Titanium mediated lignin oxidation and its application in catalytic epoxidation

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Titanium mediated lignin oxidation and its application in catalytic epoxidation

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op dinsdag 1 juni 2021 om 16:00 uur

door

Mónica Raquel Caseiro Fernandes

geboren te Peso da Régua, Portugal

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“All events, all experiences, have as their purpose the creating of opportunity.
Events and experiences are Opportunities.
Nothing more, nothing less.”

Neale Donald Walsch

To my grandparents Ilda and Alberto

Aos meus avós Ilda e Alberto

Titanium mediated lignin oxidation and its application in catalytic epoxidation

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Chapter 1

Introduction and Scope

The industrial revolution in the 19th century changed the world and pressed technology forward, creating new habits, generating new materials, and increasing mankind's dependence on machinery [1]. During the last two decades, Earth's fossil resources have become the precursors of fuels that power transportation and devices and of chemicals from which many consumer products are made. These developments also led to the information age when mankind gained a conscience of the harmful effects of its actions on the environment [2]. It has been realized in the last decades that the ozone layer was being depleted, the environment was impacted by acid rain and that, most worryingly, the increase of large amounts of carbon dioxide in the atmosphere due to combustion of fossil fuels is leading to climate change with unpredictable outcomes with respect to the environment and the quality of life [3–5]. Technologies that replace the fossil resources by renewable ones are being prioritized, preferred, and established [6].

Among renewable energy sources, tapping into the energy delivered by the sun via wind or solar remains the most promising option [7]. Implementing such renewable resources at the short term is not realistic given the scale of the various sectors that depend on fossil fuels. Biomass from living and dead plants is currently increasingly used as a renewable source of energy and fuels and this option is expected to contribute increasingly to a mix of renewable energy options in the coming decades during the energy transition [7–10]. An advantage of biomass is that it can also serve as a source of renewable carbon from which chemicals can be obtained to replace fossil-derived bulk chemical building blocks for the products that are used nowadays [11].

Efficient and clean utilization of biomass requires the development of separation/extraction and conversion processes that make use of all the components contained in lignocellulosic biomass. In the past decades, many were the publications addressing this pertinent challenge [11,12]. A basic approach is to transform selectively the highly functionalized sugars and lignin-derived chemicals into aliphatic fuels, platform molecules and aromatics that are similar or behave similarly to the intermediates and fuels currently produced from fossil fuels [13–16]. Biorefineries are the facilities that will process biomass as a feedstock and transform it into value-added products. Fast-growing crops, urban waste, and forest residues are abundant and carbon-neutral bioresources.

From wood-based biomass, three main components can be extracted: cellulose, hemicellulose, and lignin. The sugars produced from (hemi)cellulose can be transformed into bioethanol by well-established processes, which are also scalable [12,17,18]. On the other hand, the transformation and industrial use of lignin for other purposes that energy recovery is still far from its promised potential [19]. Traditionally, lignin is considered a waste or a low-value by-product. In 2015, approximately 100 million tonnes of lignin were produced worldwide and valued at USD 732.7 million [12]. The pulp and paper industry was initially the sole producer of lignin, which still holds the majority of its annual production of about 50 - 70 tonnes of lignin isolated world-wide [8,12,20]. With the implementation of cellulosic biorefineries, another supplier entered the scene, i.e., extracting lignin as a by-product of biofuel production. The main application of lignin is as a source of electricity and heat [21]. Currently, only 2% of lignin finds other applications, for example as adhesives, dispersants, surfactants, and high-value products such as vanillin [12,19,22]. Because the market for these materials is small and the amount of available lignin is rapidly increasing, it is necessary to find other methodologies to render lignin a valuable feedstock. The lignin valorisation market has its main focus on converting lignin into valuable products like biofuels, biochemicals, and bio-materials that can be introduced in established industrial procedures.

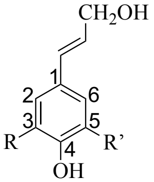
1.1 Lignin – A natural resource

Lignin is the second most abundant naturally occurring complex organic material after cellulose. It is present in almost all dry-land plant cell walls and exists mostly in xylem cells [23]. Lignin is responsible for plant cells lack of water permeability and offers protection against pathogens, pests, and natural wounding, contributing also to the strength and rigidity of the cell walls [24,25]. Its main function is to assist the movement of water by forming a barrier from evaporation and allowing water to reach critical parts of the plant. The botanist Candolle was the first to describe lignin in 1813 and he named it after *lignum,* which is the Latin word for wood [26].

Woody biomass typically contains between 15 and 35 wt% lignin, depending on the plant. Grass contains lignin in the range of 17 – 24 wt%, softwood 18 – 25 wt%, and hardwood 27 – 33 wt% [24,25]. Despite the significant potential of lignin, the industrial production of high-value lignin-derived products remains a challenge because of lignin's unique chemical reactivity, the presence of impurities (organic and inorganic), and its non-uniform structure, which make it difficult to isolate it without modifying its native structure [27].

1.2 Lignin building blocks

Lignin's molecular structure is highly recalcitrant and ill-defined, which can be traced to its biosynthesis following a random assembly of the three basic monomers via oxidative coupling resulting in an amorphous polymer [24,28–31]. It is almost impossible to find two identical "lignin molecules" with the same primary sequence of phenyl units [19]. The primary building blocks of lignin are called monolignols, phenylpropane, or C_9 units and differ in the substituents at the positions 3 and 5 of the aromatic ring (**Fig. 1.1**). Lignin is characterized by various functional groups formed during biosynthesis (**Fig. 1.2**). The monolignols are randomly linked to eachother by C-C and C-O-C bonds, sometimes also involving ring structures. The side-chain carbons linking the aromatic rings are called the aliphatic groups and its carbons are designated by α, β, and γ, with the C_α being the one attached to the aryl ring. The aromatic ring region is called the aryl group and the aromatic carbons are numbered from 1 to 6. The monolignols *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol originate from the commonly called *p*-hydroxyphenyl (H),



R = R' = H, ***p*-coumaryl alcohol**
R = H, R' = OCH_3 , **coniferyl alcohol**
R = R' = OCH_3, **sinapyl alcohol**

Fig. 1.1 Lignin monomeric building blocks.

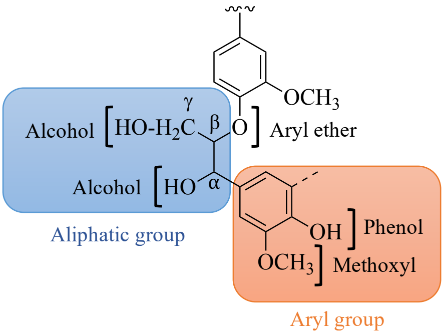


Fig. 1.2 Lignin functional groups.

guaiacyl (G), and the syringyl (S) lignin units, respectively [24]. H units are mostly associated with softwood lignin with 90-95 % of *p*-coumaryl alcohol involved in its synthesis, while G and S units are mostly found in hardwood lignin with 25-50 % and 50-75 % of, respectively, coniferyl and syringyl alcohols as motives [25,32].

1.3 Monolignol linkages

The monolignols can be linked in diverse manners, explaining the ill definition of lignin. The most common bond formed among the three monolignols is the β-O-4 linkage, but there are several others that are frequently present in common lignins, like the β-β, β-5, β-1, α-O-4, 5-5 and 4-O-5 bonds (**Fig. 1.3**) [24,30,31]. The natural occurrence of such linkages relates to the wood source: hardwood or softwood [25]. Hardwood lignin polymer has more linear structures in comparison with softwood. That is due to the formation of 5-5 and dibenzodioxocin linkages in softwood. On the hardwood lignins, the formation of those linkages is prevented by additional methoxy groups on the aromatic rings [19]. Typical ranges are listed in **Table 1.1**. This diversity needs to be taken into consideration when a methodology is developed to convert lignin into new products with a lower molecular weight. Although the linkage diversity in native lignin is high, this diversity changes when the lignin is extracted and isolated [33]. The wood source and the extraction process of lignin will influence these properties [34].

Table 1.1 Relative abundance in softwood and hardwood lignin of the common linkages between monolignols [25].

Linkage	Occurrence per 100 phenylpropane units	
	Softwood	Hardwood
β-O-4	43 – 50	50 – 65
5-5	10 – 25	4 – 10
β-5	9 – 12	4 – 6
α-O-4	6 – 8	4 – 8
4-O-5	4	6 – 7
β-β	2 – 4	3 – 7
β-1	3 – 7	5 – 7

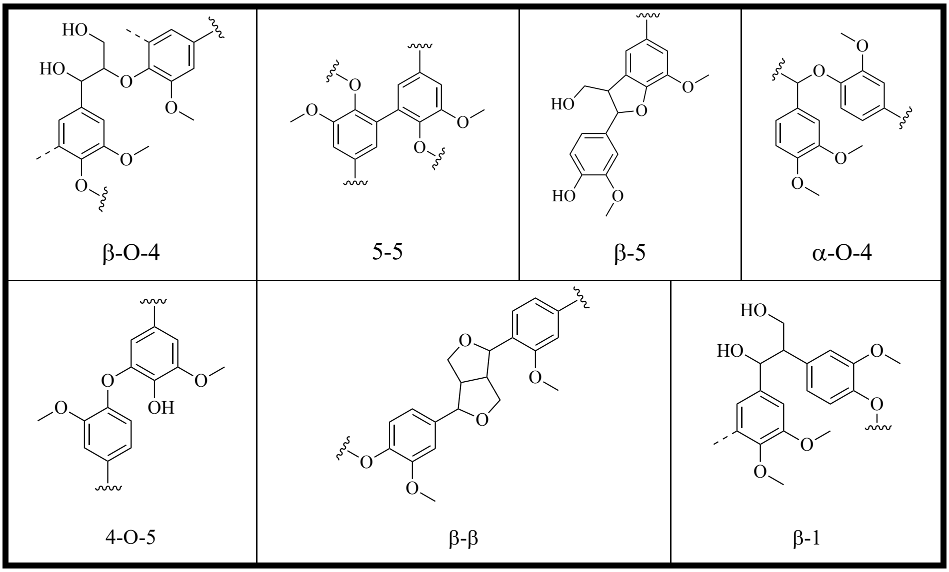

β-O-4
5-5
β-5
α-O-4
4-O-5
β-β
β-1

Fig. 1.3 Schematic representations of common linkages between monolignols.

1.4 Extraction and isolation

Based on the lignin extraction and isolation method, the final product (typically called technical lignin) can be usually categorized as a sulphur-containing lignin or a sulphur-free lignin (**Fig. 1.4**). Sulphur-containing lignins are available in large amounts, as it is a by-product of the paper and pulp industry. The use of Na_2S explains the high sulphur

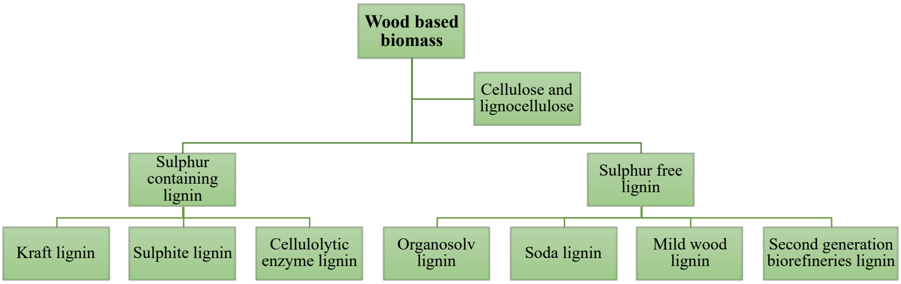


Fig. 1.4 Schematic representation of the main sources of lignin being currently extracted and isolated.

content of the lignin products. Biorefineries use other methods to isolate carbohydrates from lignin and typically render lignin products free from sulphur, bringing advantages in the further upgrading to useful products (e.g., less odour, less sulphur poisoning of catalysts) [35].

1.4.1 Sulphur-containing lignin

The Kraft process, which currently is the largest lignin-producing process, breaks the bonds that link lignin to cellulose by cooking the wood chips with sodium hydroxide (NaOH) and sodium sulphide (Na_2S). The key ingredient is Na_2S that will, in water, form NaSH responsible for promoting lignin degradation without compromising much the structure of cellulose [24,36]. The resulting lignin is highly modified and partially fragmented. The products of this process are a cellulose-rich pulp and black liquor, which is mixed with an acidic solution to isolate the lignin [35]. New types of linkages are formed during the processing, like stilbene linkages. The recondensation of lignin also leads to additional very stable C-C bonds, and new thiols groups are introduced in the derived lignin [19,24]. This Kraft lignin is currently used in fertilizers, pesticides, carbon fibres, binders, and resins. Moreover, it is the source of some fine chemicals like vanillin, hydroxylated aromatics, or quinine [12]. Most of the Kraft lignin is however incinerated by the industry where it is produced to generate energy [12].

Sulphite lignin is the most abundant type of commercial lignin for other applications than energy recovery. It is isolated by processing wood chips with sulphur dioxide (SO_2)

with a base of calcium, sodium, magnesium or ammonium [35]. Its sulphur content can go up to 8 %, which is mostly incorporated on lignin structure in the form of sulphonate groups. As sulphite lignin is water-soluble, it is in high demand by the building and construction industry markets [37]. It has been used for instance to make colloidal suspension, stabilizers, dispersants, binders, or additives for cement [12,19,31].

The last lignin type of this group is obtained by an enzymatic pre-treatment process. Cellulolytic enzymes hydrolyze and dissolve carbohydrates, retaining lignin as insoluble residue. This enzymatic action mimics the natural process of biomass decomposition, leading to a lignin with structural features similar to the native structure. The downsides of this process are the time necessary to obtain a good yield of lignin (from hours to days), the fact that some carbohydrates cannot be removed, and the large number of impurities remaining (ash, proteins, etc.) [25,38].

1.4.2 Sulphur-free lignin

Sulphur-free lignin has very distinct properties when compared with sulphur-containing lignin. The main source of such lignin is the conversion of lignocellulosic biomass in biorefineries, organic solvent pulping process, and soda pulping industries [32,39].

Organosolv lignin is extracted based on solvent fraction methodologies, where an organic solvent mixed with water is employed. A common mixture used is that of ethanol/water, but the use of benzene/water or butanol/water is also reported, among others [40–42]. To cleave the hemicellulose bonds, acid catalysts like HCl or Lewis acids are added, which contribute to the degradation and recondensation of the macromolecule structure [40]. The final lignin is separated through precipitation. Organosolv lignin is highly soluble in organic solvents but insoluble in water due to its high hydrophobicity. The main advantage of this process is extraction of a relatively pure lignin [43]. It is considered an environmentally friendly process but it has a high cost associated with solvent recovery necessary upon the isolation [25].

Milled wood lignin is extracted from a ball-milled wood with a mixture of neutral solvents, normally dioxane/water in a ratio of 9/1 respectively (physical pre-treatment)

[44,45]. Its structure is very similar to unaltered lignin, being considered the best model to elucidate its native structure, although the interpretation may be hampered by the possible depolymerization occurring during the extraction process. This depolymerization generates new free hydroxyl groups through the cleavage of β-aryl ether linkages [46].

Soda lignin from the soda pulping process is isolated from annual plants (non-wood fibres) like straw, flax and sugarcane bagasse [47,48]. Soda lignin has normally a very low molecular weight and it is insoluble in water. As it is sulphur-free and structurally similar to native lignin, it is often used as feedstock in lignin valorisation studies [33]. So far, it is applied in the production of resins, animals nutrition, as well as in polymer synthesis, for instance [12].

The lignin coming from second-generation refineries, as a by-product, is generated during the hydrolytic pre-treatment of biomass. Cellulose is fermented to ethanol, hemicellulose converted into pentoses, and lignin is subsequently isolated by precipitation. There are two approaches that can be used. The first one removes lignin prior to carbohydrates hydrolyzation, and the other targets the conversion of the carbohydrates prior to lignin removal [49].

1.5 Lignin valorisation

Lignin has the characteristics to be a source of high-value products but its complexity is immense, challenging researchers and industries in finding ways to generate value from it. Despite many studies, few technologies have reached a commercial scale [19,50–52].

The most common application is as a source of energy. Pyrolysis (where the end products are biochar, bio-oils and gases) [53] and syngas (producing H_2, CH_4, CO, and CO_2) [54] from lignin are other low-value applications explored. Besides these uses of lignin, some other applications can be appreciated from literature [12,39,55–63].

Direct use of lignin as a macromolecule is common practice in the construction industry [64–67]. Examples of such applications are components for low-cost binders [68] and, after proper chemical modifications, oligomers for inclusion in urethanes and epoxy resins [69–72].

Lignin depolymerization is gathering vast interest currently due to its immense potential [16,19,53,73–78]. Breaking lignin into lower molecular weight compounds, which can afterwards be integrated into pathways to produce fuels and platform chemicals, is the main goal to add value to this by-product of lignocellulosic biomass valorisation. A typical class of products targeted are aromatic compounds such as benzene, toluene, xylene or phenols. The production of vanillin was the first and remains the most well-known example of a lignin depolymerization methodology being employed at an industrial scale [68]. Nonetheless, only 20% of vanillin on the market is produced from lignin (i.e., by oxidation of Kraft lignin in an alkaline medium) [79,80]. Current technologies are not adapted to treat and transform molecules with the complexity of lignin. Therefore, new catalytic approaches are necessary to overcome this depolymerization challenge. The development of new catalysts and new protocols, as well as the test of old catalytic approaches, are proposed methodologies [81].

The fragmentation of lignin can be categorized into three distinct groups: cracking or hydrolysis reactions, catalytic reduction reactions, and catalytic oxidation reactions [19]. Cracking reactions are well known from petroleum refining and they are very often employing zeolites (e.g., HY and H-ZSM-5) as catalysts targeting C-C bond cleavage [82–85]. In principle, the use of such catalysts will lead to cleavage of the β-O-4 bonds and the less stable C-C bonds [82]. The products are low molecular weight aromatic compounds, yet char and coke formation are known problems. Reductive lignin depolymerization received substantial as well [86]. The production and the upgrading of bio-oils to fuel products is the focus of this research. The presence of reducing conditions (hydrogen or hydrogen-donating compounds) are beneficial leading to higher reaction yields and less coke formation than cracking processes without hydrogen [87]. Some disadvantages of this approach are the presence of contaminations (e.g., sulphur), poisoning by water, and the rapid deactivation of the catalyst by coke formation [88]. While reductive depolymerization reactions remove functional groups from the products, oxidative depolymerization reaction increase the complexity by adding functionalities to the resulting aromatics. The purpose of such oxidative depolymerization is to produce platform chemicals that may be integrated in the synthesis of organic intermediates for instance for fine chemicals. One of the most promising approaches involves the use of homogeneous catalysis, because this allows the development of catalysts that will target specifically the desired linkage-type to be disrupted by choosing appropriate ligands [19,89–91]. The remaining functional groups can then be left intact, which is of the utmost importance when developing a rational valorisation of lignin to high-value products. Although there are many methodologies and catalysts developed to depolymerize lignin through model compound studies, there is little information about performance on actual lignin streams.

1.6 Scope of the study

Lignin holds great potential as an alternative feedstock due to its rich polyaromatic nature, which can be used to obtain renewable fuels, bulk and specialty chemicals, and new lignin-based materials. However, despite intensive research, lignin valorization is still far from industrial practice. The objective of this thesis work is to find new ways to valorise lignin considering that the methodologies employed have to be simple to implement, reach for cost-effective reagents, and mitigate side-products production. To achieve this purpose, two unconventional routes are explored: (i) catalytic lignin oxidation pretreatment to weaken its structure and ease its depolymerization into lower molecular weight components, and (ii) lignin modification for applications as catalyst support. The lignin oxidation pretreatment will be investigated in two different catalytic approaches both using an organic peroxide, namely (i) using a titanium silsesquioxane as a homogeneous catalyst, and (ii) an unconventional alternative using titanium grafted to lignin as a heterogenized catalyst. Both employ a titanium mediated catalytic system to oxidize the macromolecule structure. The most promising path identified will be evaluated for the depolymerization of organosolv and soda lignins using copper-magnesium aluminium oxide as catalyst in supercritical ethanol. With respect to developing new lignin-based catalysts, the goal is to synthesize a new material by introducing a metal (titanium) functionality into the macromolecular structure. Upon characterization, the novel material will be evaluated as an epoxidation catalyst, by testing its catalytic power in different reactor types, and exploring which lignin functionalities are responsible for the activity expressed.

The first part of the thesis, which includes Chapters 2 and 3, is focused on lignin oxidation methodologies as a pretreatment prior to depolymerization. **Chapter 2** reports lignin oxidation using a titanium silsesquioxane catalyst (Ti-POSS) and *tert*-butylhydroperoxide (tBHP) as oxidant. Initially, this oxidation system is applied to several mono-aromatic lignin model compounds containing functional groups characteristic for lignin. Exploring Ti-POSS as a homogeneous catalyst, the purpose is to understand which lignin functional group will be most affected by such oxidation (defining the oxidation target). Upon such understanding, the work also explores the oxidation of an organosolv lignin (real feedstock). Based on the catalytic results, the catalyst interaction with lignin structure is further investigated.

In **Chapter 3**, we explore lignin oxidation by grafting titanium to lignin (taking advantage of the ability of titanium to react with lignin's OH groups) and oxidize it using an organic peroxide. To evaluate these approaches, we characterize the lignin functional groups before and after oxidation using solid-state NMR and IR spectroscopy. Upon this oxidative pretreatment, lignin depolymerization is evaluated as well and the monomeric products are analyzed by GC-MS. Lignin model compounds are used to understand the depolymerization yields and the effects of the pre-treatment methods.

The second part of the thesis, which includes Chapters 4 and 5, explores the use of lignin as a catalyst support in epoxidation reactions. In **Chapter 4**, a new lignin-based material is synthesized and used as a heterogeneous catalyst in olefin epoxidation with tBHP as the oxidant. The catalyst is evaluated both in batch and flow reactors.

In **Chapter 5**, a comparative study with model compounds and two different lignin types is presented to further gain understanding about the role of titanium grafted to lignin as an oxidation catalyst. The purpose is to understand how the nature of lignin influences the catalytic performance of the resulting materials. For this purpose, oak lignin is titanated and evaluated in the model epoxidation reaction and compared to the earlier results obtained for organosolv lignin. By comparison with lignin model compounds, the role of different functional groups is investigated, thereby making it possible to select the optimum lignin type for application as a catalyst support.

Finally, the work is summarized in **Chapter 6** and an outlook on the further challenges in the directions explored in this thesis is given.

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Chapter 2

Enabling Oxidation of Lignin Model Compounds and Lignin with an Organic Peroxide by a Silsesquioxane Titanate

Summary

In this study a catalytic approach is demonstrated to oxidize an organosolv lignin using a titanium catalyst and an organic peroxide. A titanium silsesquioxane catalyst (Ti-POSS), well-known for its ability to oxidize organic compounds, was initially evaluated for the oxidation of simple mono-aromatic molecules considered as lignin model compounds. The use of model compounds having hydroxyl groups mimicking the Cα, Cγ, and the phenolic moieties in lignin allow evaluation of the potential of this approach for lignin oxidation. The hydroxyl in the Cα position proved to be most reactive. The oxidation of real organosolv lignin was obstructed by a grafting phenomenon involving the catalyst and the lignin aromatic hydroxyl groups, resulting in Ti-O-Ar units. Although limited in scope, this study demonstrates how to activate specific lignin functional groups in complexation with metals, specifically titanium.

2.1 Introduction

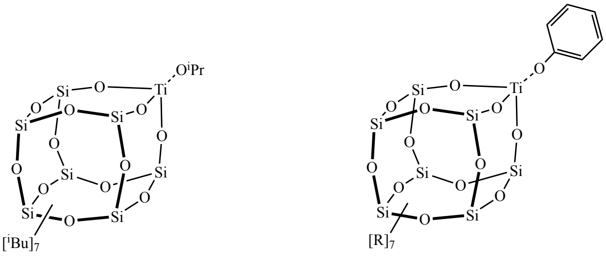
Lignocellulosic biomass, which is dry matter from land-based plants such as wood, straw, and grasses, can be separated into cellulose, hemicellulose, and lignin. While cellulose and hemicellulose have been established as and cost-effective valuable bioresources for many materials [1,2], lignin currently remains a side-product of cellulose valorisation processes and, therefore, regarded a waste material primarily utilized for heat recovery by burning [3,4]. Although lignin has an important biological function, i.e., to provide support for plants due to its rigid structure [5], its highly cross-linked polymeric nature makes lignin conversion to fuels and chemicals a challenge. Given its affordable price and renewable properties, it is important to develop efficient catalytic technologies for the upgrading of lignin to value-added products [3,6–8].

Lignin is the second most abundant wood-based polymer and the only large-scale biomass source containing aromatic functionalities. It is biosynthesized from three monomerics units: p-coumaryl alcohol, conifery alcohol, and sinapyl alcohol, which form respectively p-hydroxyphenyl, guaiacol, and syringyl lignin sub-units. All the units contain a phenyl group, a propyl side-chain, and differ in the number of methoxy groups bonded to the aromatic ring. Those units crosslink in many possible bonding patterns by carbon-carbon bonds and carbon-oxygen bonds. These bonds are part of lignin aliphatic region and the carbons (originally from the propyl groups) are labelled as α, β, and γ (**Fig. 1.2**) [9, 10].

Depolymerization of lignin into small aromatic monomers offers the possibility to create a new class of renewables to be used by the fuel and chemicals industry [7, 11–13]. Unlocking the potential of lignin by conversion technologies has attracted increasing interest from researchers from industry and academia [14, 15]. Challenges start with the extraction and isolation of the polymer. The methods employed to separate it from the other wood components and the accumulation of minerals and organic acids during those processes are some of the difficulties found. The preservation of the delicate native structure of lignin is often compromised and, therefore, results in a polymeric structure more recalcitrant to chemical cleavage than in planta lignin. Depending on the wood source and the extraction method employed, lignin might acquire different structural features increasing its complexity and decreasing its reactivity [10, 16–19] which should be taking into account when aiming for depolymerization.

Due to lignin's complex bonding patterns in connecting aromatic units, it has been a challenge to find a single method to selectively break numerous carbon-carbon and carbon-oxygen bonds present in this raw material. While some bonds can be easily broken, such as β-O-4 bonds, others are relatively strong such as the 5-5 bond (**Fig. 1.3**). A catalytic approach coupled for example with the use of high pressure and high temperature has been so far the most successful in this depolymerization processes [20, 21]. Many other methodologies were widely explored, albeit with modest success [22]. The use of supercritical solvents to overcome lignin's low solubility in combination with a catalytic system that results in mono-aromatics is among the promising methodology as shown by the groups of Hensen [23, 24] and Barta [25].

Another promising approach involves lignin pre-treatment prior to depolymerization, e.g., lignin oxidation [26, 27]. Such procedures aim to weaken the polymer structure so that the subsequent depolymerized can occur under milder conditions. Many studies showed the benefit of an oxidative pre-treatment of lignin, using distinct catalysts and oxidants [28, 29]. Oxidation of lignin results in an improved catalytic depolymerization. Usually, oxidation targets the aliphatic chain's hydroxyl groups, because they are the most vulnerable linkages and, thus, the weakest link in the polymeric chains in lignin. Titanium supported on silica has been successfully explored as a catalyst for oxidation [30, 31]. In this study, we will investigate the use of an industrial homogeneous titanium catalyst, i.e., a titanium polyhedral oligomeric silsesquioxane (Ti-POSS, **Fig. 2.1**), on the oxidation of organosolv lignin. The Ti-POSS is synthesized from an incomplete condensed silsesquioxane containing 3 silanol groups, which are the functional group targets of titanium isopropoxide. The resulting organosilicon molecule has a cage-like structure made of Si-O-Si and Ti-O-Si linkages with 7 tetrahedral silica vertices and one titanium vertices can react with the oxidant in order to initiate the oxidation of a substrate [31, 32]. Ti-POSS is known for its excellent catalytic properties in oxidation reactions, mainly in olefin epoxidation. It is a homogeneous catalyst, very soluble in organic solvents and is



Ti-POSS

(ArO)Ti-POSS

Fig. 2.1 Representation of two silsesquioxane based catalyst.

described as having remarkable properties with respect to catalysis with organic peroxides as oxidants, i.e., tert-butylhydroperoxide (tBHP) or cumene hydroperoxide. Herein, we report the oxidation using Ti-POSS on simple lignin model compounds using tBHP to evaluate the reactivity to various functional groups. The developed oxidation method was evaluated for its utility to oxidize organosolv lignin.

