



**IEA Bioenergy**  
Technology Collaboration Programme

Task 42  
Biorefining in a circular economy



# Sustainable Lignin Valorisation

Simulation tools for lignin valorisation

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# Cooperation IEA Bioenergy, LIGNOCOST Network and Universities



Know-how and data input



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AGRICULTURAL UNIVERSITY OF ATHENS

Extra report activity regarding the modelling of the biorefinery processes for the transformation of lignin to target products.

In order to carry out the assessment of the economical parameters (e.g. maximum lignin market price) to make convenient the utilization of low quality/high quality lignin to produce high-added value compounds.

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Agenzia nazionale per le nuove tecnologie,  
l'energia e lo sviluppo economico sostenibile

Mathematical model  
construction for the  
Lignin valorization



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Know-how and  
data input



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THESSALONIKI

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data input



UNIVERSITÀ DEGLI STUDI  
DI SALERNO

Tools and methods for the  
mathematical model construction

Extra report activity regarding the modelling of the biorefinery processes for the lignin conversion to target products.

To carry out the assessment of the economic parameters (e.g. maximum lignin market price) to make convenient the utilization of low quality/high quality lignin to produce high-added value compounds.

# State of the art on techno-economic assessment

Lignin source	Main lignin-based product	Main conversion processes	Reference
Organosolv pretreatment of olive tree pruning	Catechol	Alkaline treatment	(Mabrouk et al., 2018) - (Mabrouk et al., 2017)
Dilute acid pretreatment of corn stover	Propyl guaiacol		(Han, 2017)
Dilute acid pretreatment of corn stover	Phenols	HTL	(Bbosa et al., 2018)
Ionic Liquid pretreatment	Eugenol and phenols	Hydrogenolysis by Isopropanol	(Martinez-Hernandez et al., 2019)
Kraft lignin (Lignoboost)	Polyols/phenols	Depolymerization by glycols	(Dessbesell et al., 2018) - (Ou et al., 2020)
Several lignins	Phenols	Depolymerization	(Fernández-Rodríguez et al., 2021)
Kraft lignin	Vanillin, Syringaldehyde	Oxidation	(Rodrigues et al., 2018)
Kraft lignin	Vanillin	Oxidation	(Wongtanyawat et al., 2018)
Kraft lignin (Lignoboost)	Vanillin, formic acid, acetic acid, guaiacol	Oxidation	(Abdelaziz et al., 2020)
Dilute acid pretreatment of corn stover	Jet-fuel	HDO	(Shen et al., 2018a)
Kraft lignin	Aromatic monomers	Lignin pyrolysis, HDO, hydrothermal upgrading	(Vural Gursel et al., 2019)
Kraft lignin	BTEX	HTL + HDO	(Funkenbusch et al., 2019)
Kraft lignin	Jet-fuel/Resins	HDO	(Giuliano et al., 2020)
Lignin cake after fermentation	Adipic Acid	Biological conversion	(Corona et al., 2018) - (Unlu et al., 2020)
Organosolv/Steam explosion	Formaldehyde	Gasification + synthesis	(Tey et al., 2021)
Kraft lignin (Lignoboost)	Colloidal Lignin Particles	Dissolution in THF	(Bangalore Ashok et al., 2018)
Kraft lignin	Carbon Fibres	HTL	(Otromke et al., 2019)

# Challenges of the approach

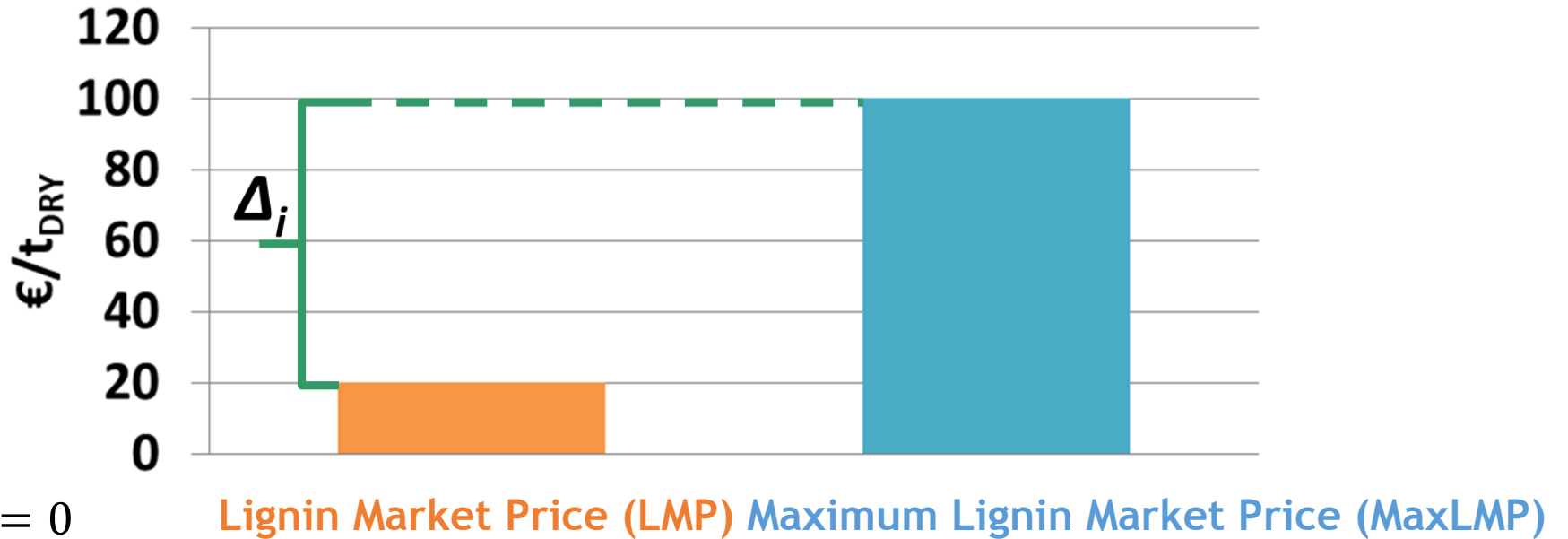
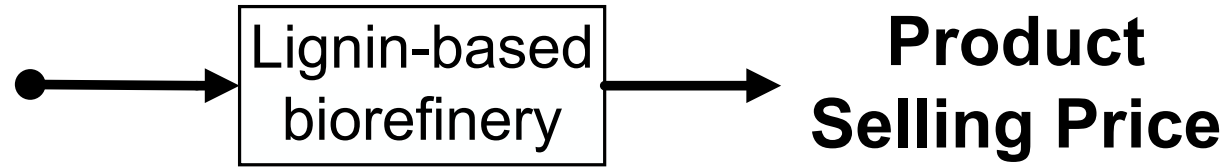
- a. Development of relationships between specific lignin characteristics (i.e., purity, composition, molecular weight, H/S/G ratio,...) and applicability in processes producing target products
- b. Lack of data relating to the lignin conversion (e.g., yields, process conditions,...)
- c. Difficulty to compare the performances of the products obtained using a specific kind of lignin and another (e.g., resin performances)

