Lignin biomass conversion into chemicals and fuels

Melián Rodríguez, Mayra; Riisager, Anders; Kegnæs, Søren; Shunmugavel, Saravanamurugan

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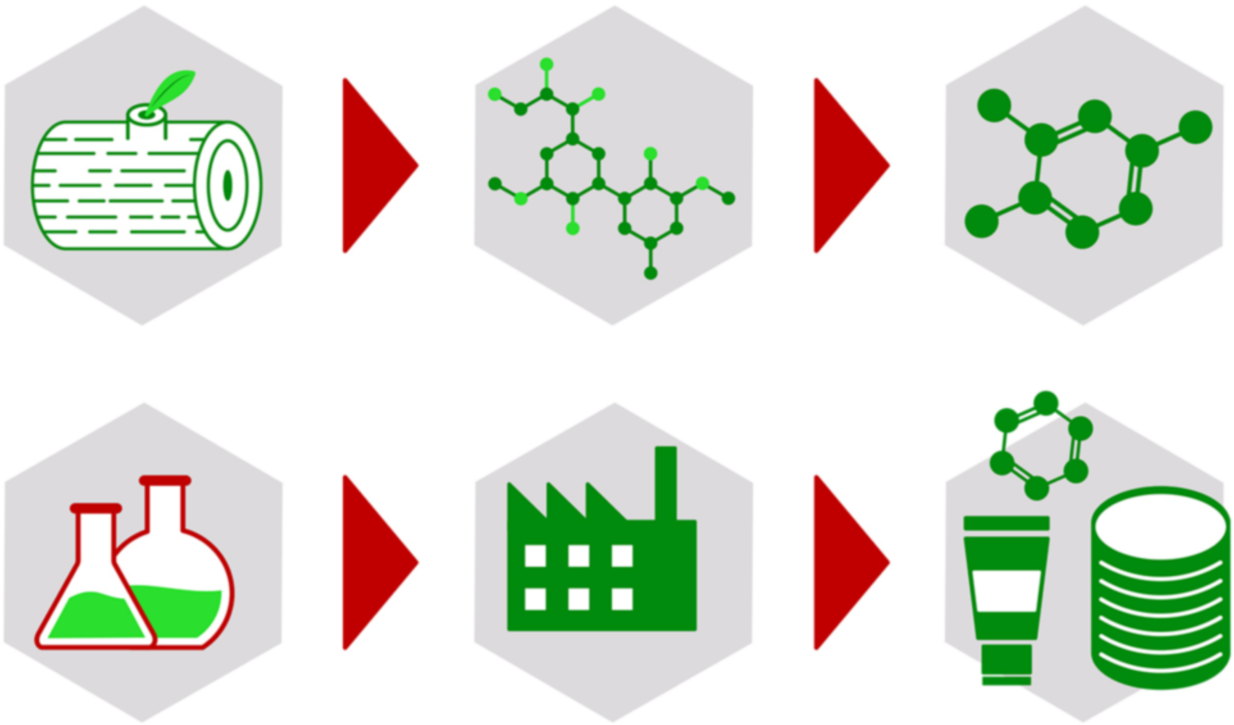
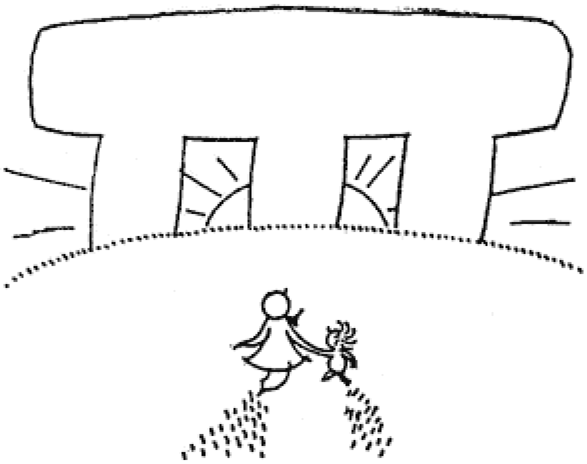


Mayra Melián Rodríguez
Technical University of Denmark
March 2016

DTU Chemistry
Department of Chemistry



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Piet Hein

Preface

The work presented in this thesis was mostly performed at the Centre for Catalysis and Sustainable Chemistry, Department of Chemistry at the Technical University of Denmark, under the supervision of Associate Professor Anders Riisager, Associate Professor Søren Kegnæs and Senior Researcher Saravanamurugan Shunmugavel between March 1st 2013 and February 29th 2016. The Danish Agency for Science, Technology and Innovation (International Network Programme, 12-132649), Haldor Topsøe A/S and the Technical University of Denmark funded the project.

Within the PhD period, an external stay was conducted at Dalian Institute of Chemical Physics between March 1st 2015 and May 31st 2015 under the supervision of Professor Jie Xu, and Professor Fang Lu. The results of the external stay in Dalian were the two-step lignin valorization in Chapter 4, and a project related article in progress (see Appendix B)

First of all, I would like to thank my supervisors Associate Professor Anders Riisager, Associate Professor Søren Kegnæs and Senior Researcher Saravanamurugan Shunmugavel for giving me the great opportunity to spend three years researching at DTU on this exciting topic, their continuous instruction, support and encouragement. I am very grateful for all their help not only concerning the academic work, but also with regards to my career and personal development.

I would also like to thank Esben Taarning for all his guidance, help and suggestions during the development of this PhD work. Special thanks go to Martin Spangsberg Holm for his advice and helpful suggestions during my first year as a PhD student in Denmark. I am grateful to Professor Jie Xu and Professor Fang Lu for letting me visit their group at Dalian Institute of Chemical Physics during my external stay in China. I would also like to thank Jiazhi Chen, for scientific discussions, inspiration and collaboration.

There are several of my senior DTU colleagues, beside my supervisors, who offered me guidance during my PhD study and for this I am truly grateful. A few of them deserve a special recognition for the time they have invested in me: Senior Researcher Eduardo J. García-Suaréz for always taking the time to guide me when I needed it and his encouragement during my PhD. Postdoc Jerrik Jørgen Mielby for great collaboration and all the guidance he has offered me through his knowledge on zeolites and heterogeneous catalysis. Postdoc Leo Schill for all his advice and helpful suggestions. In addition, Senior Researcher Sebastian Meier for his valuable guidance and collaboration concerning NMR spectroscopy.

I would thank PhD students Jacob Oskar Abildstrøm, Agata Gallas-Hulin, and Amalie Modvig for all their advice, grateful suggestions and encouragement. Furthermore, I would like to thank my colleagues at CSC, both past and present, for creating the great working environment and atmosphere, which exists in this group. Thanks also to all the technicians, in particular Bodil Fliis Holten, for the plentiful help and support she has given me in the lab during these three years. I warmly thank Lotte Skafte Jespersen for her assistance and support.

My sincere appreciation goes to Jennifer Houghton for the enthusiastic help, discussion, friendship and her valuable comments on this thesis. I would also like to thank Søren Birk Rasmussen for his help during my early time at DTU, and María Consuelo Alvaréz Galván to encourage and guide me to start this PhD.

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Mayra Melián Rodríguez

Lyngby, February 29, 2016

Abstract

Second-generation biomass or lignocellulosic biomass, which is mainly composed of cellulose, hemicellulose and lignin, is a very important and promising feedstock for the renewable production of fuels and chemicals of the future. Lignin is the second most abundant natural polymer, representing 30% of the weight and 40% of the energy content of lignocellulosic biomass. While designated applications for cellulose already exist in form of the current pulp and paper production as well as its prospective hydrolysis and fermentation into biofuels (mainly bio-ethanol), sustainable ways to valorize the lignin fraction of wood are yet to be established, due to its poor solubility and complex heterogeneous structure. This constitutes a major drawback in the economic viability of a biorefinery, where complete valorization of lignocellulosic biomass is necessary. For this reason, and due to its potential as a valuable feedstock for the production of organic chemicals, lignin valorization has become an important issue to solve.

For a better understanding and analysis of the catalytic performance of lignin, it is common to use lignin model compounds, which contain the most significant linkages present in lignin and show similar, although simplified, characteristics to the natural biopolymer. Among them, the most abundant structural unit is the β-O-4, representing approximately 60% of the bonds in hardwood and 45-50% of those in softwood.