2.2 Experimental Section

2.2.1 Chemicals

Tert-butylhydroperoxide (tBHP) (70% aqueous solution, Sigma Aldrich) was extracted with n-octane before use. The catalyst used in this study — the titanium polyhedral oligomeric silsesquioxane, Ti-POSS — was provided by Hybrid Catalysis B.V. The organosolv lignin was extracted from beech wood and provided by Energy Centrum Nederland (ECN, now TNO). All the other chemicals were obtained from Sigma Aldrich and used as received.

2.2.2 Product Analysis

The GC-MS analysis were executed in a Shimadzu 2010 GC-MS system equipped with RTX – 1701 column (60 m x 0.25 mm x 0.25 μm) and a flame ionization detector (FID) together with a mass spectrometer detector. Identification of the products was achieved based on a search of the MS spectra with the NIST11 and the NIST11s MS libraries.

Catalytic tests were performed on a Chemspeed ASW2000 automated synthesizer, containing a block with 16 reactor vessels of 10 mL each with vortex shaking. All reaction vessels were equipped with a heating mantle, which were connected to a thermostat, and cold finger reflux condensers. Samples were collected in time and monitored by gas chromatography (GC) involving determination of the respective model compound (MC), the respective oxidized MC, cyclooctene, cyclooctene oxide, tBHP and *tert*-butanol (tBuOH) through comparison with an internal standard (1,3,5-trimethylbenzene). GC analysis was done on a Shimadzu GC2010 gas chromatograph equipped with a 30.0 m x 0.21 mm x 1.00 μm dimethyl polysiloxane column, in which He was used as the carrier gas (injector temperature 250 ºC). The oven temperature program was from 45 – 120 ºC at a ramp rate of 10 ºC/min, followed by 120 – 250 ºC at 20 ºC/min. The initial and final temperature isothermal dwells were 3 and 2 min, respectively. The retention time (R_t) and the response factor (Rf_y) of substrates and products are given in **Table A.1** of Appendixes. The response factors were determined for every component concerning the 1,3,5-trimethylbezene using **Eq. 2.1**, and the concentration of the component 'y' (C_y) in % was determined by **Eq. 2.2**. Rf_y is the response factor of component 'y' with respect to the internal standard, while Area SI and Area component are the peak area of the internal standard and of the component peak, respectively, M SI, M 1 and M component are the weights (g) of the initial amount of internal standard, the initial amount of model compound 1 and the component, respectively, and MW 1 and MW component are the molecular weight (MW; g/mol) of model compound 1 and the component, respectively. The reaction yield was calculated using **Eq. 2.3**. $C1_{t=0}$ is the initial concentration calculated for the model compound 1, and the $C2_{t=t}$ is the corresponding model compound 2 concentration calculated at a given time. In case of the cyclooctene epoxidation reaction, the same equations and calculations were implemented. For this reaction, the factores M1, MW1, and C1 correspond respectively to the initial amount, the molecular weight, and the initial concentration calculated for the cyclooctene, C2 corresponds to the cyclooctene oxide concentration at a given time. Each sample was prepared by adding 100 μL of the reaction mixture to 1,00 mL of n-octane.

$$\mathrm{Rf_y}=\frac{\text{Area IS}}{\text{Area component}}\times\frac{\text{M component}}{\text{M IS}} \qquad \textbf{(Eq. 2.1)}$$

$$\mathrm{Cy}=\frac{\dfrac{\text{Area component}}{\text{Area IS}}\times\dfrac{\text{M IS}}{\text{MW component}}\times\mathrm{Rfy}}{\dfrac{\text{M 1}}{\text{MW 1}}}\times 100 \qquad \textbf{(Eq. 2.2)}$$

$$\text{Yield (\%)}=\frac{\text{C2 t=t}}{\text{C1 t=0}}\times 100 \qquad \textbf{(Eq. 2.3)}$$

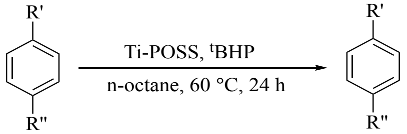
2.2.3 Procedures

2.2.3.1 Oxidation of model compounds

Unless stated otherwise, 2.5 mL of a solution of substrate (2.0 M) and 1,3,5-trimethylbenzene (2.0 M) in n-octane, and 2.5 mL of a solution of tBHP (2.4 M) in n-octane were added to a Chemspeed 10 mL reactor containing the refereed amount of Ti-POSS (**Table 2.1**). The reaction vessels were heated to 60 °C and vortexed at 600 rpm. At suitable time intervals, samples of 0.1 mL were collected automatically from the reactors and injected into GC vials containing 1 mL of n-octane to be analysed by gas chromatography.

2.2.3.2 Lignin oxidation

A sample of 200 mg of pre-dried organosolv lignin was dispersed in a volume of n-octane. 2.5 mL of tBHP (2.4 M) and 22 mg of Ti-POSS were added to the solution containing lignin and n-octane was added to reach a total volume of 10 mL. The mixture was heated to 60 °C, and it was stirred at 600 rpm for 24 hours. Subsequently, the suspension was centrifuged and the residue was washed with n-octane. This solid was dried in vacuo.



1a: R'= $CHOHCH_3$, R''= H
1b: R'= CH_2CH_2OH, R''= H
1c: R'= OCH_3, R''= H
1d: R'= OH, R''= H
1e: R'= OH, R''= CH_3

2a: R'= $COCH_3$, R''= H
2b: R'= CH_2CHO, R''= H

Fig. 2.2 Schematic representation of the model compounds oxidation using Ti-POSS and tBHP. 1 are the model compounds and 2 are the respective oxidized product.

2.2.3.3 Cyclooctene epoxidation in the presence of lignin

An amount of 15 mL of a catalyst solution was made by dissolving Ti-POSS (25.1 mg, 0.028 mmol, 1.9 mM), cyclooctene (3.31 g, 2.0 M), and 1,3,5-trimethylbenzene (3.61 g, 2.0 M) in n-octane. 2.5 mL of the catalyst solution and 2.5 mL of a solution of tBHP in n-octane (2.4 M) were added to a Chemspeed 10 mL reactor containing an amount of organosolv lignin (**Table 2.2**). The reaction vessel were heated to 60 °C and vortexed at 600 rpm. At suitable time intervals, samples of 0.1 mL were collected automatically from the reactors and injected into GC vials containing 1 mL of n-octane to be analysed by gas chromatography.

2.3 Results and Discussion

2.3.1 Oxidation of simple model compounds

Oxidation targeted the hydroxyl groups present in lignin. These OH groups are part of different lignin bond types and, therefore, exhibit distinctly different reactivities. Generally, for a common organosolv lignin, the OH groups are at the β-O-4 bonds and the aromatic rings. In order to define which of the hydroxyl groups would be more susceptible to oxidation using Ti-POSS as catalyst and tBHP as oxidant, the conversion of several model compounds were tested (**Fig. 2.2**). Model compound 1a is a mimic for the OH groups at the Cα position in β-O-4 bonds, while model compound 1b is representative for the OH group at the Cγ position of the aliphatic chains. Model compounds 1d and 1e were chosen to mimic the phenolic moieties in lignin, model compound 1c without OH groups served as a reference.

A 10 mL reactor of a Chemspeed ASW2000 automated synthesizer was charged with an appropriate amount of Ti-POSS (**Table 2.1**, m_{cat}), followed by addition of 1 equivalent model compound solution and 1.2 equivalents of tBHP solution in n-octane. The reaction proceeded at 60 °C and with a stirring speed of 600 rpm for 24 h. The solvent was n-octane, because it dissolves both the catalyst and the model compounds. The conversion, selectivity and yield are listed in **Table 2.1**.

Table 2.1 shows that only hydroxyl-containing substrates were converted under the employed reaction conditions. The reference model compound 1c (**Table 2.1**, Entry 7 and 8) was not converted both in the absence and the presence of a catalyst. This was not only evident from the absence of a decrease in the substrate concentration but also from the absence of product formation as established by GC analysis. In contrast, the MC 1a and 1b were successfully converted to the expected products 2a and 2b, respectively. The results also show that the oxidation of 1a (**Table 2.1**, Entry 2 and 3) occurs faster than the oxidation of 1b (**Table 2.1**, Entry 5 and 6) with maximum yields of 37.9 % and 7.6 %, respectively. It is an indication that the oxidation of the Cα OH in lignin might proceed at a higher rate than the oxidation of the Cγ OH in aliphatic chains of lignin. Thus, the Cα position (secondary carbon) is more reactive towards oxidation than the Cγ position (primary carbon) under the employed conditions. Observing the reaction plots, the higher reactivity of 1a hydroxyl group is clear, because the majority of the 2a is formed during the first reaction hour (**Fig. 2.3**, a), while the 2b formation is more gradual and slower in time (**Fig. 2.3**, b). Similar trends are observed in for the conversion of tBHP into tBuOH.

Table 2.1 Results obtained on the MC1a-c oxidation with tBHP using different amounts of Ti-POSS at the end of 24 hours. Reaction was held at 60 ˚C and stirred at 600 rpm.

Entry	MC	m_{cat} (mg)	Conv.[1] (%)	Select.[1] (%)	Yield[1] (%)
1	1a	0.0	1.4	0.0	0.0
2		22.0	40.5	93.7	37.9
3		107.0	21.8	91.1	19.9
4	1b	0.0	1.0	48.2	0.5
5		24.0	8.4	90.5	7.6
6		99.0	10.3	58.6	6.0
7	1c	0.0	0.0	-	0.0
8		40.0	0.0	-	0.0

The impact of the catalyst amount on the oxidation of model compound 1 to model compound 2 was also investigated. For 1a, the conversion was 40 % with a selectivity to 2a of 94% using a Ti-POSS concentration of 5.0 mM (**Table 2.1**, Entry 2). By using 4 times more catalyst ([Ti-POSS] = 22 mM), the conversion decreased to 22 % and the selectivity to 91 % (**Table 2.1**, Entry 3). For 1b, the conversion was 8 % with 91 % selectivity to 2b using a Ti-POSS concentration of 5.0 mM (**Table 2.1**, Entry 5). Increasing the catalyst concentration ([Ti-POSS] = 22 mM, 4 times more) led to a slightly higher conversion of 10 %, but the selectivity to 2b dropped substantially to 58 % (**Table 2.1**, Entry 6), resulting in a lower reaction yield (6.0 %). Thus, an increasing amount of catalyst did not result in higher yields.

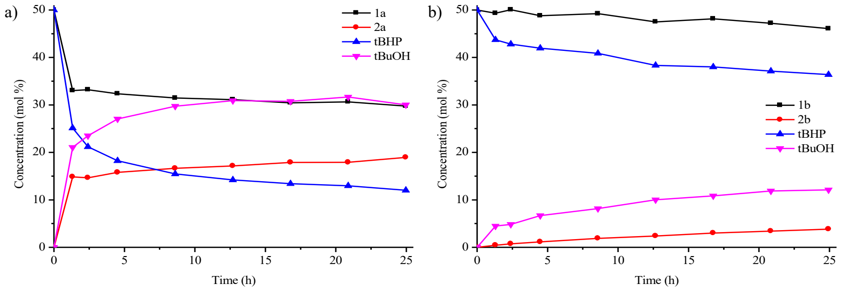


Fig. 2.3 Plot of the concentration of substrates and products in time with Ti-POSS as catalyst and tBHP as oxidant. The results correspond to the Table 2.2 **a**) Entry 2, and **b**) Entry 5.

The model compounds mimicking the phenolic moieties (1d and 1e) had very different reactivities compared to 1a-c. Reactions with 1d and 1e for 24 h led to the formation of a black precipitate. This precipitate formed immediately after the addition of the tBHP solution. The precipitate was separated from the liquid fraction for further analysis. For model compound 1d, GC analysis of the liquid fraction showed a substrate conversion of 16 %, but no identifiable reaction products of 1d could be detected in the solution. Decomposition of the peroxide, however, was demonstrated to give small amounts of two new compounds. These were identified through GC-MS as 2-(*tert*-butylperoxy)-2-methylpropane and as isobutylene, both common in reactions with tBHP (side products derived from radical reactions during the oxidation or the oxidant degradation). For 1e, a similar result was obtained. About a quarter of the initial amount of the model compound was lost after 24 hours of reaction. Also in this case, GC-MS analysis showed the appearance of 2 side-products from tBHP decomposition.

The analysis of the precipitate was inconclusive. Due to the amorphous nature of this black solid and the consumption of the substrates, it can be concluded that a complex and random structure was formed by the action of the catalyst and the oxidant on the mentioned model compounds. The phenolic model compounds prove to be very reactive under employed conditions and no means of control over precipitate formation was found.

In summary, this model compound study shows that the reactivity of the OH groups towards oxidation increases in the order:

OH at the Cγ position < OH at the Cα position < aromatic OH.

2.3.1 Lignin oxidation

Cleaving the β-O-4 bond is the most important target for an oxidative pre-treatment of lignin. This bond, as others like β-1 or β-5, has hydroxyl groups at Cα and Cγ atoms, which represent secondary and primary carbon atoms, respectively. Following the results of model compound 1a-b oxidation with Ti-POSS and tBHP, the Cα position appears to be favored in oxidation.

To verify this, we suspended a pre-dried organosolv lignin in n-octane and added tBHP and Ti-POSS. After 24 h reaction at 60 °C, the lignin was isolated and characterized by ^{1}H-^{13}C HSQC NMR spectroscopy. The NMR sample was prepared by dissolving the lignin sample in deuterated dimethyl sulfoxide. It was observed that this method led to the formation of a precipitate in the NMR tube, hindering its analysis. After filtration, the lignin concentration in solution was too low for NMR characterization. In order to explain this, the liquid fraction obtained from the oxidation reaction was analyzed by gas chromatography. Among the reaction products, *iso*-propanol was observed, which suggests that the catalyst has been modified and may have developed strong interactions with lignin. Specifically, it is speculated that the isopropyl group of the Ti-POSS catalyst will react with the lignin OH functional groups.

The earlier observation of the formation of a precipitate during oxidation of the model compounds with phenolic moieties (1d and 1e) is similar to the reactions that might have occurred between the lignin phenolic moieties and Ti-POSS. Experiments performed with a similar silsesquioxane-based catalyst (**Fig. 2.1,** (ArO)Ti-POSS) which has the Ti binding phenolate group instead of an *iso*-propoxylate group, showed that it has lower catalytic activity reacting with tBHP [33]. In case of interaction of the Ti-POSS with the OH groups of the aromatic moieties in lignin, it is expected that the activity of the catalyst will drop.

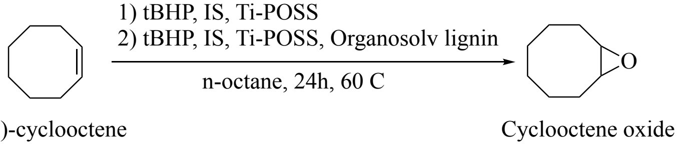


Fig. 2.4 Schematic representation of the cyclooctene epoxidation reaction with tBHP catalysed by Ti-POSS in the 1) absence and 2) presence of organsolv lignin.

Ti-POSS displays a very high catalytic activity in cyclooctene epoxidation with tBHP (**Fig. 2.4**, 1). If one or more of its ligands are replaced by lignin, a lower activity can be expected. As such, addition of lignin to a cyclooctene model epoxidation reaction using Ti-POSS and tBHP can slow the conversion of the olefin into the corresponding epoxide (**Fig. 2.4**, 2). To verify this, 4 reactors in the Chemspeed robot were loaded with different amounts of organosolv lignin (**Table 2.2**), while the same amounts of cyclooctene, Ti-POSS and tBHP were added. The reaction was monitored over time by automatic sample collection for subsequent GC analysis. The results of the reaction for 24 h are presented in **Table 2.2**, while the corresponding conversion plots are shown in **Fig. 2.5**.

Table 2.2 Conditions used to verify the effect of the organosolv lignin on the catalytic activity of Ti-POSS in the cyclooctene epoxidation reaction using tBHP as oxidant. The conversion, selectivity, and yield values are calculated based on the substrate and product concentrations at the end of approximately 24 hours of reaction.

Entry	m_{lignin} (mg)	$n_{Ti\text{-}POSS}$ (mmol)	Lignin Phenol content (mmol)	Ratio (Ti-POSS/ Phenol content)	Conv.[1] (%)	Select.[1] (%)	Yield[1] (%)
1	-	5.20E-03	-	-	94.0	98.7	98.1
2	100.4		0.36	1.44E-02	89.0	94.1	88.6
3	251.0		0.90	5.75E-03	93.7	95.3	90.6
4	500.6		1.80	2.89E-03	91.3	95.7	88.5

[1] Values determined by gas chromatography.

Fig. 2.5 shows that the catalytic activity is impeded by the addition of organosolv lignin. Normally, the cyclooctene epoxidation reaction in batch catalyzed by Ti-POSS occurs predominantly during the first 2 h (**Fig. 2.5**, Entry 1, blue). With an increasing amount of lignin present, the rate of the reaction was clearly compromised. By observing the reaction plots during the first 5 h, it is clear how lignin is affecting the catalytic process (**Fig. 2.5**, Entry 2-4, grey area highlighted). After 24 h, the concentrations of cyclooctene and cyclooctene oxide were essentially the same in the reactors containing lignin. This shows that the remaining Ti-POSS was involved in cyclooctene oxidation and that an increasing amount of lignin did not significantly change the final reaction outcome, but slowed down the reaction significantly. The final conversion was not strongly impacted

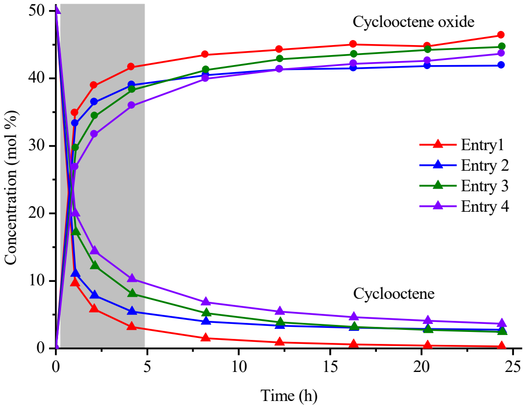


Fig. 2.5 Evolution of the cyclooctene (circles) and the cyclooctene oxide (triangles) concentrations in the absence and presence of organosolv lignin in the reaction medium. Reaction plots of the epoxidation catalysed by Ti-POSS and using tBHP as oxidant. The entry number correspond to the conditions stablished on Table 2.3.

by the presence of lignin with the cyclooctene conversion after 24 h being in the range of 89 – 94 % (**Table 2.3**). The selectivity to cyclooctene oxide, on the other hand, displayed a small decrease from 99 % for the reaction without lignin (**Table 2.3**, Entry 1) to values around 95 % in the presence of lignin (**Table 2.3**, Entry 2-4). This decrease could be due to side-reactions of cyclooctene or cyclooctene oxide with lignin or because the predominance of phenolic OH groups in lignin leads to deactivation of the catalyst. Overall, this led to a decrease of the cyclooctene yield with increasing lignin loading: while in the control experiment Ti-POSS showed an optimized yield of 98 %, the yield decreased to 89 %, 91 %, and 88 % upon charging the reaction mixture with 100 mg, 250 mg, and 500 mg of organosolv lignin, respectively.

Although the presence of the lignin did not completely deactivate the catalyst, it is evident that an interaction is occurring between the natural polymer and the Ti-POSS (**Fig. 2.6**), which reduces the reaction rate of epoxidation. Given above the cyclooctene epoxidation results, the presence of phenolic moieties in lignin will significantly contribute to deactivation of the Ti-POSS catalyst. Accordingly, we did not pursue the oxidation of lignin using this approach.

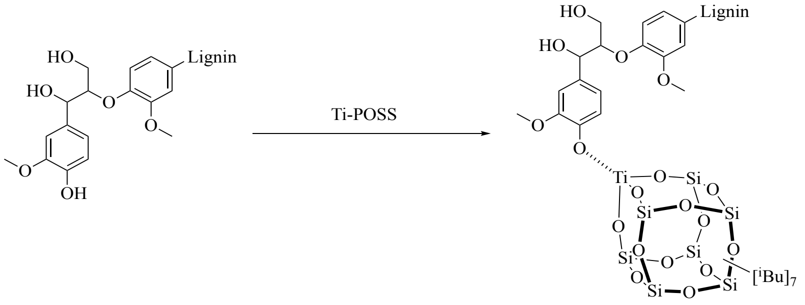


Fig. 2.6 Schematic representation of the interaction between the phenolic moieties of the organosolv ligninn an the Ti-POSS during the oxidation. Structures are a suggestive representation.

2.4 Conclusions

Ti-POSS is an active catalyst for the oxidation of aliphatic hydroxyls to the corresponding carbonyls in simple lignin model compounds. Nevertheless, the highly reactive nature of phenolic moieties with Ti-POSS led to the formation of an unidentified, possibly titanated precipitate, which leads to deactivation of the catalyst. By attempting real lignin oxidation with Ti-POSS as catalyst and by using tBHP as oxidant, the results were in part similar to what was observed for the model compounds. The organosolv lignin oxidation remains elusive, but an interesting interaction between the natural polymer and the catalyst was found. The presence of *iso*-propanol in solution after the oxidation attempt indicated that the *iso*-propoxyl group of the Ti-POSS was replaced by lignin, by reacting with a free OH group, potentially a phenolic OH. A catalytic activity determination (using a cyclooctene epoxidation reaction) showed that in the presence of lignin the Ti-POSS activity decreases significantly. Albeit that the original goal of oxidizing lignin was not achieved, the findings help to understand better the reactivity of hydroxyl groups in lignin towards (homogeneous) oxidation.

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Chapter 3

Lignin oxidation with an organic peroxide and subsequent aromatic ring opening

Summary

The oxidation of an organosolv lignin with tert-butylhydroperoxide initiated by titanium grafting on the lignin structure was investigated. Titanation of reactive hydroxyl groups of lignin is responsible for crosslinking of the lignin structure. IR and MAS ^{13}C *NMR spectra confirmed the oxidation of lignin and other pronounced structural changes. A study with guaiacol as a model compound helped to understand that aromatic ring opening occurs under the given conditions catalysed by the grafted titanium. The structure of the oxidized lignin become less recalcitrant and, therefore, potentially more susceptible to be depolymerised and converted into products, although the aromatic ring opening decreased the yield of aromatic monomers.*

This chapter is based on the published work in Int. J. Biol. Macromol. ***2019****, 123, 1044-1051.*

3.1 Introduction

Lignin is a natural polymer fundamental to the plant cell walls, together with cellulose and hemi-cellulose. Its main functions are to bring rigidity and contribute to the structural integrity of plants [1]. Lignin biosynthesis involves radical polymerization of *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which form respectively *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) lignin subunits. As this polymerization is a random process, lignin has a high structural diversity [2].

Over the past decades, lignin has been studied as a natural resource for a wide variety of applications. As its structure is rich in aromatic moieties, lignin is potentially a cheap alternative source for producing gasoline fuel components and base chemicals [3]. The lingering challenge is to break the recalcitrant lignin structure into aromatic monomers at conversion rates and with a production distribution that can lead to a commercially viable process. So far, catalytic depolymerization is the most promising approach to achieve this goal [3,4]. Among the many approaches, alcohols such as methanol or ethanol used as supercritical solvents and hydrogen donors represent a new medium and reactant for lignin depolymerisation [5–7]. This and other catalytic approaches remain at the research stage. Another challenge in this respect is associated with the recalcitrant nature of the lignin extracted from the lignocellulosic biomass matrix. Methods for isolating lignin at an industrial scale such as Kraft pulping or organosolv extraction result in a substantial change in the molecular structure of the lignin [8]. The strong carbon-carbon bonds between the aromatic constituents increases at the expense of the weaker oxygen-containing bonds, primarily weak ether bonds. These changes are the result of repolymerization reactions involving radicals obtained during the isolation step. As a result, *ex planta* or technical lignins are much more difficult to depolymerize than *in planta* lignin. Therefore, the lignin-first process present a novel approach with higher yields of a limited number of aromatic products, which is based on extraction of lignin from wood instead of cellulose [9]. However, the depolymerization of lignin extracted by this approach cannot be considered a waste recovery approach, because it does not substantially contribute to the recovery of the 50 million tonnes of lignin isolated per year as industrial waste, mainly from the pulp and paper industry [10,11].

As a contribution to lignin valorisation, oxidative pre-treatment of lignin has been described as a way to weaken the lignin structure, making it more susceptible to depolymerisation [12]. Several reports mention the oxidation of hydroxyl groups from primary and secondary carbons of the lignin aliphatic chains. Oxidation results in a higher susceptibility of lignin to depolymerisation, achieving higher reaction rates under milder conditions. Stahl and co-workers explored the use of TEMPO as a catalyst and proposed a mechanism in which a C_α benzylic carbonyl group formed by oxidation can polarize the $C_ß$-H bond, promoting acid-catalysed ether bond cleavage [13,14]. Westwood and co-workers combined C_α oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and a zinc catalyst to promote C-O-Aryl bond cleavage [15]. Bolm and co-workers reported a one-pot reaction with a TEMPO catalyst, which starts with C_γ oxidation followed by a retro-aldol reaction and, consequently, depolymerisation [16].

In this study, we also explore the oxidation of lignin by using *tert*-butylhydroperoxide (tBHP) as the oxidant. tBHP is a widely used oxidizing agent in diverse applications and known for its high reactivity towards organic compounds in a mild environment, e.g. in Sharpless epoxidation [17,18]. As a catalyst, we explored the use of Ti bound to the free hydroxyl groups of the lignin structure. Both the incorporation of Ti and the oxidation of lignin with tBHP were accomplished under mild conditions. The Ti-modified and the oxidized lignins depolymerization were tested thereafter to access how the oxidation will interfere in the monomeric mixtures obtained. The methodology used employs supercritical ethanol as a solvent and a copper magnesium catalyst (CuMgAlOx) with proven results on literature [5,19]. Guaiacol was used as a model compound to understand in detail the transformations on lignin aromatic moieties.

3.2 Experimental Section

3.2.1 Chemicals

Organosolv lignin (BLg) extracted from beech wood was provided by ECN (now TNO). Protobind P1000 soda lignin (P1000) was obtained by soda pulping of wheat straw, purchased from GreenValue and used as received. tBHP (70% aqueous solution, Sigma Aldrich) was extracted with n-octane prior to use. Titanium (IV) isopropoxide

($Ti(O^iPr)_4$, Sigma Aldrich) was distilled before use. 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was synthesized from pinacol and phosphorus trichloride according to a method described in the literature [20]. The catalyst used for the depolymerization studies was a copper-magnesium-aluminium-oxide catalyst, $CuMgAlO_x$ which was synthetized according to a literature procedure [5]. All other chemicals were obtained from Sigma Aldrich and used as received.

3.2.2 Product analysis

2D Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance spectroscopy (^1H- ^{13}C HSQC NMR) spectrum was recorded using a VARIAN INOVA 500 MHz spectrometer equipped with a 5 mm ID AutoX ID PFG Probe. Spectra were obtained using the phase-sensitive gradient-edited HSQC program (gHSQCAD). The main parameters were as follows: 16 scans, acquired from 0 to 16 ppm in F2 (^1H) with 1200 data points (acquisition time 150 ms), 0 to 200 ppm in F1 (^{13}C) with a 2 s relaxation delay and 256 t_1 increments (acquisition time 10 ms). The samples were prepared with a concentration of 100 mg of the lignin in 0.6 mL dimethyl sulfoxide-d_6 (DMSO-d_6). Data processing was carried out using the MestReNova software. The central DMSO solvent peak was used as an internal reference (δ_C 39.5, δ_H 2.49 ppm). The cross-peaks were assigned according to the literature [21]. Phosphorus, proton, and carbon (^{31}P, ^1H, and ^{13}C) NMR spectra were recorded at 296 K using a Bruker 400 MHz spectrometer. To record a quantitative ^{31}P NMR spectra we used a 25 s relaxation delay between 30° pulses, 128 scans and an inverse gated decoupling pulse sequence. The chemical shift was calibrated relative to the internal standard for which the cyclohexanol peak signal centred at δ_P 144.2 ppm was used. Integration regions that were used to assign the signal and relative signal intensities used to calculate the concentration of the hydroxyl group are highlighted (**Fig. A3.1** and **Table A3.1**). ^{13}C NMR spectra were recorded with a 1.5 s relaxation delay, 16 scans and 256 time increments. The chemical shift was calibrated relative to the $CDCl_3$ resonance signal centred at δ_C 77.0 ppm. MAS ^{13}C NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer, using a 4 mm zirconia rotor at a spinning rate of 10 kHz and a frequency of 125 MHz. ^{13}C chemical shifts were referenced to adamantane.

The acquisition was performed with a standard CP pulse using 2 ms proton 90° pulse, an 800 ms contact pulse and an acquisition time of 20 ms.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyser with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K_{α}= 1486.6 eV) operating at 72 W and a spot size of 400 μm; samples were not handled under an inert atmosphere and should be considered passivated. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure of the UHV chamber was $2x10^{-8}$ mbar. Compounds were calibrated by setting the C 1s adventitious carbon position to 284.8 eV.

Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on a Shimadzu MIRacle 10 single reflection ATR accessory in the 4000-500 cm^{-1} wavelength region.

The metal content was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) on a Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing. All the samples (20 mg) were dissolved in 50 ml aqueous solution with 10 ml of H_2SO_4 and 2 ml of H_2O_2.

For lignin depolymerization, a 100 mL AmAr stirred high-pressure autoclave was used. The monomers in the resulting mixture were analysed by GC-MS on a Shimadzu 2010 GC-MS system equipped with an RTX – 1701 column (60 m x 0.25 mm x 0.25 μm) and a flame ionization detector (FID) together with a mass spectrometer. Product identification was based on a search of the MS spectra with NIST11 and NIST11s MS libraries. The monomeric content weas determined according to a method developed by Chaintreau and his co-workers [22] and the yields were calculated following **Eq. 3.1**.

$$\text{Yield of monomers (wt \%)}=\frac{\text{weight of monomers (calculated from GC-FID)}}{\text{weight of starting lignin}}\times 100 \qquad \textbf{(Eq. 3.1)}$$

3.2.3 Procedures

3.2.3.1 Synthesis of Ti-modified Organosolv Lignin

Experiments were carried out under inert atmosphere using standard Schlenk techniques. Pre-dried organosolv lignin (BLg, 1.0 g) was dissolved in 50 ml dry ethyl acetate. 5.6 ml $Ti(O^iPr)_4$ were added dropwise to this solution (18.9 mmol, 0.38 M). The mixture was kept at room temperature and under argon atmosphere for 2 hours. Upon completion, the suspension was dried under vacuum and the solid was washed with ethyl acetate to remove traces of unreacted $Ti(O^iPr)_4$. Due to its insoluble character in common solvents, the product (Ti-modified lignin, BLgTi) was characterized by elemental analysis, IR spectroscopy, XPS and MAS ^{13}C NMR.

3.2.3.2 Oxidation of Ti-modified lignin with tBHP

For a typical oxidation reaction, approximately 100 mg of BLgTi were suspended in 5.0 ml solution of tBHP (1.0 M in n-octane). The heterogeneous mixture was stirred (600 rpm) at 60 °C for 24 hours. After completion, the oxidised Ti-modified lignin was separated by centrifugation, washed with n-octane and dried under vacuum. The product was insoluble and, therefore, it was only characterized by IR and MAS ^{13}C NMR spectroscopy.

3.2.3.3 Lignin depolymerization

Typically, the autoclave was charged with 500 mg of catalyst, 1000 mg of lignin, and 40 mL of ethanol. The sealed reactor was several times purged with nitrogen to remove all the oxygen. The initial pressure was set to 10 bar, the stirring to 500 rpm, and the temperature to 340 °C. Heating to the desired temperature took 1 hour. The reaction mixture was kept under the described conditions for 4 hours more. After cooling to room temperature, a sample of the mixture was filtrated. To the filtrate, 20 μL of n-dodecane was added as internal standard and the resulting mixture solution was analysed by GC-MS to determined its monomer composition. The products of depolymerization were identified based on their MS profile and reaching to compounds libraries. For general analysis purposes, the monomeric units resulting from lignin depolymerization were subdivided into two categories: hydrogenated cyclic compounds and aromatic compounds.

3.2.3.4 Synthesis of Ti-modified guaiacol

Experiments were carried out under inert atmosphere using standard Schlenk techniques. Guaiacol (1.5 g, 11.9 mmol, 1 eq.) was dissolved in 20 ml of ethyl acetate and $Ti(O^iPr)_4$ (3.5 mL, 11.9 mmol, 1 eq.) was added dropwise under vigorous stirring. The reaction was kept at these conditions for 2 hours. The final mixture was dried under vacuum. The product (Ti-modified guaiacol 1:1, Ti-gua(1)) was characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. Analysis showed that the yellow powder obtained is a mixture of two compounds: $Ti(O^iPr)_3(OC_6H_4OMe)$ and $Ti(O^iPr)_2(OC_6H_4OMe)_2$. As determined by ICP analysis the Ti content was 13.2 wt% of Ti. The ratio between the grafted Ti and the added Ti is 0.35. Experiments were repeated using 4 equivalents of guaiacol instead of 1. The product (Ti-modified guaiacol 4:1**,** Ti-gua(4)) is a mixture of compounds, mainly $Ti(O^iPr)_1(OC_6H_4OMe)_3$ and $Ti(OC_6H_4OMe)_4$.

3.2.3.5 Oxidation of Ti-modified guaiacol with a tBHP solution

An amount of approximately 100 mg of Ti-gua(1) was dissolved in 5.0 mL solution of tBHP in n-octane**.** A total of 9 solutions of tBHP were prepared with the following oxidant concentrations: 0.02 M, 0.05 M, 0.08 M, 0.10 M, 0.25 M, 0.50 M, 0.75 M, 1.00 M and 2.00 M. The reaction mixture was kept at 60°C and stirred at 600 rpm for 24 hours. The product (oxidised Ti-modified guaiacol, Oxi-gua) precipitated during the reaction and was isolated by centrifugation, washed with n-octane to remove traces of side products and dried under vacuum. Due to its insoluble character, Oxi-gua was characterized only by IR and MAS ^{13}C NMR spectroscopy.

3.2.3.6 Derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

A stock solution was made by dissolving 6.2 µl cyclohexanol and 8.4 mg chromium(III)acetylacetonate in 1.5 ml pyridine/CDCl3 (1.6:1; v/v). 13 mg of organosolv lignin was dissolved in 200 µL of pyridine/CDCl3 (1.6:1 v/v) and 400 µL of stock solution was added. Finally, 30 µl of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added to the prepared lignin solution and stirred to form a homogeneous mixture.

3.3 Results and discussion

3.3.1 Lignin characterization

We used an organosolv lignin extracted from beech wood (a hardwood) via the solvent extraction method [23]. NMR spectroscopy was applied to characterize the resulting lignin before modifying it further. 2D HSQC NMR spectra of the BLg are shown in **Fig. 3.1**. We followed relevant literature for the identification [21] and quantification [24] of the predominant linkages present in this sample. Two regions of the spectra are of particular interest. The oxygenated side-chain region at δ_C/δ_H: 92 - 45/2.6 - 5.6 ppm represents the carbon-proton cross-peaks of the linkages between lignin building blocks (**Fig. 3.2a**). The aromatic region at δ_C/δ_H: 125 - 100/6.2 - 7.6 ppm relates to cross-peaks of the different C_9-units (**Fig. 3.2b**). The most representative linkages in the lignin are β-O-4, β-β and β-5 bonds. The α position of β-β (δ_C/δ_H: 85/4.63 ppm) and β-5 (δ_C/δ_H: 87/5.47 ppm) bonds are easily distinguished in these spectra. On the other hand, the assigned resonance signal for the α proton/carbon cross-peak of the β-O-4 linkage is weaker (δ_C/δ_H: 72/4.89 ppm; low intensity). In the aromatic region, the predominant C_9-unit is $S_{2,6}$ at δ_C/δ_H: 104/6.62 ppm. The aromatic cross-peaks of H (δ_C/δ_H: 119/6.78 ppm) and G_2 (δ_C/δ_H: 113/6.77 ppm) units are identified as well. Bond quantification is based on the integration of the C_α cross-peaks and uses the integrated G_2 signal as a reference and the results are presented on **Fig. 3.2**. The calculations indicate a β-O-4 linkage content of 1.9 per 100 Ar, which is low compared to the β-β content (11.1 per 100 Ar) and the β-5 content (3.5 per 100 Ar). The lignin interlinkage distribution emphasizes the relatively high content of C-C interlinkages, which leads to a low reactivity of the lignin.

Derivatization of the lignin with 2-chloro-4,4,5,5-tetra-methyl-1,3,2-dioxaphospholane followed by quantitative ^{31}P NMR spectroscopy was employed to determine the number of OH groups (see **Fig. A3.1** and **Table A3.1**) [25–27]. The aliphatic

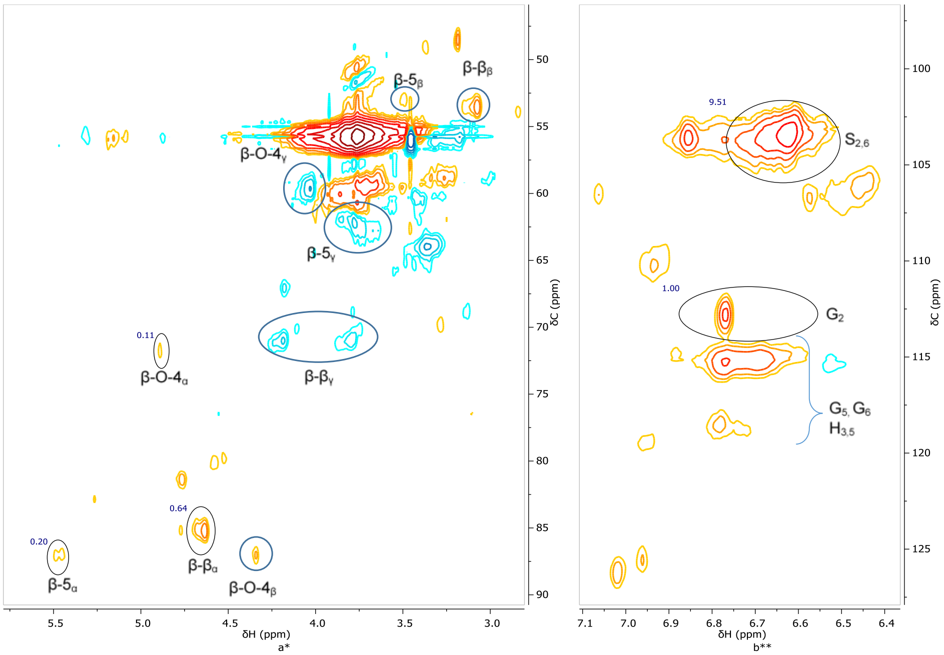
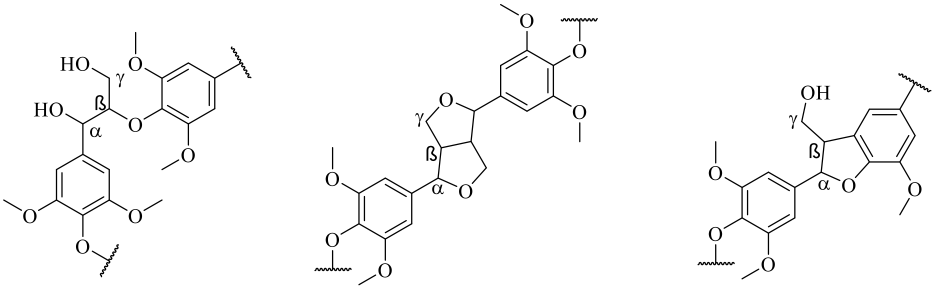


Fig. 3.1 BLg $^{1}H,^{13}C$-HSQC NMR of **a)** the side-chain region with the integration of α resonance signals of β-O-4, β-β, and β-5 bond types, and **b)** of the aromatic region with the integration of G_2 and $S_{2,6}$ resonance signals used in the quantification. The quantification was made according to the literature and the integration signal of the G_2 (δ_C/δ_H: 113/6.77 ppm) was used as reference [24]. *Highlighted the carbon-proton correlation signals of α, β and γ atoms. **Identification of carbon-proton correlation signals of other important aromatic features.

OH content is 0.95 mmol/g, which is relatively low and in agreement with the low content of β-O-4 interlinkages. On the other hand, the phenolic OH content of this lignin is relatively high: 2.54 mmol/g of phenolic syringyl groups (δ_P: 144 - 141.5 ppm) and 1.06 mmol/g of phenolic guaiacyl and demethylated hydroxyl groups (δ_P: 140.5 - 139.8 ppm). The low number of aliphatic OHs and the high content of syringyl groups is in good agreement with the 2D HSQC NMR analysis. Signals due to 4-O-5’ condensed phenolic units at δ_P 144.3 - 142.8 ppm and p-hydroxylphenolic groups at δ_P 138.6 - 136.9 ppm were not observed for this lignin.



ß-O-4 (1.9 per 100 Ar) ß-ß (11.1 per 100 Ar) ß-5 (3.5 per 100 Ar)

Fig. 3.2 Chemical structure, identification, and quantification per C_9-unit of the three main linkages find on lignin determined by the ^{1}H-^{13}C HSQC NMR.

3.3.2 Lignin titanation and oxidation

The first attempt to oxidise lignin was done with a simple and commercially available titanium catalyst: titanium(IV) isopropoxide ($Ti(O^iPr)_4$). n-Octane was used as the solvent because of the stability of the organic peroxide in this solvent. A drawback is however that lignin cannot be dissolved in n-octane. BLg was suspended in n-octane followed by addition of the catalyst and tBHP. After 2 h reaction at 60 °C, the IR spectrum of the solid product was compared to that of the parent lignin (**Fig. A3.2**). The resulting spectra are similar and, specifically, there is no indication of oxidation. GC analysis of the reaction mixture showed that more than 90% of the tBHP added was converted into tBuOH. This indicates that the organic peroxide was decomposed by the Ti catalyst. The results indicate that lignin was not affected by this procedure, which can be attributed to its insolubility in n-octane.

In order to overcome this problem, we explored the grafting of the Ti catalyst to organosolv lignin followed by oxidation with tBHP. For this, we made use of the relatively high hydroxyl content of this lignin. Given the strong Lewis acidity of $Ti(O^iPr)_4$, we did not use a base to catalyse the grafting process. Lignin titanation was done in ethyl acetate by adding $Ti(O^iPr)_4$ dropwise, which resulted in a brown precipitate (BLgTi). Analysis of the Ti-modified lignin showed that the Ti content was 14.3 wt%, which means the ratio between the grafted Ti and the added Ti is 1.58×10^{-2}. An XPS analysis revealed a (surface) Ti content of 13.5 wt%. The ratio between the free OH

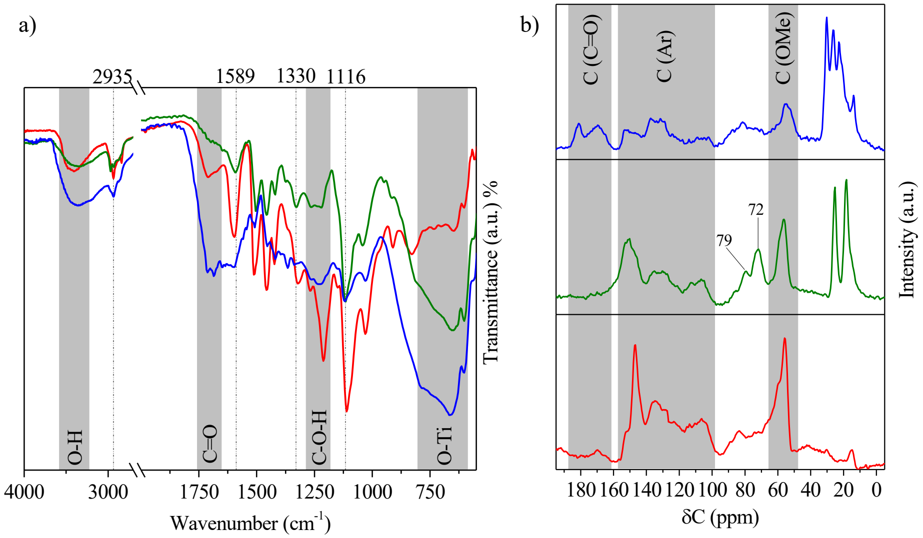


Fig. 3.3 a) IR and **b**) MAS ^{13}C NMR spectra of the BLg (red), BLgTi (green) and Oxi-BLgTi (blue). The main structural changes are highlighted.

groups (measured by derivatization with a phosphorous compound) and the grafted titanium is 0.24. As the resulting lignin cannot be dissolved in common solvents, we could not further characterize it using 2D HSQC NMR. Therefore, we turned to IR and MAS ^{13}C NMR spectroscopy to track the changes due to the titanation step.

The IR spectra of the Ti-modified and the parent lignin are shown in (**Fig. 3.3a**). Two main differences are observed. A band at 656 cm^{-1} in the BLgTi is a Ti-O bond stretching vibration, while the decreased intensity of the band at 3410 cm^{-1} indicates the consumption of hydroxyl groups. Also, the band at 1330 cm^{-1} (C-O-H bending vibration (C-O deformation) has a lower intensity after titanation. The band at 2935 cm^{-1} (CH stretch from aromatic methoxy and side-chain methyl) became more intense, which is likely due to the isopropoxide groups remaining as ligands to Ti. The position of this band is consistent with the C-H vibration of CH_3 groups in $Ti(O^iPr)_4$.

The MAS ^{13}C NMR spectrum of the parent lignin contains signals in three main regions, i.e., between 50 - 90 ppm due to lignin side-chain carbons, between 95 - 160 ppm due to aromatic carbons and between 165 - 180 ppm due to carbonyl carbons [28,29]. Comparison to the NMR spectrum for the BLgTi (**Fig. 3.3b**) revealed two types of changes. In the regions between 15 - 30 ppm and 70 - 80 ppm, new peaks are seen, which originate from some the isopropyl groups of $Ti(O^iPr)_4$ that were not substituted when the Ti was loaded on the lignin. The peaks at 19 and 26 ppm correspond to primary carbons of the isopropyl group (CH_3) and the peaks at 72 and 79 ppm to tertiary carbons (CH). The fact that there are two peaks for each carbon indicates that there are at least two different types of grafted Ti with different substitution degrees of the parent ligands. The changes registered in the aromatic region were less obvious, but still significant. The ^{13}C NMR signals due to aromatic C can be divided into three groups represented by regions (i) between 125 - 103 ppm for non-substituted aromatics, (ii) between 141 - 125 ppm for C-substituted aromatic carbons and (iii) between 160 - 141 ppm for O-substituted aromatic carbons. There was a small shift of the signal at 128 ppm for the parent lignin to 134 ppm for the Ti-modified counterpart and a significant intensity decrease of the signal at 147 ppm. These changes are the result of the titanium binding to the phenolic moieties, shifting the signals to a less protected region of the spectrum. The intensity reduction of the signal belonging to the O-substituted aromatic carbons after titanation might be related with the extensive transformation of the phenolic moieties.

As a next step, we explored tBHP oxidation using Ti-modified lignin both as a substrate and as a catalyst. The modified lignin was suspended in a tBHP solution in n-octane. After 24 hours reaction at 60 ºC, the oxidized Ti-modified lignin (Oxi-BLgTi) was isolated and characterised by IR and solid-state NMR spectroscopy, as it remained insoluble in common solvents. The results indicate that lignin lost a large part of its aromaticity. Analysing the IR spectra (**Fig. 3.3a**), it is seen that a new band located at 1715 cm^{-1} appears, which is indicative of a larger amount of -C=O stretching vibrations. On the other hand, bands representing the bond stretching vibrations of the aromatic rings became weaker. The characteristic bands of the aromatics at 1116 cm^{-1} (aromatic C-H in-plane deformation), 1421 cm^{-1} (aromatic skeletal vibration combined with C-H deformation), 1503 cm^{-1} (asymmetric aryl ring stretching) and 1589 cm^{-1} (symmetric aryl ring stretching) have lower intensity when compared with the starting Ti-modified lignin. In the ^{13}C NMR spectrum, new peaks located at 169 ppm and 181 ppm confirm the formation of new –C=O bonds. The region between 180.0 - 168 ppm are the resonance signals of carboxylic acids (–COOH) and esters (-COOR'). Comparing the aromatic rings resonance signals of the titanated with the oxidised lignin, there is a loss of half of the signals due to aromatic rings upon the oxidative treatment.

3.3.3 Depolymerization of Ti-modified and Oxidized lignins

We employed our approach to modify soda lignin P1000 and establish its impact on lignin depolymerization in supercritical ethanol assisted by a copper-magnesium-aluminium-oxide catalyst ($CuMgAlO_x$) [5,19]. We chose P1000 for this purpose to compare the reference results to earlier work. P1000 was titanated and oxidized prior to depolymerization utilizing the same conditions as for organosolv lignin. XPS analysis of the Ti-modified P1000 revealed a Ti content of 11.6 wt%, while the Ti content was 9.1 wt% for oxidised Ti-modified P1000 (Oxi-P1000). The partial loss of Ti during oxidation with tBHP was also observed in the organosolv lignin experiments.

Table 3.1 Yield (wt%) subdivided into hydrogenated cycles, aromatics, and total, and total weight of monomers obtained by depolymerization of 6 lignin samples using supercritical ethanol as solvent and $CuMgAlO_x$ as catalyst at 340 °C.

Entry	Lignin	Yield (wt%)			Total weight of monomers (mg)
		Hydrogenated cycles	Aromatics	Total	
1	P1000	10.2	8.3	18.5	184.8
2	Ti-modified P1000	7.7	9.2	16.9	168.6
3	Oxi-P1000	8.4	3.3	11.7	116.7
4	BLg	1.3	3.2	4.6	46.0
5	BLgTi	1.7	3.7	5.5	54.7
6	Oxi-BLgTi	1.7	1.5	3.2	32.4

Depolymerization experiments were carried out for 6 lignin samples: **1**) P1000, **2**) Ti-modified P1000, **3**) Oxi-P1000, **4**) BLg, **5**) BLgTi, and **6**) Oxi-BLgTi. At the end of each

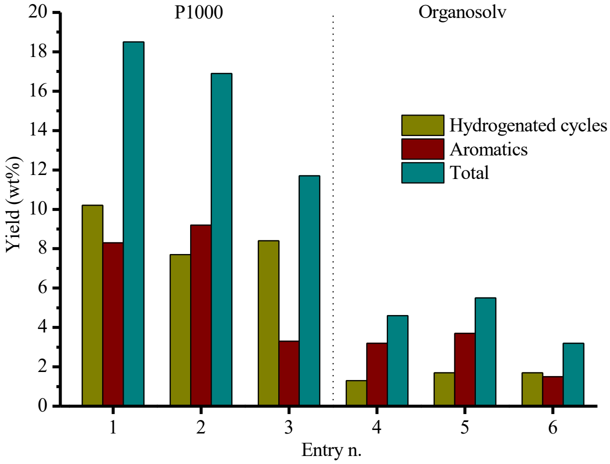


Fig. 3.4 Monomers yield (wt%) subdivided into hydrogenated cycles, aromatics, and total obtained from 6 different lignin depolymerization experiments using supercritical ethanol as solvent and $CuMgAlO_x$ as catalyst at 340 °C. Entry numbers are according to **Table 3.1**.

reaction experiment, the liquid phase was sampled and analysed by GC-MS. We grouped the monomeric products in the resulting oil in two categories: hydrogenated cyclic compounds and aromatic compounds. The resulting compositions are presented in **Table 3.1** and **Fig. 3.4** with detailed information about the monomers being provided in **Tables A3.2 – A3.7** of Appendix. The presence of titanium in both lignins and the subsequent oxidation step did not significantly improve its depolymerization. In fact, the highest depolymerization yield of 18.5 wt % was obtained for P1000 not exposed to any pre-treatment (control sample, **Table 3.1** and **Fig. 3.4**, Entry 1). The lignin oxidation method mainly affects the aromatic features of the lignin. It is difficult to determine how the aliphatic parts of the lignin were modified upon oxidation and depolymerization, because ethanol is also converted yielding a range of aliphatic products with more than 2 carbon atoms [19].

Fig. 3.4 and **Table 3.1** demonstrate the expected higher reactivity of the soda lignin P1000 in comparison with the organosolv lignin. This difference can be understood by analysing the lignin bond types by 2D HSQC NMR of P1000 (**Fig. A3.3**), which indicates a β-O-4 linkage content of 16.2 per 100 Ar and a β-β linkage content of 15.9 per 100 Ar. The signal of the C_α cross-peak of the β-5 linkage was absent. Structurally, the P1000 has more ether bonds on its aliphatic regions when compared with the organosolv lignin, a feature which makes it more susceptible to depolymerization. The low aromatic content associated with the depolymerization of the oxidized samples and the IR and solid-state NMR analysis indicated that the aromatic region was greatly compromised by the oxidation step with tBHP. As we expected that this can be due to ring opening of aromatics moieties in lignin, we used guaiacol as a simple model compound for lignin to study the oxidation step upon titanation.

3.3.4 Guaiacol oxidation – a model compound study

We explored the intrinsic chemistry of the suspected aromatic ring opening by grafted Ti using guaiacol as a model compound. This approach was chosen because the reactions with lignin showed a high titanation degree of phenolic OH groups. The same Ti source ($Ti(O^iPr)_4$) was used to titanate guaiacol. Two Ti-modified guaiacol substrates were synthesized at guaiacol-to-$Ti(O^iPr)_4$ ratios of 1:1 and 4:1. The resulting products were characterized by ^1H and ^{13}C NMR spectroscopy.

The ^1H NMR spectra of both products (**Fig. 3.5a**) showed the disappearance of the guaiacol OH resonant signal at δ_H 5.94 ppm. This indicates that this functional group can react with the Ti precursor. A shift of the aromatic resonant signals was noticed from δ_H 7.05 - 6.90 ppm to 6.95 - 6.60 ppm, which can be explained by the influence of Ti on the signal of aromatic protons. The broadening and increasing number of these features with increasing guaiacol-to-Ti ratio indicates the formation of a mixture of compounds. A new functional group between δ_H 1.29 - 1.15 ppm is assigned to the resonance signals of isopropyl groups (CH_3), which were not removed during the grafting process. The integration of the $^iPr(CH_3)$ and Ar(H) resonant signals indicates a ratio of 4 Ar(H) to 12.6 $^iPr(CH_3$ protons) for the Ti-modified guaiacol 1:1 (Ti-gua(1)) and 4 Ar(H) to 1.5 $^iPr(CH_3$ protons) for the Ti-modified guaiacol 4:1 (Ti-gua(4)). The higher substitution of O^iPr groups for Ti-gua(4) is expected in view of the higher guaiacol amount.

The ^{13}C NMR spectra (**Fig. 3.5b**) clarified the extent of the molecular diversity by the number of aromatic C resonant signal located between δ_C 155 - 100 ppm. In the experiment with an equimolar ratio of guaiacol and $Ti(O^iPr)_4$, the number of aromatic carbons is consistent with a mixture of $Ti(O^iPr)_3(OC_6H_4OMe)$ and $Ti(O^iPr)_2(OC_6H_4OMe)_2$. On the other hand, the experiment with a 4-fold excess guaiacol contains a larger number of species. The data suggest that we deal predominantly with $Ti(O^iPr)(OC_6H_4OMe)_3$ and $Ti(OC_6H_4OMe)_4$ (high intensity ^{13}C signals) and traces of guaiacol, $Ti(O^iPr)_3(OC_6H_4OMe)$ and $Ti(O^iPr)_2(OC_6H_4OMe)_2$ (**Fig. 3.5d**). The same pattern is observed for the ^{13}C resonant signals of the methoxy group between δ_C 57 - 55 ppm, and it also shows a larger number of signals for the mixture prepared with excess guaiacol. By contrast, the number of isopropyl group ^{13}C resonant signals for the Ti-gua(4) mixture is lower than for the Ti-gua(1) sample, specifically considering the CH_3 signal between δ_C 26 - 25 ppm and the CH signal between δ_C 82 - 80 ppm. These differences confirm the lower number of isopropyl groups when more guaiacol is added. In fact, it was observed that, upon addition of more guaiacol to a solution of Ti-gua(1), the substitution of the isopropoxide groups continues.

The finding that free hydroxyl groups are consumed by substitution of the isopropoxide groups on Ti can explain the low solubility of lignin in common solvents after titanation (such as ethyl acetate or THF, which previously dissolved it). We suspect that the introduction of Ti as the isopropoxide complex leads to crosslinking of the lignin structure, resulting in a bulkier structure. This could not be tested by GPC due to the insolubility problem.

We carried out guaiacol oxidation using Ti-gua(1), because this model compound is a better representative of Ti-modified lignin due to the larger amount of isopropyl groups. The oxidation of the Ti-gua(1) was evaluated in solutions containing different concentrations of tBHP (reaction at 60 ºC for 24 h). The products are insoluble in common solvents, similar to the oxidized Ti-modified lignin, and were therefore characterized by IR and MAS ^{13}C NMR spectroscopy.

