

Mechanistic insights of hydrogenative lignin depolymerization reactions

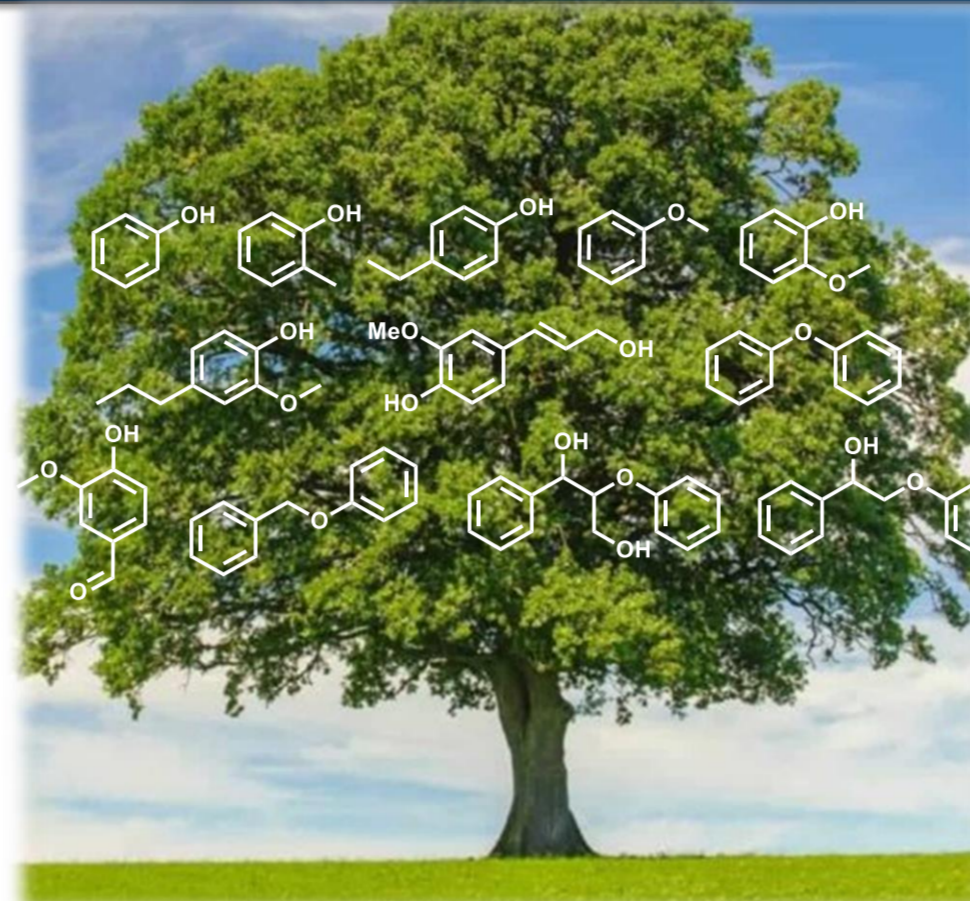
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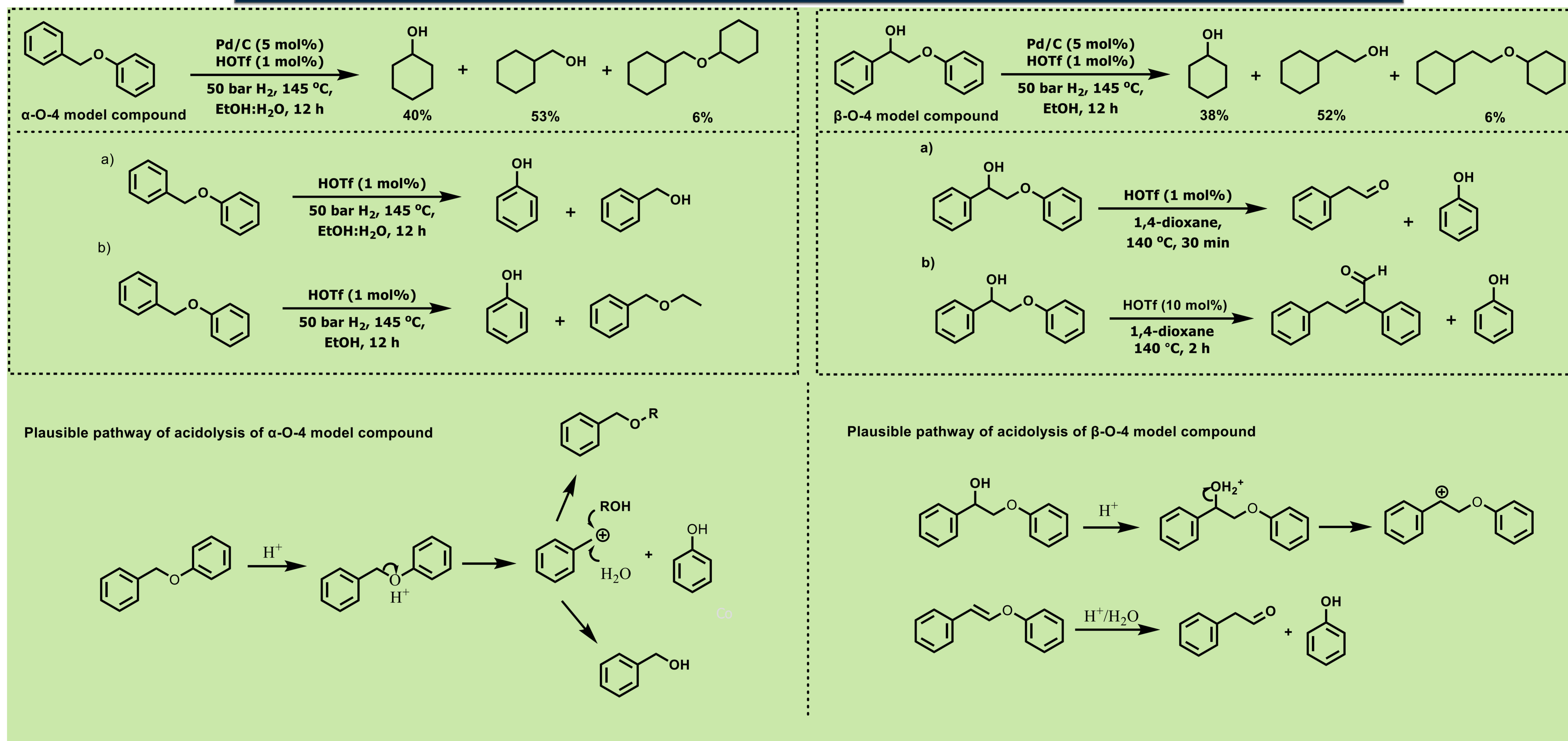
Lignin is an aromatic polymer having complex structure formed from interlinkages between methoxylated alkyl-phenol units. More specifically, lignin contains a variety of linkages interconnected by carbon-carbon (C-C) and ether (C-O) bonds such as β -O-4-aryl linkage (45–60%), α -O-4 (6–8%), 4-O-5 (4–9%), β -1 (7–9%), and 5–5 (3–27%)¹. Lignin provides mechanical rigidity and strength to the plant tissues and might be used as a renewable and abundant source for value-added chemicals in the future. In general, it covers up to 30 % of lignocellulosic biomass, and its content differs according to type of plants². Due to the complexity of lignin, model compounds are widely used to attain a better understanding of lignin chemistry.

