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Conversion of lignin into chemicals with heterogeneous catalysis - Current and future technologies

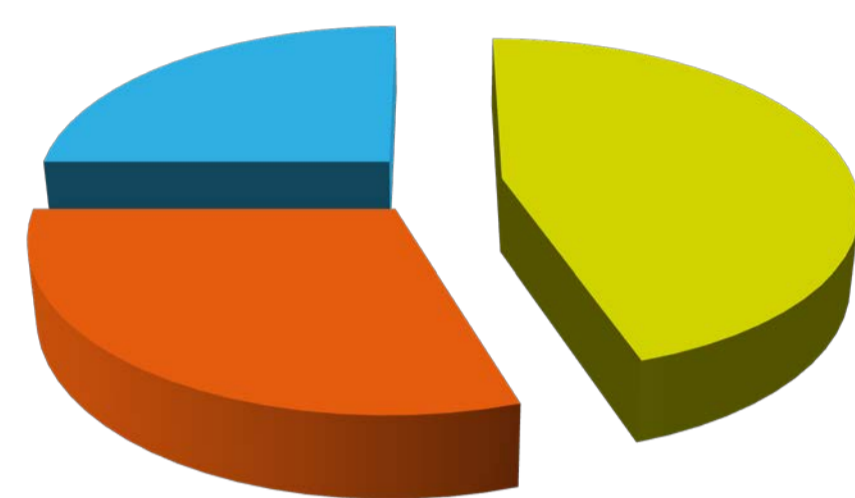
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Introduction

The research interests in biomass conversion to fuels and chemicals has increased significantly in the last decade in view of current problems such as global warming, high oil prices, food crisis and other geopolitical scenarios. Many different reactions and processes to convert biomass into high-value products and fuels have been proposed in the literature, giving special attention to the conversion of lignocellulosic biomass, which does not compete with food resources and is widely available as a low cost feedstock.

Lignocellulose biomass is a complex material composed of three main fractions:

- cellulose (40-50%),
- hemicellulose (25-35%)
- lignin (20-30%)



Lignin constitutes up to 30% of the weight and 40% of the heating value of lignocellulosic biomass. It is the most complex fraction and is harder to process compared to the sugar fractions. The complexity has led lignin to be treated as a waste stream, and typically burned to produce energy. However, lignin is a significant portion of the total carbon in biomass, and better use of this fraction is a requirement to improve the economic balance of any bio-refinery. For this reason, research on upgrading lignin has become of recent interest, as many interesting products, mainly aromatics, can potentially be produced from lignin. Here we present an overview conversion of lignin into chemicals with heterogeneous catalysis