The IR spectra of Ti-gua(1) and guaiacol are shown in **Fig. 3.5c**. The differences between these spectra are the appearance of the band at 629 cm^{-1} (Ti-O stretching vibration), the disappearance of the band at 3410 cm^{-1} (OH stretching vibration) and the intensifying of the bands at 2859 cm^{-1}, 2924 cm^{-1}, and 2967 cm^{-1} (stretch vibrations of CH bonds of the isopropyl groups). For the aromatic stretching region, we found that the

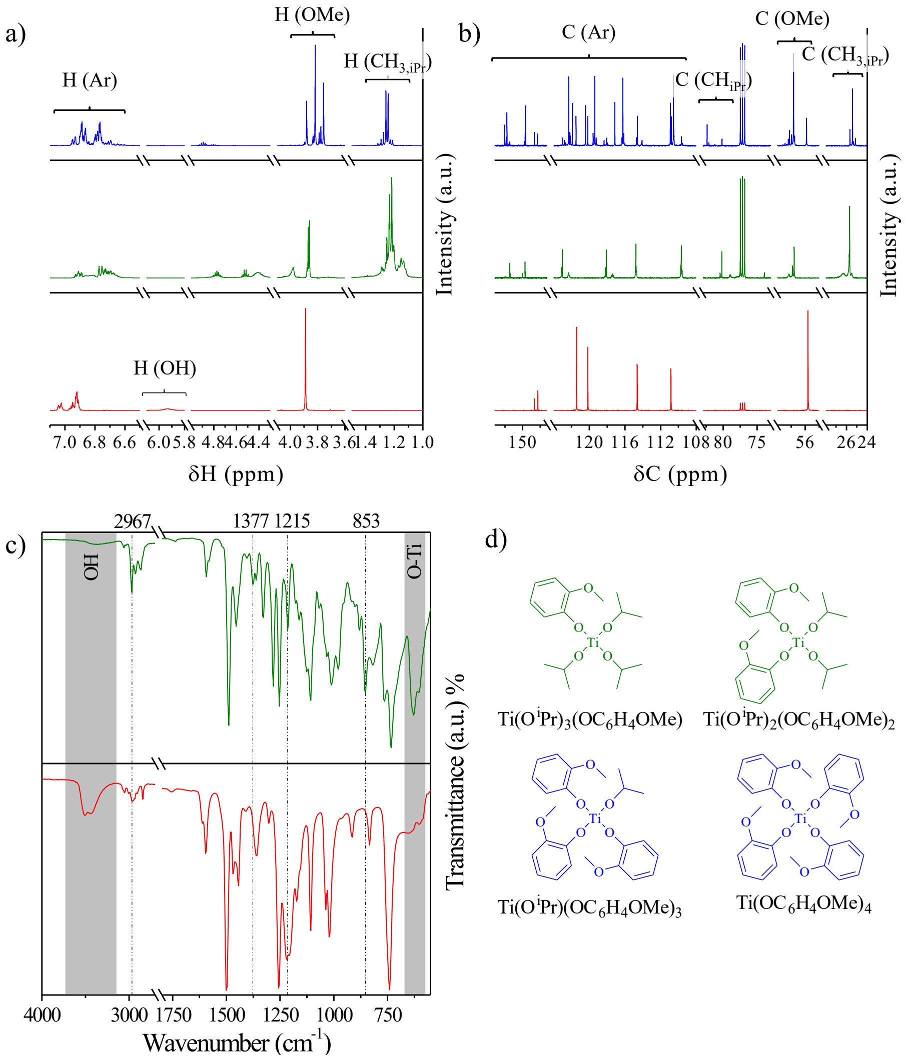


Fig. 3.1 Comparison between the **a)** ^{1}H NMR and **b)** ^{13}C NMR spectra of guaiacol (red), Ti-gua(1) (green) and Ti-gua(4) (blue). **c)** IR spectra of guaiacol (red) and Ti-gua(1) (green) with the most important bands highlighted identifying the structural changes. **d)** Chemical structures of Ti-gua formed in the guaiacol titanation reactions.

band at 853 cm^{-1} (Ar C-H out-of-plan deformation vibration) became more intense, while the bands at 1215 and 1377 cm^{-1} (C-O-H bending vibration and C-O stretching vibrations, respectively) became weaker. These changes match the expected results for the grafting of Ti through the guaiacol OH group.

The IR spectra of the products after oxidation with tBHP (Oxi-gua) are presented in **Fig. 3.6a** (respective tBHP concentration used to treat the sample is highlighted on the graphic). With increasing oxidant concentration, the structure of the reactant was more affected. The bands at 853 cm^{-1} and 735 cm^{-1} (C-H out-of-plane deformation vibrations), at 1255 cm^{-1} and 1107 cm^{-1} (C-H in-plan deformation vibrations), and at 1490 cm^{-1} and 1592 cm^{-1} (-C=C- stretch vibration) are disappearing with the increase of the tBHP concentration. A new band at 1736 cm^{-1} appeared due to the C=O stretching vibration of unconjugated carboxyl acids. This new band is a clear indication that the reactant was oxidised.

Oxi-gua samples treated with a low concentration of tBHP (0.1 M) and with a higher oxidant concentration (2.0 M) were analysed by MAS ^{13}C NMR (**Fig. 3.6b**). In comparison with the Ti-gua(1), the product treated with less tBHP displays minor changes of its structure with the exception of two new peaks appearing at 166 ppm and 173 ppm, reflecting the formation of new carbonyl moieties. At higher tBHP concentration, the changes are more pronounced. The peaks corresponding to the aromatic C resonant signals disappeared and new ones appeared at 84 ppm (alkene C resonant region) and at 172 ppm. The shift of the C from the methoxy group resonant signal from 57 ppm to 53 ppm is consistent with the structural change from MeO-Ph to MeO-CH(-CH=)$_2$.

These substantial changes in the aromatic region of the titanated materials (i.e,, for lignin and guaiacol) upon oxidation indicate that aromatic ring opening occurred. The MAS ^{13}C NMR and IR spectra of the oxidised materials demonstrate similar structural changes: new carbonyl group signals and less intense aromatic signals. The partial ring cleavage by oxidation with tBHP is associated with Ti grafting on the lignin. In all our blank experiments and in an attempt of oxidizing lignin with Ti(O^{i}Pr)$_4$ reported initially on Chapter 2, there was no indication that the aromatic content of lignin was affected by the oxidant. This extensive structural modification of lignin was already described in the literature as a degradation pathway caused by using, for example, H_2O_2, organic peroxides and peracids [2]. Gellerstedt and Agnemo reported that ring opening was found exclusively in the presence of a catalytic metal that was able to interact with lignin [30]. Another work reported reactions introducing a similar effect on lignin that were promoted

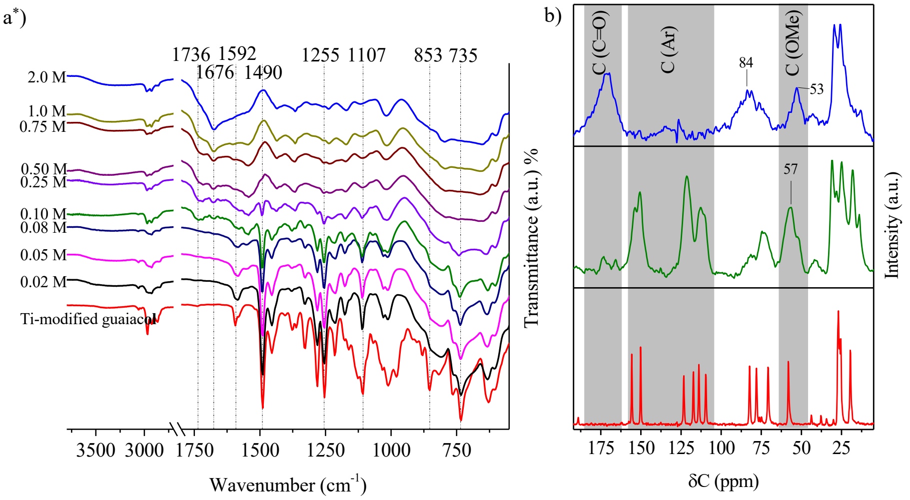


Fig. 3.2 a) IR spectra of the Ti-gua(1) after oxidation with different concentrations of tBHP and respective **b**) MAS ^{13}C NMR spectra of guaiacol (red), Oxi-gua after oxidation with 0.10 M (green) and 2.0 M (blue) of ^{t}BHP. The most important signals, identifying the changes with the increase of the oxidation, are highlighted. * Spectra stacked for clarity.

by elaborated catalysts like porphyrin-based ones [31,32]. In their studies, the reaction mechanism was thought to involve aromatic ring opening leading to muconic acid type products. In a typical ring-opening reaction by oxidation forming this species, a quinone intermediate is formed as indicated in **Fig. 3.7** [2,33]. The typical ^{13}C NMR resonant signal of quinones lies around δ_C 180 ppm (carbonyl groups in adjacent carbons) and its IR band is located between 1690 - 1675 cm^{-1}. The oxidized Ti-modified lignin MAS ^{13}C NMR spectrum has a peak at δ_C 181 ppm and its IR spectrum has a band at 1680 cm^{-1}, which might be an indication of an intermediate stage prior to opening of the aromatic ring. The C resonant signal at δ_C 169 ppm and the IR band at 1736 cm^{-1} represent the carbonyl group from the muconic acids species having their signals in the carboxylic acids regions assigned to lignin.

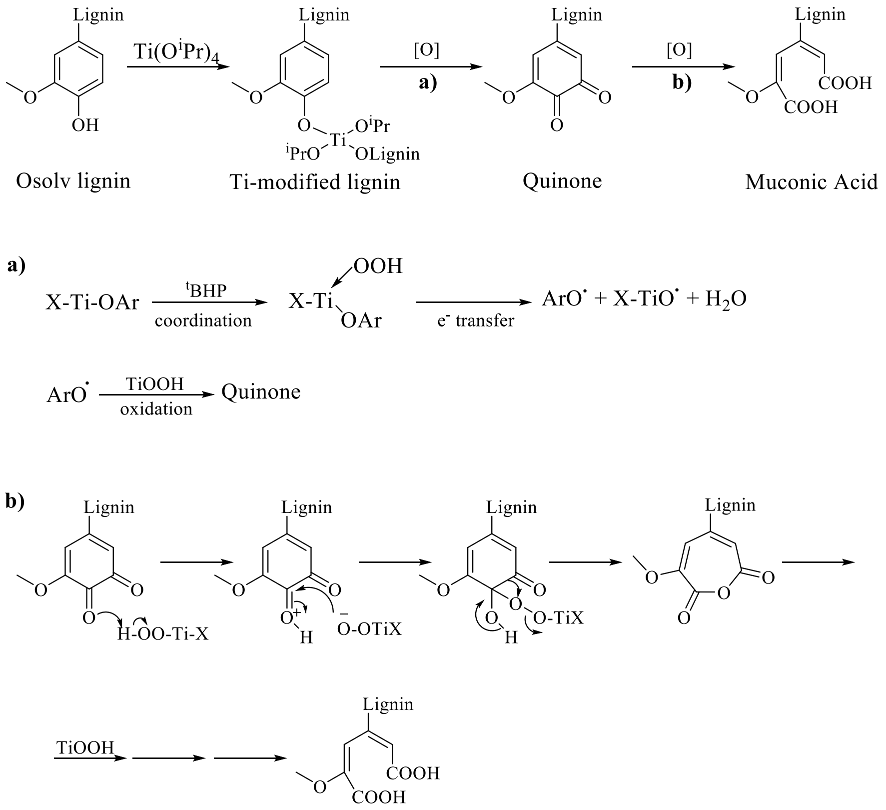


Fig. 3.3 Reaction pathway of aromatic ring opening in a typical oxidation with peroxides resulting in the formation of **a**) quinone and **b**) muconic acid species thereof [2,33–35].

3.4 Conclusions

We demonstrated a lignin oxidation process involving the titanation of lignin followed by oxidation with tBHP. Ti(O^{i}Pr)$_4$ reacted with the hydroxyl groups of lignin. The resulting Ti-lignin complexes acted both as substrate and catalyst in the oxidation of the modified lignin. Lignin oxidation led to a decreasing amount of aromatic monomers after depolymerization in ethanol using a CuMgAlO$_x$ catalyst in comparison with the parent lignin. The surmise that the decreased yield is caused by opening of aromatic rings due to oxidation was verified by studying the interaction of Ti(O^{i}Pr)$_4$ with guaiacol as a model for lignin. Detailed characterization evidenced the reaction of the phenolic OH group of guaiacol with Ti(O^{i}Pr)$_4$ giving rise to a number of Ti-guaiacol compounds. Oxidation by tBHP led to ring opening and muconic acid type species as evidenced by spectroscopic investigations. Therefore, the employed oxidation approach is limited with respect to obtaining a high yield of monomeric aromatics.

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Chapter 4

Lignin modified by titanium as a solid catalyst for alkene epoxidation

Summary

The use of lignin as a building block for hybrid catalytic materials is demonstrated. Technical lignin was functionalized with titanium by a facile reaction with titanium isopropoxide ($Ti(O^{i}Pr)_4$). Titanated lignin was used as a heterogeneous epoxidation catalyst with moderate activity for cyclooctene epoxidation with organic peroxide. The heterogeneous nature of the catalyst was proven by hot filtration tests and application in a continuous process. Titanated lignin could be recycled at least 5 times in consecutive batch epoxidation experiments. Next, the catalyst was used in a continuous flow reactor. With this study, a novel concept for lignin valorisation is demonstrated, i.e., lignin as a catalyst support.

4.1 Introduction

Biomass has been in vogue over the past decades as an alternative and renewable source of energy and chemicals. Besides cellulose and hemicellulose, biomass contains a substantial amount of lignin. In the past, many studies [1–5], patents [6,7] and even policies [8] have been developed involving this natural polymer as a way to solve environmental problems and, simultaneously, to replace fossil fuels [9,10]. Every year, approximately 50 million tonnes of lignin are produced as a side-product of the paper and pulping industry. Although 1.1 million tonnes are isolated and then used in industrial processes, the majority of lignin waste is incinerated recovering only its energy content [11,12]. The most successful case developed so far concerning high-added value products involves industrial production of vanillin from lignin [13].

Lignin is one of the three main components extracted from wood-based biomass, being the second most abundant natural polymer (only overcome by cellulose) [4,14]. Its exploitation and implementation at industrial scale has been a challenge. Complications in lignin valorisation arise from its highly complex and recalcitrant molecular structure [14,15]. These structural characteristics are a consequence of a random biosynthetic process involving three monomeric units (monolignols): *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The monolignols are connected through carbon-carbon and ether bonds, building up a structure that is composed of aliphatic chains and aromatic moieties. During this process, a variety of bonds are created with distinctive, notorious (un)reactivity and high structural complexity [14].

The majority of studies involving lignin are focused on catalytic cleavage of the polymeric structure into smaller phenolic units that can be further used as bio-fuels or as fine and bulk chemicals precursors [16–19]. However, only little work has been reported with lignin being employed as a whole structure [20,21]. The synthesis of phenol-formaldehyde resins is a major application in this respect, which is based on lignin without depolymerization. The lignin polyphenolic units can act as a substitute for phenol [22–25]. Taking advantage of the same properties, a method was patented in which lignin from processed wood waste was used as an ingredient to manufacture rubber [6]. Mullick proposed that lignin can also be used as a concrete additive, helping to control a set of desired properties of the material (such as hydration) and, at the same time, reducing the amount of cement used [26]. Recently, Bolm and co-workers presented lignin as an activator in the Strecker reaction. The lignin hydroxyl groups facilitate the formation of α-aminonitiles by enhancing the cyanation step of imines [27]. All these applications contribute to the valorisation of lignin in a broad sense and in particular those that do not require further treatment such as purification or depolymerization, thus increasing the overall economic viability of second-generation biorefineries.

The functionalization or transformation of lignin into new materials, exploiting its sturdiness, was the inspiration for this study. Previously on Chapter 3, we established the reluctance of lignin to undergo titanium-mediated oxidation [30]. This provided inspiration for a new approach, demonstrated here, in which lignin is used as a support for a heterogeneous catalyst. Titanation of lignin was found to result in catalytic materials for alkene epoxidation. Catalyst synthesis exploited the high amount of free hydroxyl groups on the lignin structure and their reactivity to titanium alkoxide. Given the relevance of titanates in alkene epoxidation [28,29], also titanated lignin was found to be catalytically active. As a heterogeneous catalyst, the new lignin-based catalyst was successfully applied in cyclooctene epoxidation using an organic peroxide as the oxidant. Its catalytic performance was first tested in batch, but its activity proved also to be adequate for use in a continuous-flow reactor.

4.2 Experimental Section

4.2.1 Chemicals

tert.-Butylhydroperoxide (tBHP) (70% aqueous solution, Sigma Aldrich) was extracted with n-octane before use. The catalysts used in this study - Ti-modified organosolv lignin (BLgTi) [30] and the titanium-silica catalyst (SiTi) [31] - were synthesised according to literature procedures. For the synthesis of BLgTi**,** organosolv lignin extracted from beech wood and provided by Energy Centrum Nederland (ECN, now TNO) was used. For the catalytic epoxidation test under flow conditions, the BLgTi was crushed and sieved and a sieve fraction of 180-250 μm was used. All other chemicals were obtained from Sigma Aldrich and used as received.

4.2.2 Product analysis

^{13}C MAS NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer, using a 4 mm zirconia rotor at a spinning rate of 10 kHz and a frequency of 125 MHz. ^{13}C chemical shifts were referenced to adamantane. The acquisition was performed with a standard CP pulse using 2 ms proton 90º pulse, an 800 ms contact pulse and an acquisition time of 20 ms.

Titanium metal content was determined by elemental analysis and X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyser with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K_α= 1486.6 eV) operating at 72 W and a spot size of 400 μm; samples were not handled under an inert atmosphere and should be considered passivated. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure of the UHV chamber was $2x10^{-8}$ mbar. Compounds were calibrated by setting the C 1s adventitious carbon position to 284.8 eV.

Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on a Shimadzu MIRacle 10 single reflexion ATR accessory in the 4000-500 cm^{-1} wavelength region.

For the thermogravimetric analysis (TGA) of the Ti-modified lignin, a Mettler Toledo TGA/DSC 1 instrument was applied. An amount of ca. 20 mg of material was placed in an uncovered alumina crucible, which was heated to 750 ºC at a rate of 5 ºC/min in a 40 mL/min He + 20 mL/min O_2 flow. The X-ray diffraction (XRD) was performed with a Bruker D2 power diffraction system.

The nitrogen sorption isotherms of the lignin-based materials were measured at -196 °C on a Micromeritics TriStar II system in static measurement mode. The samples were outgassed at 120 °C for 3 h, prior to the soption measurements. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area (S_{BET}) from the adsorption data obtained (p/p0 = 0.05-0.25).

Catalytic tests in batch were performed on a Chemspeed ASW2000 workstation using 10 mL double-walled reactors which are vortex shaking. Catalytic tests in flow were performed on a Thalesnano X-Cube plug flow reactor (**Fig. A4.1**). The plug-flow reactor bed dimensions were 65 mm of length and 4 mm of internal diameter, as standard for ThalesNano cartridge. Samples, both from batch or flow experiments, were collected in time and monitored by gas chromatography (GC) involving determination of cyclooctene, cyclooctene oxide, tBHP and tert-butanol (tBuOH) through comparison with internal standards. Analysis was done on a Shimadzu GC2010 gas chromatograph equipped with a 30.0 m x 0.21 mm x 1.00 µm dimethyl polysiloxane column, in which He was used as the carrier gas (injector temperature 250 ºC). The oven temperature program was from 45 – 120 ºC at a ramp rate of 10 ºC/min, followed by 120 – 250 ºC at 20 ºC/min. The initial and final temperature isothermal dwells were 3 and 2 min, respectively. 1,3,5-Trimethylbenzene and *tert*-butylbenzene were used as internal standards (IS). The retention time and the response factor of substrates and products are given on **Table A4.1**. The response factors (Rf_y) were determined for every component concerning the 1,3,5-trimethylbezene using the **Eq. 4.1**, and the concentration of the component 'y' (C_y) in % (mol/mol cyclooctene$^{t=0}$) was determined by the **Eq. 4.2**. Rf_y is the response factor of component 'y' with respect to the internal standard; Area IS and Area component are the peak area of the internal standard and of the component peak, respectively; M IS, M cyclooctene and M component are the weights (g) of the initial amount of internal standard, the initial amount of cyclooctene and the component, respectively; MW cyclooctene and MW component are the molecular weight (MW; g/mol) of cyclooctene and the component, respectively. Each sample was prepared by adding 100 µL of the reaction mixture to 1,00 mL of n-octane.

$$Rf_y = \frac{\text{Area IS}}{\text{Area component}} \times \frac{\text{M component}}{\text{M IS}} \qquad \textbf{(Eq. 4.1)}$$

$$\mathrm{Cy}=\frac{\dfrac{\text{Area component}}{\text{Area IS}}\times\dfrac{\text{M IS}}{\text{MW component}}\times \text{Rfy}}{\dfrac{\text{M cyclooctene}}{\text{MW cyclooctene}}}\times 100 \qquad \textbf{(Eq. 4.2)}$$

4.2.3 Procedures

4.2.3.1 Batch reactions

Unless stated otherwise, 2.5 mL of a solution of cyclooctene (2.0 M) and 1,3,5-trimethylbenzene (2.0 M) in n-octane, and 2.5 mL of a solution of tBHP (2.4 M) in n-octane were added to a Chemspeed 10 mL reactor containing the required amount of catalyst. The mixture was stirred (600 rpm) for 24 h at the required temperature. Samples were collected automatically in time and analysed by gas chromatography.

For the catalyst recycling experiments, at the end of each cycle, the catalyst was separated by filtration, washed 3 times with n-octane to remove traces of substrates and products, dried under vacuum at room temperature and then reused in another cycle.

4.2.3.2 Hot filtration test

To a 5.0 ml vial were added cyclooctene (0.631 g, 5.0 mmol), 1,3,5-trimethylbenzene (0.601 g, 5.0 mmol), 2.5 mL of a 2.0 M solution of ^{t}BHP in n-octane, and the remaining volume was filled with n-octane to afford a total volume of 5 mL. The solution was homogenised, and 50.0 mg of BLgTi was added. The reaction was stirred (600 rpm) at 60 ºC for 2 hours, and samples were collected in time. After 2 hours, the reaction mixture was immediately filtrated removing the catalyst, and the liquid fraction was placed back in a vortex stirred reactor vessel at 60 ºC for the next 24 hours. Samples were again collected in time and analysed by GC.

4.2.3.3 Continuous-flow reactions

A catalyst bed was packed with the required amount of catalyst diluted in silica carbide. Two solutions were prepared independently in n-octane. Solution 1 was a mixture of cyclooctene (1.0 M) and 1,3,5-trimethylbenzene (1.0 M). Solution 2 was a mixture of tBHP (1.2 M) and tert-butylbenzene (1.0 M). Two pumps were used to drive an equal pre-determined volume of each solution through the reactor at known flow rates, with an internal pressure set to 10 bar. The reactor schematics are shown in **Fig. A4.1**. Samples were collected in time and analysed by GC.

4.3 Results and discussion

4.3.1 Catalyst characterization

BLgTi was made by treatment of Lignin with titanium isopropoxide as previously described [30]. Before evaluating the BLgTi performance as an epoxidation catalyst, its basic physico-chemical properties were determined and compared to known data [30]. The corresponding data are given in the SI.

XPS and elemental analysis showed that the titanium content was approximately 14 %. ^{13}C MAS NMR and IR spectroscopy confirmed that the titanium was grafted by conversion of previously lignin OH groups to Ti-O-Lg groups as evident from the disappearance of the band at 3410 cm^{-1} in the IR spectrum and the appearance of some isopropanol from the $Ti(O^iPr)_4$ source (**Fig. 3.3a**). The presence of residual isopropoxy ligand was also evident from the ^{13}C MAS NMR spectrum.

The analysis of the nitrogen adsorption isotherm of the BLgTi shows that it possesses a total BET surface area of 7.4 m^{2}g^{-1} (**Fig. 4.1a**, green). XRD measurements showed that no crystalline TiO_2 had formed in the BLgTi sample.

The thermogravimetric behaviour of BLgTi was determined and compared to lignin starting material. In general, for typical lignin the thermogravimetric (TG) curve exhibits three stages. The first stage of mass loss is between 30 – 120 ºC (due to evaporation of absorbed water), the second stage occurs between 180 – 350 ºC (due to decomposition of carbohydrates) and the last stage of mass loss is at temperatures above 350 ºC (due to degradation of phenolic, alcohols, and aldehydes) [32]. The organosolv lignin used in preparing BLgTi has a similar mass loss sequence (**Fig. 4.1b**, red). The major mass loss percentage starts around 200 ºC and continues until 540 ºC. In contrast is the TG curve of the BLgTi (**Fig. 4.1b**, green) where thermal degradation already starts at lower temperature. The most significant mass loss begins around 150 ºC and continues until 500 ºC. At approximately 360 ºC, 50% of the BLgTi mass was volatized. The earlier onset

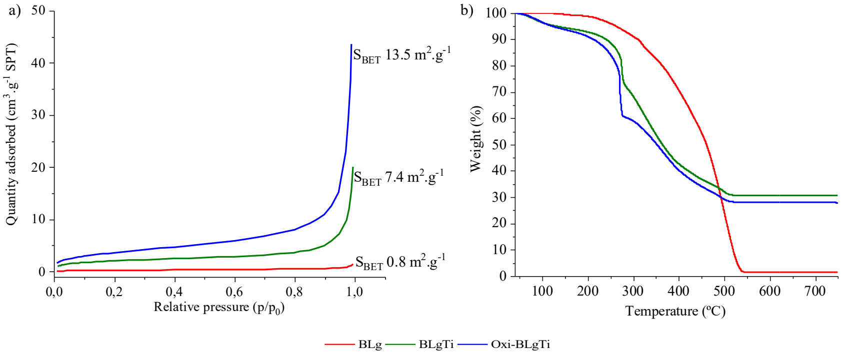

Fig. 4.1 **a**) N_2 adsorption isotherm of the BLg (red), BLgTi (green), and the Oxi-BLgTi (blue). **b**) TG curves of the BLg (red), BLgTi (green), and the Oxi-BLgTi (blue) obtain under He and O_2 atmosphere at a heating rate of 5 ˚C.min.

of degradation suggests that the presence of titanium accelerates combustion in air. After 520 ºC, there is no more mass loss registered. The remaining mass corresponds to approximately 30 % of the original sample. After the TG analysis was completed, a white powdery residue remained on the sample holder. This powder was identified as titanium dioxide formed upon the degradation of the organic part of the material, which the mass corresponds to the titanium content indicated by the elemental analysis.

4.3.2 Batch catalytic test

Previously, we reported that titanium grafted into the native lignin acts as a catalyst in oxidizing lignin with tBHP as the oxidant [30]. Inspired by this catalytic action, we explored the potential of BLgTi and tBHP for catalytic alkene epoxidation (**Fig. 4.2**).

As BLgTi is found to be insoluble in common solvents such as ethanol, methanol, THF, toluene, chloroform, water, ethyl acetate, diethyl ether, dimethylformamide, the catalytic activity was determined using BLgTi as a suspension in a reagent solution. This represents a heterogeneous system, potentially containing BLgTi as a heterogeneous

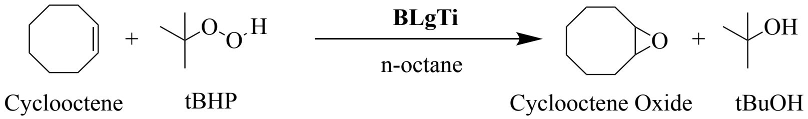

Fig. 4.2 Schematic representation of the cyclooctene epoxidation reaction with the tBHP catalysed by BLgTi.

catalyst. Initial experiments were carried out in batch at 60 °C with a total reaction time of 24 h. Samples were automatically collected in time, and the concentration of reagents and products were monitored by gas chromatography. The resulting conversions are listed in **Table 4.1**, Entry 3. Clearly, the BLgTi catalyst can epoxidize cyclooctene with high conversion and moderate selectivity to cyclooctene oxide. The BLgTi activity, however, is less than that of the SiTi reference catalyst (**Table 4.1**, Entry 2) . On the other hand, the conversion is enhanced with respect to the blank reaction (**Table 4.1**, Entry 1). Observing the reagents concentration over time (**Fig. 4.3a**), it is clear that the oxidant is being consumed faster than the alkene during the first reaction hours. As such 50 % of the cyclooctene conversion occurs during the first 4 hours, and subsequent conversion levels off after 12 hours of reaction (**Fig. 4.3b**). This demonstrates that the activity is higher in the first hours of reaction, albeit with moderate selectivity in oxidant. These results can be explained by the lower oxidant concentration at higher conversion as well as by potential catalyst deactivation.

Moderate selectivity in the application of BLgTi clearly relates to unproductive decomposition of tBHP releasing molecular oxygen as no other reaction products were found than cyclooctene oxide and tBuOH.