Oxidative depolymerization is one of the most viable methods for lignin valorization. It involves the cleavage of ether bonds, such as β-O-4 and other linkages present in lignin and its model compounds, giving aldehydes or carboxylic acids as products, depending on the reaction conditions used. In Chapter 2 of this thesis, the preparation, characterization and catalytic performance of heterogeneous catalysts for the aerobic oxidation of β-O-4 lignin model compounds (veratryl alcohol and guaiacyl glycerol-β-guaiacyl ether) is discussed.

The use of an environmentally friendly process, the organosolv process, for treating lignocellulosic biomass in the presence of a solvent and using reaction conditions under which at least part of the lignin is separated from the biomass, is described in Chapter 3. Different catalysts and reaction conditions have been studied in order to optimize the organosolv process for the production of high-quality lignin for further upgrading.

At the end of this thesis, Chapter 4, a catalytic process is described for the valorization of lignin, consisting of a two-step catalytic system. The two-step catalytic system involved catalytic oxidation, followed by hydrogenolysis. A catalytic system was developed for lignin hydrogenolysis and the influence of the temperature and reaction time was studied for the catalytic oxidation of lignin.

The results presented in this thesis contribute to a better understanding of the various factors influencing the production of bulk aromatic chemicals from lignin, including valuable knowledge regarding catalyst activity and stability, optimal conditions for the valorization of lignin and lignin model compounds, and a process for the extraction of lignin from wood. Hence, it is necessary to further develop catalytic processes to enable the transformation of lignin from a low quality, low-price waste product into a high-quality, high-value feedstock for bulk and specialty chemicals by the development of the appropriate catalytic technology.

This transformation is critical because lignin represents the only viable renewable source to produce the aromatic compounds on which society currently depends.

Abstrakt

Anden generations biomasse består først og fremmest af lignocellulose indeholdende cellulose, hemicellulose og lignin. Lignocellulose er et meget vigtigt og lovende råstof til produktion af vedvarende brændstof og kemikalier i fremtiden. Lignin er den næstmest udbredte naturlige polymer og repræsenterer 30% af vægten samt 40% af energiindholdet i lignocellulose biomasse. Mens der allerede eksisterer et anvendelsesområde for cellulose i form af nutidig papir og papirmasse produktion, såvel som fremtidig hydrolyse og fermentering til bio-brændstof (først og fremmest bio-ethanol), så er der ikke etableret bæredygtige måder hvor på der kan skabes værdi ud af den ligninholdige del af træ, som har lav opløselighed og en kompleks heterogen struktur. Dette gør økonomien af et bio-raffinaderi ufordelagtig, da en total værdiskabelse af lignocellulose biomasse er en nødvendighed for at skabe rentabilitet. Af denne årsag, og grundet lignins potentiale som et værdifuldt råstof i produktionen af organiske kemikalier, er værdiskabelsen af lignin blevet et vigtigt problem at løse.

For at kunne forstå og analysere lignins katalytiske opførsel er det almindeligt at anvende lignin modelblandinger, som indeholder de mest signifikante bindingstyper der er til stede i lignin, og som viser de samme karakteristika som den naturlige biopolymer. En af de mest udbredte strukturelle enhed er β-O-4 typen, som repræsenterer ca. 60% af bindingerne i løvtræ (hårdt træ) og 45-50% af bindingerne i nåletræsved (blødt træ). Oxidativ depolymerisering er en af de mest anvendelige metoder til værdiskabelse af lignin. Det indebærer spaltningen af etherbindinger, som f.eks. β-O-4 og andre koblinger der findes i lignin og lignins modelblandinger, under dannelse af aldehyder eller carboxylsyre som produkter.

Kapitel 2 i denne afhandling omhandler forberedelse, karakterisering og undersøgelse af den katalytiske aktivitet af heterogene katalysatorer i aerob oxidation af β-O-4 lignin modelblandinger med veratrylalkohol og guaiacyl glycerol-β-guaiacyl ether.

I kapitel 3 beskrives anvendelse af en miljøvenlig proces - Organosolv-processen - til behandling af lignocelullose biomasse med et opløsningsmiddel og reaktionstilstande hvorved en del af ligninen separeres fra biomassen. Forskellige katalysatorer og reaktionsbetingelser er blevet undersøgt med henblik på at optimere processen for at kunne fremstille høj-kvalitets lignin til yderligere opgradering.

I slutningen af denne afhandling beskrives i kapitel 4 et to-trins katalytisk proces system, som kan omdanne lignin til højere-værdi kemikalier. Systemet består af katalytisk oxidering fulgt af hydrogenolyse. Der blev udviklet et katalytisk system til hydrogenolysen af lignin og indflydelsen af temperatur og reaktionstid på den katalytiske oxidering af lignin blev undersøgt.

Resultaterne som præsenteres i denne afhandling bidrager til en bedre forståelse af de forskellige faktorer, som har indflydelse på produktionen af aromatiske storskala kemikalier fra lignin. Deriblandt værdifuld viden om katalysatoraktivitet og -stabilitet, optimale betingelser for omsætning af lignin og lignin modelblandinger og en proces til isolering af lignin fra træ.

Det er dog nødvendigt at udvikle den katalytiske teknologi yderligere for at ændre lignin fra at være et spildprodukt af lav kvalitet og pris til at være et værdifuldt højkvalitets råstof anvendeligt til storskala kemikalieproduktion. Denne udvikling er kritisk, fordi lignin udgør den eneste bæredygtige kilde til at producere de aromatiske forbindelser, som vores samfund er afhængigt af på nuværende tidspunkt.

List of Abbreviation

Acac	Acetylacetonate
AFEX	Ammonia Fiber Explosion
ASAM	Alkaline Sulfite Antraquinone Methanol process
BET	Brunauer Emmett Teller surface area
BTX	Benzene, Toluene and Xylene
CF	Carbon fibers
DICP	Dalian Institute of Chemical Physics
DMSO	Dimethyl sulfoxide
EIA	Energy Information Administration
EtOH	Ethanol
EU	European Union
EQ	Environmental Quotient
GC-FID	Gas Chromatography – Flame ionization detector
GC-MS	Gas Chromatography – Mass Spectroscopy
GHG	Greenhouse Gas
GGGE	Guaiacyl glycerol-β-guaiacyl ether
HPLC	High Performance Liquid Chromatography
IEA	International Energy Agency
ILs	Ionic Liquids

IPCC	Intergovernmental Panel on Climate Change
MeOH	Methanol
m/v	mass/volume
NMR	Nuclear Magnetic Resonance
PAN	Poly-Acrylic-Nitrile
ppmv	Parts per million by volume
RPCs	Representative Concentration Pathways
SEC	Size exclusion chromatography
TEM	Transmission electron microscopy
TEMPO	2, 2, 6, 6-tetramethylpiperidine-N-oxyl
TON	Turnover Number
U.S.	United States
VA	Veratryl alcohol
VA-ether	1,2-dimethoxy-4-(methoxymethyl) benzene
VAld	Veratraldehyde
vol. %	volume percent
wt. %	weight percent

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Chapter 1

Introduction

1.1 Current global energy situation.

Unquestionably, the use of fossil fuels has become the engine during the development of society since the Industrial Revolution. Unfortunately, this resource is in serious depletion, and the accompanying environmental hazards make it unfavorable. Therefore, the need for a transition to a carbon-neutral renewable system for the production of bioenergy and biomaterials becomes more apparent [1]. Moreover, the European Union (EU) has outlined a number of targets regarding energy savings and the use of renewable and alternative energy source instead of fossil fuels. In 2020, the EU aims to cut greenhouse gas emissions by 20% (or 30% if the conditions are right), increase the proportion of renewable energy to 20% and boost energy efficiency by a minimum of 20% [2]. In 2050, the EU has also committed itself to reducing greenhouse gases by 80 to 95% in order to create a low-carbon economy, as part of global efforts to combat climate change and air pollution, reduce dependence on foreign fossil fuels and keep energy affordable for companies and consumers [3]. To fulfill these objectives, the EU set out five priorities:

1. Achieving an energy-efficient Europe, so the current relationship between economic growth and increasing energy consumption must be broken.
2. Ensure the free movement of energy to create a more integrated, interconnected and competitive market, applying the current EU legislation and developing a general plan to allow energy to flow from one country to another.
3. Provide secure, safe and affordable energy for citizens and businesses, generating more consumer-friendly policy based on the benefits competition brings.