Introduction



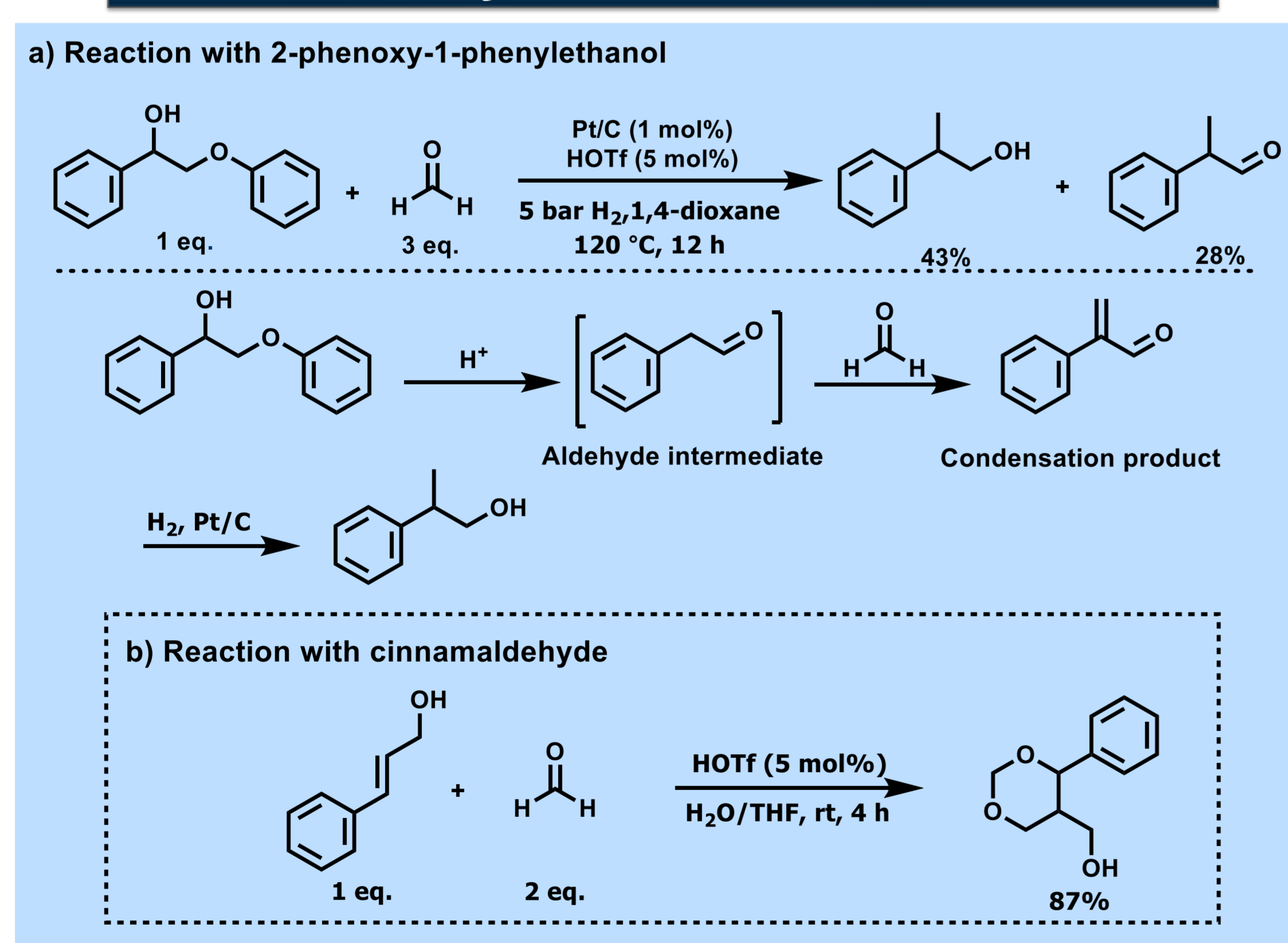
Acidolysis along with stabilization of reactive functional groups is one of the most significant tools for monomer yield augmentation in lignin depolymerization³. We performed palladium catalyzed hydrogenation of α -O-4 and β -O-4 model compounds in the presence of catalytic amounts of triflic acid. Reactive intermediates (benzylic carbocation intermediates) which can lead to condensation reactions have been identified. To prevent unwanted oligo- and polymerizations of reactive intermediates, methanol is introduced as so-called capping agent. Moreover, the role of formaldehyde which is released from the α -carbon of the alkyl side chains in lignin is examined.