# Methodology

- a. Mathematical model of a process Superstructure converting lignin to target products
- b. Process yields based on literature/partner data
- c. Simplified approach to differentiate the quality of the lignin (% of “reactive” lignin)
- d. Maximization of the Maximum Lignin Market Price

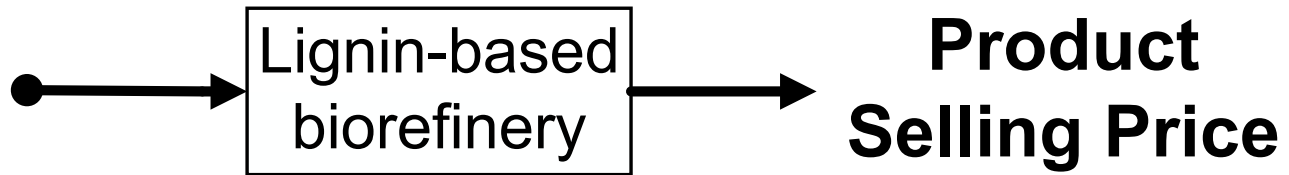
# Lignin Market Price vs Maximum Lignin Market Price

**Lignin Market Price**  
(biomass, pretreatment, pulping processes,...)

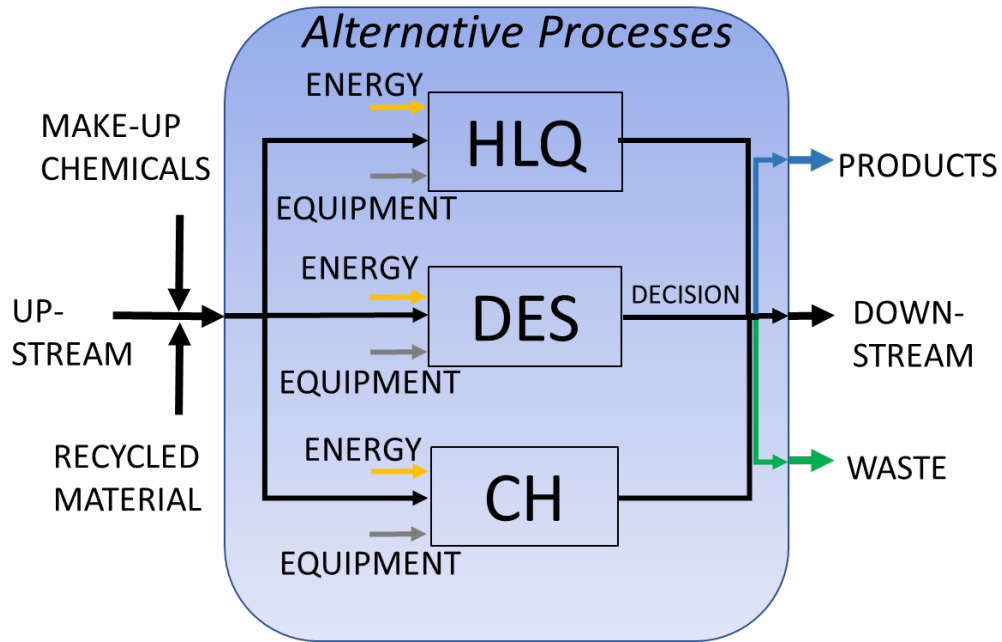


Fixing:  
 $NetPresentValue = f(LMP) = 0$

**Maximum Lignin Market Price**



# Mixed-Integer Non-Linear Programming



Mass balances:

- Input/Output, recycling, waste streams

Energy balances:

- Electricity, heat, cooling

Investment costs:

- Equipment costs (non-linear)

Operating costs:

- Energy, waste, chemicals

Treated lignin and product output:

- Derived from mass balances

Decisions:

- Only one option can be chosen (binary)

