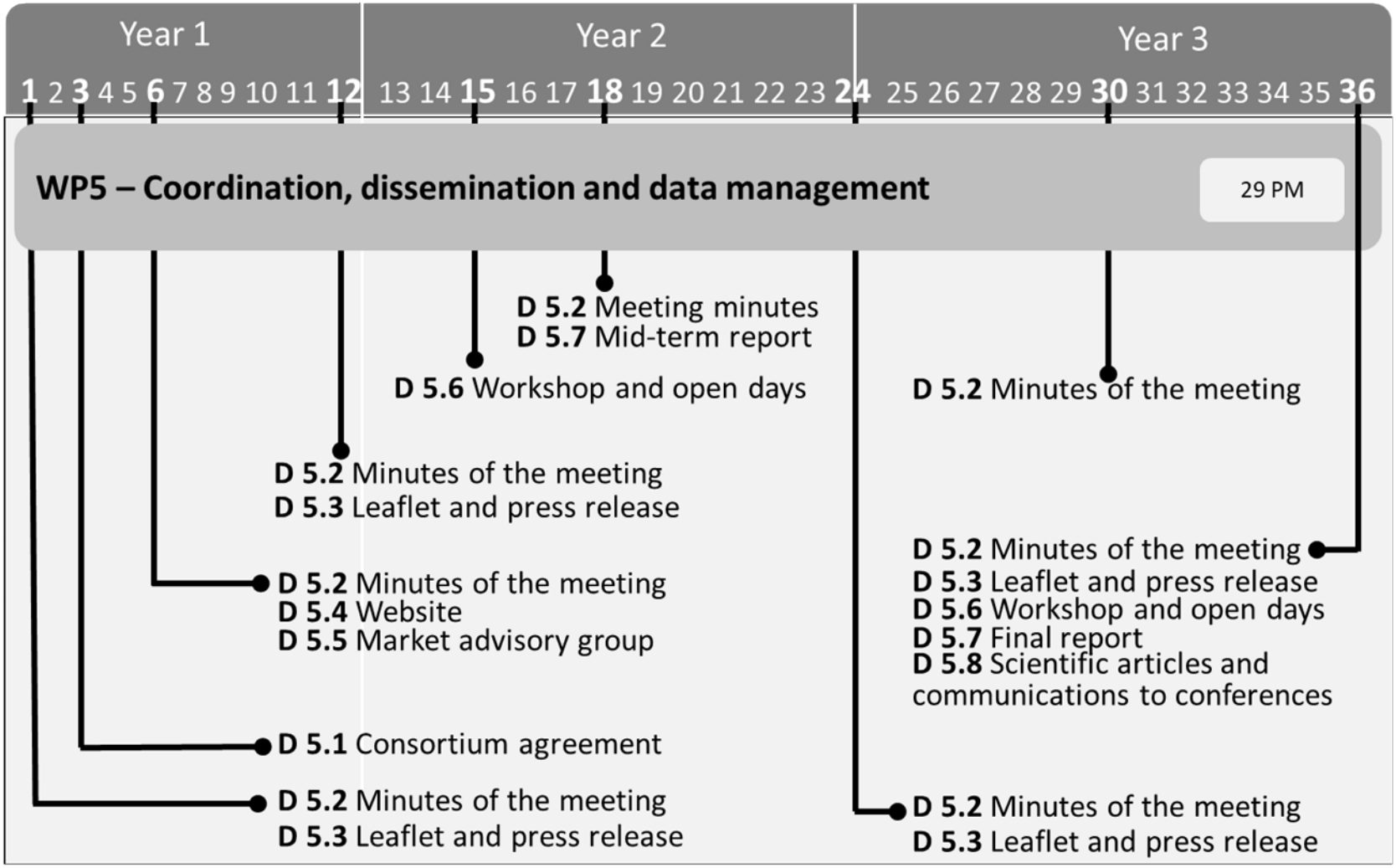
5.2 Communication & dissemination — USC, all

1-36

5.3 Data management — USC, all

1-36

Deliverables WP5



ERA CoBioTech (ERA-Net Cofund on Biotechnologies)

ACHEMA2018

Kick-off session: "Biotechnology for a sustainable bioeconomy"

Project name: Environmental-friendly bioadhesives from renewable resources

Project acronym: WooBAdh

Name: Maria Teresa Moreira

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Frankfurt am Main, 13.06.2018