4. Extending Europe's leadership in energy technology and innovation. Without a major technological shift, the EU will not be able to achieve their ambitions to eliminate fossil fuels for electricity and transport by 2050.
5. Consolidate and secure strong international partnerships. Many of the challenges facing the EU (climate change, access to oil and gas, technology development and energy efficiency) are also important for other countries [2].

However, despite the efforts made by the EU, many countries do not foresee achieving the objectives marked by 2020 let alone 2050. The existing strategy is wholly inadequate to meet the challenges [4].

1.1.1 The natural resource challenge.

The world population is expected to increase from the current total of 7.1 billion to 8.2 billion in 2030, meaning the Earth will have to feed more than a billion more people in fourteen years time. This only exacerbates the challenge currently faced by the developing countries (Figure 1.1).

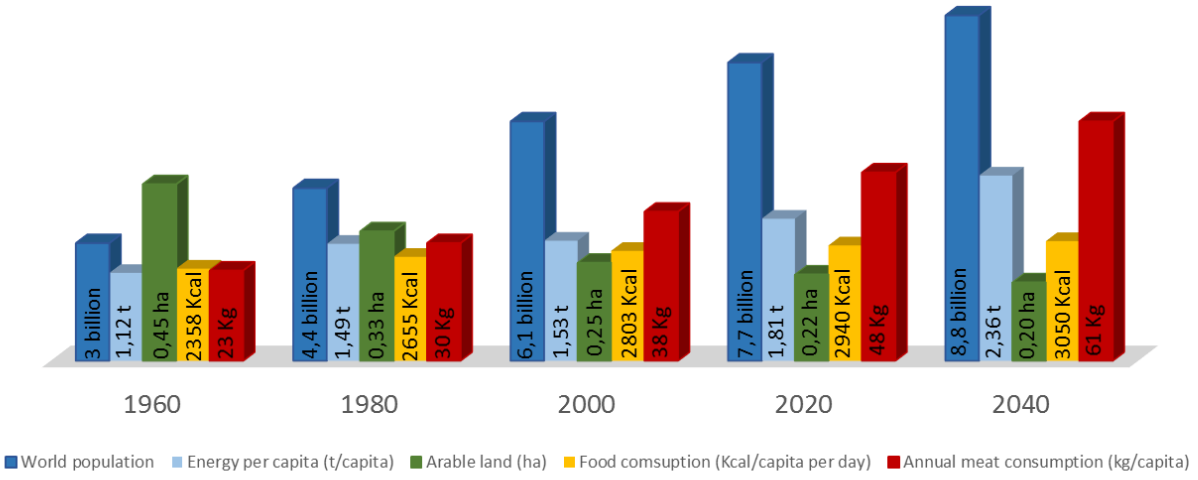


Figure 1.1. Data showing the development and the projection of the global population from 1960 to 2040, and per capita development in energy use, arable land, calorie intake and annual meat consumption [5-7]

The exploitation of valuable natural resources, including oil, gas,metals, minerals and timber, is often noted as a key factor in the development, intensification or continuation of violent conflicts around the world. In addition, there is growing competition for increasingly scarce resources, such as arable land or water. This is further exacerbated by environmental degradation, population growth and climate change [5]. To face these challenges, the chemical industry has created a wide range of materials, medicines, fertilizers and fuel at low cost, relying almost solely on petroleum feedstocks. During the 20th century, oil was a cheap and abundant feedstock, becoming the main product and the great ally of capitalism. Given the finite nature of this resource, it is expected that oil prices will rise as the dwindling supplies struggle to keep pace with increasing demand. This is expected to have a major impact on the chemical industry of the 21st century [4].

An important point to consider is that energy demand is increasing every year (Figure 1.2.). Although there are many resources for electricity production (oil, gas, coal, nuclear, wind, solar, geothermal, hydroelectric etc.), fuels used for transport come mainly from fossil fuels. Energy, as a resource, has therefore two challenges to face; sustainable power generation and production of sustainable fuels for transport.

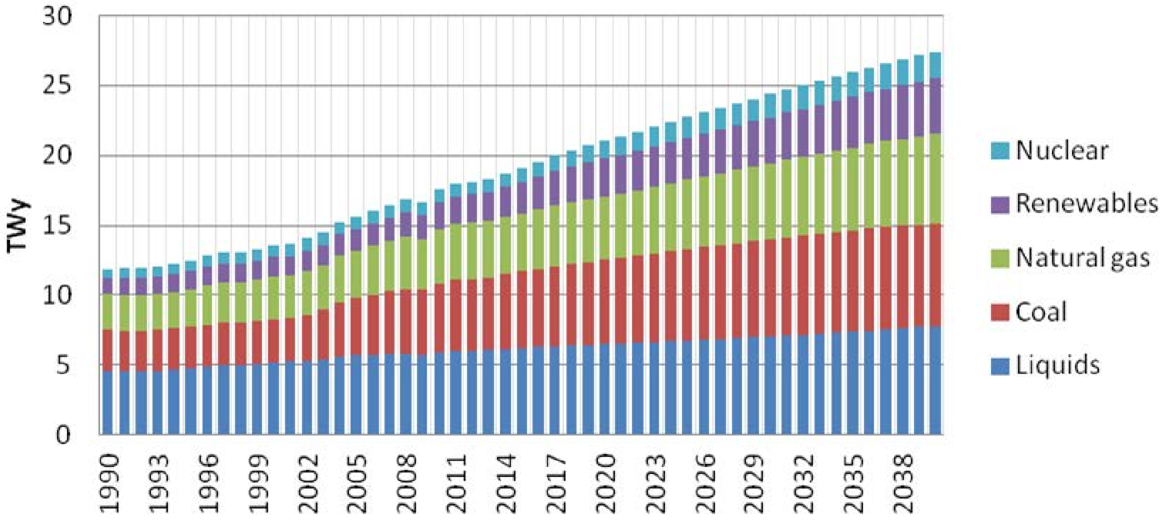


Figure 1.2. World energy consumption by fuel type. Historical data and projection by EIA [8]

Electricity production should be considered separately to the production of transport fuel, which is expected to double in capacity over the period 2000-2030 mainly in Asia and Africa. Currently, it is estimated that the reserves of fossil fuels in the world will last for at least hundred years. In addition, there are now technologies for the production of clean and sustainable electrical energy, such renewable energy (solar, geothermal, wind, etc.) that have registered a gradual increase in recent years. The importance of sustainable energy generation lies in the concern that the vast amounts of carbon dioxide released from coal-generated electricity, will contribute to climate change. Additionally, there is a desire to be less dependent on energy supplies from foreign nations [4].

It is estimated that the transport and industrial sectors will account for 92% of the demand for liquid fuels until 2040, while in other sectors the consumption of liquid fuels will diminish around the world [8]. For this reason, sustainable transport fuel generation is without a doubt the greatest component of the resource challenge, simply because of the sheer amount of fuel needed. It seems that there is no single key to solve this challenge, but rather many different approaches are needed. First generation biofuels, which are produced directly from food crops, such as corn or sugar cane, can perhaps supply 30% of the current fuel demand if fully developed [1]. The increasing use of electric and hybrid cars will reduce fuel consumption. Technologies such as hydrogen and fuel cells will help reduce the demand for liquid fuels. However, these approaches have their own drawbacks. First generation biofuels require large areas of arable land, and will therefore compete with the production of food for a growing world population. To overcome this problem, second generation biofuels are being developed from lignocellulosic biomass or woody crops, agricultural residues or waste, which require less land and are therefore more desirable. One disadvantage of the second generation biofuels, however is that it is relatively difficult to extract the required fuel. Electric and hybrid cars require batteries and/or electricity. Hydrogen production is not simple and requires a lot of energy and heavy security. Currently, most of the hydrogen used in the word is produced from fossil fuels, meaning the green credentials of hydrogen-fueled vehicles are debatable. It seems evident that transport costs will increase in the future as oil reserves dwindle. In order to reduce our dependence on fossil fuels and transform the energy sector into, more research and development of existing technologies is needed, with the chemical industry, playing a key role in this challenge.

1.1.2 The climate challenge.

Global warming is possibly the most dramatic side effect of fossil fuels usage. Fossil fuels are converted into energy through combustion reactions, leading to the emission of greenhouse gases (GHG) such as CO_2, CH_4 and N_2O. In the atmosphere, CO_2 concentrations have increased considerably over the past century. In 2015, the concentration of CO_2 in the atmosphere exceeded 400 ppmv. This represents an increase of more than 120 ppmv since the pre-industrial era. More than half of this increase has occurred since 1980, with an average growth of 2 ppmv / year in the last ten years. Fossil fuel emissions are not limited to CO_2, as levels of other GHG, CH_4 and N_2O have significantly increased in the atmosphere since the mid-20th century. The human influence on the climate is reflected clearly in anthropogenic emissions of GHG, which are now reaching their highest levels in history (Figure 1.3.) [8-9].