$$\text{Max}_{z^d, x^c, y} LMP = LMP(z^d, x^c, y)$$

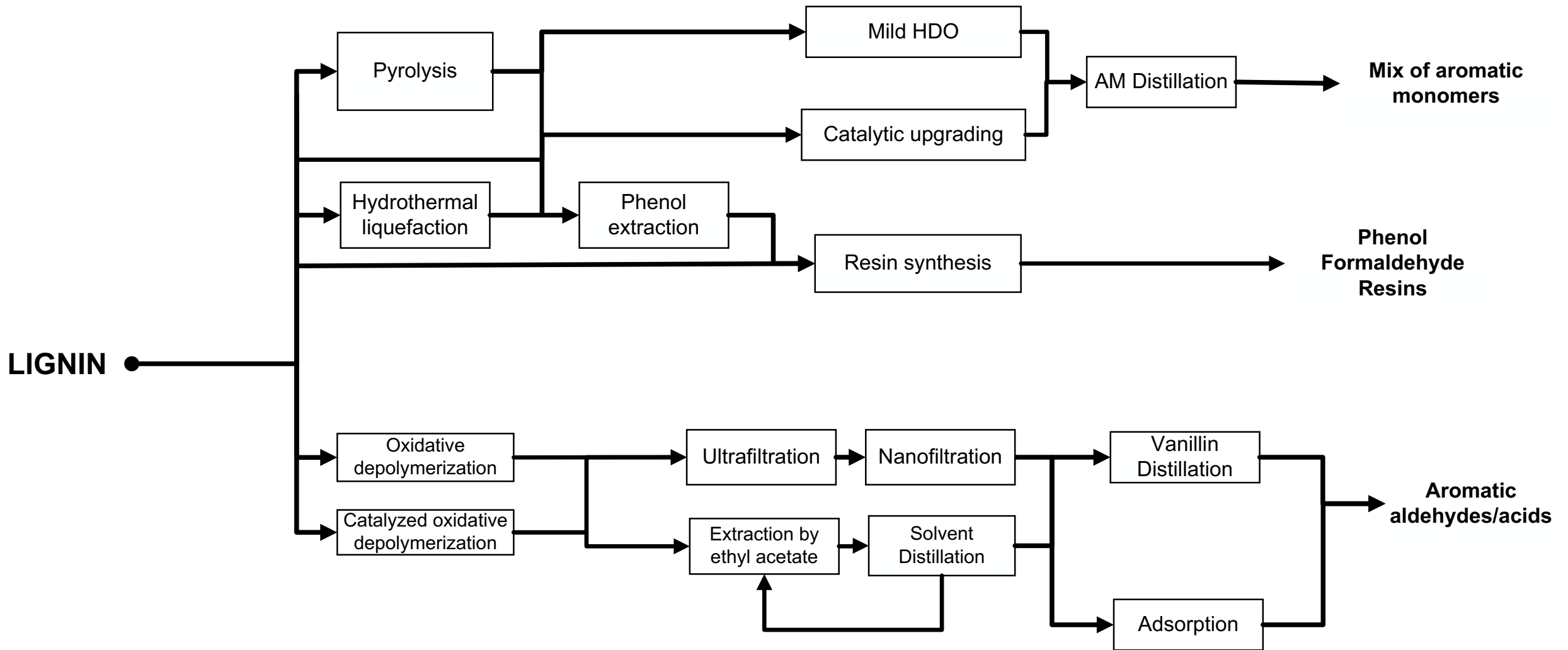
$$\text{NetPresentValue}(LMP) = 0$$

$$h(z^d, x^c) = 0$$

$$g(z^d, x^c, y) \leq 0$$

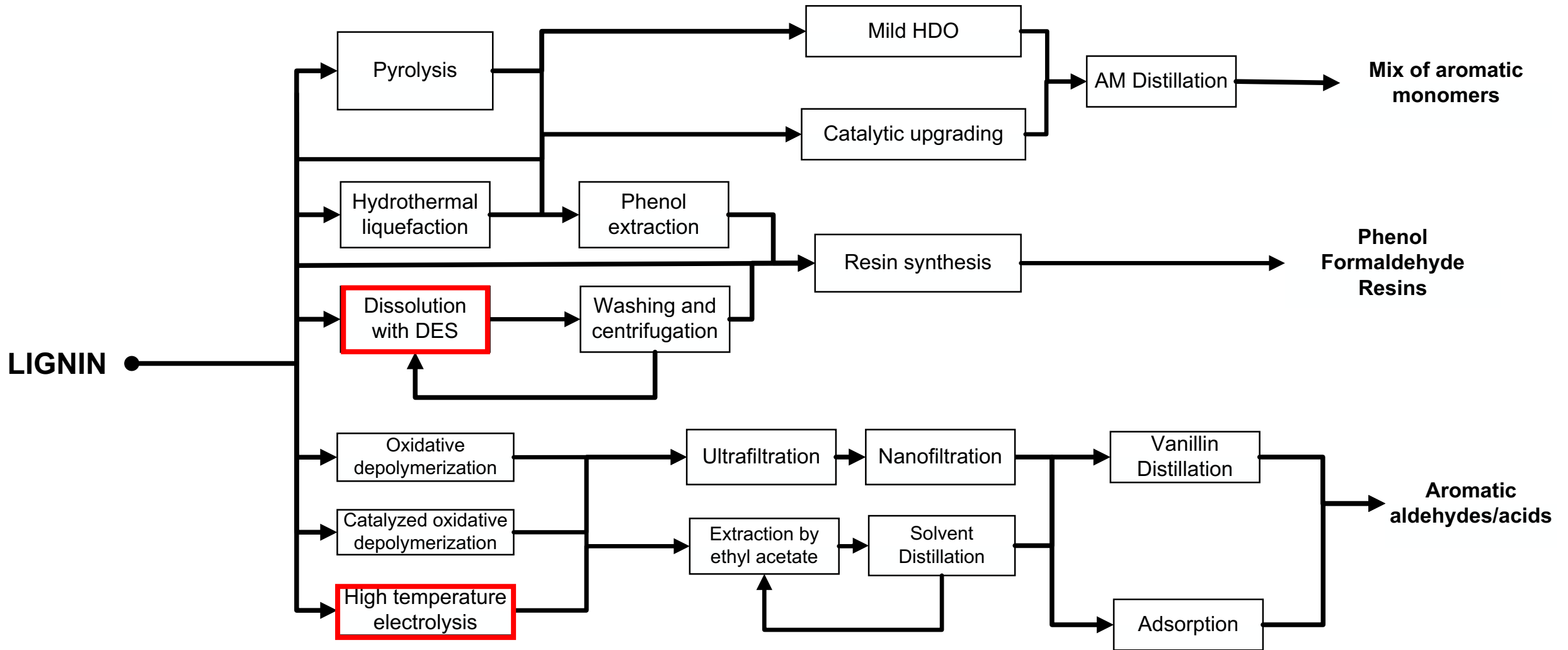
$$z^d, x^c \in X, y \in \{0, 1\}^m$$

# Process Superstructure



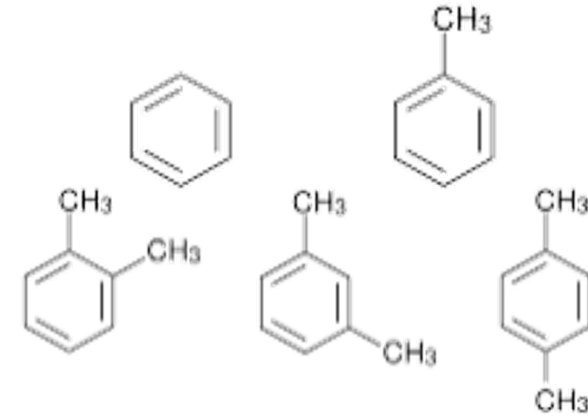
# Process Superstructure

Lab-scale processes