Regarding the reaction selectivity to cyclooctene oxide, the results show that selectivity improves over time, going from 68 % in the first hour to 76% at the end of the experiment (**Fig. 4.3b**). The same phenomenon was previously observed in degradation of virgin lignin with tBHP catalysed by titanium grafted into its structure.

Subsequently, the degree of titanium leaching and the heterogeneity of the catalyst were investigated in hot filtration experiments. In these experiments, after 2 hours of reaction, the catalyst was removed by filtration of the hot reaction mixture. The filtered reaction mixture was further monitored in time to verify if filtration stops further conversion. The conversion plots of hot filtration experiments are shown in **Fig. A4.3**. No further conversion was observed after the catalyst was removed by filtration. The conversion over a period of 24 hours after filtration, was essentially unchanged compared to when the catalyst was removed. This clearly demonstrates that BLgTi acts as a heterogeneous epoxidation catalyst.

Table 4.1 Results obtained for the cyclooctene epoxidation with tBHP using different amounts of BLgTi and different temperatures, in a batch reactor.

Entry	Catalyst	$m_{Cat.}$ (mg)	T (°C)	Conv.[1] (%)	Select.[1] (%)
1	-	0.0	60.0	10.4	11.2
2	SiTi	50.0	60.0	95.7	91.6
3	BLgTi	50.0	60.0	63.9	76.3
4			100.0	69.2	84.1
5		100.0	60.0	67.8	85.4
6		200.0		71.9	82.9

[1] Value determined by gas chromatography after 24 hours of reaction.

The time over which a catalyst remains active and the ease of reuse are important characteristics, particularly for industrial application. To evaluate the recyclability of BLgTi, several recycles with fresh reagents were performed. After each run, the original BLgTi was filtrated off, washed 3 times with n-octane to remove any reagents or products excess, dried under vacuum at room temperature, and reused using the same reaction conditions as in the previous cycle. The results of these recycling experiments are represented in **Fig. 4.4**. The results show that the BLgTi can be recovered and reused up to 5 times. Although there was a considerable drop in the catalyst activity after the first two catalytic cycles, activity stabilized in the last three cycles with a steady cyclooctene

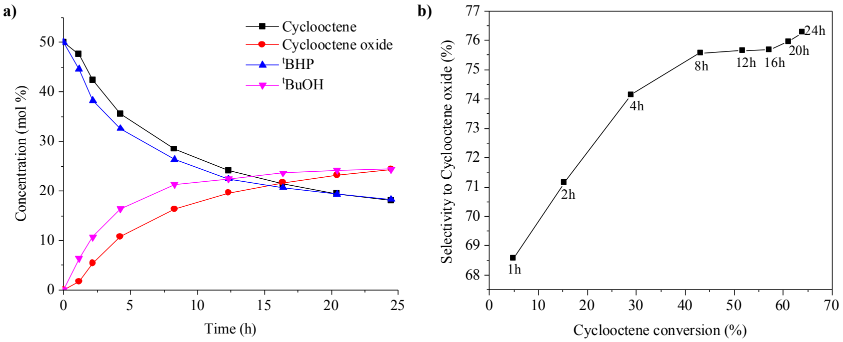

Fig. 4.3 **a**) Conversion plots of cyclooctene epoxidation with BLgTi as catalyst and tBHP as oxidant. **b**) Selectivity to cyclooctene oxide as a function of cyclooctene oxide.

conversion at around 35%. Noteworthy, there was an improvement on the selectivity to cyclooctene oxide with the increase in the number of cycles, from 76% in the first cycle to 90% in the fifth cycle.

From the IR spectrum of the catalyst after the 5th cyclooctene epoxidation cycle (Oxi-BLgTi) it is apparent that the structure of the catalyst changed. Changes in the IR spectrum are minor with respect to the aromatics moieties stretching bands, and major with respect to a new band at the C=O stretching region (1736 cm^{-1}). Similar changes were reported in the literature for oxidation reactions involving BLgTi and lignin [30,33] (**Fig. 3.3a**).

The surface area and the thermogravimetric properties of Oxi-BLgTi were determined as well. The physisorption results show that the surface area of BLgTi almost doubles during the epoxidation process. The total BET surface area for Oxi-BLgTi is 13.5 m^2g^{-1} (**Fig. 4.1a**, blue). On the other hand, the TG curve does not show significant differences with respect to the original sample, only a faster mass loss starting around 270 ºC and a lower percentage of non-volatized fraction after completion (**Fig. 4.1b**, blue). The minor decrease in the residual amount of sample is indicative for some titanium loss during epoxidation, thus implying some titanium leaching. Titanium loss is also confirmed by XPS analysis which showed that 33% of the initial titanium amount was gone at the end of the 5th epoxidation cycle. The titanium leaching can explain the activity drop observed

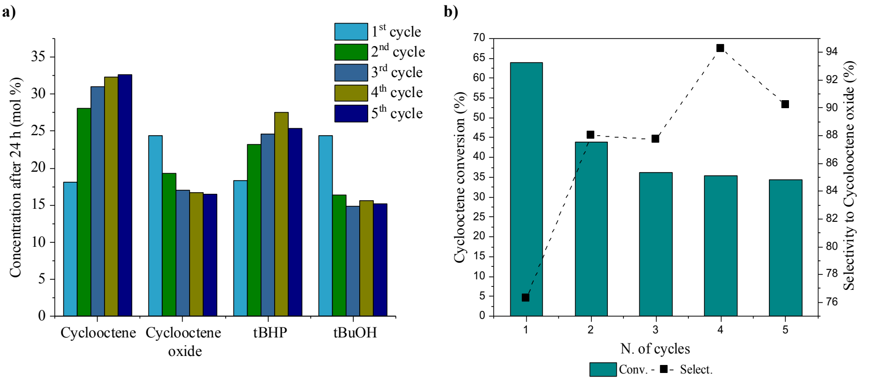

Fig. 4.4 BLgTi recycling activity tested during 5 catalytic cycles in batch. **a**) Concentration of reagents and products monitored by GC. **b**) Conversion of cyclooctene (bars) and selectivity to cyclooctene oxide (stars) values between reaction cycles. Data obtained after 24 hours of reaction.

during catalyst recycling experiments. Based on the hot filtration tests (*vide supra*), this leached titanium has no catalytic activity in the epoxidation reaction.

In pursuit of improving catalyst conversion rate, the temperature and the amount of catalyst were subsequently changed. Increasing the temperature proves to be beneficial to the catalytic process (**Table 4.1**, Entry 5). A 40 ºC increase of the temperature to 100 °C improved the conversion of cyclooctene as well as the selectivity to cyclooctene oxide from 63.9% to 69.2%, and from 76.3% to 84.1%, respectively. Increasing of the amount of catalyst also showed some improvement, both in conversion and in selectivity (**Table 4.1**, Entry 5 and 6). Nonetheless, doubling or quadrupling the amount of catalyst only increased the cyclooctene conversion to a maximum of 72% (8% increase), and the selectivity to cyclooctene oxide to a maximum of 85% (9% increase). These values thus show that only a minor activity improvement can be achieved at the cost of a substantial increase in the amount of catalyst.

4.3.3 Continuous-flow catalytic test

The BLgTi catalytic activity in batch demonstrated that it has the right characteristics to be tested in a flow process: heterogeneous catalysis, acceptable conversion rates and recyclability. The cyclooctene epoxidation reaction in n-octane was carried out in a ThalesNano plug flow reactor (X-Cube) holding a catalyst sample in a fixed bed (bed size = 65mm x 4mm, volume = 0.82 mL) (**Fig. A4.1**). PEEK tubing and standard HPLC connectors were used. The X-Cube reactor bed was filled with BLgTi catalyst (77 to 407 mg) diluted in silica carbide, and was held in place by stainless steel frits. The reactor was connected to the fluidic system by screw caps at the reactor entrance and exit. Two HPLC pumps were used to drive a pre-determined volume of two solutions (containing known amounts of reagents and internal standards in n-octane) through the reactor heated at a set temperature. Catalyst were on stream for up to 10 hours, relevant conditions are listed in **Table 4.2**.

Table 4.2 Results obtained for the cyclooctene epoxidation with tBHP using different amounts of BLgTi per catalyst bed and its test in different runs, in a flow reactor.

Entry	Cat.	$m_{cat.}$ (mg)	Run	$t_{on\ stream}$ (min.)	Conv.[1] (%)	Select.[1] (%)
1	BLgTi	77.1	1st	190	34	81
2			2nd	355	19	77
3			3rd	235	11	72
4		406,7	1st	540	31	79

[1] At the end of the run.

Initial experiments were performed at 60 °C for 3 h, at a constant flow of 7,4 μL.min.$^{-1}$ for each reagent. This corresponds to a total flow of 0.88 mL.h^{-1} and a residence time of ca. 1 h. As in previously conducted batch experiments, samples were collected in time and analysed by gas chromatography. Conversion and selectivity data are listed in **Table 4.2** (Entry 1) and **Fig. 4.5a**. As anticipated, the BLgTi is active for cyclooctene epoxidation in the flow process with modest conversion yields. Initially, the cyclooctene conversion was around 25 %, but during the first hour it increased up to 38 %. The cyclooctene conversion remained stable for the next two hours at conversion rates of approximately 35 %. During the entire run the selectivity to cyclooctene oxide, was around 80 %. Compared to batch experiments (**Table 4.1**, Entry 3), the conversion in flow experiments, as well as the space time yield, was approximately cut by half, but the

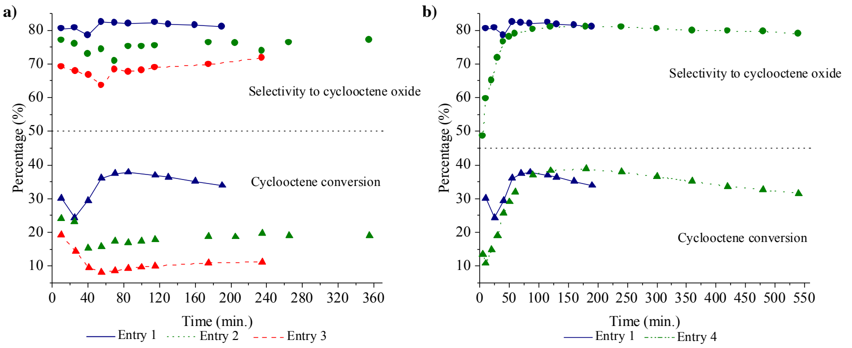

Fig. 4.5 Conversion and selectivity plots to cyclooctene oxide. **a**) Repeated runs over the same catalyst bed, and **b**) runs with different amount of catalyst (entry numbers corresponding with **Table 4.2**).

selectivity was higher.

The same BLgTi catalyst packed bed was tested in two new runs. Between runs, the packed bed was flushed with n-octane to remove traces of reagents, products or side products from the previous run. The results are presented in **Fig. 4.5a**, and in **Table 4.2** (Entry 2 and 3). The conversion plots show that the catalyst loses its activity with longer time on stream. The conversion values decrease immediately after the first 3 hrs on stream to values around 19 %, resp. 11 % after 6, total of 9 hrs on stream. Also the selectivity to cyclooctene oxide gradually dropped with time on stream from 80% to 72 %. The flow process appears to accelerate BLgTi deactivation, presumably as titanium leaching is stimulated by the ongoing stream of fresh reagents that directly wash out leached species from the reactor bed.

Aiming to improve the catalyst activity, new experiments were planned. A new bed was packed with 5 times more catalyst, and it was tested at the same temperature and flow rate conditions (**Table 4.2**, Entry 4). Samples were collected in time and analysed by gas chromatography. The results of cyclooctene conversion and selectivity to cyclooctene oxide in time are shown in **Fig. 4.5b**. Almost no improvement resulted on conversion as it increased from 38 to 40 %. Using more catalyst, however, did result in an extended period of activity for time on stream. Comparing both experiments (**Fig. 4.5b**), in order to reach a conversion level of approximately 32%, the bed with 5 times more catalyst was running for 540 minutes (**Fig. 4.5b**, green) while the other reached the same conversion level already in 190 minutes. The marked conversion drop (**Fig. 4.5**) for the bed with 5 times the amount of catalyst occurred after the 5th h of reaction, 4 h later than the experiment with less catalyst. Comparing the selectivity to cyclooctene oxide, there is no significant deviation observed on increasing the amount of catalyst in the fixed bed. Data from the flow experiments are typical for loss of catalyst activity through gradual leaching of (inactive) titanium species.

4.4 Conclusion

This is one of the first, albeit modest, examples of the exploitation of lignin as a support for a heterogeneous catalyst. It was demonstrated, both in batch and in flow processes, that a titanium catalyst supported on lignin is active in cyclooctene epoxidation with modest conversion and selectivity results. In batch, the cyclooctene conversion amounts to 72 % with 83 % selectivity to cyclooctene oxide, and in flow the conversion is 40 % with 80 % selectivity. There were noticed drops on BLgTi activity in both processes, but complete deactivation of the catalyst was not observed.

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Chapter 5

A study of alkene epoxidation catalysis by titanates of lignin and lignin model compounds

Summary

The application of lignin as a building block for hybrid catalytic materials exploiting specific structural features is reported with a case study for titanium-catalyzed epoxidation. The presence of phenolic moieties is mandatory for obtaining best epoxidation catalysts from organosolv lignin upon titanation. The use of related diaromatic lignin model compounds was likewise explored and helped to shape a clear idea of which type of organosolv lignin would be a suitable precursor for obtaining a promising epoxidation catalyst. In this context, phenolic moieties, resulting from the cleavage of β-O-4 linkage during harsh organosolv extraction, are preferred. Catalytic materials now represent an established area of lignin chemistry.

5.1 Introduction

Lignin is the second most abundant polymer on the wood-based biomass, only overcome by cellulose [1,2]. It is a natural biopolymer made of methoxylated phenylpropane structures biosynthesized to conceive rigidity, support and protection to vascular plants [3]. Its structure is very complex and difficult to map as it can vary with the wood source (hardwood and softwood) and as its synthesis follows a random assembly of three different mono phenolic units - the monolignols (*p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) [1,4,5]. Due to the arbitrary coupling of the monolignols, there are no two equal lignin structures. Several types of linkages can be formed between the units, as are examples the β-O-4, 5-5, β-5, 4-O-5, β-1, and β-β. The ether β-O-4 bond is dominant, consisting usually in more than 50 % of the linkages in the native lignin (protolignin) [4,6].

As lignin has been studied for decades [7,8] and as it has a role in processes taking place in biorefineries [2], many ways to extract and isolate it are known. Physical, chemical, or biological pretreatment and solvent extraction procedures are common methods used to pretreat and to isolate lignin [9]. For each method employed, the temperature, pressure, pH range, and solvents used are some of the factors that matter, resulting in final products with varying characteristics [4,5,10]. The aromatic nature of lignin remains a common feature, but the linkages connecting the aromatic rings (aliphatic moieties) differ. Not only will the kind of bonds be different, but also the relative occurrence of each bond will vary [1,4]. This phenomenon adds complexity to an already complex structure *per se* as the structure of the isolated lignin will be dependent of the isolation method employed.

Two of the most well-known processes for lignin isolation are the Kraft process and the organosolv process [11], originating from pulp and paper industry and from biorefineries, respectively. The Kraft process causes the highest degree of structural changes on lignin as it uses high pH, high amounts of aqueous sodium hydroxide and sodium sulfide, combined with high extraction temperatures. Most of the original linkages are broken during the Kraft process (5-5 bond type normally resists) but also new linkages are formed (such as stilbene units). The lignin purity is also compromised because of the amount of sulphur that becomes part of the polymeric structure [1,4,12]. The organosolv process, on the other hand, was introduced as a more environmentally friendly method, which delivers high purity lignins [1,4,13]. The method is based on extracting lignin using organic solvents (e.g. ethanol and methanol) with typically sulphuric acid as catalyst under milder conditions. The major drawback of this process is that it leads to extensive cleavage of the β-O-4 linkage followed by repolymerization rendering a lignin with considerably fewer ether bonds, higher phenolic content and more carbon-carbon bonds [4,5].

Lignin is yearly isolated at enormous scale as a by-product of some industries (paper and pulp, biorefineries) and it is used mainly for heat production by burning it [14,15]. There is a lack of application in industry to better exploit the full potential of this aromatic polymer. Its recalcitrant structure and the complexity of the linkages are some of the challenges hindering more added value applications. Due to the complexity of lignin and driven by the desire to study certain of its functionalities in detail, model compounds (MCs) are often used as starting point in lignin research [16–21]. These MCs often mimic one or two monolignols and are considerate to be representative for the system that is replicated in real lignin polymers. The most common MC mimics the β-O-4 linkage, which combines two aromatic moieties mimicking C_β of the aliphatic chain to C_4 of the aromatic ring through an ether bond (**Fig. 5.1**). The functionalization of the aromatic ring may further vary.

The transformation of lignin into catalytic materials was demonstrated in catalytic epoxidation on the previous chapter. Here the scope of catalyst synthesis is further investigated by exploring various types of organosolv lignin and lignin model compounds. Aim is to find a correlation between the type of lignin hydroxyl groups present and the catalytic activity of the resulting titanated lignins. By using model compounds containing different hydroxyl groups (titanium binding functional group), systematic variation in titanate synthesis is also accomplished. Finally, a correlation is found between the catalytic activity of various titanated lignins and various titanated model compounds for alkene epoxidation.

5.2 Experimental section

5.2.1 Chemicals

tert-Butylhydroperoxide (tBHP) (70% aqueous solution, Sigma Aldrich) was extracted with n-octane before use to afford water free peroxide solutions. The catalysts used in this study - Ti-modified beech lignin (BLgTi) and Ti-modified oak lignin (OLgTi) - were synthesized according to a literature procedure [22]. For the synthesis of BLgTi**,** organosolv lignin extracted from beech wood (BLg) was used as provided by Energy Centrum Nederland (ECN, now TNO). For the synthesis of the OLgTi, a dioxane soluble lignin (OLg) was used as extracted according to a literature procedure [23]. The model compounds 3 and 4 were synthesized, isolated and purified according to literature methods [16]. All other chemicals were obtained from Sigma Aldrich and used as received.

5.2.2 Product analysis

2D Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance spectroscopy (^{1}H- ^{13}C HSQC NMR) spectrum was recorded using a VARIAN INOVA 500 MHz spectrometer equipped with a 5 mm ID AutoX ID PFG Probe. Spectra were obtained using the phase-sensitive gradient-edited HSQC program (gHSQCAD). The main parameters were as follows: 16 scans, acquired from 0 to 16 ppm in F2 (^{1}H) with 1200 data points (acquisition time 150 ms), 0 to 200 ppm in F1 (^{13}C) with a 2 s relaxation delay and 256 t_1 increments (acquisition time 10 ms). The NMR samples were prepared with a concentration of 100 mg of the lignin in 0.6 mL dimethyl sulfoxide-d_6 (DMSO-d_6). The central DMSO peak was used as the chemical shift (δ) reference (δ_C 39.5, δ_H 2.49 ppm). The cross-peaks were assigned according to the literature. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded in a Bruker Advance 500 MHz spectrometer with the THF-d_8 shift used as the chemical shift reference (δ_C 67.2 and 25.3 ppm, δ_H 3.58 and 1.72 ppm). The NMR tubes were prepared using an inert atmosphere. Data processing was carried out using MestReNova software.

Titanium metal content was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyser with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K_{α} = 1486.6 eV) operating at 72 W and a spot size of 400 μm; solid samples were not handled under an inert atmosphere and were considered passivated. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure of the UHV chamber was $2x10^{-8}$ mbar. Compounds were calibrated by setting the C 1s adventitious carbon position to 284.8 eV.

Catalytic tests were performed on a Chemspeed ASW2000 workstation using 10 mL double-walled glass reactors with vortex shaking. Liquid reaction samples were collected in time and analyzed by gas chromatography (GC) involving determination of cyclooctene, cyclooctene oxide, tBHP and tert-butanol (tBuOH) through comparison with a internal standard (1,3,5-trimethylbezene). Analysis was done on a Shimadzu GC2010 gas chromatograph equipped with a 30.0 m x 0.21 mm x 1.00 μm dimethyl polysiloxane column, in which He was used as the carrier gas (injector temperature 250 ºC). The oven temperature program was from 45 – 120 ºC at a ramp rate of 10 ºC/min, followed by 120 – 250 ºC at 20 ºC/min. The initial and final temperature isothermal dwells were 3 and 2 min, respectively. The retention time and the response factor of substrates and products are given on **Table A5.1**. The response factors (Rf_y) were determined for every component concerning the 1,3,5-trimethylbezene using the **Eq. 5.1**, and the concentration of the component 'y' (C_y) in % (mol/mol cyclooctene$^{t=0}$) was determined by **Eq. 5.2**. Rf_y is the response factor of component 'y' with respect to the internal standard; Area IS and Area component are the peak area of the internal standard and of the component peak, respectively; M IS, M cyclooctene and M component are the weights (g) of the initial amount of internal standard, the initial amount of cyclooctene and the component, respectively; MW cyclooctene and MW component are the molecular weight (MW; g/mol) of cyclooctene and the component, respectively. Each sample was prepared by adding 100 μL of the reaction mixture to 1,00 mL of n-octane.

$$Rf_y = \frac{\text{Area IS}}{\text{Area component}} \times \frac{\text{M component}}{\text{M IS}} \qquad \textbf{(Eq. 5.1)}$$

$$\mathrm{Cy}=\frac{\frac{\text{Area component}}{\text{Area IS}}\times\frac{\text{M IS}}{\text{MW component}}\times\text{Rfy}}{\frac{\text{M cyclooctene}}{\text{MW cyclooctene}}}\times 100 \qquad \textbf{(Eq. 5.2)}$$

5.2.3 Procedures

5.2.3.1 Synthesis of Ti-modified model compounds

All titanation reactions were carried out under inert atmosphere in a glove box. The model compound (1 eq.) was dissolved in 2.5 ml of deuterated THF (THF-d_8) and $Ti(O^iPr)_4$ (1 eq.) was added dropwise under vigorous stirring (**Table 5.1**, entry 1 and 3). The reaction colour changed after the addition of the first drop of $Ti(O^iPr)_4$ to yellow. After 3 hours a sample was taken for analysis by proton and carbon NMR. The clear reaction mixture was subsequently dried under vacuum. The resulting solid was washed with hexane, filtered off and dried.

For the titration of the model compounds with $Ti(O^iPr)_4$, a solution was prepared with a given amount of model compound dissolved in 2,0 ml of THF-d_8. 100 μL of a $Ti(O^iPr)_4$ stock solution (59.8 μmol, 12.0 mM) were added to the model compound solution. The vial was vigorously stirred for 30 minutes. The reaction mixture was than analyzed by proton NMR. The procedure was repeated several times (**Table 5.1**, Entry 2 and 4). NMR spectra of titration experiments are shown in **Fig. 5.2**.

5.2.3.2 Catalytic epoxidation tests

Unless stated otherwise, 2.5 mL of a solution of cyclooctene (2.0 M) and 1,3,5-trimethylbenzene (2.0 M) in n-octane, and 2.5 mL of a solution of tBHP (2.4 M) in n-octane were added to a Chemspeed 10 mL reactor containing the required amount of catalyst (**Table 5.2**). The mixture was stirred (600 rpm) for 24 h at 60 °C. Samples were collected automatically in time and analyzed by gas chromatography.

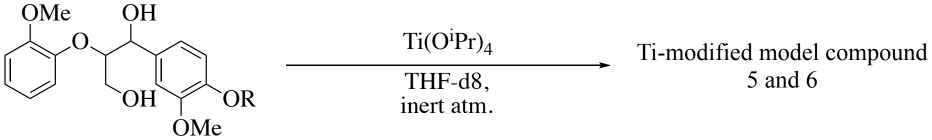
5.3 Results and discussion

5.3.1 Ti-modified model compounds synthesis and characterization

The Ti-modified MCs were made by adding titanium isopropoxide to a MC solution (**Fig. 5.1**). The metal will bind the MCs through the hydroxyl functional groups rendering titanium alkoxy or –aryloxy units. Two β-O-4 linkage mimicking MCs were chosen. Both have two hydroxyl groups on the aliphatic moieties (mimicking the Cα and the Cγ OH groups on lignin) and at least one methoxy group in each aromatic ring. The difference is that one MC has a phenolic moiety (3) and the other has an extra aromatic methoxy group instead (4). The premise is to compare the activity as epoxidation catalyst of each titanated MC and, through correlation, to predict which type of titanated lignin will be more suitable for this application: the one that is richer in β-O-4 or the one that had its ether bonds cleaved to render more phenolic moieties instead.

The β-O-4 mimicking model compounds were synthesized according to the literature [16]. After the purification, proton and carbon NMR were measured and the resonant signals identified (**Fig. A5.1 – A5.3**). The NMR spectra of 3 (**Fig. A5.1**) show some vestigial peaks which correspond to the resonance of a minor isomer of the MC, which is also formed during the synthesis.

The titanation reaction of both MCs was initially attempted in ethyl acetate as this solvent gave good results in a similar reaction with lignin. After the addition of $Ti(O^iPr)_4$ a yellow precipitated formed, which disappeared after 30 minutes of vigorously stirring. The solutions were dried under vacuum and two dark yellow powders were obtained. It



3, R= H
4, R= Me

Fig. 5.1 Reaction scheme of the of the titanation of model compounds 3 and 4 using $Ti(O^iPr)_4$ as metal source. The resonant signals are identified according with the lignin position that they are mimicking.

was found that the isolated products of both reactions were insoluble in common deuterated solvents. This fact hinders the analysis of the MCs structure by NMR, as comparison of spectra with those of the substrate 3 and 4 became impossible. In order to analyze the formation of the Ti-modified MCs, the reaction solvent was switched to a deuterated solvent – deuterated tetrahydrofuran (THF-d_8) (**Fig. 5.1**). The reaction procedure was the same as applied before. Thus an equivalent of $Ti(O^iPr)_4$ was added dropwise to a 2.5 mL solution containing one equivalent of the respective model compound (**Table 5.1**, entry 1 and 3). The reaction was kept under inert atmosphere (glove box) and stirred for 3 hours. Before drying the products under vacuum, a sample was taken to be analyzed by proton and carbon NMR. The spectra with the titanated MCs 3 and 4, respectively MC 5 and 6, proved to be very complex. The presence of side products, such as isopropanol and remains of the $Ti(O^iPr)_4$ reagent impede spectra analysis due to signal overlap. As the resonant signals of the products were not clear, the titanation was made with a gradual increment of the concentration of $Ti(O^iPr)_4$ added to the MC solution. Intermediate NMR spectra were measured after each portion of titanium alkoxide added. To this purpose a stock solution of $Ti(O^iPr)_4$ was prepared and aliquots of 100 μL were added to the MC solution. The reaction mixture was stirred for 30 minutes after each addition, then a NMR was measured. The procedure was repeated and the spectra obtained are shown in **Fig. 5.2**.

Table 5.1 Reagents quantities added for the titanation reaction of the model compounds 3 and 4.

Entry	Model compound (MC)	m_{MC} (mg)	n_{MC} (mmol)	$n_{Ti(OiPr)4}$ (mmol)
1	3	70.0	0.22	0.22
2		53.0	0.17	0.014[i]
3	4	50.0	0.15	0.15
4		52.0	0.16	0.011[i]

[i] Added in aliquots of 100 μL of a stock solution of $Ti(O^iPr)_4$ ($[Ti(O^iPr)_4]$= 12.0 mM).

