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Oxidative Cleavage of C-C Single/Double Bond by H₂O₂ and V₂O₅ in Cinnamic acids and Lignin for Selective Synthesis of various aromatic compounds

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PURPOSE OF THE ABSTRACT

Selective oxidative cleavage of carbon-carbon double bonds is a synthetically important reaction to introduce oxygen functionality into molecules or to degrade complex compounds, especially those from natural sources and biomass, i.e. oils, terpenes, cinnamic acids. It is important for the preparation aromatic compounds from lignin as a sustainable alternative to conventional crude oil-based methods.¹ It is also a very fundamental reaction in industrial organic synthesis and in valorisation of biomass i.e. oils, terpenes.²

Vanillin is a commonly used aromatic compound for flavouring and is also used as a fragrance and food preservative.³ The only commercial source of natural vanillin is the pods of the Vanilla orchid. More than 12 000 tons of vanillin are produced each year, but only 1% of this is natural vanillin from the pods of the Vanilla orchid.. Nowadays, the conversion of lignin into vanillin represents a very attractive field of research. The main natural sources for vanillin are lignin and ferulic acid. Lignin is the second most abundant polymer on Earth and an only naturally available aromatic heterogeneous compound with a highly complex three-dimensional cross-linked network structure.⁴ The main source of lignin are paper and bioethanol industries. The pulp and paper industry produces 50-70 million tonnes of lignin annually, and the bioethanol industry is estimated to increase its production to 225 million tonnes per year by 2030.⁵ Softwood Kraft lignin represents the best source because it accounts for over 90% of the lignin extracted worldwide and because the coniferyl alcohol predominate in it. Lignin can be converted to ferulic acid by alkaline or enzymatic hydrolysis, while ferulic acid is also found in the lignocellulosic biomass in the cell walls of plants, grasses, grains, vegetables, flowers, fruits, leaves, seeds, nuts.⁶

Selective oxidative cleavage of unsaturated bonds such as carbon-carbon double bonds is a synthetically important reaction to introduce oxygen functionality into molecules or to degrade complex compounds, especially those from natural sources and biomass. A classical ozonolysis was followed by development of various catalytic methods with different oxidants.⁷ The most appropriate oxidants would be oxygen and hydrogen peroxide, however this area C=C and C-C oxidative cleavage reactions is still underexplored.

We will present our research on the catalytic oxidative depolymerization of Kraft lignin with hydrogen peroxide catalyzed by vanadium(V) oxide to different high value chemicals. Depending on the type of biomass and the chemical composition of lignin, various products can be obtained including cost effective method for lignin to vanillin conversion. The method is simple and cost-effective for the oxidative cleavage of the C-C double bond in cinnamic acid derivatives, where the choice of solvent determines the selectivity towards benzaldehydes, benzoic acids, and benzoquinones. The selectivity and efficiency of the process was demonstrated on ferulic acid to vanillin conversion. The green metric was used to evaluate the conversion of ferulic acid to vanillin with other similar methods.

FIGURES

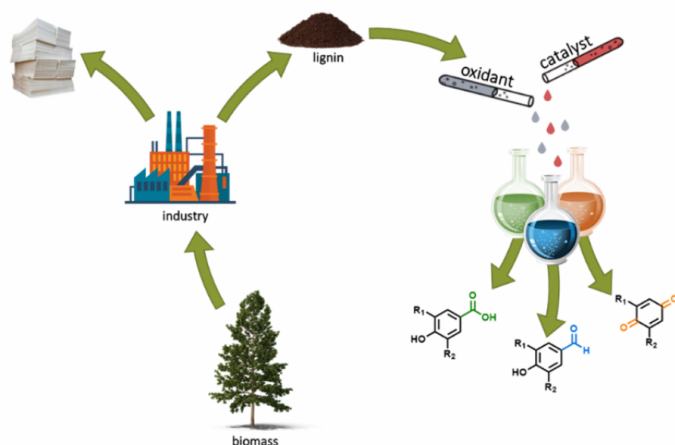


FIGURE 1

Figure 1

From lignocellulosic biomass to various aromatic molecules by oxidative depolymerization of lignin by H₂O₂

FIGURE 2

KEYWORDS

lignin depolymerization | oxidative cleavage | cinnamic acids | hydrogen peroxide

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