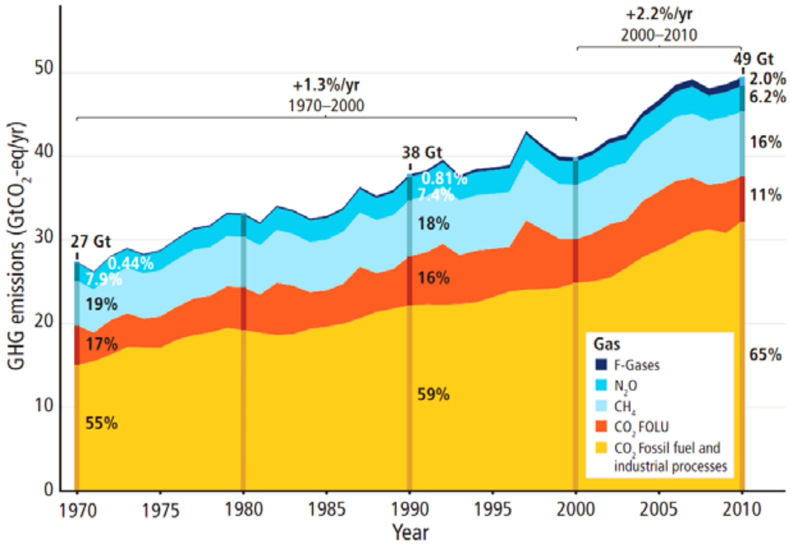


Figure 1.3. Total annual anthropogenic GHG emission by gases 1970-2010. CO_2 from fossil fuel combustion and industrial processes; CO_2 from Forestry and Other Land Use (FOLU); methane (CH_4); nitrous oxide (N_2O); fluorinated gases covered under the Kyoto Protocol (F-gases) [9].

Cumulative emissions of CO_2 largely determine mean global surface warming by the late 21st century and beyond. Projections of greenhouse gas emissions vary over a wide range, depending on both socio-economic development and climate policy (Figure 1.4). Most aspects that influence climate change will last for many centuries, even though the current anthropogenic CO_2

emissions will stop. It is inevitable that the climate will continue to change for centuries, due to past, present and future CO_2 emissions [9].

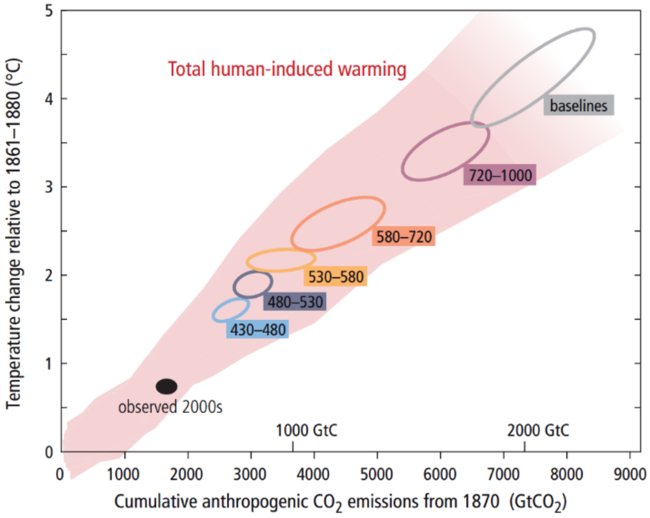


Figure 1.4. Warming versus cumulative CO2 emissions. Colored plume shows the spread of past and future projections from a hierarchy of climate carbon cycle models driven by historical emissions and the four Representative Concentration Pathways (RCPs) over all times out to 2100, and fades with the decreasing number of available models [9].

Two sectors produced nearly two-thirds of global CO_2 emissions in 2013: electricity and heat generation, by far the largest, which accounted for 42%, while transport accounted for 23% (Figure 1.5) [10]. 72% of the energy production came from coal-fired power plants, with the largest emissions coming from China – contributing 30%, followed by the U.S at 19% [11].

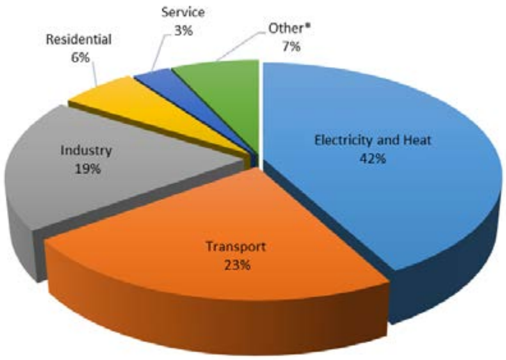


Figure 1.5. World CO2 emissions by sectors in 2013 [10]. * *Others include agriculture/forestry, fishing energy industries other than electricity and heat generation, and other emissions not specified elsewhere*

By adopting stronger climate change policies, governments could slow down or change the course of these emission trends, and ultimately stabilize the level of greenhouse gases in the atmosphere. Mitigation efforts over the next two to three decades will largely determine the long-term increase in mean global temperature and the corresponding impact on climate change that can be avoided. Policies on climate change can be properly constructed as an integral part of sustainable development, and the conclusions of the IPCC's report on climate change confirmed that a change towards sustainable development can reduce greenhouse gas emissions and prevent further climate change [9].

1.2 Green and sustainable chemistry.

Green and sustainable chemistry is in very simple terms a different way of thinking about how chemistry and chemical engineering can be done.

Green chemistry involves the creation, design and development of products and processes that reduce or eliminate the use and generation of substances hazardous to human health and the environment [12]. As well on focusing on protecting the environment and preventing pollution, green chemistry research also investigates ways to increase efficiency and reduce production costs of existing processes [13].

The concept of sustainable development, first introduced in the Brundtland report in 1987, is defined as *development that meet the needs of the present generation without compromising the ability of future generations to meet their own needs* [14].

These two concepts, green chemistry and sustainable development have been the focus over the last decade, of both industry and academia. In fact, the two concepts go hand in hand; sustainability is the ultimate goal and green chemistry tells us how to get there [12].

1.2.1 Atom economy and E-factor.

The quantification of how green or how environmentally friendly a chemical reaction or product is, can be very difficult. However, to get an estimate, two useful measures of the environmental impact of chemical processes are accepted: the E factor and the atom efficiency.

Atom efficiency is a useful tool for evaluating the amount of waste that will be generated by a chemical process. It is calculated by dividing the mass ratio of the desired product by the sum of the mass ratio of all the reactants in the stoichiometric equation of the reaction involved (equation 1.1) [16].

$$atom\ economy = \frac{M_{product}}{\sum M_{reactants}} \tag{1.1}$$

In 1992, Sheldon introduced another tool, the E-factor, which evaluates the environmental impact of a particular reaction based on the amount of waste generated, defined as everything but the desired product. It takes the chemical yield into account and includes reagents, solvent losses, all process aids and, in principle, even fuel. There is one exception: water is generally excluded from the calculation of the E factor. A higher E factor means more waste and, consequently, a greater negative environmental impact. The ideal E factor is zero. [15]. Table 1.1 compares typical E factors in different sectors of the chemical industry.

$$e - factor = \frac{total\ waste\ generated\ in\ kg}{total\ product\ in\ kg} \tag{1.2}$$

Table 1.1. E- Factors and typical production in the chemical industry [16].

Industry segment	Annual tonnage	E-factor
Petrochemicals	10^6 -10^8	< 0.1
Bulk Chemicals	10^4 -10^6	1 – 5
Fine Chemicals	10^2 -10^4	5 – 50
Pharmaceuticals	10 -10^3	25 - 100

In order not only to evaluate the environmental impact of waste by its amount, but also by its nature, Sheldon introduced the Environmental Quotient (EQ). The EQ can be obtained by multiplying the E factor with an arbitrarily assigned unfriendliness quotient (Q) based on an assessment of how harmful a particular type of waste is. The value of Q is debatable and difficult to quantify, but in principle, it is possible to make a quantitative assessment of the environmental impact of a chemical process using this method [17].