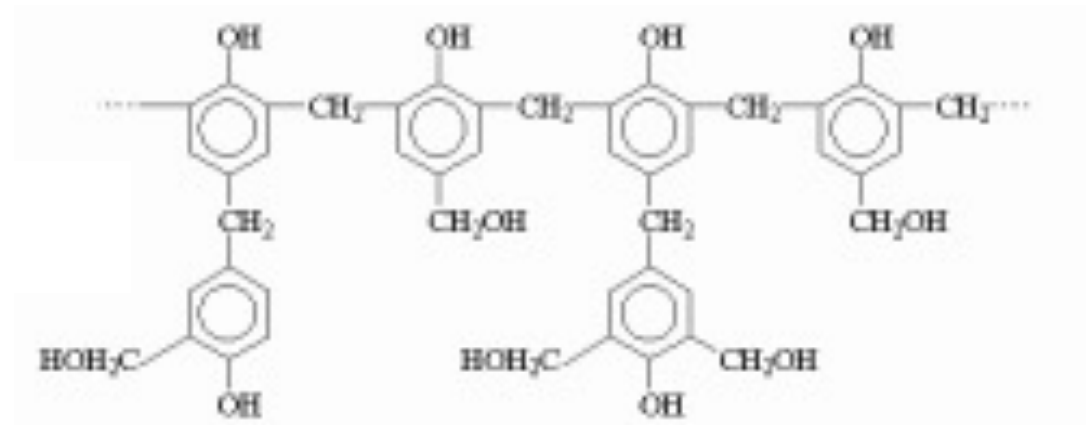


# Target products

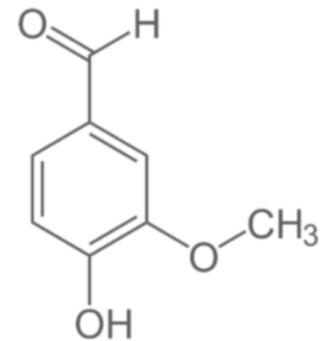
✓ **AM** - Aromatic Monomers (mixture of BTX, phenols,...)



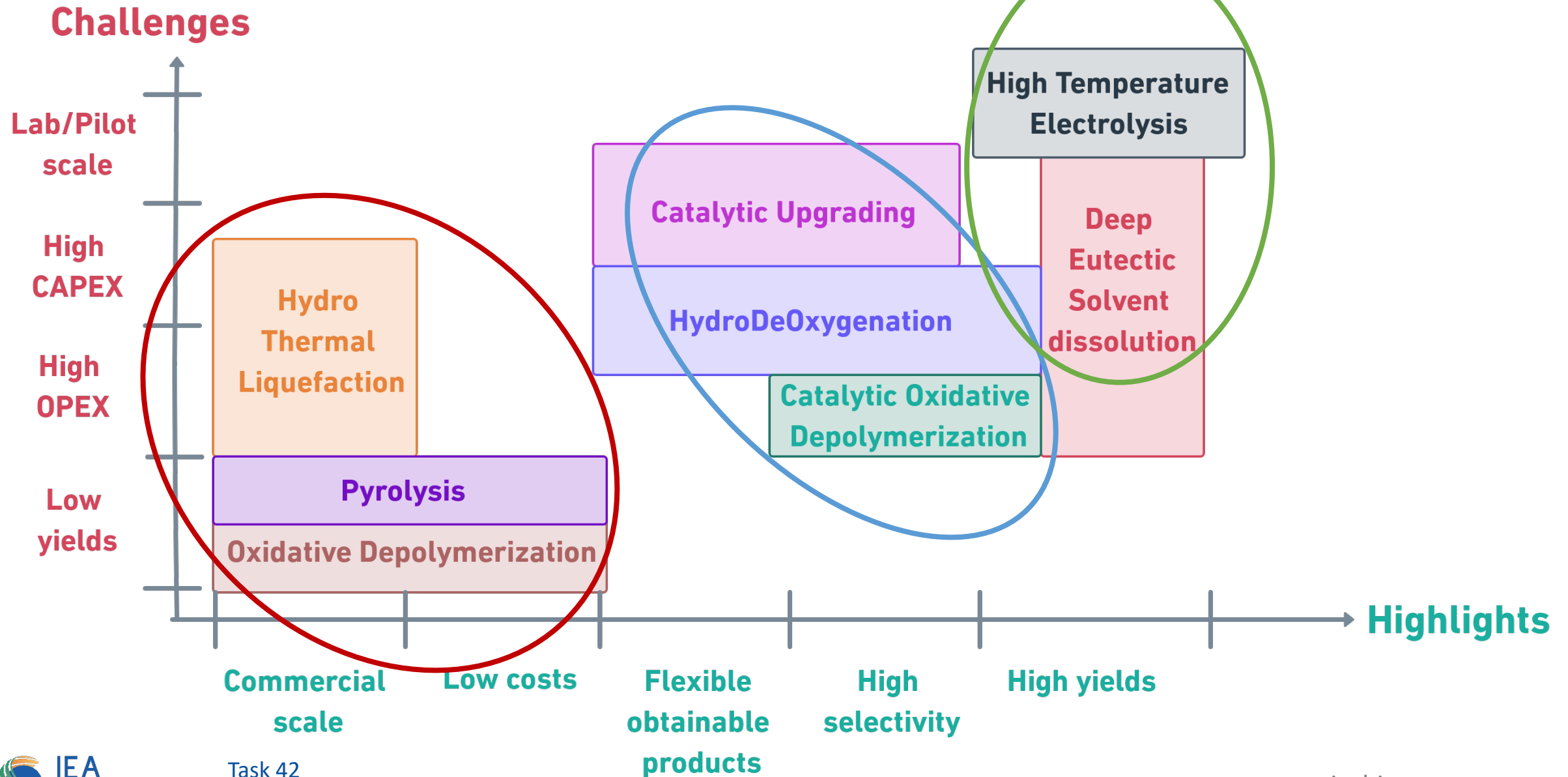
✓ **RES** - Phenol-Formaldehyde Resins



✓ **VAN** - Aromatic Aldehydes/Acids (mixture of Vanillin, Acetovanillone, Vanillic Acid,...)