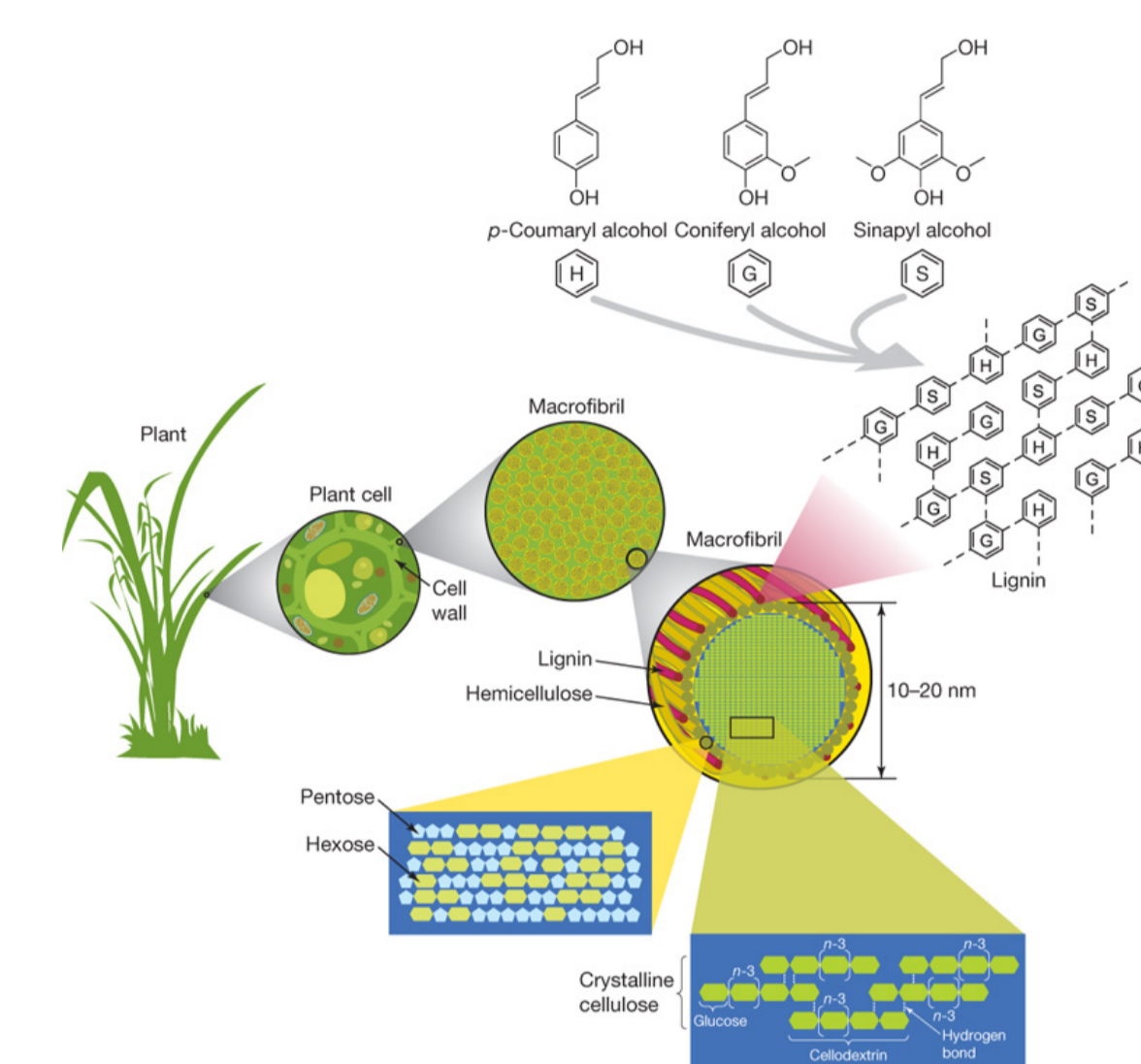


Fig. 1. View of the role of lignin, cellulose and hemicellulose in a typical plant.

Lignin structure

Lignin is a three-dimensional amorphous polymer consisting of methoxylated and phenylpropane moieties. The exact structure of the lignin found in plants is variable but the biosynthesis of lignin is thought to involve the polymerization of three monomers: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Despite the variability, lignins have different structural linkages in common with the β -O-4 linkages being the most dominants.