1.2.2 Catalysis: the pillar of green and sustainable chemistry

One of the fundamental pillars of green and sustainable chemistry is catalysis. The design and application of new catalysts and catalytic systems achieves simultaneously the two goals of green and sustainable chemistry; environmental protection (achieving through greater atom efficiency and lower energy usage), and economic profit [18].

In this thesis, heterogeneous catalytic systems have been used to the lignin biomass conversion into chemicals and fuels, following the green and sustainable chemistry principles.

By definition, catalysis increases the rate of a reaction by the participation of an additional substance that does not go through any permanent change in the process; the catalyst. The catalyst increases the reaction rate by offering an alternative pathway that proceeds through a lower energy transition state, and requires a lower activation energy (E_a). Figure 1.6. shows how the activation energy (E_a) for a hypothetical exothermic reaction X + Y to give Z decreases when the reaction occurs in presence of a catalyst. [19-22].

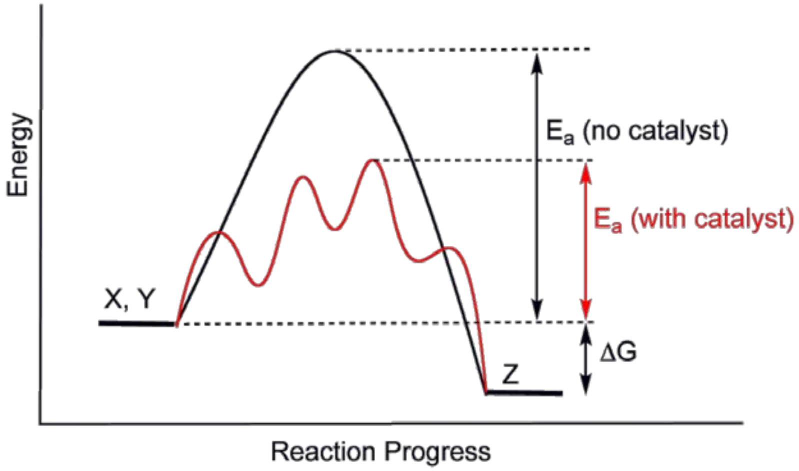


Figure 1.6. The energy diagram for a generic exothermic reaction X+Y to give Z [21].

In order for a catalyst to be suitable for a chemical process, it is necessary for it to possess three main properties:

- **Activity**. The activity measures how fast one or various reaction proceed in the presence of a catalyst [20].
- **Selectivity**. The selectivity gives the fraction of the starting material that is converted into the desired product [20].
- **Stability**. The thermal, chemical and in case of heterogeneous catalysts, mechanical stability of a catalyst determines its lifetime in an industrial reactor. The catalyst stability is determined by many different factors, such decomposition, and poisoning. The deactivation of a catalyst can be followed by activity and selectivity measurements as function of time. This property is of crucial important in chemical industry because it determines the catalyst lifetime and, hence the economics of a process [20].

Catalysts are divided into three main groups: homogeneous catalysts, heterogeneous catalysts and biocatalyst [19].

Biocatalysis.

Biocatalysis is the term used for catalysis taking place in living systems or using catalysts found in living systems (enzymes). In bio-catalytic processes, protein enzymes or other biological catalysts perform chemical transformations on organic and/or inorganic compounds. Both enzymes that have been isolated and enzymes still residing inside living cells are employed for this task [19].

Homogeneous catalysis.

In homogeneous catalysis, the catalyst is in the same phase as the reactants. Homogeneous catalysts are regularly used in the pharmaceutical industry and are often employed to carry out relatively complex transformations in comparison to heterogeneous catalysis.

Homogeneous catalysts are difficult to separate from the products, as both, catalyst and products are in the same phase [19-20].

Heterogeneous catalysis

In heterogeneous catalysis, the reactant and the catalyst are in different phases. The catalyst is usually a solid material while the reactants are in gas or liquid phase [22]. Heterogeneous catalysis have a vital importance advantage, separation. Heterogeneous catalysts are either automatically removed in the process (usually in fixed – or fluidized bed reactor in gas phase), or they can be separated by sedimentation, centrifugation or filtration (usually in liquid phase in batch reactors).

Heterogeneous catalysts are used not only in the production of commodity chemicals, materials, and fuels, but also in energy conversion and in food production, being applied in numerous industrial process in chemical, pharmaceutical, food, automotive and petrochemical industries. The continued research in heterogeneous catalysis is a requirement for accosting environmental and energy issues that as have being seen is facing our industrializing society (*Chapter 1* - 1.1 Current situation) [22].

1.3 Biomass.

Biomass is the most abundant carboneous renewable resource available and is viewed as an alternative feedstock to fossil fuels [23]. Biomass can be defined as any biological material derived from living organisms. In the context of biomass for energy, biomass often refers to plant derived material, but the meaning itself is equally applicable to resources coming from both animals and plants [24].

Vegetable biomass, mainly composed of carbohydrates, is generated by carbon dioxide (CO_2) and water (H_2O) using solar energy source and producing oxygen (O_2) as a byproduct photosynthesis [23]. In this process, CO_2 is removed from the atmosphere, converted into organic carbon, and stored in woody biomass. Trees release the stored carbon as CO_2 to the atmosphere, when they die, decay or burn. When this occurs, the carbon cycle is completed (Figure 1.7). So long as biomass is sustainably managed and replenished with new growth, its use results in no net increase in atmospheric CO_2 levels, and is therefore carbon neutral [25].

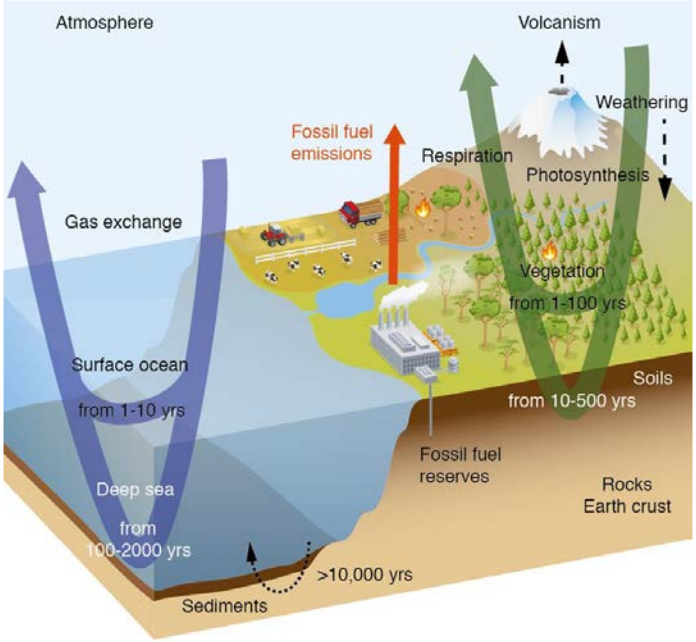


Figure 1.7. Simplified diagram of the carbon cycle showing the typical time scales of renewal for the transfer of carbon through the main reservoirs [9].

As mentioned previously, fossil resources are unable to meet the growing demand for energy and commodity chemicals. Because of this, new markets are being establish to meet these demands, using clean and green technologies, and renewable raw materials, such as biomass [25]. Biomass is the only renewable energy source that can provide fuel in a gaseous, liquid or solid state. It can be used to generate electricity, as fuel for transport or as heat, mainly for high-temperature industrial applications. Bioenergy is easy to store when demand is low, and conveniently transformable when the energy is required. Depending on the process, bioenergy can be used in the production of electricity, as can other forms of renewable energy, as wind energy. However, due to the possibility of storage, generation of heat from biomass plays an important role, because it is able to meet seasonal demand, as is commonly observed in the Nordic countries [26].

1.3.1 Biorefineries.

Biorefineries are named by analogy with conventional refineries, which aim to maximize the utilization of the raw material producing a wide range of fuels and chemicals [27]. According to the International Energy Agency (EIA), "*a biorefinery is the sustainable processing of biomass into a spectrum of marketable products ranging from energy, food, feed, chemicals and material applications*" [10].

Biomass conversion is currently performed in separate facilities in which all the economic potential has not been exploited. However, future biomass applications will be based on a single integrated facility called a biorefinery where all fractions and by-products of biomass will be used to produce a variety of products including energy, either as heat or electricity , biofuels, biomaterials and chemical substances [1, 25-30]. Thereby, the profitability of biomass will increase and more flexibility will be achieved making it possible to withstand market fluctuations and changes in consumer needs. In addition, the integrated biorefinery concept is associated with complex biochemical and thermochemical conversion methods, from which a wide range of products can be obtained. These conversion processes have improved energy efficiency, increasing the sustainability of global processes [31].