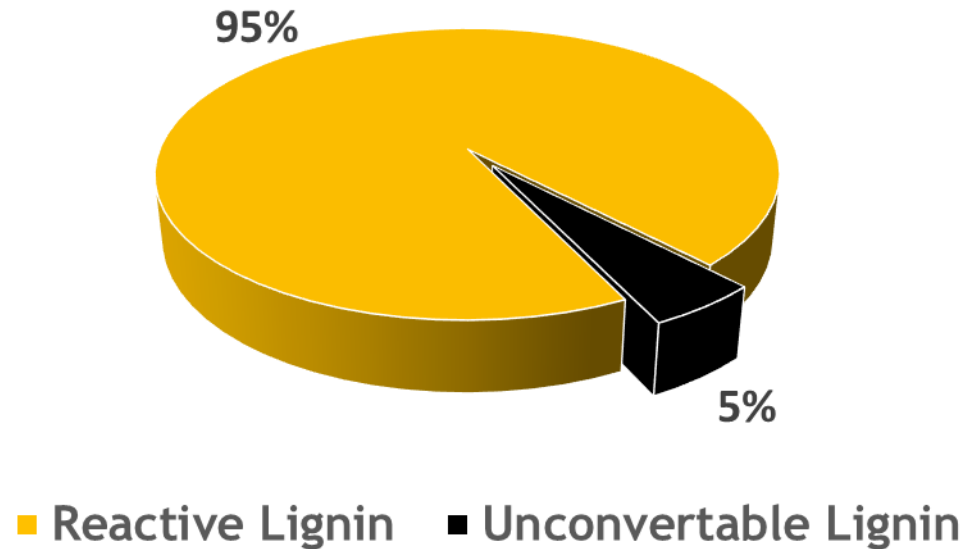


# Main lignin valorization processes



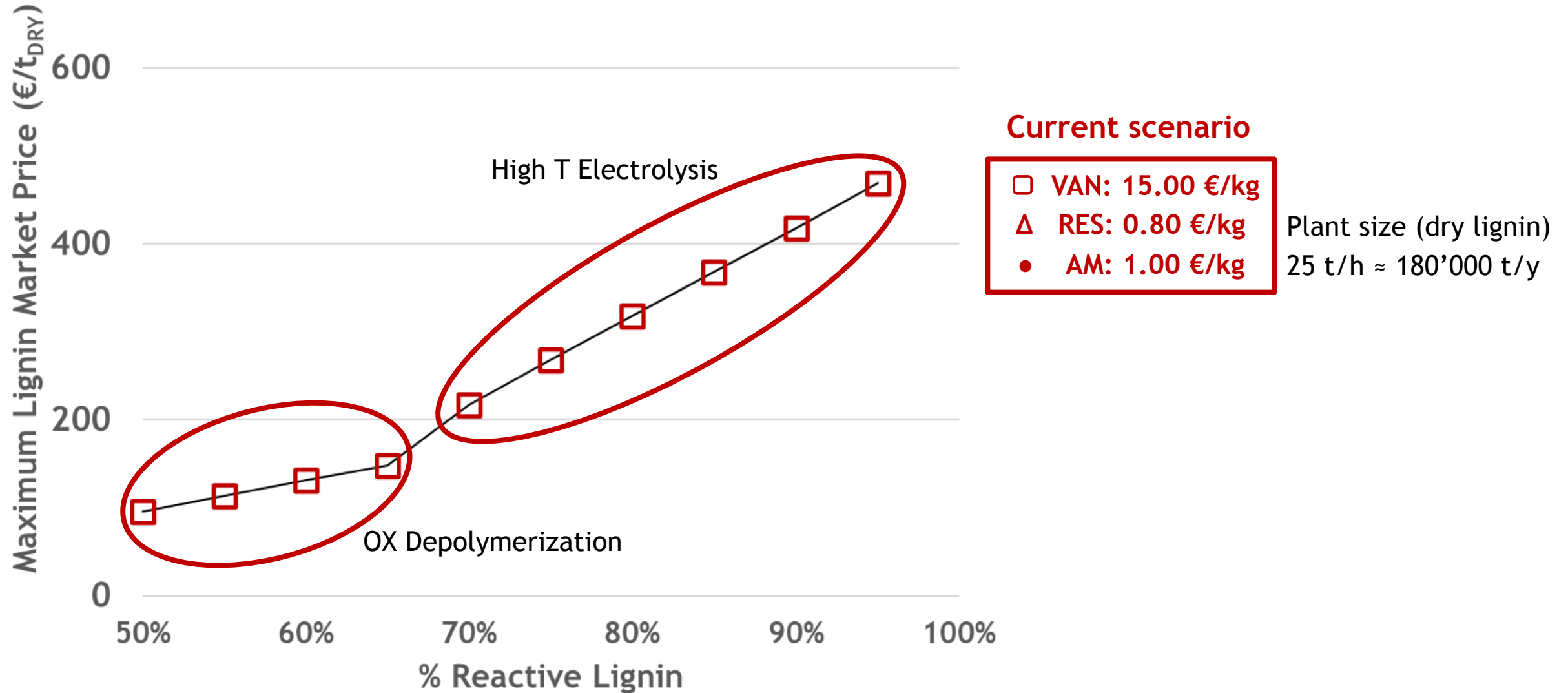
# 'Reactive' Lignin

- ✓ Lignin conversion and product yields depend on quantity of reactive/depolymerized lignin
- ✓ Composition (H/S/G), kind of bonds ( $\beta$ -o-4,  $\beta$ - $\beta$ ,...), impurities, Molecular Weight distribution are the main parameters to consider in order to estimate the fraction of lignin 'reactive' to convert in