Acid catalyzed hydrogenative cleavage of α -O-4 and β -O-4 model compounds

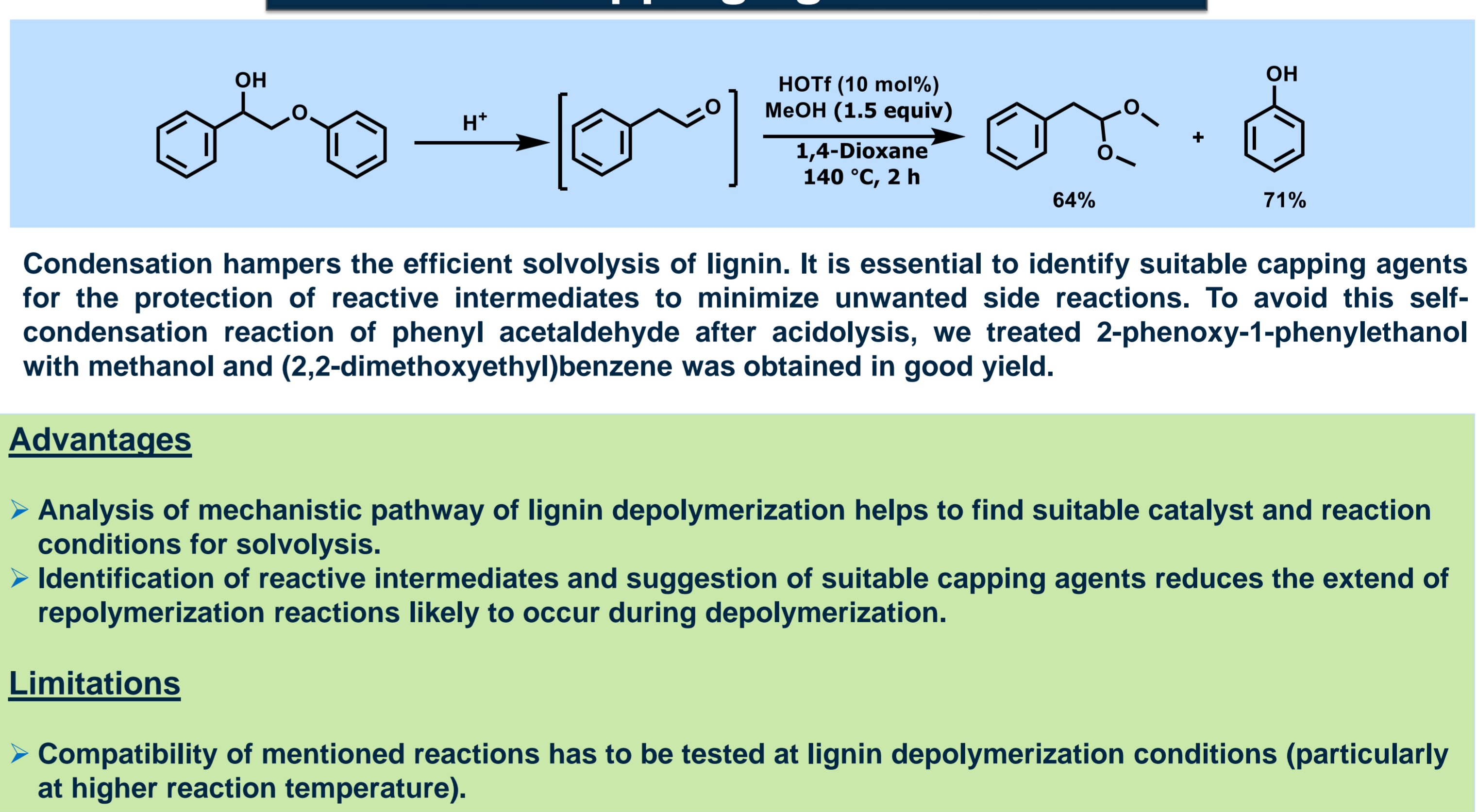


During acidolysis of benzyl phenyl ether, after the protonation by triflic acid, phenol and a primary benzylic carbocation are formed. This carbocation reacts with water to give respective benzyl alcohol product in the presence of water. In case of alcoholic solvents (EtOH) benzyl ethyl ether is formed. Similarly, acidolysis of 2-phenoxy-1-phenylethanol starts with the protonation as well as dehydration of the α -OH, readily forming a benzylic carbocation, which subsequently undergoes productive C-O cleavage aided by rehydration to form phenylacetaldehyde and phenol. Acidolysis of both β -O-4 and α -O-4 linkages, leads to the formation of benzylic carbocation intermediates, which react with electron-rich lignin aromatic rings and result in the further condensation of lignin to form higher molecular weight products.

Formaldehyde mediated reactions



Capping agents



Summary

Identification and stabilization of reactive functional groups during solvolysis is a tool to improve lignin depolymerization reactions. Mechanistic investigations explain possible side reactions in lignin solvolysis processes. Active functional groups and potential reactive intermediates which undergo condensation reactions were identified. Alcohols were successfully used as capping agents to avoid such unwanted side reactions.

References

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