The selection of a specific type of biomass, such as lignocellulosic biomass, available as feedstock for the production of energy and other products (biofuels, biopolymers, and chemical molecules) will be determined by the characteristics of the region (for example the climate and topography of the land) and the activities which occur: including agricultural and industrial land usage. The products desired determine the type of biomass and process required in a biorefinery [27-34].

Borregaard in Norway operates an example of an industrial biorefinery. This biorefinery uses wood as raw material. Wood fibers are converted into advanced grades of specialty cellulose for products used in the construction and oil industries, and for the production of foodstuffs, tablets, cosmetics, filters, hygiene products, and paints. Additionally, part of the dissolved lignin is converted by catalytic oxidation into vanillin, and the sugar extracted is fermented to make bioethanol, as a second generation biofuel. (Figure 1.8) [35].

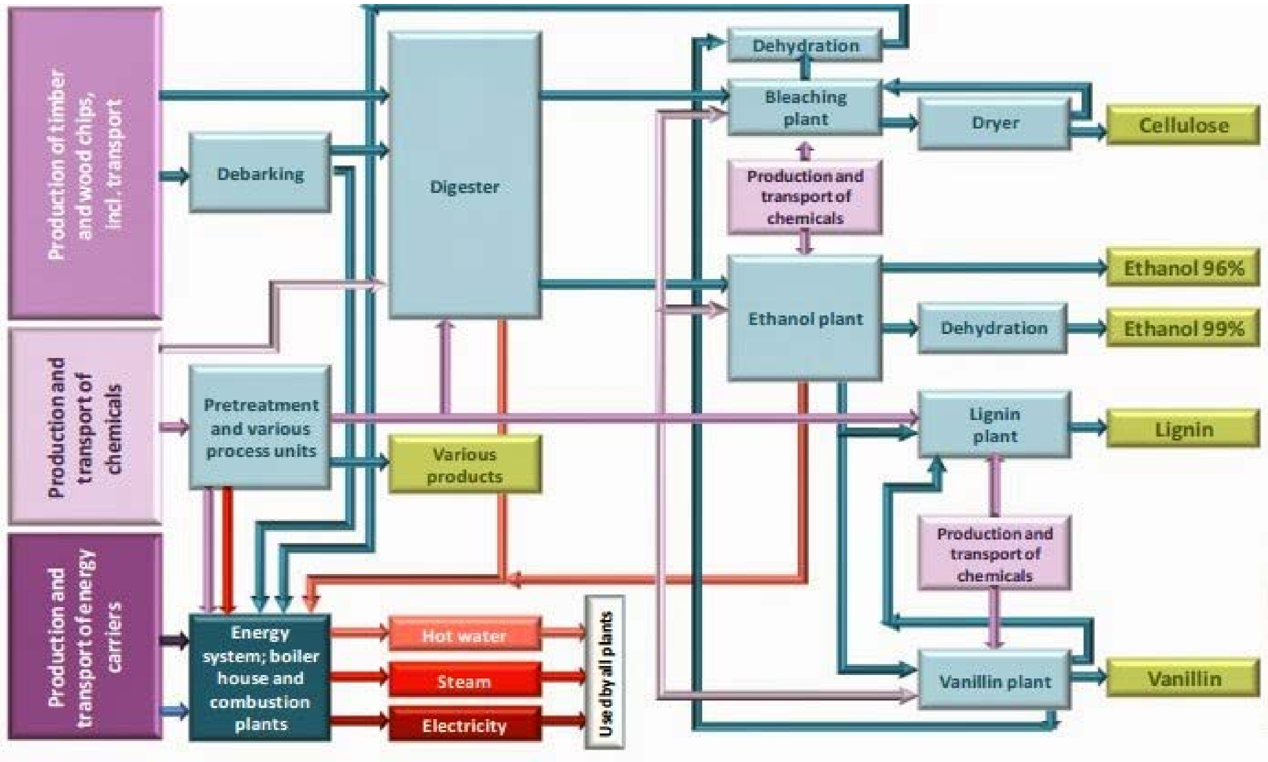


Figure 1.8. Schematic overview over the flows of raw material and energy through the different processing steps towards the end products for Borregaard Sarpsborg Biorefinery [35].

Various technologies are under development for lignocellulosic biorefineries, in which the lignin fraction is only consider as an energy source. However, there has been an increase in biorefinery technologies, which make use of the possibility of separating the biomass into carbon-rich and lignin-rich fractions. Borregaard biorefinery provides a good example of this. They used lignin mainly for the production of synthetic -vanillin, which is a well know flavorant and is also find use in medical applications or as a platform chemical for pharmaceutical production [35]. However, the vanillin market is not big enough to warrant the complete integration of lignin into the bio-based economy of a biorefinery. A better understanding of the ways in which lignin can be converted to bulk chemicals and fuels is clearly desirable, as a better use of this fraction could significantly boost the carbon economy, as well as improve the profitability of any biorefinery.

1.3.2 Lignocellulosic biomass.

The biomass-based chemicals and fuels generally are produced by sugar and starch containing crops such as beet, corn and grain, the so-called first-generation biomass. These crops are also used for food and animal feed, resulting in an undesirable competition between food and fuels. To counter rising food prices and food shortages in the world's developing countries, it is therefore important to develop the use of the so-called second-generation biomass, in which waste products are used as raw material instead. Second-generation biofuels and chemicals are usually made from lignocellulosic biomass [36-38].

Lignocellulosic biomass consists of plant tissues composed of cells with cell walls formed from cellulose microfibrils frameworks. Hemicellulose and lignin polymers are interlinked with microfibrils structures [29]. The structure of the cell wall gives strength to the plant and protects the plant against pathogens. The complexity of this structure makes it difficult to extract the potential lignocellulosic biomass compounds, meaning pretreatment and fractionation procedures are required to access them. However none of them is able to completely isolate each component without modifying or degrading them.

Lignocellulosic biomass can be divided into three organic components with the following representative fractions by dry weight: cellulose (40-50 wt. %), hemicellulose (25-35 wt. %) and lignin (20-30 wt. %) (Figure 1.9). A number of other minor components are also found:

proteins (3-10 wt. %), lipids (1.5 wt. %), soluble sugars and mineral called extractive (10.5 wt. %). These are often referred to as “ash” [37-40].

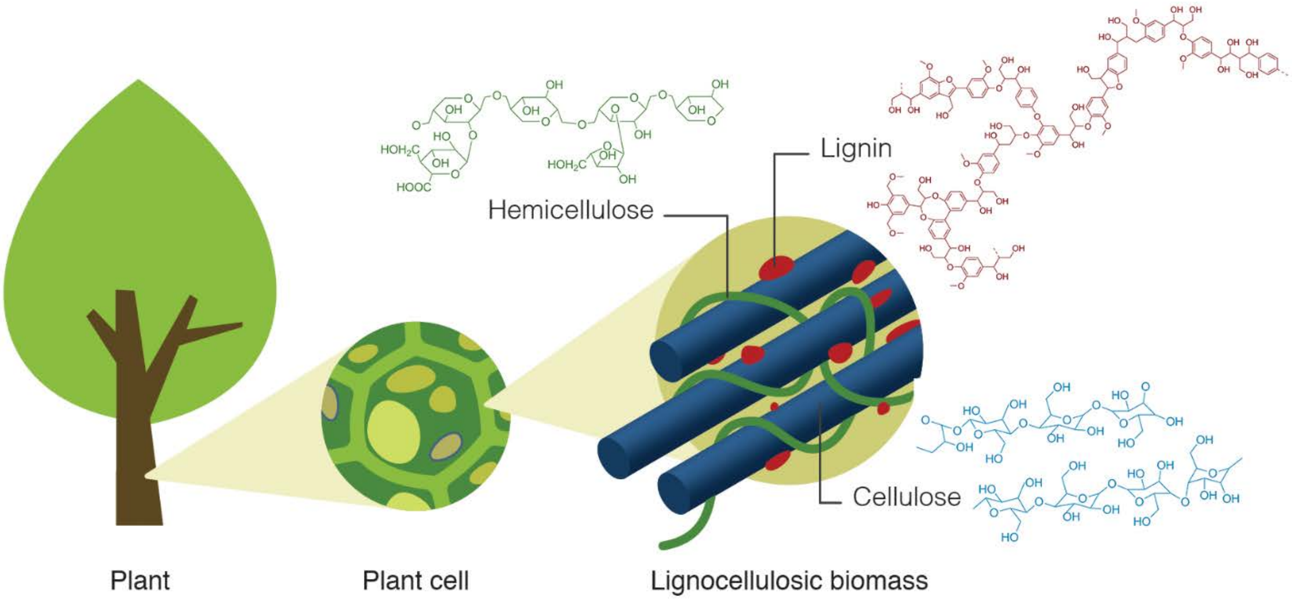


Figure 1.9. Representation of lignocellulosic biomass and of its main fractions. [41-43].