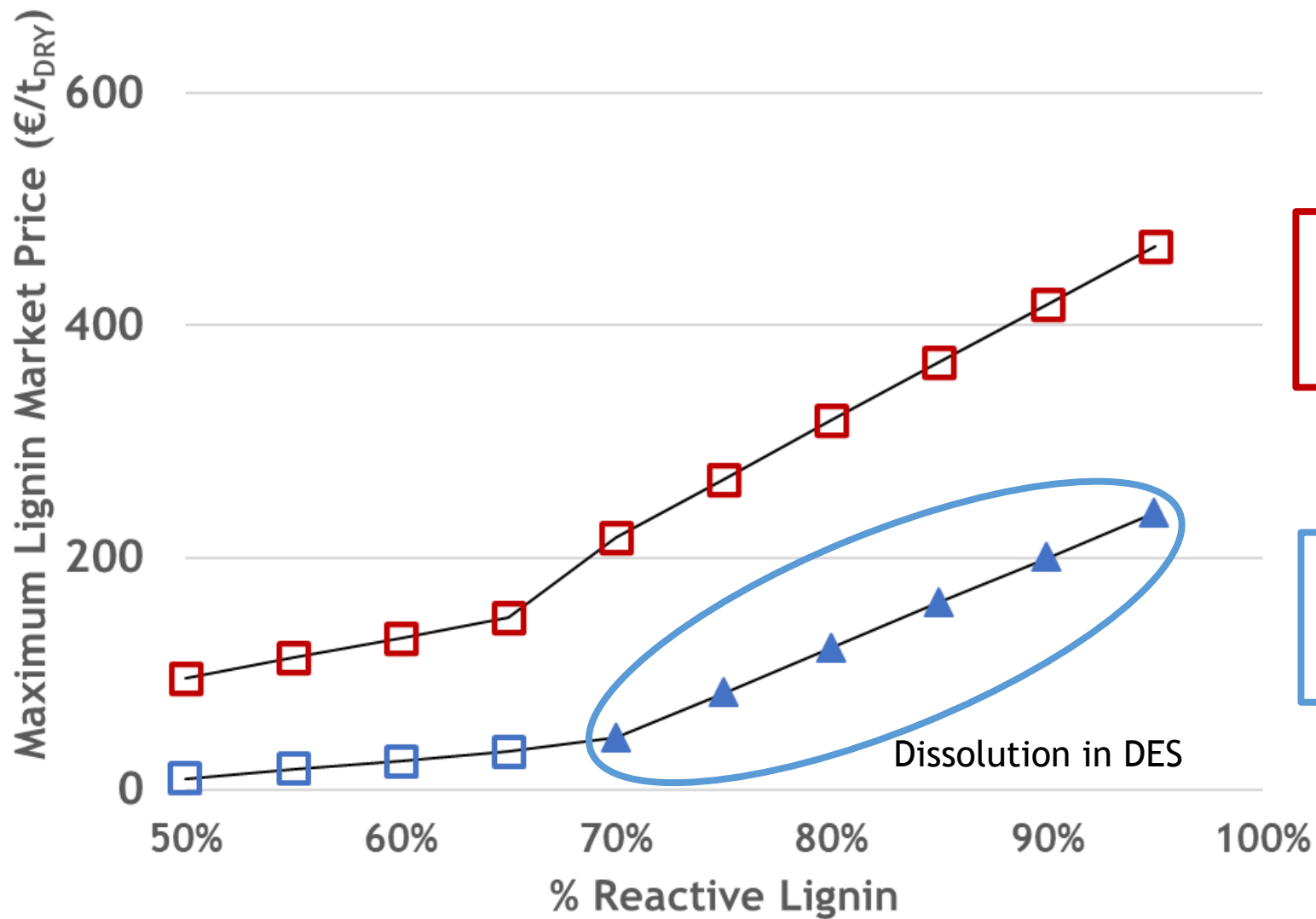


- ✓ A simplified model was built considering variable this fraction (from 50% to 95%)

# Maximum Lignin Market Price vs product selling price



# Maximum Lignin Market Price vs product selling price



## Current scenario

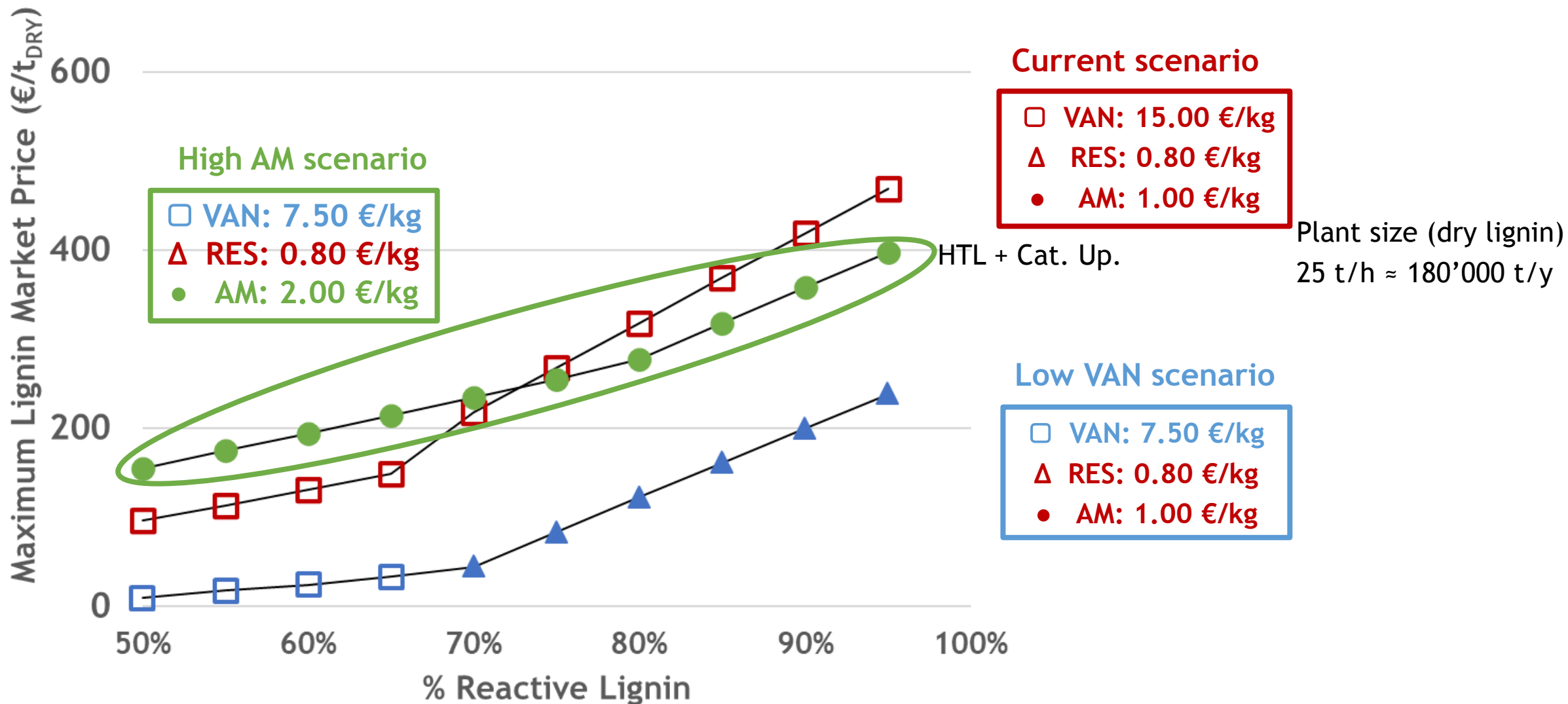
- VAN: 15.00 €/kg
- △ RES: 0.80 €/kg
- AM: 1.00 €/kg