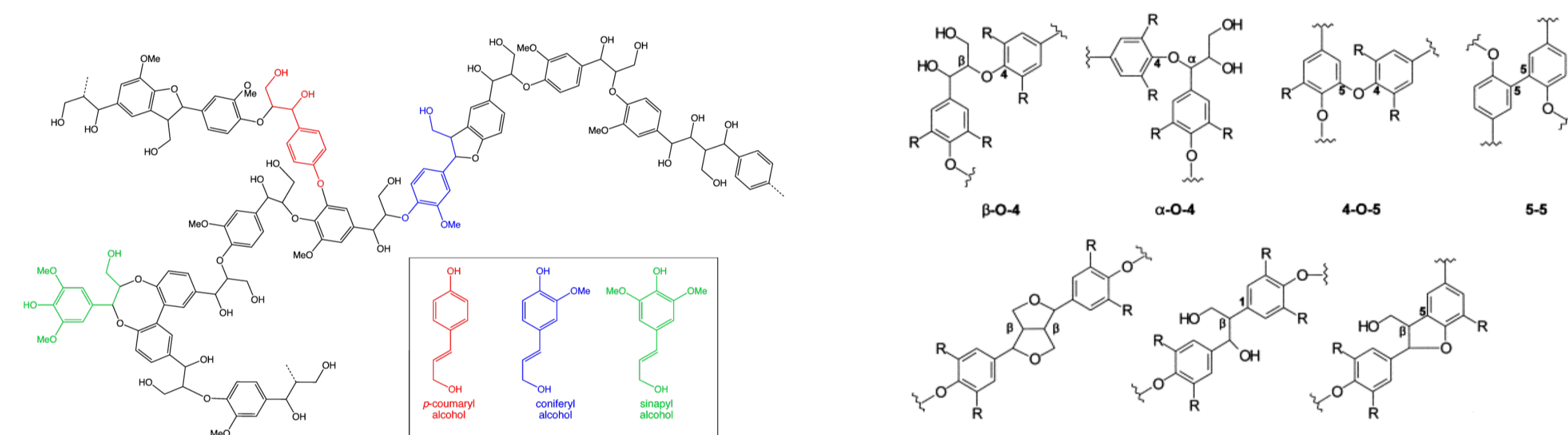


Fig. 2. Example of softwood lignin structure with the three monolignol monomers constituent

Fig. 3. Type of bonds in lignin

| Linkage type | Dimer structure | Softwood lignin Total linkages (%) | Hardwood lignin Total linkages (%) |
|-------------------|--------------------------------------|------------------------------------|------------------------------------|
| β -O-4 | Phenylpropane β -aryl ether | 45-50 | 60 |
| 5-5 | Biphenyl and dibenzodioxocin | 19-22 | 9 |
| β -5 | Phenylcoumaran | 9-12 | 6 |
| β -1 | 1,2-Diaryl propane | 7-9 | 7 |
| α -O-4 | Phenylpropane α -aryl ether | 6-8 | - |
| 4-O-5 | Diaryl ether | 4-7 | 6,5 |
| β - β | β - β -linked structures | 2-4 | 3 |

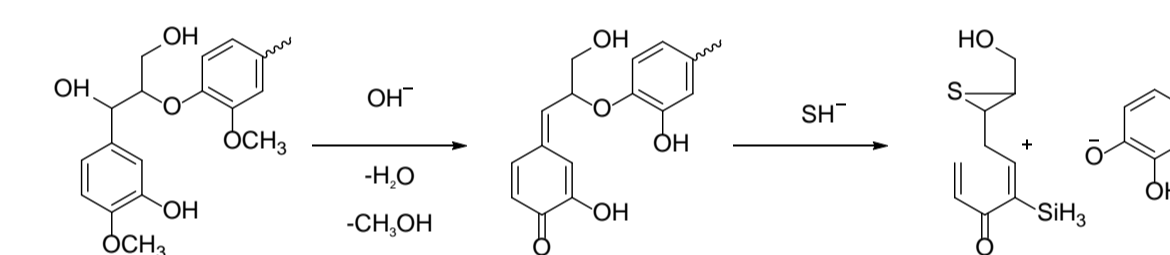
Pretreatment methods

Bergius process

Based on the liquefaction of coal to synthetic oil, where brown coal, also known as lignite, is converted into synthetic oil by hydroliquefaction in the presence of a catalyst, that included tungsten or molybdenum sulfides, tin or nickel oleate and others under high hydrogen pressure.

Kraft lignin process

Typical process in the production of paper. Pulping is caused by nucleophilic attack on electron-deficient conjugated and carbonyl structures, while bleaching is caused by electrophilic attack of electron-rich centers in aromatic nuclei and unsaturated, ring-conjugated side chain.

