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Feature Article

Oxidative upgrade of lignin – Recent routes reviewed

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ABSTRACT

Lignin is the second most abundant natural polymer. Its use and targeted functionalisation within biomass refinery processes, however, still needs to be further explored and developed. The oxidative functionalisation, and thus valorisation of lignin, is a very promising way to go, since it holds the possibilities to yield highly functionalised, monomeric or oligomeric products that can serve as starting materials for other valorisation processes in the chemical and pharmaceutical industries. Gaining a profound knowledge about the structure of lignin, being able to analyse structural features, and understanding the mechanisms that guide the reactions leading to the oxidative derivatisation, depolymerisation and functionalisation of lignin samples from different renewable sources are key requirements for developing successful valorisation protocols for lignin. In this review, we wish to revisit, and set into context, some important achievements in the field of oxidatively upgrading lignin. We will focus on organometal catalyses (MTO, salen complexes, POMs), biomimetic catalyses (porphyrins), and enzymatic catalyses (laccase, peroxidase) for upgrading lignin and lignin model compounds. Details of mechanistic implications and means of potential manipulations of reaction outcomes are discussed.

Contents

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1. Introduction

The development and exploitation of renewable, non-fossil-based resources has become increasingly important, since the use of fossil-based resources is no longer justifiable for practical, ecological, and socio-economic reasons. Many technologies have been developed and successfully implemented in order to end fossil-dependent energy production; many of these technologies are based on the use of biomass [1,2]. Biomass represents a readily available and renewable, and thus versatile alternative resource, and research focused on exploring the possibilities to exploit this resource is gaining momentum in light of the dwindling of our fossil-based resources. Fuels obtained from biomass-refinery processes are already replacing fossil-based fuels in everyday life; the use of biomass components and derivatives thereof, as substrates for the chemical industry that produces higher value applications, ranging from building materials to pharmaceutical applications, is, however, still in fledging stages [3].

Forest biomass comprises a rather complex mixture of carbohydrates, aromatics, lipids, proteins, and a wide range of smaller molecules such as vitamins, colourants and odorants. New mechanical and chemical processes are needed to obtain analytically pure and defined substances out of – or from – this mixture [4], allowing the use of these substances to be used in downstream industrial chemical transformations. Ideally, the biomass-derived substances should be readily usable in already established chemical processes that utilise other, already commercially available substances for further derivatisation [5]. Today, biorefinery processes aiming at the valorisation of the lignocellulosic part of the biomass, which consists of cellulose, lignin, and hemicellulose, produce, in analogy to petroleum refinery processes, several products including fuel for energy production, and chemicals [1–4]. From the viewpoint that an economically viable biorefinery program comprises the use of all components of the biomass in parallel processes that aim at the production of both, fuels and fine chemicals [6], the lignin component is currently still under-utilised [7].

Lignin, that is currently mostly obtained as "waste" in paper and biofuel productions, but that could also be isolated by more tailor-made processes with respect to the specificities of further transformations within the biorefinery cascades [3,8], is the second-most abundant renewable polymer: it contributes as much as 30% of the weight, and as much as 40% of the energy content of lignocellulosic biomass [9]. Lignocellulosic biorefinery thus receives enormous amounts of lignin, and the development of truly sustainable and efficient biorefinery processes should aim at the valorisation of lignin not only as energy, but also as a resource for starting materials for the chemical industries [10,11]. Noteworthy, lignin represents the only renewable source of aromatic fine chemicals [12–14], and direct and efficient conversion of lignin to discrete molecules or classes of lower-molecular weight aromatic, monomeric building blocks for polymer productions is a very interesting future opportunity. The controlled breaking of carbon–carbon and carbon–oxygen bonds in lignin represents a very selective depolymerisation that could produce a whole series of monomeric, aromatic species [14]. Technologies that rely on selective bond cleavages in lignin also have the potential to yield new types of building blocks for block-polymers [4,7]. Selective modifications of the polymer lignin itself are suitable to transform it into a structural base for complex co-polymers with various potential applications [15]. In the medicinal and pharmaceutical areas, potential applications of lignin-derived substances could comprise the use as building blocks for the fabrication of microcapsules, or the exploition of the antioxidant features of the polyphenolic structural features of lignin [16]. Existing and potential applications of lignin are summarised in Fig. 1.

Several reviews have been written to cover and present research on lignin, and on processes aiming at its valorisation [1,2,7,8]. The methods used for the valorisation of lignin range from classical chemical approaches such as pyrolysis (thermolysis) [17–20], hydrolysis [21,22], reduction (hydrogenolysis) [23–25], or oxidation [26,27], to newer biotechnological approaches [22]. In this review, we wish to focus on methods and technologies aiming at the oxidative upgrade of lignin *via* radical pathways, since the native structure of lignin comprises several distinct functional groups that can – in principle – be selectively further functionalised *via* oxidation [28]. After briefly revisiting the most important structural features of lignin, the most important methods to isolate lignin, and the tools used characterise lignin and the products obtained upon (oxidative) functionalisation, we will summarise important work in the field of