Plant size (dry lignin)  
25 t/h ≈ 180'000 t/y

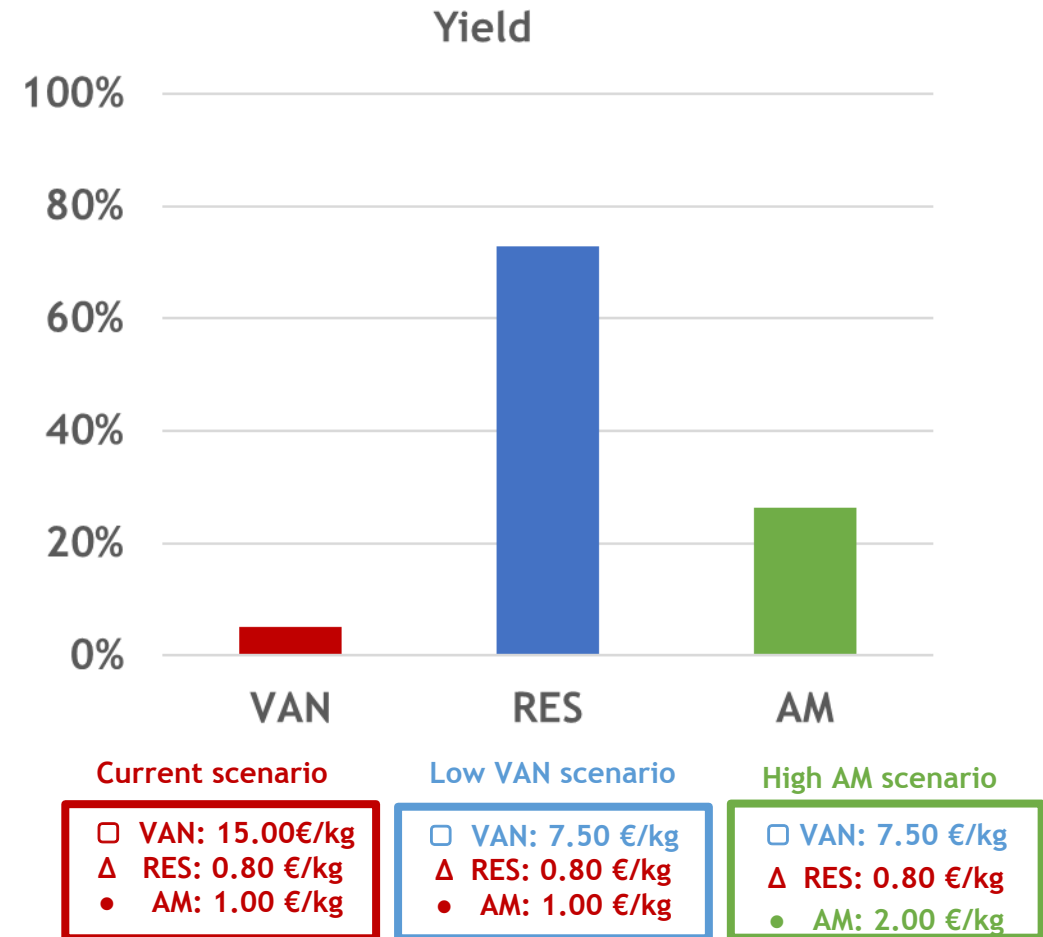
## Low VAN scenario

- VAN: 7.50 €/kg
- △ RES: 0.80 €/kg
- AM: 1.00 €/kg

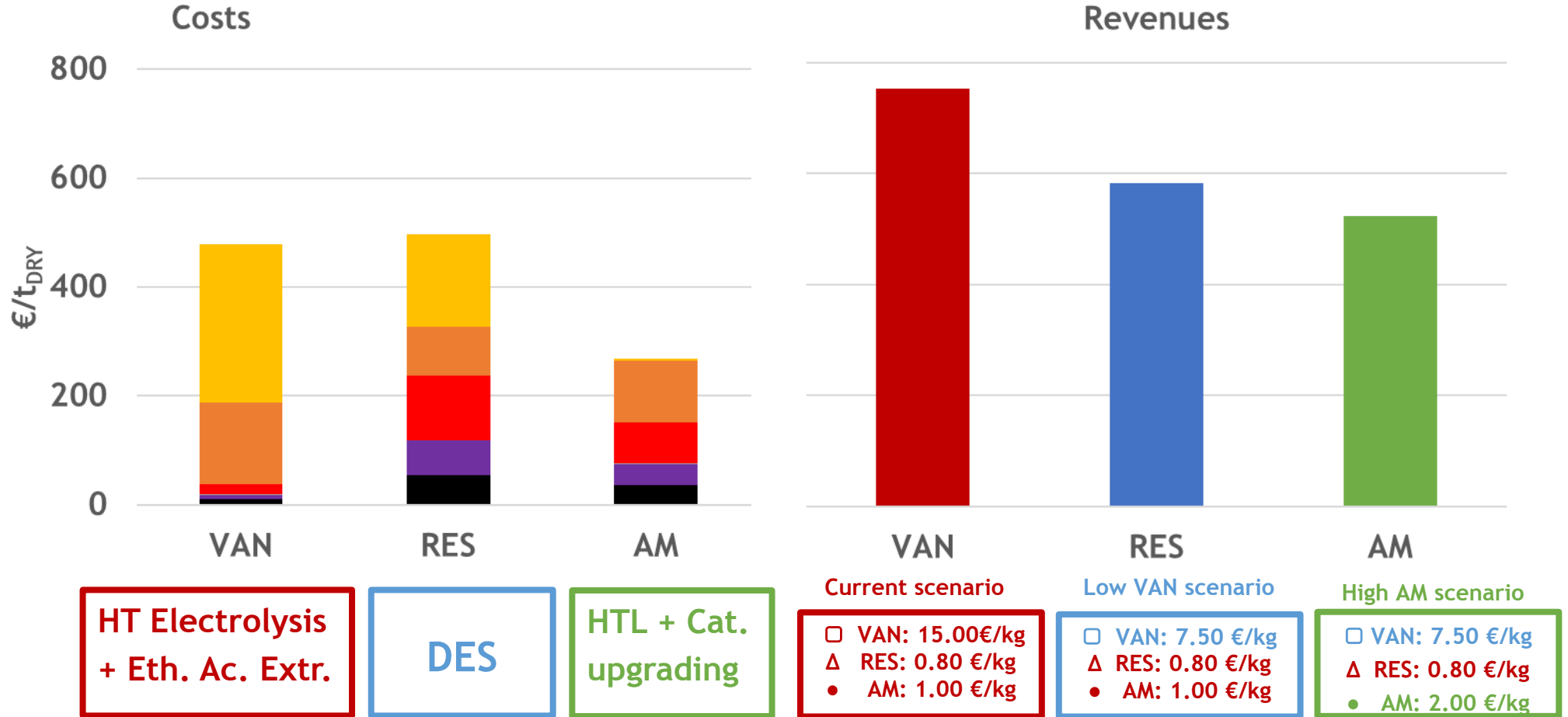
# Maximum Lignin Market Price vs product selling price



# Cost Analysis (75% 'reactive' lignin)



# Cost Analysis (75% “reactive lignin»)



# Limits

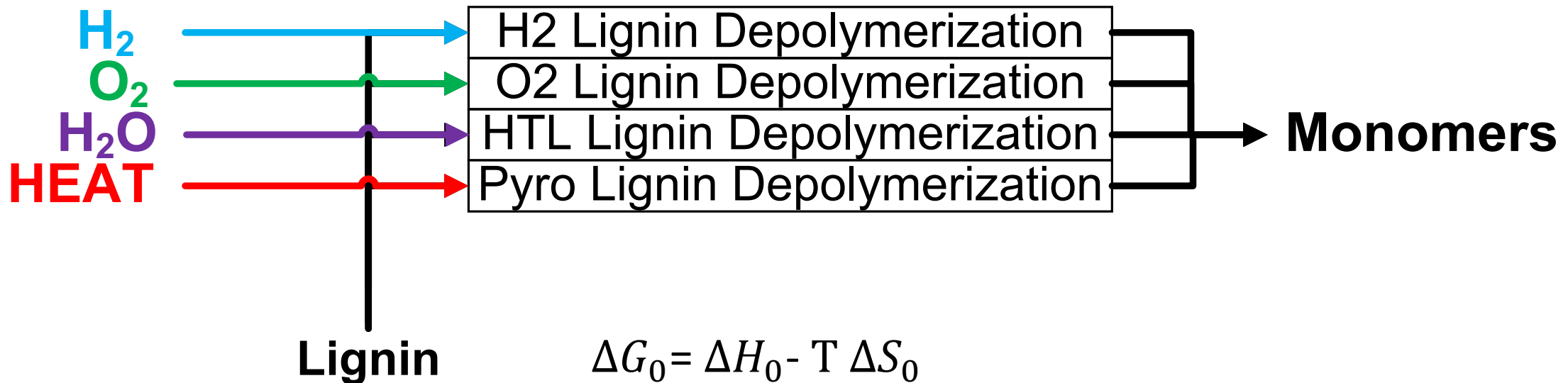
- ❑ The limit of the model lies in linking the lignin source (Kraft, Organosolv,...) and the considered values of “reactive lignin”
- ❑ The highlighted results, Maximum Lignin Market Prices, are lower than the current Lignin Market Prices of most technical lignins (which are higher only for products with high selling price scenarios and high “reactive lignin”)

# Opportunities

- ✓ Simple use of the results obtained with the model for an LCA analysis
- ✓ Individuate the process thresholds making a lignin substrate economically viable with respect to another kind of lignin, or with respect to different technical/market scenarios
- ✓ Provide lignin producers in pulp industries (e.g., as a side-product for energy generation) the best way to valorise it, while providing the biorefinery industries the best lignin to use/optimal purchase price

# Future perspectives

- ✓ Find a transfer function linking “reactive lignin” parameters and the lignin source/conversion process
- ✓ Improve the process Superstructure adding other products (e.g. phenols)
- ✓ Develop a rigorous depolymerization simulation model based on the thermodynamic analysis considering specific lignin characteristics (kind of bonds, monomers nature,...), obtaining a simulation of the lignin depolymerization behavior for different process conditions and reactants



$$\text{Min } \Delta G_0(\text{reaction}) = \Delta G_0(\text{products}) - \Delta G_0(\text{reactants})$$

Thanks to

- ✓ ENEA - Isabella De Bari, Silvio Mastrolitti, Elisabetta Borsella, Maria Teresa Petrone
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