Observing the evolving proton spectra of the Ti-modified MCs facilitated their interpretation. On spectra following the formation of 5 it is clear that the resonant signals

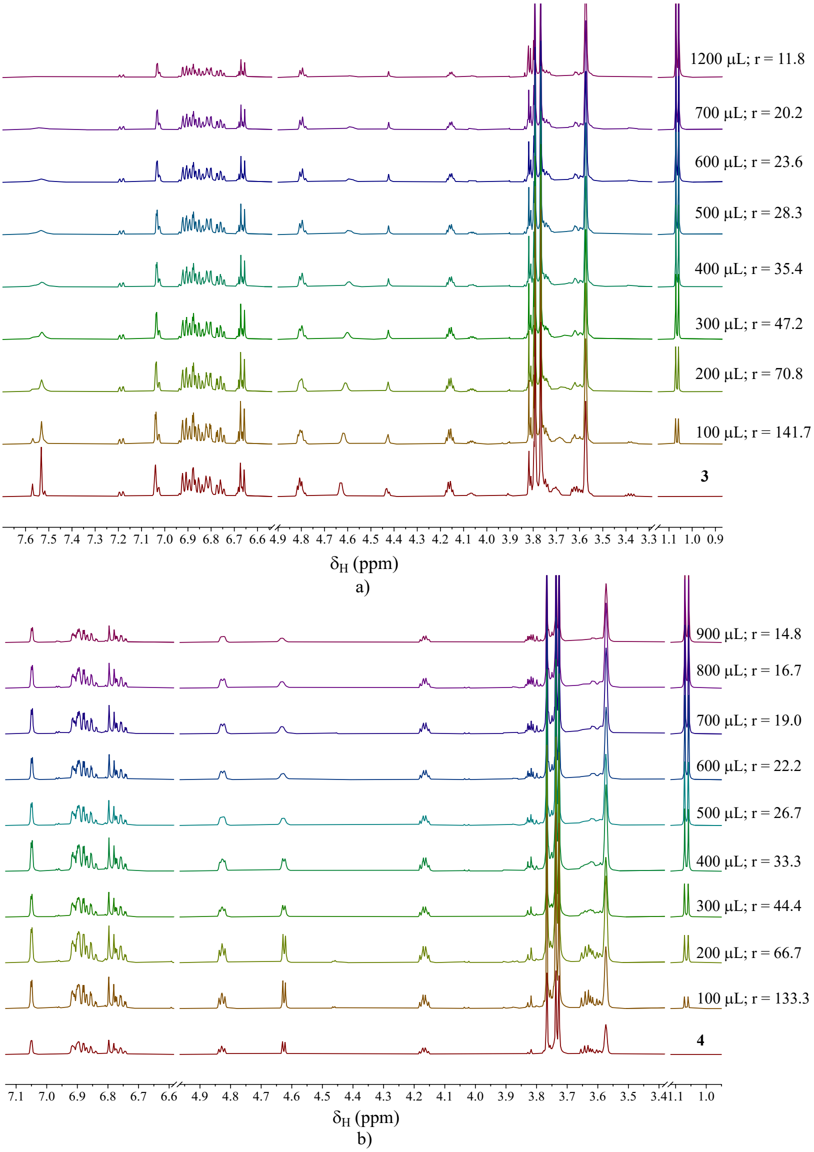


Fig. 5.2 Proton NMR evolution of MC **a**) 3 and **b**) 4 with the addition of aliquots of $Ti(O^iPr)_4$ in deuterated THF. The values given describe the volume of added stock solution of $Ti(O^iPr)_4$ ($[Ti(O^iPr)_4]$ = 12.0 mM) and the ratio (r) between the amount of MC and the amount of $Ti(O^iPr)_4$ in solution.

of the OH groups, both phenolic (δ_H 7.53 ppm) and aliphatic (Cα OH, δ_H 4.63 ppm), slowly disappear. This confirms that reaction of these hydroxyls with the titanium reagent occurs. The Cγ OH was difficult to trace because it resonates in the same region as the methyl protons belonging to the methoxy groups (δ_H 3.82-3.74 ppm), but the integral over these signals decreased as expected to account for one proton with the gradual increase of added titanium. The resonant signals of the α and γ protons registered minor differences in chemical shift, but their multiplicity pattern changed. The multiplicity of the α proton resonant signal (δ_H 4.80 ppm) changes from a triplet (MC 3 spectrum) to a doublet for 5. The γ protons resonant signal (δ_H 3.73 and 3.62 ppm) shifts to a more shielded region and changed from a multiplet to a double-doublet. Regarding the aromatic proton resonant signals located between δ_H 7.04 – 6.66 ppm, there were no chemical shifts observed, but the peaks split in two. The β proton resonant signal was not affected by the titanation reaction as the corresponding peaks remain the same as in the spectrum of 3. The same happened to the methoxy groups proton resonant signals (δ_H 3.77 ppm and 3.79 ppm) which also remain unchanged. As expected the resonant signals of the isopropanol (CH_3 at δ_H 1.05 ppm, and the CH at δ_H 3.80 ppm) were visible in the spectra after the first aliquot of $Ti(O^iPr)_4$ was added. This is expected as isopropanol is a reaction product of the substitution of the isopropyl groups of the $Ti(O^iPr)_4$ by the MC. As there were no signals of other isopropyl groups visible all the isopropyl groups were substituted. This result was anticipated, because the concentration of the titanium is very low compared to the MC concentration. Regarding the ^{13}C NMR spectra, comparing the spectra of 3 with the spectra of 5 (**Fig. A5.2** and **A5.4**, respectively), the number of signals increased. The most significant changes are the shift of the resonant signals of the Cα (3, δ_C 74.0 ppm) and the Cγ (3, δ_C 61.9 ppm) to a less shielded region around δ_C 78.4 ppm and δ_C 63.8 ppm, respectively. Also, a small shift on the substituted aromatic carbons resonant signals (3, between δ_C 152.2 and 147.0 ppm) to a region with higher chemical shifts (between δ_C 154.0 and 148.6) was noticed. These shifts of the carbon resonant signals are an effect of the titanium incorporation.

From spectra following the formation of the MC 6, similar trends could be derived. On the proton NMR, the disappearing of the α OH group resonant signal (δ_H 4.63 ppm) was noticed. Likewise, the multiplicity of the Cα and the Cγ proton resonant signals changed from a triplet to a doublet (δ_H 4.83 ppm) and from a multiplet to doublet (δ_H 3.67 – 3.60 ppm), respectively. In the aromatic region the same splitting effect of the MC 5 proton NMR was observed (δ_H 7.05 – 6.75 ppm). There were no differences in the signals chemical shift. Also, the resonant signals of isopropanol were found.

5.3.2 Catalytic tests of Ti-modified model compounds

As described above, complete titanation of the model compounds used in this study affords the final products 5 and 6 which are insoluble in common solvents. This characteristic offers potential for their application as heterogeneous catalysts. Titanated MCs 5 and 6 could therefore be tested, in the same way as titanated lignins, for activity in alkene epoxidation. These tests involved epoxidation of *cis*-cyclooctene epoxidation to cyclooctene oxide using *tert*-butylhydroperoxide as oxidant. The experiments were carried out in batch at 60 °C with a total reaction time of 24 h. Samples were automatically collected in time and transferred to GC vials for further analysis by gas chromatography. This allows the monitoring of the concentration of reagents and products in solution in time. The conversion and selectivity values obtained are listed in **Table 5.2** (Entry 1 and 2). From these data it is clear that both MCs are active epoxidation catalysts under the conditions chosen. From the conversion plots in time (**Fig. 5.3**), it is clear that 5 performed better than 6. The conversion of cyclooctene amounted to 69.8 % for MC 5 while only 13.3 % was found for MC 6. Thus MC 5 was 5 times more active in epoxidation than MC 6. Comparing the values of the selectivity to cyclooctene oxide, there is also a noticeable difference between both model compounds. While 5 has an excellent selectivity of 96 %, 6 registered only 65 %. Observing the graphics of selectivity as a function of the conversion (**Fig. 5.3**), both model compounds had stable selectivities through most of the conversion period.

Table 5.2 Conversion of cyclooctene and selectivity to cyclooctene oxide obtained with Ti-modified materials using tBHP as oxidant at 60 °C during 24 h.

Entry	Catalyst	$m_{Cat.}$ (mg)	Conv.[1] (%)	Select.[1] (%)
1	5	24.0	69.8	96.4
2	6	17.0	13.3	65.7

[1] Value determined by gas chromatography after 24 hours of reaction.

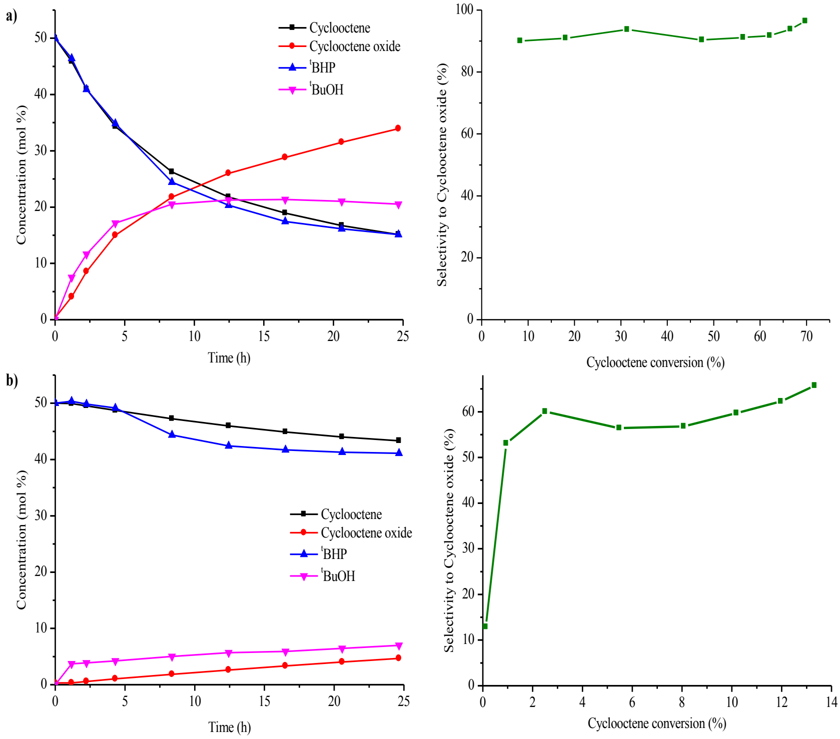


Fig. 5.3 Concentration plots of the cyclooctene epoxidation and of the selectivity to cyclooctene oxide as a function of cyclooctene conversion with **a**) 5 and **b**) 6 as catalyst and tBHP as oxidant at 60 ˚C during 24 h.

According to these results, the presence of the aromatic OH group on MC 5 appears to be beneficial for catalytic application. This indicates that, like for real lignin, highest catalytic activity can be expected from use of a type of lignin with a high number of phenolic moieties.

5.3.3 Ti-modified lignin as epoxidation catalyst

In order to test this hypothesis on lignin, two types of organosolv lignin were chosen: beech wood lignin (BLg, used on the previous chapter) and oak wood lignin (OLg). Normally, an organosolv lignin has a low number of β-O-4 linkages, which are disrupted during the extraction process, and its final structure becomes very rich in hydroxyl groups. Both lignins were characterized by $^{1}H,^{13}C$-HSQC NMR and the amount of each linkage type present was quantified to determine the degree of depolymerization/repolymerization during the extraction process (**Fig. 3.1** and **Fig. A5.5**). The most representative linkages in both lignins are the β-O-4, β-5, and β-β bonds. The bond quantification is based on the integration of the C_α cross-peaks and uses the integrated G_2 signal as reference. According to the calculations, it is estimated that the β-O-4 linkage content is very high on the OLg (46.7 per 100 Ar) compared with BLg (1.9 per 100 Ar). The β-5 linkage content is also higher on the OLg (16.4 per 100 Ar) compared to BLg (3.5 per 100 Ar). Contrary, the β-β linkage content is lower for OLg (7.8 per 100 Ar) than for BLg (11.1 per 100 Ar). The major difference on the β-O-4 linkage content between the two lignins indicates that the extraction of the oak lignin involved milder conditions and the structural changes induced during the process did not dramatically affect the initial structure. The beech lignin was extracted at forcing conditions, which transforms the initial structure completely by cleaving essentially all the ether bonds.

The synthesis of the Ti-modified beech (BLgTi) and oak (OLgTi) lignin was done according to the literature procedure, detailed on the previous chapter for BLg [22]. For the synthesis of the OLgTi dioxane was used as solvent, because the OLg is not soluble in ethyl acetate (previously preferred solvent). To graft titanium on the lignin structure it is vital to completely dissolve the lignin prior to the addiction of the reagent $Ti(O^{i}Pr)_4$. The titanium content was determined by XPS analysis. As a result of the structural differences between both lignins used, the titanium loading on BLgTi (13.5 %) was almost 4 times higher than that on OLgTi (3.7 %).

The titanated lignins were tested as cyclooctene epoxidation catalysts using the same conditions as employed for testing of MCs 5 and 6. The conversion and selectivity data are listed in **Table 5.3**, entry 1 and 2, and the conversion plots are shown in **Fig. 5.4**.

Table 5.1 Conversion of cyclooctene and selectivity to cyclooctene oxide obtained with Ti-modified materials using ^{t}BHP as oxidant at 60 °C during 24 h.

Entry	Catalyst	$m_{Cat.}$ (mg)	Conv.[1] (%)	Select.[1] (%)
1	BLgTi	50.0	63.9	76.3
2	OLgTi	52.0	18.9	65.9

[1] Value determined by gas chromatography after 24 hours of reaction.

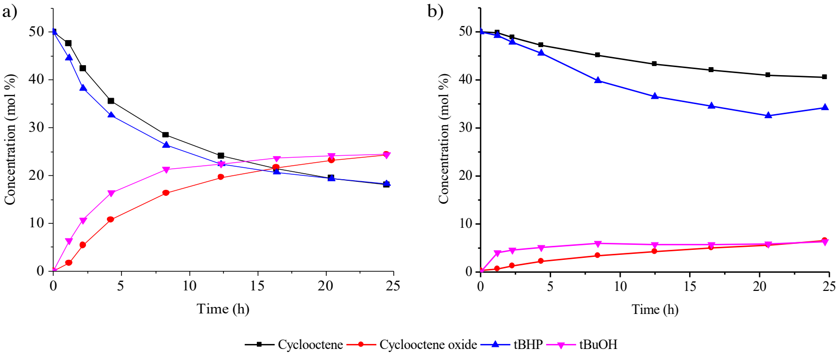


Fig. 5.4 Concentration plots of the cyclooctene epoxidation reagents and products using as catalyst **a**) BLgTi (same as in the Fig. 4.3 repeated here for comparison purposes) and **b**) OLgTi and tBHP as oxidant.

The results obtained show that the BLgTi is a better epoxidation catalyst than OLgTi. The cyclooctene conversion upon using BLgTi was 63.9 %, which is 3 times higher than that for OLgTi (18.9 %). Employing BLgTi also results in somewhat higher selectivity to cyclooctene oxide (76.3 %) than for OLgTi (65.9 %). The concentration plots show that the epoxidation reaction occurs slower with OLgTi. At the end of 24 hours, the amount of cyclooctene oxide formed using OLgTi was similar to that obtained after 2 hours reaction using BLgTi as catalyst.

These results can be attributed to the difference in the amount of titanium present in each lignin sample. Clearly, the catalyst containing more titanium is performing better. Nevertheless, the initial lignin structure is also expected to contribute to this result. The titanation of beech and oak lignin was done under the same conditions and using the same amount of reactant, but one structure was capable of grafting more titanium (BLgTi) than the other (OLgTi). The BLgTi has a higher amount of phenolic moieties resulting from the cleavage of the β-O-4 and further repolymerization forming the phenolic hydroxyls that have ideal reactivity with titanium isopropoxide. This leads to an increased amount of metal that can be grafted on the lignin.

5.4 Conclusion

Both titanated phenolic model compounds and real organosolv lignins were shown to provide building blocks for heterogeneous Ti-mediated epoxidation catalysts. Especially preferred is the use of organosolv lignin with a high amount of hydroxyl groups that enables catalytic materials with high titanium content. Ideal starting material for catalyst preparation therefore results from the cleavage of the β-O-4 linkage, as occurs under forced conditions of organosolv lignin production. The best performing lignin-based catalysts in this study therefore resulted from titanated beach wood organosolv lignin BLgTi. Use of BLgTi enabled conversion of 64 % and an oxide selectivity of 76 % in cyclooctene epoxidation. Also, titanated model compound 5, which precursor has a phenolic moiety, was capable of epoxidation of 70 % of the tested alkene with a selectivity of 96 %. In contrast, titanated model compound 6, which precursor has only aliphatic hydroxyls, gave a low conversion of 17 % in epoxidation tests. Likewise, an oak derived catalyst OLgTi, which precursor structure resembles more the protolignin with low phenolic content, gave only 19 % of conversion with 66 % of selectivity in epoxidation tests. Highly transformed organosolv lignins are therefore preferred to alternatives having structures similar to the native form of the natural polymer.

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Titanium mediated lignin oxidation and its application in catalytic epoxidation

Lignin is one of the most abundant resources on Earth. With second-generation biorefineries and pulp and paper industry isolating this macromolecule as a coproduct on a daily basis, lignin is amply available. To a certain degree, lignin can be considered a waste material for which industry has no real use. Therefore, its valorisation holds the potential for a source of high profits with the additional advantage of being environment friendly. As lignin is investigated as the only renewable bulk source of aromatics in nature, it holds great potential to be transformed into fuels, fine chemicals, and other high-value products. Lignin valorisation can be the key to start shifting from fossil fuels to reusable carbon sources. In spite of a large research effort, the natural polymer is still underutilized by the industry as cost-effective lignin valorisation technologies are still scarce.

The aim of this PhD thesis was to investigate new ways to convert lignin into valuable products. The work followed two approaches. Firstly, we attempt to oxidize lignin as a pre-treatment approach to facilitate its depolymerization into new aromatic value-added chemicals. Secondly, a new use for lignin was sought by its transformation into a catalyst. The routes explored were unconventional but the results, albeit modest, were encouraging in the context of lignin valorisation.

In **Chapter 2** a catalytic approach was followed to oxidize an organosolv lignin. A titanium silsesquioxane (Ti-POSS) was chosen as a catalyst due to its well-known ability to oxidize organic compounds in reaction with organic peroxides as oxidants. Initially, the Ti-POSS activity was evaluated in the oxidation of simple mono-aromatic molecules considered as lignin model compounds. These phenolic models have hydroxyl groups mimicking the ones on real Cα and Cγ lignin sidechains but could be more readily characterized than real lignin oxidation products. The results showed that the hydroxyl group in the Cα position (secondary carbon, model compound 1a) proved to be most reactive with the methodology employed, enabling a conversion of 40.5 % to its expected oxidated product. Though with a lower conversion, the Cγ mimicking model compound (primary carbon, 1b) could also be oxidized (Conv. = 8.4 %). The Ti-POSS proved to be an active catalyst for the oxidation of aliphatic hydroxyls to the corresponding carbonyls. The same method was applied in the oxidation of real organosolv lignin. Disadvantageously, the oxidation of lignin was obstructed by a grafting phenomenon that involved the catalyst and the lignin aromatic hydroxyl groups, resulting in the formation of Ti-O-Ar units. The highly reactive nature of phenolic moieties with Ti-POSS (also demonstrated with the test on the model compounds 1d and 1e) headed to the formation of an unidentified precipitate, possibly containing titanium, which led to catalyst deactivation. Iso-propanol was detected in solution after the oxidation attempt indicating that the iso-propoxy groups of the Ti-POSS were replaced by lignin through reaction with a free OH group (potentially phenolic OH). An additional test with Ti-POSS showed that in the presence of lignin its activity in other reactions decreases significantly. This approach thus enabled a deeper understanding of the reactivity of lignin hydroxyl groups towards (homogeneous) oxidation and metalation. In this chapter, it was demonstrated how to activate specific lignin functional groups, namely the hydroxyl groups, to form complexes with metals, e.g., titanium. The organosolv lignin oxidation using this methodology was abandoned. Nevertheless, the underlying interaction between the natural polymer and the metal was established and its potential was explored in the remaining chapters.

Chapter 3 initially focused on the new findings regarding the lignin capacity to accommodate titanium in its structure. Instead of doing the oxidative pre-treatment of lignin by reaction with a catalyst and an oxidant, the methodology developed started by first grafting titanium onto the lignin structure by adding $Ti(O^iPr)_4$ to a solution containing dissolved lignin. The $Ti(O^iPr)_4$ reacted with the hydroxyl groups of lignin releasing isopropanol. Using NMR and IR techniques, the new titanated material (Ti-modified lignin, BLgTi) was characterized, and its features compared with the initial structure of the organosolv lignin. The analysis strongly indicated that the incorporation of titanium is responsible for crosslinking the lignin structure. The oxidation of the Ti-modified lignin was investigated by its heterogeneous reaction with tBHP. The IR and MAS ^{13}C NMR spectra of the product confirmed the oxidation of lignin with concomitant structural changes. In other words, the Ti-modified lignin was acting both as substrate and as catalyst in its oxidation. The depolymerization of lignin with a copper-magnesium-aluminium oxide catalyst (CuMgAlOx) in supercritical ethanol advanced to test the capacity of the oxidative pre-treatment. The quantification of the monomeric content after the depolymerization highlighted a dramatic drop of the aromatic monomeric units on the oxidated samples in comparison with the parent lignin. Intrigued with the results and aiming to understand the causes of it, a study with guaiacol as a model compound was performed. The guaiacol was submitted to the same modifications with titanium (reaction with $Ti(O^iPr)_4$) and to the oxidation thereafter. A detailed characterization confirmed the linkage of the hydroxyl moieties of the guaiacol to the titanium. A careful analysis of the outcome upon oxidation showed that an aromatic ring opening occurs, under the given conditions, promoted by the grafted titanium given origin to a muconic acid type species. The structural modifications observed in the guaiacol study were agreeing with the ones observed on the tested lignin. The methodology explored was dramatically changing the lignin's valuable features by compromising its aromatic content. Although the structure of the oxidized lignin becomes less recalcitrant and, therefore, potentially more susceptible to be depolymerized, the aromatic ring opening decreases its value as a natural source of aromatics. Therefore, the employed oxidation approach is limited with respect to obtaining a high yield of monomeric aromatics.

The second part of this thesis explores a new way of giving value to lignin and how an one step transformation can convert the macromolecule into a catalytic material. This unprecedented use establishes lignin as a building block for hybrid, catalytic materials. **Chapter 4** is entirely aimed at exploring the potential of lignin as metal support (titanium). The lignin titanate is able to catalyse alkene epoxidation reactions. The Ti-modified lignin introduced before was thus tested as a catalyst for cyclooctene epoxidation with an organic peroxide as oxidant (tBHP). The catalyst showed, in batch reactions, moderate activity with a cyclooctene conversion between 64 – 72 % and a selectivity to cyclooctene oxide between 76 – 85 %. The heterogeneous nature of the catalyst was demonstrated by hot filtration tests and its recyclability demonstrated up to 5 cycles in repetitive batch experiments. As the batch reactor results were promising for further process development, the epoxidation was consequently investigated in a continuous process. Using a flow reactor, the Ti-modified lignin catalyst could be used for a considerable time on stream (up to 9 hours) with a conversion maximum of 40 % and a selectivity to cyclooctene oxide of 81 %. There were drops observed in catalyst activity in both processes, but complete deactivation of the catalyst never occurred. It was demonstrated with this study, both in batch and in flow processes, that a titanium catalyst supported on lignin is active in cyclooctene epoxidation with modest conversion and selectivity results.

The lignin application as a building block for hybrid catalytic materials, as reported in the previous chapter, opens a new path to lignin valorisation. This was possible by exploring lignin structural features, specifically the reactivity of the hydroxyl groups. In order to investigate which hydroxyl moieties were responsible for the catalyst formation, titanation of model compounds was studied. For this purpose, in **Chapter 5** diaromatic lignin model compounds mimicking the β-O-4 linkage-type were used as these are the most abundant in native lignin structures. These model compounds differ just in the C_4 position where one has a hydroxyl group (phenolic) and the other a methoxyl group. Both were titanated through a reaction with $Ti(O^iPr)_4$ and used as catalysts in cyclooctene epoxidation. The results imply that the presence of phenolic moieties is very important to obtain the best epoxidation catalyst. The titanate model compound with the phenolic feature gave the best conversion rate (70 %) with a selectivity for cyclooctene oxide of 96 %. This experiment helped to predict which type of lignin would be a better precursor for obtaining a promising epoxidation catalyst. To verify if these results reflect what happens with the real lignin feedstock, two types of lignin were selected based on the number of phenolic moieties previously quantified by ^{31}P NMR, upon derivatization with a phosphorus compound. Both lignins were titanated and had their catalytic activity tested. The best performing lignin-based catalysts in this study resulted from titanated beach wood organosolv lignin (BLgTi) enable to convert 64 % of the tested alkene with a 76 % selectivity to the epoxide. This lignin was the one with a higher number of phenolic moieties prior to the titanation. In fact, the reactions with diaromatic model compounds were a perfect model for the results obtained using the depicted lignins because they do replicate the catalytic performance observed with the real lignin. In this context, the phenolic moieties resulting from the cleavage of β-O-4 linkage during harsh organosolv extraction, for example, are preferred to build a lignin-based catalyst than lignins which have structures similar to the native form of the natural polymer.

This dissertation explored the grafting of titanium on the lignin structure and the new properties of the resulting hybrid materials. Initially the oxidation was investigated of the natural polymer catalysed by a grafted metal. The extent of the subsequent oxidation was too high leading to a ring-opening effect that hindered a depolymerization process aimed at maximum yield of aromatics from lignin. Nonetheless, the oxidative pre-treatment proposed can be of help in future research where the focus will be at a potential route to aliphatic products from lignin. The recalcitrant lignin structure was weakened and is probably more susceptible to be disrupted.

On the other hand, the grafting of titanium on the lignin structure converts this into a metal supported catalyst, as was demonstrated for alkene epoxidation. The synthesis of this lignin-based catalyst took advantage of the lignin's acidic phenolic moieties. The application of the new catalyst, its structural changes resulting from the catalytic process, and its characteristics to deliver a better performance were also successfully explored. In this way, catalytic materials now represent a completely new area of lignin chemistry. Further research can focus as well on alternative metals to coordinate to the lignin functional groups to facilitate selective lignin conversion and transformation. Lignin depolymerization is in fact a field that can bring many advantageous applications of this exciting natural polymer, but it is also important to keep in mind that, as a macromolecule, lignin can be equally useful if its features and reactivity are explored, for instance its interaction with metals.

Appendices

"You can have data without information, but you cannot have information without data."

Daniel Keys Moran

Table A.1 Retention time (Rt) and response factors (Rfy) of reagents and products with respect to 1,3,5-trimethylbenzene (internal standard) from the chromatography analyses.

Component (y)	R_t (min)	R_{fy}
tBuOH	1.911	1.2998
tBHP	4.705	2.2958
Cyclooctene	9.031	1.0076
1,3,5-trimethylbenzene	10.257	-
tert-butylbenzene	10.754	0.9618
2-phenylacetaldehyde (2b)	11.253	1.3203
1-phenylethanol (1a)	11.600	1.1926
Acetophenone (2a)	11.650	1.2103
2-phenylethanol (1b)	12.306	1.3758
Cyclooctene oxide	12.312	1.1843

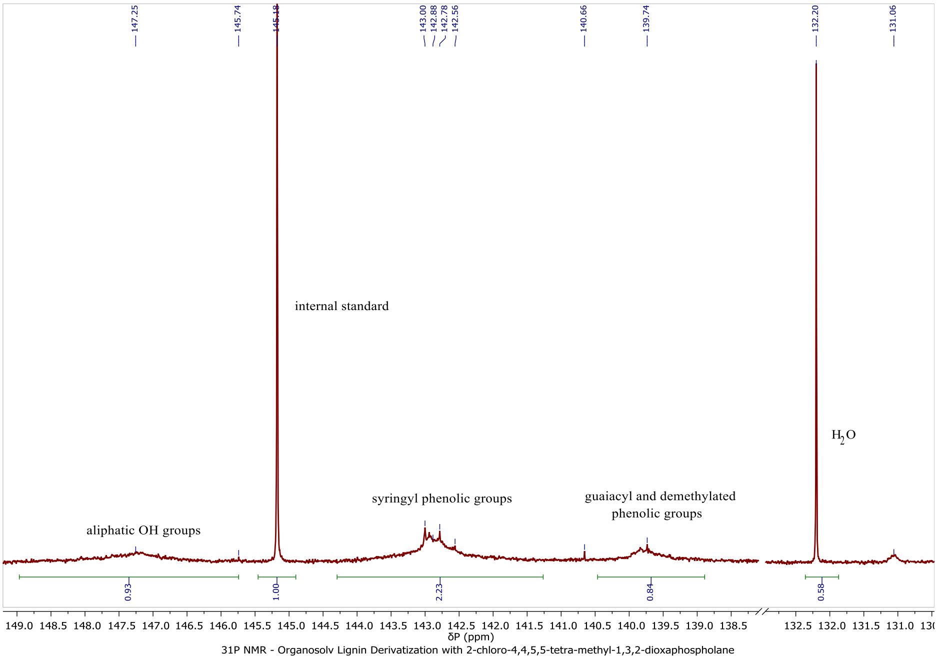


Fig. A3.1 Derivatization reaction of the lignin with 2-chloro-4,4,5,5-tetra-methyl-1,3,2-dioxaphospholane and ^{31}P NMR spectrum of the derivatized lignin. Free OH groups resonant signals identified according to the literature using cyclohexanol as internal standard [2,26,27].

Table A3.1 Amount of OH groups on lignin quantified based on the integration of the derivatized resonant signals on the ^{31}P NMR spectrum using cyclohexane as internal standard. Results are expressed in mmol of OH group per g of dry lignin.