Cellulose and hemicellulose valorization has been widely examined, and many different studies have during the last year focused on obtaining biofuels and high value chemicals from these fractions. In fact, monomeric sugars can be used for commercial production of second-generation biofuels such as bioethanol or bio-propylene, by fermentation. Sugars can also be converted to other molecules (e.g. succinic acid, ethylene glycol or propylene glycol) using fermentation or conventional chemical conversion technologies. Nevertheless, a commercial process for lignin valorization is yet to be developed and lignin conversion technology lags far behind the other two fractions [23-25, 44].

1.4 Lignin.

The term lignin was introduced in 1819 by de Candolle and originates from the Latin word *lignum*, meaning wood [45]. Lignin, alongside cellulose and hemicellulose, is one of the major constituents of the cell walls of all higher vascular land plants. It is a three-dimensional biopolymer which is found together with hemicellulose and cellulose filling the spaces between them and acting as a resin which holds the lignocellulosic matrix together, protects the cell wall from microbial attacks, and provides shear and compressive strength to the plant tissues (Figure 2.0) [36-38, 45-44].

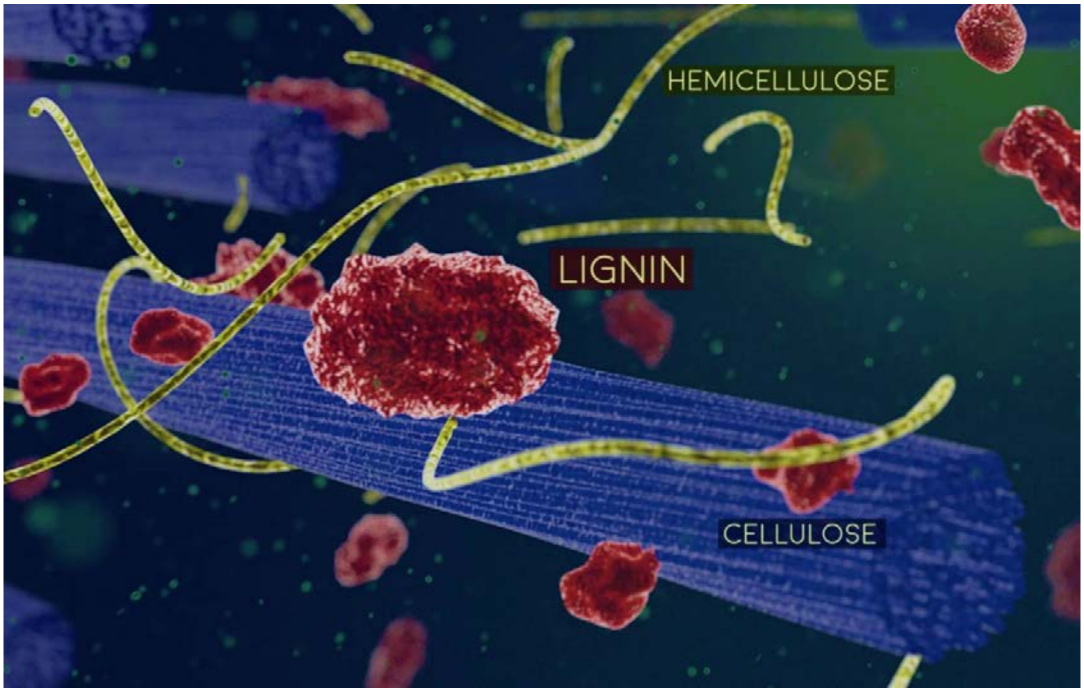


Figure 2.0. Artistic representation of lignocellulosic biomass with cellulose fibers (blue), lignin (red) and hemicellulose (light green) [41-43].

The amount of lignin found in a plant depends on the species, and can vary between 15 to 40% by weight. In herbs, lignin content is less than 15% by weight. In wood stems the portion of lignin is from 24% to 33% in normal softwood (gymnosperm trees), and from 19 to 28% in normal temperature zone hardwood (angiosperm trees) [46-45].

Lignin is a natural biopolymer, but unlike other polymers and despite many research efforts, its chemistry, biosynthesis and molecular biology has not been completely elucidated. It is currently accepted that the biosynthesis of lignin is the result of the random polymerization via oxidative phenolic coupling of three basic monolignol units: p-coumaryl, coniferyl and sinapyl alcohol (Figure 2.1).

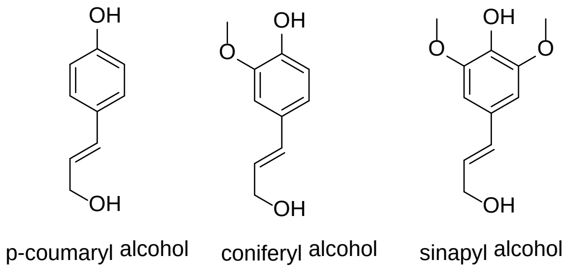


Figure 2.1. The three monolignol monomers, the building blocks of lignin.

The composition of lignin polymers varies not only between species but also between tissues of an individual plant. Both the proportion of monolignol monomers and linkages between them vary. Softwood lignin is almost exclusively derived from the polymerization of coniferyl alcohol (over 95%) and the rest is mainly coumaryl alcohol, while in hardwood lignin the predominant building unit is sinapyl alcohol (from 45 to 75 %), followed by coniferyl alcohol (from 25 to 50%), with coumaryl alcohol almost inexistent (from 0 to 8 %) [38, 46, 47].

The monolignol monomers, are linked randomly through carbon – carbon and carbon – oxygen bonds. The main interunit linkages are illustrated in Figure 2.2, and their abundance in spruce (softwood), and beech and birch (hardwood) are listed in Table 1.2. In general, β-O-4 and α-O-4 ether bonds are the most abundant in lignin, making up about 70% of the linkages found in native lignin. Hence, the cleavage of β-O-4 linkages, represent the most promising strategy for depolymerization of lignin into simpler substructures [37-39]. Figure 2.3 shows a schematic representation of softwood and hardwood lignin fragments with their common linkages. These structures are pictorial and do not imply any particular sequence [38].

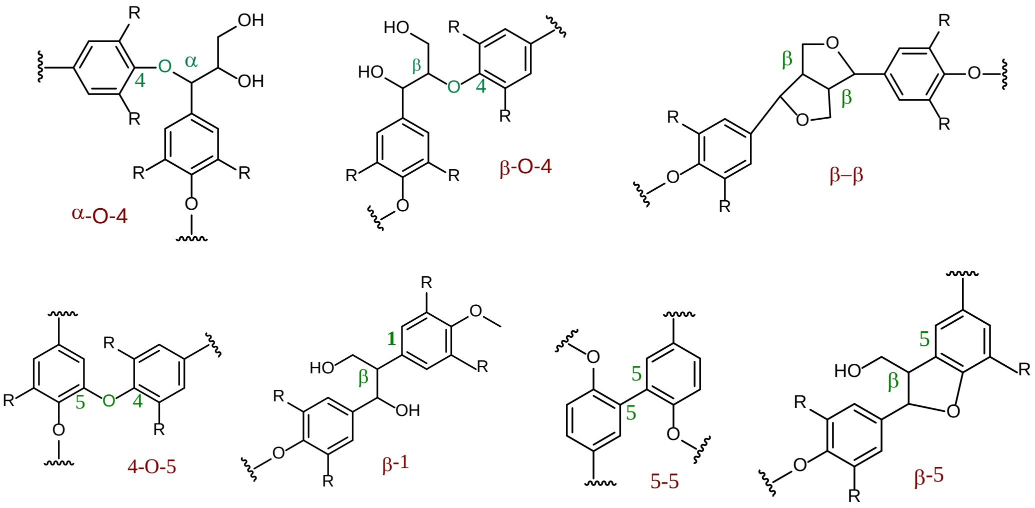


Figure 2.2. Schematic representation of the common linkages in native lignin.