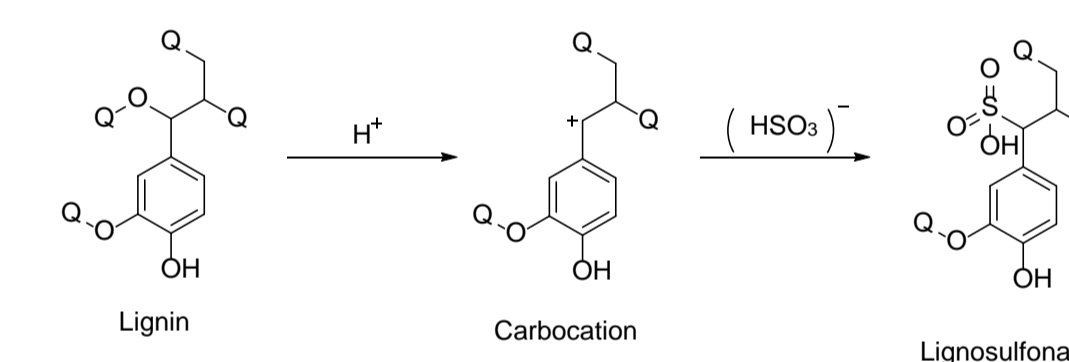


Pyrolysis

High temperature reaction performed in the absence of oxygen. It is a thermochemical decomposition of organic compounds, and might therefore be useful to break down lignin to low molecular weight compounds

Lignosulfonate process

The sulfite pulping treatment is also relatively common in the pulp and paper industry. Involves acidic cleavage of ether bonds, which connect many of the constituents of lignin. Carbocations produced during ether cleavage react with bisulfite ions (HSO_3^-) to give sulfonates.

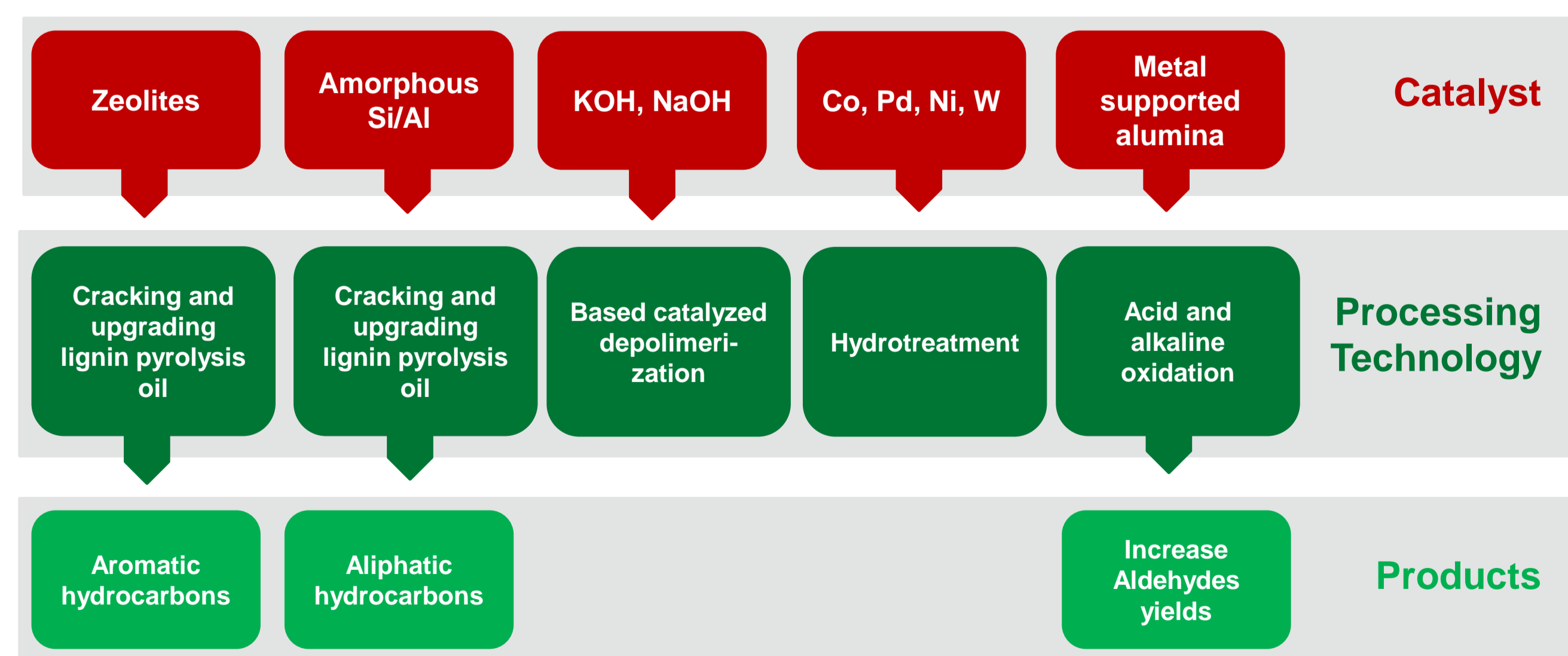


Organosolv process

Uses organic solvent mixture with inorganic acid catalysts (eg. HCl or H_2SO_4) to break the internal lignin and hemicellulose bonds. The solvents commonly used in the process are methanol, ethanol, acetone, ethylene glycol, triethylene glycol, and tetrahydrofurfuryl alcohol