Lignin group	Free OH (mmol/g)
Side-chain	0.95
Syringyl phenolic	2.54
Condensed phenolic units (4-O-5' type)	-
Guaiacyl and demethylated phenolic	1.06
p-Hydroxyphenolic	-

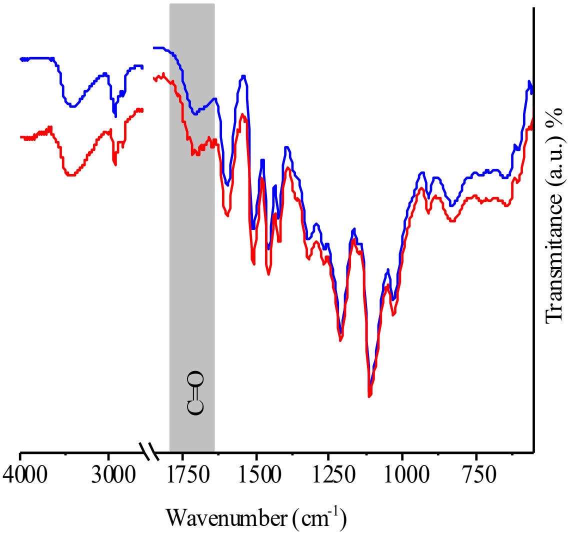


Fig. A3.2 IR spectra of the organosolv lignin (blue) and the product of the lignin oxidation with tBHP as oxidant and $Ti(O^{i}Pr)_4$ as catalyst (red) in n-octane.

Table A3.1 Identified product list of the P1000 lignin monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified by MS)	Retention time (min)	Mass (m/z)	Weight of monomer^{i} (mg)
1	Cyclohexene	5.6	77	37.5
2	Benzene	5.8	78	8.8
3	Cyclohexene, 3-methyl-	6.9	96	1.2
4	Cyclohexene, 4-methyl-	6.9	96	2.9
5	Cyclohexanol, 2-methyl-	7.2	114	8.8
6	Toluene	8.7	92	18.4
7	Cyclohexene, 1-ethyl-	9.2	110	2.3
8	Cyclohexene, 1,4-dimethyl-	9.6	110	1.9
9	4-Ethylcyclohexene	10.5	110	3.8
10	Cyclohexene, 1-ethyl-	11.2	110	5.1

11	Ethylbenzene	12.3	106	6.1
12	p-Xylene	12.6	106	4.0
13	Cyclohexanol	15.1	100	12.0
14	Benzene, 1-ethyl-3-methyl-	16.3	120	0.5
15	o-Cymene	21.4	134	1.4
16	2-Cyclohexen-1-one, 4,5-dimethyl-	22.3	124	0.8
17	3-Cyclohexene-1-carboxaldehyde, 4-methyl-	22.7	124	1.4
18	Dodecane (internal standard)	23.4	170	0.0
19	Benzyl alcohol	24.1	108	6.8
20	(4-Methyl-cyclohex-3-enyl)-methanol	24.3	126	19.7
21	Cyclohexanemethanol, 4-methylene-	24.8	126	4.8
22	Benzenemethanol, 2-methyl-	27.8	122	8.9
23	Benzenemethanol, 4-ethyl-	30.5	136	5.7
24	1,4-Benzenediol, 2,5-dimethyl-	31.1	138	2.9
25	Phenol, 2-methyl-5-(1-methylethyl)-, acetate	31.1	192	2.3
26	Phenol, 4-ethyl-2-methoxy-	31.5	152	1.9
27	1,4-Dimethoxy-2,3-dimethylbenzene	32.1	166	1.8
28	Phenol, 3-methoxy-2,5,6-trimethyl-	33.1	166	1.2
29	Benzenemethanol, 4-(1,1-dimethylethyl)-	33.6	164	0.5
30	2,4,6-Trimethylbenzyl alcohol	33.8	150	2.2
31	2,5-Diethylphenol	33.9	150	5.0
32	Benzenemethanol, 4-(1,1-dimethylethyl)-	34.2	164	1.2
33	4',6'-Dihydroxy-2',3'-dimethylacetophenone	35.4	180	1.7
34	Propofol	35.8	178	0.9
35	2H-1-Benzopyran-2-one, 7-hydroxy-6-methoxy-4-methyl-	40.3	206	0.3

[i] Calculated from GC-FID.

Table A3.3 Identified product list of the Ti-modified P1000 lignin monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified by MS)	Retention time (min)	Mass (m/z)	Weight of monomer[i] (mg)
1	Cyclohexene	5.6	82	28.7
2	Benzene	5.8	77	8.9
3	Cyclohexene, 3-methyl-	6.8	96	0.5
4	Cyclohexene, 4-methyl-	6.9	96	0.4
5	toluene	8.7	92	12.1
6	Cyclohexene, 1,2-dimethyl-	9.2	110	1.8
7	Cyclohexene, 1,4-dimethyl-	9.6	110	1.5
8	Cyclohexene, 4-ethenyl-	10.2	110	2.9
9	Cyclohexene, 1-ethyl-	10.5	110	1.9
10	4-Ethylcyclohexene	10.5	110	8.6
11	Cyclohexene, 1-ethyl-	11.2	110	6.2
12	1-Methyl-2-methylenecyclohexane	11.4	110	5.0
13	Ethylbenzene	12.3	106	5.1
14	p-Xylene	12.6	106	4.0
15	p-Xylene	12.7	106	0.6
16	Benzene, propyl-	15.9	120	4.5
17	Benzene, 1-ethyl-4-methyl-	16.3	120	0.2
18	Valeric acid, 4-phenyl-	20.0	178	4.8
19	Benzene, 1-ethyl-2,3-dimethyl-	21.4	134	1.5
20	Ethanone, 1-(3-cyclohexen-1-yl)-	22.0	124	4.4
21	Cyclohexane, 1-methyl-3-(1-methylethyl)-	22.5	148	1.8
22	3-Cyclohexene-1-carboxaldehyde, 1-methyl-	22.7	124	0.5
23	Benzene, 2-ethenyl-1,4-dimethyl-	23.3	132	0.1
24	Dodecane (internal standard)	23.4	170	0.0
25	4-Acetyl-1-methylcyclohexene	24.1	138	0.5
26	Benzyl alcohol	24.2	108	0.6
27	(4-Methyl-cyclohex-3-enyl)-methanol	24.8	126	8.0

28	: 2-Cyclohexen-1-one, 4,4,5-trimethyl-	25.1	138	2.5
29	Formic acid, (2-methylphenyl)methyl ester	25.2	150	1.9
30	3-Cyclohexene-1-carboxylic acid, 4-methyl-, methyl ester	25.5	154	1.7
31	Benzenemethanol, 4-methyl-	27.6	122	1.5
32	Benzenemethanol, 2-methyl-	27.9	122	4.7
33	Phenol, 3,4-dimethyl-	28.9	122	3.4
34	2,5-Diethylphenol	31.1	150	1.6
35	1,4-Benzenediol, 2,3,5-trimethyl-	32.2	152	0.6
36	Benzene, 1-ethoxy-2-methoxy-4-methyl-	32.5	166	1.7
37	1,4-Benzenediol, 2,3,5-trimethyl-	33.0	152	0.4
38	Ethyl 3,5-dimethylbenzoate	33.1	178	0.6
39	Phenol, 2-(1,1-dimethylethyl)-6-methyl-	33.6	164	0.4
40	2,5-Diethylphenol	33.9	150	2.3
41	Benzene, 1-methoxy-4-methyl-2-(1-methylethyl)-	34.2	164	0.5
42	Benzene, 4-ethyl-1,2-dimethoxy-	34.3	166	2.4
43	Phenol, 2-(1,1-dimethylethyl)-4-methyl-	34.8	164	0.4
44	Phenol, 2,4-bis(1-methylethyl)-	35.8	178	2.5
45	Butylated Hydroxytoluene	36.0	220	0.4
46	Phenol, 2,5-bis(1-methylethyl)-	36.2	178	1.4
47	5-Methyl-2,4-diisopropylphenol	38.5	192	0.8
48	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-4-methyl-	38.7	178	0.6
49	2,6-Diisopropylanisole	38.9	192	0.3
50	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-4-methyl-	39.0	178	0.4
51	5-Methyl-2,4-diisopropylphenol	39.2	192	0.7
52	5-Methyl-2,4-diisopropylphenol	39.5	192	0.4
53	Phenol, 2,6-bis(1,1-dimethylethyl)-	40.1	206	1.7
54	Phenol, 2,5-bis(1,1-dimethylethyl)-	40.3	206	0.3
55	Phenol, 3,5-bis(1,1-dimethylethyl)-	40.4	206	1.4

56	Phenol, 3,5-bis(1,1-dimethylethyl)-	42.6	206	0.4
57	Phenol, 2,6-bis(1,1-dimethylethyl)-	43.4	206	1.2
58	Butylated Hydroxytoluene	43.5	220	1.0
59	2,6-Di-t-butyl-4-methylphenol acetate(ester)	43.6	262	0.7
60	Phenol, 2,4,6-tris(1-methylethyl)-	44.1	220	0.6
61	4-tert-Butyl-2,6-diisopropylphenyl acetate	44.1	276	1.6
62	4'-tert-Butyl-2',6'-dimethylacetophenone	44.7	204	0.2
63	3,4-2H-Coumarin, 4,4,5,6,8-pentamethyl-	45.6	218	1.5
64	4-tert-Butylcatechol, dimethyl ether	45.9	194	0.6
65	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.0	208	1.1
66	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.7	208	1.2
67	1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	46.9	222	2.4
68	Benzene, hexaethyl-	48.4	246	0.7
69	3,5-di-tert-Butyl-4-hydroxyacetophenone	48.7	248	0.4
70	Phenol, 2,4,6-tris(1-methylethyl)-	48.9	220	0.6
71	Phenol, 3,5-bis(1,1-dimethylethyl)-	49.5	206	0.8
72	Phenol, 2,4,6-tris(1-methylethyl)-	49.8	220	0.6
73	2,4,6-Triisopropylbenzoic acid	51.1	248	0.3
74	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	52.3	234	0.1
75	Phenol, 2,4,6-tris(1-methylethyl)-	52.4	220	0.5

[i] Calculated from GC-FID.

Table A3.4 Identified product list of the Oxi-P1000 lignin monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified by MS)	Retention time (min)	Mass (m/z)	Weight of monomer[i] (mg)
1	Cyclohexene	5.5	82	13.1
2	3-Heptene	5.6	98	4.5
3	Benzene	5.8	78	4.7
4	Cyclohexene, 4-methyl-	6.9	96	3.4
5	Toluene	8.7	92	4.5

6	Cyclooctene, (Z)-	8.8	110	0.8
7	Cyclohexene, 1,2-dimethyl-	9.1	110	1.4
8	Cyclohexane, ethenyl-	9.6	110	2.3
9	Cyclohexene, 4-ethenyl-	10.2	108	3.4
10	4-Ethylcyclohexene	10.5	110	14.2
11	Cyclohexanol, 1-ethyl-	13.7	128	1.6
12	p-Xylene	13.7	106	1.2
13	Benzeneethanol, α,β-dimethyl-	13.7	150	5.6
14	Oxalic acid, cyclohexylmethyl ethyl ester	22.4	214	4.7
15	Phthalic acid, cyclohexylmethyl ethyl ester	23.0	290	1.6
16	Dodecane (internal standard)	23.4	170	0.0
17	(4-Methyl-cyclohex-3-enyl)-methanol	24.3	126	20.9
18	(4-Methyl-cyclohex-3-enyl)-methanol	24.9	126	8.3
19	Cyclohexaneethanol, 4-methyl-β-methylene-, trans-	30.1	154	5.3
20	Benzene, 1-ethoxy-2-methoxy-4-methyl-	32.4	166	1.3
21	Diethyl Phthalate	33.2	222	0.2
22	Durohydroquinone	34.2	166	1.6
23	Propofol	34.8	178	0.0
24	Phenol, 2,6-bis(1,1-dimethylethyl)-	40.0	206	0.5
25	Phenol, 2,5-bis(1,1-dimethylethyl)-	40.4	206	0.6
26	Dibutyl phthalate	42.2	278	0.3
27	Dibutyl phthalate	43.2	278	0.1
28	2-Methyl-4,5-dimethoxycrotonophenone	43.4	220	1.5
29	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	44.0	234	0.4
30	Dihydrocoumarin, 4,4,5,7-tetramethyl-	45.5	204	0.7
31	α,α-Diisopropyl-o-methoxybenzyl alcohol	45.7	222	0.4
32	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.0	208	1.5
33	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.6	208	1.0
34	1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	46.9	222	2.1
35	Phenol, 2,4,6-tris(1-methylethyl)-	48.8	220	0.6
36	Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters	49.5	306	0.4

37	2,4,6-Tris(1,1-dimethylethyl)-4-methylcyclohexa-2,5-dien-1-one	49.7	276	0.6
38	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	50.6	278	1.5

[i] Calculated from GC-FID.

Table A3.5 Identified product list of the BLg monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified by MS)	Retention time (min)	Mass (m/z)	Weight of monomer[i] (mg)
1	Cyclohexene, 1-ethyl-	10.5	110	0.3
2	Cyclohexene, 1-ethyl-	11.2	110	7.1
3	Cyclohexane, butylidene-	16.8	138	0.5
4	Cyclohexane, butylidene-	17.6	138	0.7
5	4,4-Dimethyl-cyclohex-2-en-1-ol	19.9	126	1.0
6	Cyclohexane, 1-methyl-3-propyl-	22.4	140	3.9
7	Dodecane (internal standard)	23.4	170	0.0
8	2,4,6-Trihydroxytoluene	28.5	140	2.4
9	6-Methyl-cyclohex-2-en-1-ol	30.6	112	0.9
10	1,4-Benzenediol, 2,5-dimethyl-	31.0	138	2.6
11	2',4'-Dihydroxy-3'-methylacetophenone	33.0	166	0.9
12	Phenol, 2,4-bis(1-methylethyl)-, acetate	35.7	220	1.9
13	Benzaldehyde, 2,4-dihydroxy-3,6-dimethyl-	36.9	166	4.0
14	2'-Hydroxy-4',5'-dimethylacetophenone	37.1	164	5.3
15	2',5'-Dimethoxypropiophenone	37.6	194	2.2
16	Phenol, 2,4-bis(1-methylethyl)-, acetate	38.6	220	2.4
17	Propofol	38.8	178	2.9
18	2-(1,1-Dimethylethyl)-6-(1-methylethyl)phenol	39.1	192	3.0
19	Propanal, 2-(4-ethoxyphenyl)-2-methyl-	40.9	192	2.4
20	Benzene, 1,2,4,5-tetraethyl-	44.0	190	1.6

[i] Calculated from GC-FID.

Table A3.6 Identified product list of the BLgTi monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified based on the library)	Retention time (min)	Mass (m/z)	Weight of monomer[i] (mg)
1	Cyclohexene, 1-ethyl-	10.5	110	0.9
2	Cyclohexene, 3-ethyl-	11.2	110	12.8
3	Cyclohexanol, 2-(1-methylpropyl)-	16.3	156	0.5
4	Cyclohexanol, 2-(1-methylpropyl)-	17.6	156	0.2
5	3,3,5,5-Tetramethylcyclohexanol	18.5	156	0.5
6	Dodecane (internal standard)	23.4	170	0.0
7	2-Ethylbutyric acid, 4-methoxyphenyl ester	25.3	222	0.8
8	(2,4,6-Trimethylcyclohexyl) methanol	28.5	156	0.5
9	2-Cyclohexen-1-ol	30.6	98	0.4
10	1,4-Benzenediol, 2,5-dimethyl-	31.0	138	1.2
11	Benzene, 1-ethoxy-2-methoxy-4-methyl-	32.4	166	0.4
12	Benzene, 4-ethyl-1,2-dimethoxy-	34.2	166	1.3
13	Propofol	35.7	178	0.8
14	Butylated Hydroxytoluene	35.9	220	0.3
15	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-4-methyl-	36.1	178	1.1
16	Benzene, 1-(1,1-dimethylethyl)-4-methoxy-	36.9	164	0.1
17	Benzene, 1-(1,1-dimethylethyl)-4-methoxy-	36.9	164	0.4
18	2-(1,1-Dimethylethyl)-6-(1-methylethyl)phenol	38.4	192	0.6
19	2-(1,1-Dimethylethyl)-6-(1-methylethyl)phenol	38.8	192	0.3
20	Propofol	38.9	178	0.8
21	2-(1,1-Dimethylethyl)-6-(1-methylethyl)phenol	39.4	192	0.3
22	Phenol, 2,6-bis(1,1-dimethylethyl)-	39.9	206	0.8
23	Phenol, 2,5-bis(1,1-dimethylethyl)-	40.3	206	0.8
24	5'-Hydroxy-2',3',4'-trimethylacetophenone	40.9	178	0.5
25	4',6'-Dimethoxy-2',3'-dimethylacetophenone	41.1	208	0.2
26	Benzene, 1,2,4,5-tetraethyl-	41.4	190	0.2
27	Benzene, 1,3,5-tris(1-methylethyl)-	42.0	204	0.3
28	5-Methyl-2,4-diisopropylphenol	42.2	176	1.0

29	Phenol, 2,5-bis(1,1-dimethylethyl)-	42.4	206	0.2
30	Phenol, 2,5-bis(1,1-dimethylethyl)-	43.0	206	0.2
31	4-tert-Butylcatechol, dimethyl ether	43.2	194	2.1
32	Phenol, 2,4,6-tris(1-methylethyl)-	43.3	220	0.7
33	Butylated Hydroxytoluene	43.4	220	0.4
34	Butylated Hydroxytoluene	43.9	220	0.4
35	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	44.0	234	0.5
36	Benzene, 1,2,4,5-tetraethyl-	44.0	190	0.5
37	Benzenepropanal, 3-(1,1-dimethylethyl)-α-methyl-	44.4	204	0.6
38	Benzene, 1,3,5-tris(1-methylethyl)-	44.9	204	0.3
39	Benzenepropanal, 3-(1,1-dimethylethyl)-α-methyl-	45.1	204	0.3
40	2H-1-Benzopyran-2-one, 6-acetyl-7-(acetyloxy)-4-methyl-	45.3	260	0.5
41	Butyrophenone, 4'-tert-butyl-2',6'-dimethyl-	45.4	232	1.6
42	p-Octylacetophenone	45.6	232	0.5
43	2,5-Cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-ethylidene-	45.6	232	0.8
44	4-tert-Butylcatechol, dimethyl ether	45.7	194	0.5
45	4',6'-Dimethoxy-2',3'-dimethylacetophenone	45.9	208	1.7
46	2,5-Cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-ethylidene-	46.1	232	0.2
47	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.5	208	1.8
48	1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	46.7	222	2.9
49	Methyl 5-acetyl-2-methoxybenzoate	47.0	208	0.5
50	3,5-di-tert-Butyl-4-hydroxybenzyl alcohol	48.1	236	0.5
51	Benzene, hexaethyl-	48.2	246	0.7
52	3,5-di-tert-Butyl-4-hydroxyacetophenone	48.5	248	0.3
53	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	48.6	234	0.3
54	Phenol, 2,4,6-tris(1-methylethyl)-	48.7	220	0.8
55	Phenol, 2,5-bis(1,1-dimethylethyl)-	49.3	206	1.9
56	Butylated Hydroxytoluene	49.6	220	1.0
57	Benzoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-	50.0	250	0.4
58	2,4-Cyclohexadien-1-one, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-	50.1	222	0.7

59	Phenol, 2,4-bis(1,1-dimethylpropyl)-	50.5	234	0.5
60	3,5-di-tert-Butyl-4-hydroxyacetophenone	50.8	248	0.3
61	2,4,6-Triisopropylphenetole	51.3	248	0.5
62	4-tert-Butyl-2,6-diisopropylphenyl acetate	52.1	276	0.7
63	Phenol, 2,4-bis(1,1-dimethylpropyl)-	52.2	234	0.8

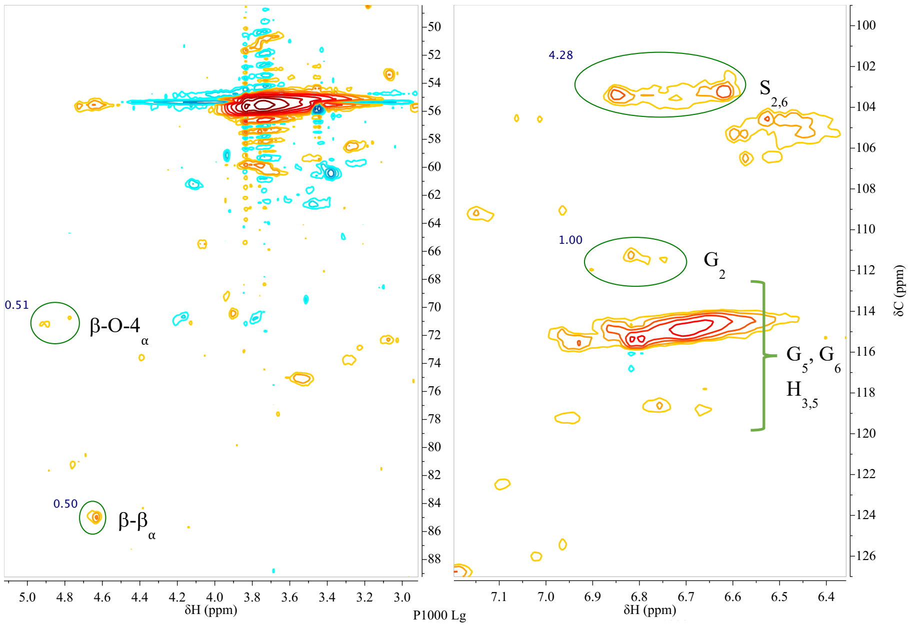
[i] Calculated from GC-FID.

Table A3.7 Identified product list of the Oxi-BLgTi monomeric mixture sample measured by GC-MS and identified based on their MS profile and reaching to compounds libraries.

Peak no.	Compound (identified based on the library)	Retention time (min)	Mass (m/z)	Weight of monomer[i] (mg)
1	Cyclohexene, 1,2-dimethyl-	9.8	110	1.7
2	4-Ethylcyclohexene	10.5	110	0.8
3	Cyclohexane, ethenyl-	11.2	110	12.7
4	Cyclohexane, butylidene-	17.5	138	0.6
5	Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1α,2β,5β)-	20.4	156	0.6
6	Cyclohexanol, 2,3-dimethyl-	21.2	128	0.8
7	Dodecane (internal standard)	23.4	170	0.0
8	Phenol, 4-methoxy-, acetate	28.2	166	1.8
9	Phenol, 5-methoxy-2,3,4-trimethyl-	34.2	166	1.4
10	Phenol, 2,5-bis(1-methylethyl)-	35.7	178	0.5
11	Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	35.9	220	0.8
12	5-Methyl-2,4-diisopropylphenol	38.4	192	0.1
13	Propofol	38.5	178	0.3
14	6-tert-Butyl-2,4-dimethylphenol	38.9	178	0.3
15	Phenol, 2,6-bis(1,1-dimethylethyl)-	39.9	206	0.2
16	2H-1-Benzopyran-2-one, 7-hydroxy-6-methoxy-4-methyl-	40.1	206	0.2
17	Phenol, 2,5-bis(1,1-dimethylethyl)-	40.3	206	0.3
18	6-tert-Butyl-2,4-dimethylphenol	40.5	178	0.1

19	2,6-Diisopropylanisole	42.1	192	0.6
20	Phenol, 2,6-bis(1,1-dimethylethyl)-	43.2	206	0.9
21	Phenol, 2,4,6-tris(1-methylethyl)-	43.3	220	0.3
22	2,6-Di-t-butyl-4-methylphenol acetate(ester)	43.4	262	0.3
23	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	43.9	234	0.2
24	Benzene, 1,2,4,5-tetraethyl-	44.0	190	0.2
25	4'-tert-Butyl-2',6'-dimethylacetophenone	45.4	204	0.6
26	Isocoumarin-3-one, 4,4,5,6,8-pentamethyl-	45.6	232	0.4
27	Acetophenone, 2',4'-dimethoxy-3'-methyl-	45.7	194	0.4
28	4',6'-Dimethoxy-2',3'-dimethylacetophenone	45.8	208	0.7
29	2,6-Di-t-butyl-4-methylphenol acetate(ester)	46.2	262	0.1
30	Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	46.3	220	0.1
31	4',6'-Dimethoxy-2',3'-dimethylacetophenone	46.5	208	0.6
32	1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	46.7	222	1.4
33	Benzene, 1,2,4,5-tetrakis(1-methylethyl)-	48.2	246	0.3
34	Phenol, 2,4,6-tris(1-methylethyl)-	48.7	220	0.3
35	Phenol, 2,5-bis(1,1-dimethylethyl)-	49.3	206	0.6
36	Phenol, 2,4,6-tris(1-methylethyl)-	49.6	220	0.3
37	Benzoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-	50.0	250	0.2
38	1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-	50.1	222	0.3
39	Phenol, 2,4-bis(1,1-dimethylpropyl)-	50.5	234	0.2
40	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	52.1	234	0.2

[i] Calculated from GC-FID.



a) **b)**

Fig. A3.3 P1000 lignin $^{1}H,^{13}C$-HSQC NMR of **a)** the side-chain region with the integration of α resonance signals of β-O-4, and β-β bond types, and **b)** of the aromatic region with the integration of G_2 and $S_{2,6}$ resonance signals used in the quantification. The quantification was made according to the literature and the integration signal of the G_2 (δ_C/δ_H: 112/6.81 ppm) was used as reference [24].

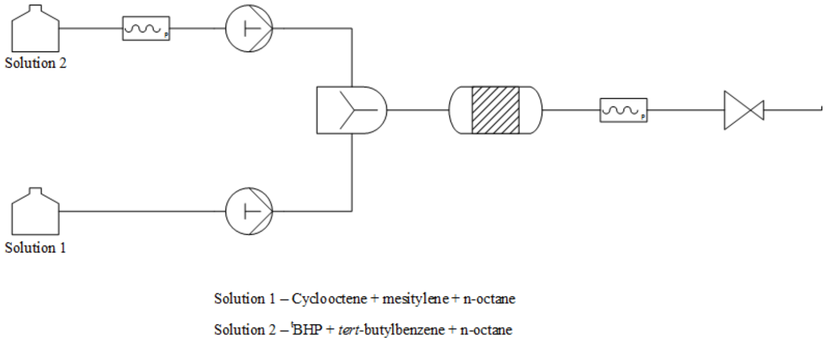


Fig. A4.1 Schematic representation of the plug flow reactor setup used to test the LgTi catalyst (catalyst bed dimensions 65 mm x 4 mm).

Table A4.1 Retention time (Rt) and response factors (Rfy) of reagents, products and internal standards with respect to 1,3,5-trimethylbenzene from the chromatography analyses.

Component (y)	Retention time (min)	Response factor
tBuOH	1.911	1.2998
tBHP	4.705	2.2958
Cyclooctene	9.031	1.0076
1,3,5-trimethylbenzene	10.257	-
tert-butylbenzene	10.754	0.9618
Cyclooctene oxide	12.312	1.1843

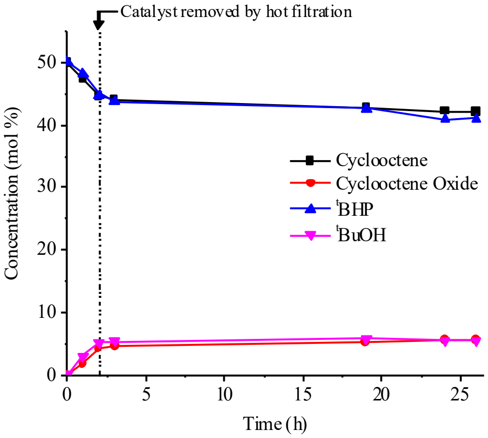


Fig. A4.3 Hot filtration conversion plots of cyclooctene epoxidation reaction with BLgTi, during 26 hours. The catalyst was removed 2 hours after the beginning of reaction (black vertical line).

Table A5.2 Retention time (Rt) and response factors (Rfy) of reagents and products with respect to 1,3,5-trimethylbenzene (internal standard) for gas chromatography.