Catalysts in lignin conversion

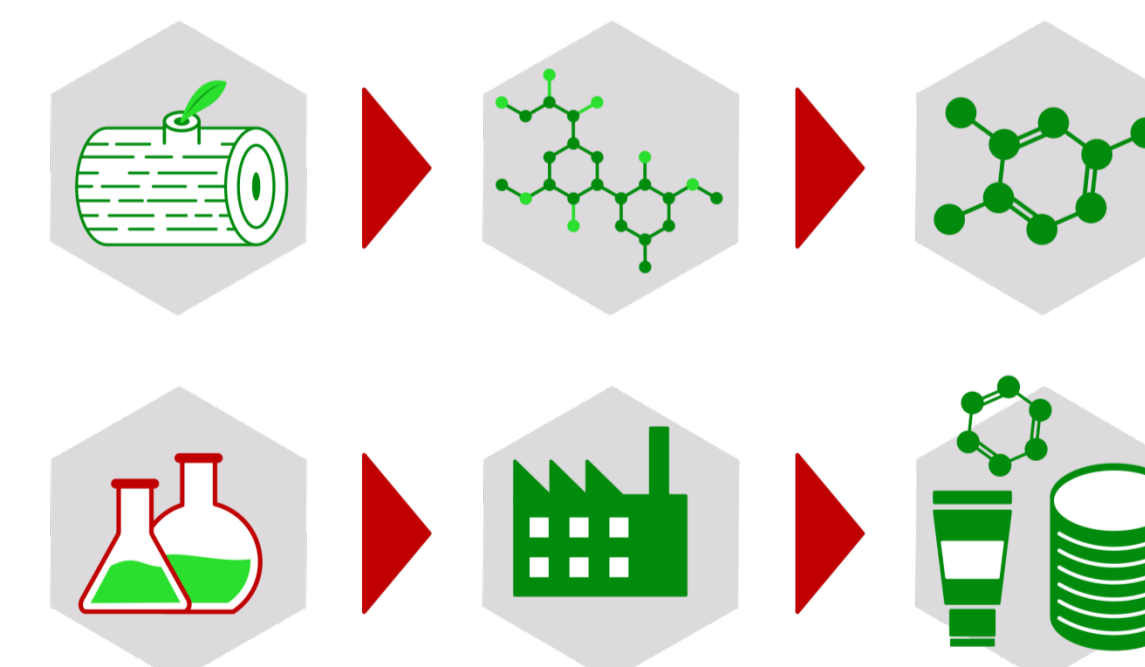
Catalysis has been considered an important technology in biomass and lignin conversion. Catalysts usually are required to assist selective bond cleavage, leading to high selectivity values for a particular compound in the product stream. Various catalysts have been tested for different processes and substrates including both model compounds and lignin extracts



Future of lignin utilization

Lignin valorization constitutes an important component of the modern biorefinery scheme, and the structure and composition of lignin offer unique routes to produce several fine and bulk chemicals. Macromolecular lignin is utilized as raw materials in many industrial processes as a substitute for phenol in phenol-formaldehyde resins and fillers in polymers, carbon fibers, binders, polyurethane foams, epoxy resins and biodispersants.

However, the most prominent lignin utilization so far appears to be its depolymerization into lower molecular weight compound. Considerable effort has already been devoted to developing a wide variety of catalytic routes specifically for lignin oxidation and reduction.



Lignin is the only viable source to produce the renewable aromatic compounds

It is necessary to further develop catalytic processes to allow transformation of lignin from a low quality, low-price waste product into a high-quality, high-value feedstock for bulk and specialty chemicals by the development of the appropriate catalytic technology.

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