Component (y)	Retention time (min)	Response factor
tBuOH	1.911	1.2998
tBHP	4.705	2.2958
Cyclooctene	9.031	1.0733
1,3,5-trimethylbenzene	10.257	-
Cyclooctene oxide	12.312	1.3025

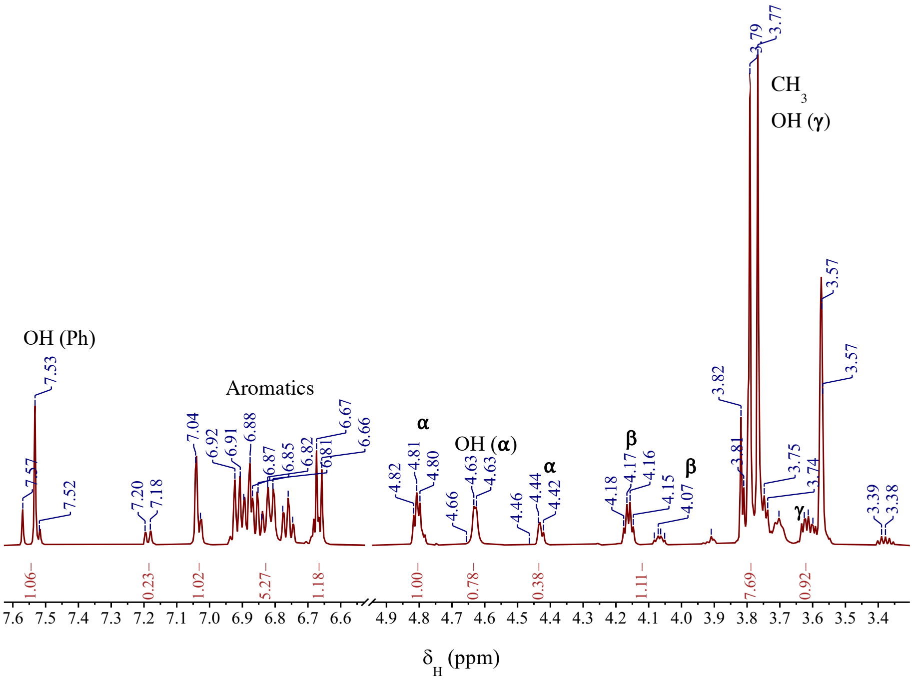


Fig. A5.1 Proton NMR of the model compound 3. The resonant signals are identified according with the lignin position that they are mimicking, represented in **Fig. 5.1**.

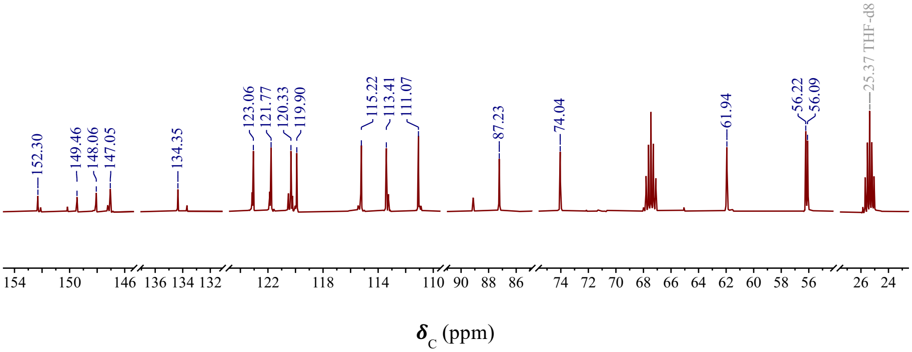


Fig. A5.2 Carbon NMR of the model compound 3.

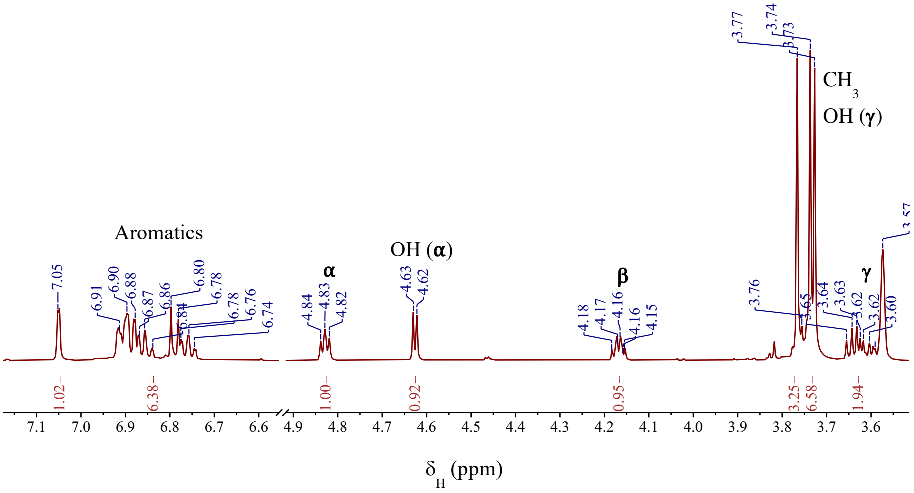


Fig. A5.3 Proton NMR of the model compound 4. The resonant signals are identified according with the lignin position that they are mimicking, represented on **Fig. 5.1**.

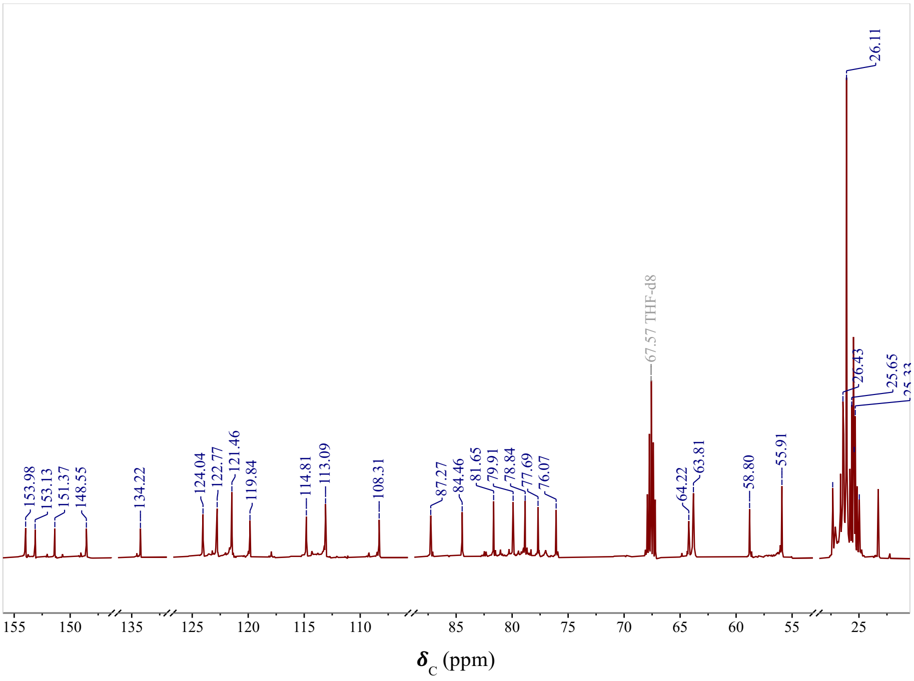


Fig. A5.4 Carbon NMR of the model compound 5.

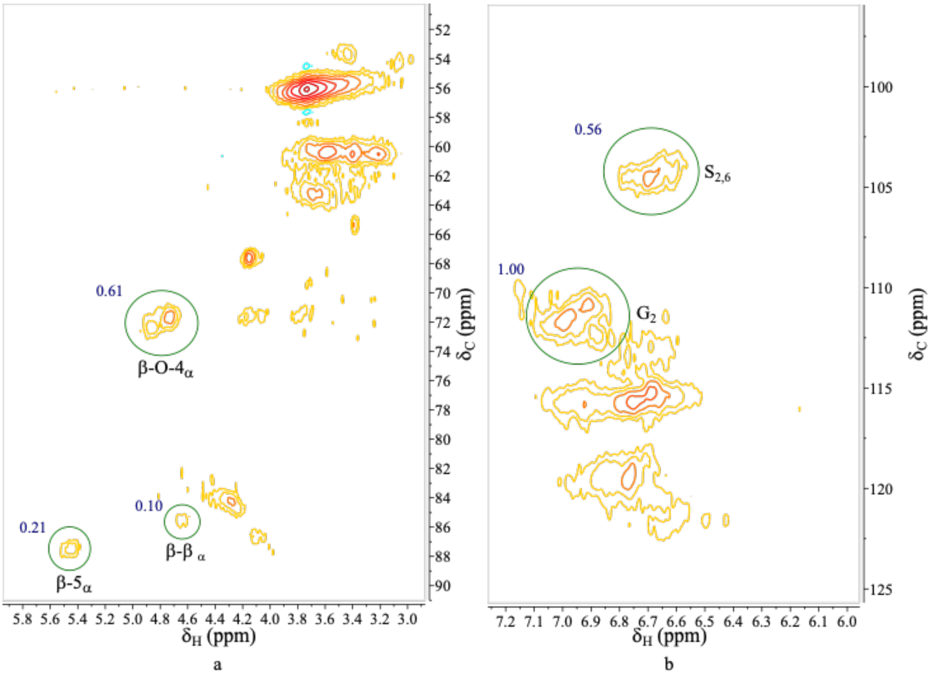


Fig. A5.5 Oak lignin ^{1}H,^{13}C-HSQC NMR of **a**) the side-chain region with the integration of α resonant signals of β-O-4, β-β, and β-5 bond types, and **b**) of the aromatic region with the integration of G_2 and $S_{2,6}$ resonance signals used in the quantification. The quantification was made according to the literature and the integration signal of the G_2 (δ_C/δ_H: 113/6.77 ppm) was used as reference. It is highlighted the carbon-proton correlation signals of α atoms.

Acknowledgements

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"Those who pass by us, do not go alone, and do not leave us alone; they leave a bit of themselves, and take a little of us."

Antoine de Saint-Exupéry

“It is good to have an end to journey toward; but it is the journey that matters, in the end.” The sentence is from Ursula K. Le Guin (*The Left Hand of Darkness*), but I would like to borrow her words to describe how I feel about the years of work that are now consolidated in this thesis. I was fortunate enough to have amazing people around me through the journey. They not only kept me company but also intervened actively in this story. The following words are how I thank them.

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You are power, you are beauty, you are a bright light! Thank you for all the laughs we had, the talks, the dinners (with Andrea as well), everything. And do not forget, we are warriors! Imelda, you are one of my favourite people! We had a quiet start (very unusual for me), but thank goodness it changed. Thank you for your love, for your amazing sense of humour (that I like so very much), and for making me feel dear every time we spoke. Even nowadays, I love to listen to you on our Zoom meetings. Sofyia, every time I think of you I recall the willpower that will take you wherever you want to go. Thank you for your *Carpe diem* example and for sharing it with me. Thank you for proving me that vegan people do smell better than others. Thank you for all the joy you spread in my life and for all the fun moments we put ourselves into experiencing! Chris, guria, eu a ti escrevo em português (com sotaque europeu), porque não faria sentido ser de outra forma. 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Many people have said this before, but I am going to state it because I now truly understand its meaning: there are two types of family, the one we are born into and the one we choose throughout life. I consider myself a very fortunate person as I have both. From now on, I will refer to both as one and will call them family.

Camarada Monteiro, minha querida Joana, obrigada por continuares a fazer parte da minha vida. Já nos conhecemos à muitos anos, já partilhámos algumas aventuras, muitos copos, rimos muitos e falamos de coisas muito sérias. Sei que a vida pode mudar, mas sempre que te encontrar nada terá mudado. Vemos o mundo com formas muito diferentes, mas isso nunca nos impediu de fazer nada juntas. Obrigada por isso. Olha, temos é de manter o velho mote "E vivam as sunguas!" e continuar a festa, porque não há festa como esta! Voltar a casa foi mais fácil porque tu, e a tua querida irmã Ana Rita, estavam por perto e imediatamente me abriram os braços e me acolheram. Obrigada.

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Mafalda, minha querida Mafaldinha, antes de mais obrigada por me permitires ser tia emprestada do teu pequeno Duarte. É uma honra. Assim como é uma honra fazer parte da tua vida. És das pessoas mais conscientes, assertivas e companheiras que eu conheci até hoje. Mas não é por isso que eu gosto de ti. O teu valor está nesse coração enorme que carregas dentro de ti, nessa tua genuinidade que deixa qualquer um desarmado, e nesse teu sentir que sem saber bem como me faz sentir a mim também. Adoro estar perto de ti e gostava de o poder fazer mais vezes. Obrigada por fazeres parte da minha história desde os nossos 18 aninhos, por aceitares sempre estas minhas manias, e por me ouvires até à exaustão falar de Luís XIV (sim, eu nunca vou esquecer isso!).

Carlita, minha Carlita, verdade seja dita, eu nunca percebi o que nos uniu na universidade. Mas, o que quer que tenha sido, foi um bênção divina. Há uma parte de mim que quer ser como tu; sempre quis. Depois há outra parte de mim que sabe que não tenho a tua coragem. És a maior! Adoro a forma como olhas a vida e como te atiras de cabeça à aventura, e sempre que posso tento aprender algo contigo. E adorava que te conseguisses ver como eu te vejo. Daqui pareces uma Super Mulher. Obrigada por seres super. Obrigada pela tua presença tantas vezes agradavelmente desconcertante na minha vida. Obrigada por todos os postais que me enviaste de tantos sítios ao longo destes anos. Obrigada por me manteres na tua lista de contactos (e espero que nunca me tires de lá). Adoro-te, adoro ter-te por perto mesmo que longe, e adoro saber que estava certa quando te disse que o facto de ires para Dinamarca não ia mudar nada. A vida é tua Carlita, sê vida!

Catarina, grande Catarina, tu sabes muito, tu sabes tudo. Eu só gostava de saber como é que tu fazes. Conheci-te num dos momentos mais solitários da minha vida. Tudo estava ao contrário. E porque no teu mundo as coisas também não estavam fáceis, unimo-nos na nossa lamentação. E fez-se luz! És uma companheira do caraças, que sempre me mostraste ativamente que uma boa dose de loucura só faz bem. Tenho pena de não ter sido mais vezes louca contigo (talvez ainda dê tempo). Nem sempre me dizes aquilo que quero ouvir, e permiti-me começar a agradecer-te por aqui. Obrigada por durante estes anos que passei a fazer este doutoramento teres estado sempre presente, nunca arredaste pé mesmo quando eu era só chata. Eu sei que nós devíamos amar incondicionalmente toda a gente, mas há pessoas que é mais fácil. Tu és uma dessa pessoas. Obrigada pelos conselhos, pelas partilhas, por todas a nossas conversas que, para quem não sabe, chegam a durar mais de 5 horas. Como temos aprendido, obrigada por seres e por sentires e por me deixares ser e sentir contigo.

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Sodona Joana Rita, sempre te ouvi dizer que "o mundo cabe na cabeça de um alfinete". As ligações que unem as nossas famílias provam que tens toda a razão. O melhor é que posso passar séculos sem falar contigo, mas quando falo, sinto que estamos tão próximas como se vivêssemos na cabeça de um alfinete. Obrigada por todos estes anos a viver no mesmo alfinete. Obrigada por partilhares comigo os teus dons, a tua emoção, a tua luz, a tua intuição; eu sei que achas que não tens nada disto mas quero que esta frase seja a prova de que não é bem assim. Se eu recebi tudo isto, foi porque tu os enviaste. Obrigada pelos ataques de riso incontroláveis, pelas horas intermináveis de converseta, pelas tuas opiniões que me abrem os olhos, por aquele tipo de informação que eu sei que só uma mente como a tua memoriza, e por aquela prende de São Valentim que me deste em 2012. Durante este doutoramento, estiveste sempre lá. Apoiaste-me quando precisei, aceitaste e sublinhaste as minha reclamações e, mais importante, reiterastes os meus insultos em todas as situações merecedoras de (ou nem por isso) como se estivéssemos dentro do carro da Carol em pleno dia de feira em Espinho. Obrigada por todos os momentos partilhados e que venham muitos mais dentro desta cabeça de alfinete em que vivemos.

Taninha amori, migita do meu coração, eu passo tanto tempo a falar contigo que nem sei bem o que mais há para dizer. Tu és uma peça muito importante deste puzzle que é a minha vida (e ambas sabemos que não é só desta vida). Uma peça que é sempre fácil de encontrar, mas que não cabe em parte nenhuma porque o seu lugar, apesar de garantido, está sempre a redesenhar-se. Com isto quero dizer que, no que quer que a minha vida se transforme, tu transformas-te comigo. Não sei que raio de simbiose é esta, mas mesmo quando sinto que a realidade me está a fugir das mãos, tu chegas, amparas-me e dizes-me que eu não sou louca (ou que estou completamente louca). Estás sempre disponível para me agarrar ao chão quando estou sem ele e sempre pronta para me deixares voar quando vês que tenho asas. Se fosses macho, fazia-te; como não és, perdi o interesse! (Infelizmente nada podemos fazer em reação à nossa natureza.) Em 2009, quando bati à tua porta pela primeira vez, acredito que desejaste que aquela tivesse sido a minha primeira e última visita. Espero que esse desejo não se volte a repetir. Obrigada pelo passado, por estares no presente, e antecipadamente grata pelo futuro.

Sasha, thank you for the many moments we shared. Thank you for the uncountable talks that many times opened my eyes. I love talking to you, your way of not taking me seriously, and the fact that you are always happy to eat whatever I cook without complaints. You helped me to grow, to be more honest with myself, and to laugh out loud with no shame. Your inner child met mine and there were pretty magic moments that I was blessed to share with you. If I recall, you taped some of those moments, like baking *pasteis* attempts, or me singing inappropriate Russian sentences (for those who are wondering what I am talking about). I would like to thank you in advance for deleting all those videos (from your cloud as well!!). Without you, my years in Eindhoven would have been shadier, sadder, and just normal. I will always want to hear from you. The doors of my house will always be open to receive you (I promise to cook something as well). You are family, so please do not become a distant cousin. Thank you!

Tobias, Tobi, to be honest, at the point I am writing this, I know nothing of your life. Somehow it is not strange. I know you are doing well, and strangely that is enough. Nonetheless, I miss you. I miss listening to you, listening to your jokes. (Before I met you, I have never heard anything about the German sense of humour; so, as far as my experience goes, Germans have a great sense of humour!) I also miss your breakdancing. Thank you for your support when I needed it, for always saying something (or simply waving) while walking as fast as one could on the corridor and, for always asking me the tough questions whose answers I did not want to face. We were not always friends, but somehow it happened. Now, it is the perfect moment to say that I want my book back. I need to 'start living'. Do not become a stranger. If at any point you wonder how to contact me, just ask Arno. He will keep us in touch.

Anton, Antoshka, incredibly we became real friends when you started doing the casual Friday thing. Thank you for that! You know I loved that tradition of yours. The same way I loved when you showed up at my place with a basket of fruit and some weed just because I was with a cold (and I got better!!). I even loved when you complained to me because I did not give you a working straw. (For your information, you were using the lemon squeezer; it was not my fault. And, by the way, no one drinks gin with a straw!) They say that we only know a person's real value when we are apart from them. When you left town, every moment you came back for a visit, or we went to visit you, was special. I love the way you always allowed me to grumble with you and your willingness to grumble with me about whatever was going on in our lives. I love listening to you talking about mundane things (and not that mundane) because I always get a new perspective. And that is a superpower, my friend! Thank you for never keeping yourself at a safe distance. Thank you for always being there when I reached out to you. Thank you for making life seem easy, even when it was falling apart. Thank you for being you, independently of where you are. That is your gold. I would like to extend my gratitude to your lady, Anastacia, that had always kindly welcomed me into your family. And please, keep me posted about the little one growing up… at least while he is still smaller than I am (after that, it will be just a shame… although I still will want to know).

I was informed that, in online defences, we do not take paranymphs. Well… I had them anyway because I invited them in advance and I was ashamed to cancel the invitation. So, I would like to take the opportunity to express my gratitude to my two knights in shining armour, my paranoid friends, my secret three sum: Doctor Arno van Hoof and Doctor Evgeny Uslamin. I love you two! There is no other way to put it. Thank you for every single time you bothered me, you annoyed me, you scared me, you made fun of – and with me. Thank you for the times that you have ignored me, that you visited, that held me, supported me, hugged me (I MISS THAT SO MUCH) and saved me. Many times, you kept me walking even when I had no will to. My dear Arno, you were the first person with whom I connected in NL; the weird ‘wanna be’ bold guy at the lunch table laughing at everything, trying to speak (in English) to me, and folding his sandwiches more times than necessary. All the moments that followed were just to establish a connection that was written in the stars. Proof of that is this telepathic communication that we developed. Or the sense of humour we share. Or that you are always ready to eat my leftovers. Or your willingness to follow my directions even knowing that I had no sense of direction. I love many things about you and hate many others. I love how you always support me and share my pain (and happiness), how you pretended to follow my “orders”, and the fact that you like the sun as much as I do. I hate that you know me so well to the point of knowing how to trigger the ‘momo-monster’, prank me, scare me, and recognize when I am not good. Thank you! Your friendship and care is something that I will always be thankful for; as you will always be part of my life. You are not like a brother to me, you are a brother! (Although sometimes I felt like the mom in the equation; I guess this qualifies me as the older sibling). My dear Evgeny, my first memory of your presence in my life was congratulating you on your birthday. Today, I know that moment happened 6 months after you arrived to the group. “It is not you, it is me.” I do not pay attention to people. Later on, I learnt that I used to scare you. Still do not know why. It is funny, I do not have powerful memories of you in my good moments, but I remember you being in every single bad moment. And that is what makes you so unique, so special. Always by my side, helping, listening, supporting me. To be honest, you never gave me the support I would like to have, but the one I needed, with powerful sentences like “I don’t know why you are like this?!” or “You are being paranoid!” or “Who cares?”. Thank you for caring. Thank you for accepting the Momo paranoia mode. Thank you for listening to me (everybody knows how demanding this can be). One last thing, thank you for raising my awareness. I spend so much time in meditation and stuff (you know), but no exercise is as efficient as you stating the obvious (in your very own way) about whatever. That is nerve-racking, but thank you anyway. One last thing (this time for real), thank you for our day in Venice. It was as romantic as Verona will never be! No words are enough to express how much I like you two, how important you are, and how special you make my life. And I know no words will ever be enough. Thank you, my favourite bastards!

My dear Lingqian, the best for last! They say that growing up, we are less likely to create true friendship bonds that last a lifetime. Well, we made it happen! During this journey, you were my companion fighting with me in every single battle. Sometimes standing in front of me for protection, other times standing behind me for support, but always by my side. We always recognize how different we are, our cultures, our ways of perceiving life. But, we always focus on what unites us instead of what divides us. And that is as rare as you are! Your friendship was the way the Universe found to bless me beyond what I thought I deserved. Thank you for everything you gave me (I could make a list, but that would be endless and these acknowledgements are already long enough). Thank you for your goodness and your kindness. You are a reminder that good people still exist in this confusing world. I treasure all the memories we have like shopping afternoons that none of us needed, having heartfelt talks while eating, laughing out loud everywhere, bonding. Thank you so very much for allowing me to be a part of your life. I would like to thank as well the saint of a husband that you have. Chao, thank you for taking such good care of my friend (we both know how much work that implicates) and for always receiving me warmly in your house.

À família que sempre me acompanhou e apoiou ao longo desta jornada, e tantas outras antes desta, o meu muito obrigada. Sou verdadeiramente abençoada por vos ter na minha vida. Apesar de todos terem um valor inestimável, há alguns agradecimentos especiais que tenho de deixar aqui. Muriel, rica prima, obrigada por me abrires, sempre que possível, as portas da tua casa ao longo destes anos. Obrigada também por me acompanhares nas visitas surpresa a casa e por guardares segredo disso. E, por fim, mas não menos importante, obrigada por todas as *sexy pics* (ou nem por isso) que fomos tirando ao longo destes anos que espelham bem a "deterioração" do meu estado mental ao longo do doutoramento. Tia Peta, muito obrigada por tomares tão bem conta da nossa preciosa Avó Alice. Sem ti andaríamos todos mais preocupados e a dormir menos descansados. Graças a ti, ela tem o melhor cuidado e qualidade de vida possível. Muito obrigada! Tia Elisabete, Tonton Tony, Eva, Tio Fernando, Tante Andre, Sandra, merci beaucoup. Merci à tous pour m'avoir reçu de bras ouverts quand je cherchais, à vos côtés, du repos et renouveler mes énergies. Votre soutien pendant mon doctorat a été très important.

Ao meu afilhado Pedro, tu és a prova viva de que um doutoramento pode durar muito tempo. Quando a Raquel começou na Holanda, tu tinhas 2 meses e qualquer coisa… Muito obrigada por tornares a minha vida mais colorida/divertida, por me lembrares que eu na realidade só sou um ano mais velha do que tu, e por despertares em mim esta vontade de ser melhor para te poder acompanhar. Prometo que vou sempre brincar contigo, chamar-te a atenção quando precisares e levar-te para os copos quando cresceres. Amo-te muito.

Liliana, maninha do meu coração, digamos que estes últimos anos não foram fáceis para nenhuma de nós. Eu tinha o doutoramento para terminar e tu tinhas que terminar outras coisas. Mas a prova de que é das trevas que nasce a luz, é que durante este processo nós nos tornamos verdadeiramente irmãs. Não sei por que é que as coisas acontecem como acontecem, só sei que se não tivessem acontecido nós não estaríamos onde estamos hoje, rijas, melhores, mais felizes! Obrigada por ouvires todas as minhas coisas sem reclamar, por compreenderes a forma como eu vejo mundo, e por me apoiares quando preciso. Eu sei que não nos escolhemos uma à outra (pelo menos conscientemente), mas quero que saibas que se me fosse dada a opção, eu escolhia-te uma e outra vez. Sempre.

Mãezinha e Paizinho, eu sei que dou muito trabalho, que às vezes digo coisas estranhas (maioritariamente acertadas :), e que nem sempre vos dou a atenção que vocês merecerem, mas quero que saibam que esta é a minha forma de dizer que vos amo muito. Obrigada por me aceitarem de volta no vosso cantinho, depois de terminado o trabalho na Holanda, sem nunca me pressionarem ou fazerem exigências. Isto mostra o quão sortuda eu sou em ter-vos como pais. Obrigada por me acompanharem nas minhas decisões, por me darem a vossa opinião, e por fazerem de mim quem sou. Sei que não vou poder estar sempre fisicamente do vosso lado, mas quero que saibam que vos levo comigo para onde quer que a vida me leve. Bom, e a partir de agora, podem finalmente dizer a toda a gente que a vossa 'mai' nova é Doutora, mas Doutora a sério :). Muito Obrigada!

During my PhD years, I also have some "invisible" supporters. Characters and people that were not physically there, but whose personality, stories and talent drove me through all the moments. I would like to thank Daenerys Targaryen (you deserved to be the queen of the seven realms!), John Snow, Tyrion Lannister, Thor, Damon Salvatore, Diana - Princess of the Amazons, Magnus Bane, Luca Guadagnino, Paulo Coelho, Tarantino, Arundhati Roy, António Zambujo, Salvador Sobral, Sara Tavares, Lucifer Morningstar, Samuel L. Jackson, Eva Green, Clair and Jamie Fraser, Louis XIV and his Versailles, André Le Notrê, Henry Cavill, Yuval Noah Harari, Eckhart Tolle, Louise L. Hay, Fiódor Dostoiévski, Mia Couto, Sara Howard, Anne Frank, Cesária Évora, and Roger Wolff, and many others. This might sound like a joke or that I am not taking it seriously, but many times I just needed to leave my life and enter someone else's story. All these names helped me to do just that, and for it I am very grateful.

Last, but not least, I would like to thank the most important person: myself. Thank you for doing this, I know you better now. Never forget the lessons you learnt and the people you met. For better and for worse, the journey ended.

Now, the future awaits you around the corner.

Love,
MoMo

Mónica R. Caseiro Fernandes was born on 30th May 1990 in Peso da Régua, Portugal.

She completed her high school with praises in Sciences and Technology in 2008 at Macedo de Cavaleiros High School in Macedo de Cavaleiros, Portugal. She continued her higher education by starting, in 2008, a three-year bachelor's in Biochemistry followed by a master's degree in Organic Chemistry and Natural Products both at the University of Aveiro in the city of Aveiro, Portugal. In 2013, she graduated within the QOPNA group where she completed a project that she was developing since the last year of her bachelor entitled “Synthesis of new calix[4]pyrroles with sulphonamide groups and its anion binding proprieties” under the supervision of Prof.dr. Augusto Tomé and Dr. Andreia Farinha. In 2013, she continued her work with the QOPNA group as a researcher within a project that aimed for the synthesis of new Porphyrin-Phthalocyanine-Fullerene conjugates. In 2014, she started a PhD project at Hybrid Catalysis B.V. in collaboration with the Inorganic Materials & Catalysis group at the Eindhoven University of Technology in The Netherlands under the supervision of Dr. Erik Abbenhuis and Prof.dr.ir. Emiel Hensen. Her PhD was developed within the SuBiCat project sponsored by the Mari-Curie Initial Training Network. The results obtained from this work are presented in this dissertation.

Throughout her academic career, she was involved in volunteer activities that she continues to develop to this day.

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