Table 1.2. Abundance of linkages from native lignin [27, 38, 47].

Linkage	Abundance (%)		
	Softwood	Hardwood	
	Spruce wood	Birch wood	Beech wood
α-O-4	11 -16	6-8	28-32
β-O-4	39 – 50	60	32 - 37
4-O-5	4 – 7	6.5	2
5-5	9 – 11	4.5	2
β-1	2	7	16
β-5	6 – 12	6	8
β–β	2 – 4	3	6.4

Lignin also contains a significant range of chemical functional groups, such as hydroxyl (aromatic and aliphatic), methoxy, carbonyl, and carboxyl. These functional groups affect the properties of the lignin molecule, especially its solubility. Lignin is quite soluble in alkaline solutions due to the ionization of hydroxyl and carboxyl functional groups [46, 49].

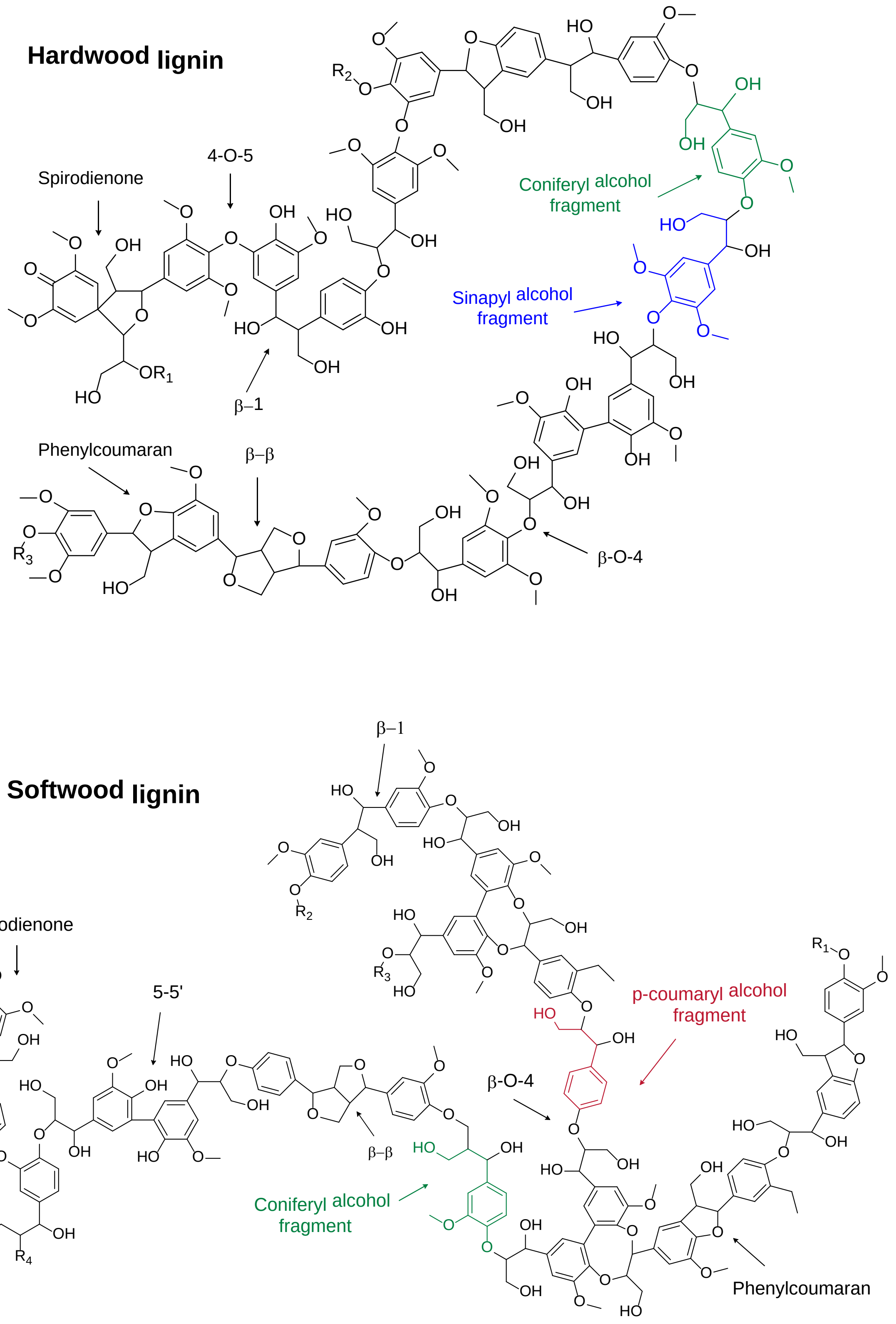


Figure 2.3. Schematic representation of hardwood lignin (top) and softwood lignin (bottom) [38].

1.4.1 Lignin dissolution and pretreatment.

Lignin properties strongly depend on the pretreatment process of lignocellulosic biomass, by which, lignin is isolated from cellulose and hemicellulose. Due to the strength and complexity of cellulose, hemicellulose and lignin, the solubilization of lignocellulosic biomass as a whole remains a challenge. Indeed, it has been admitted that the insolubility of wood in common solvents has severely inhibited efforts to valorize wood and its components [50].

The pretreatment of lignin is an important initial step in any biorefinery operation [51]. In the pretreatment process, the principal components of lignocellulosic biomass and related materials are separated, the extended polymer degrades to small compounds, which occasionally react further, for example, resulting in sulfur incorporation. The isolation method employed determines the structure of lignin polymers produced. Methods producing consistent types of lignin of high quality and purity and high cellulose yields are highly desirable isolation methods. These pretreatment or isolation technologies have been divided into four categories: physical pretreatments (ball milling, etc.), solvent fraction (organosolv process, the use of ionic liquids, etc.), chemical pretreatment (acidic, alkaline, etc.), and biological treatment (using predominantly fungi) [52]. Nowadays, the dominant fractionation process of lignocellulose is Kraft pulping, which corresponds to about 85% of the lignin produced in the world [53]. However, it is important that lignin pretreatment in biorefinery is targeted at separating all fractions of lignocellulosic material, obtaining a pure feedstock, such occurs in the organosolv process method. Lignin pretreatments methods use different conditions (temperature, pressure, solvent, pH range, etc.) and degradation techniques which can alter the chemical structure of the isolated lignin polymers produced. Hence, each pretreatment method has both advantages and disadvantages that will be discussed below. The choice of lignin pretreatment method determines the type of high-value products obtained after lignin degradation, and it is an important fact for the integration of lignin in biorefinery operation [50-53].

1.4.1.1 Steam explosion.

The steam-explosion process is a rapid treatment for lignocellulose biomass that involves the impregnation of wood or bagasse with high-pressure steam (13 – 34 bar, 180 – 230 ^{o}C) for short contact times (1-20 min), followed by a rapid pressure release [54-55]. The process is auto-catalyzed by the organic acid that is liberated from hemicellulose. During the explosion, the lignocellulosic biomass components are separated by acid-catalyzed hydrolysis or heterolytic cleavage. After the explosion, lignin can be extracted into alkali (diluted NaOH solution) or organic solvents [21]. The resulting steam explosed lignin contains a low content of carbohydrates and impurities originating from wood. It resembles the native lignin more than other treated lignin materials, as the chemical structural changes are rather limited under the process conditions applied. The main drawbacks of the process are the low pulp yield and high cost. As a result, this technique is still not commercialized [54].

1.4.1.2 Lignosulfonates.

Lignosulfonate is generated during sulfite pretreatment, which is a relative common process in the pulp and paper industry. In sulfite pulping, the wood is cooked in aqueous sulfite solution (HSO_3^- or SO_3^{2-}) at 125 - 150 ^{o}C for 3 – 7 h [21, 56]. The process is usually performed under acidic conditions, although it can be carried out in basic solutions using sodium or ammonia sulfite. The β-O-4 linkages are stable when the process is carried out in acid media, but they are prone to undergo cleavage in basic media. However, stable C-C bonds are formed, when aldol condensation takes place in the sulfite pulping [21].

Lignosulfonates are water-soluble from pH 2 to 12, making this type of lignin different from others. In addition, lignosulfonate lignin exhibit a higher average molecular weight and higher monomer molecular weight that other lignin, materials such as Kraft lignin, due to the incorporation of sulfonate groups in the structure. An example of the lignosulfonate structure can be seen in Figure 2.4. [21, 57].

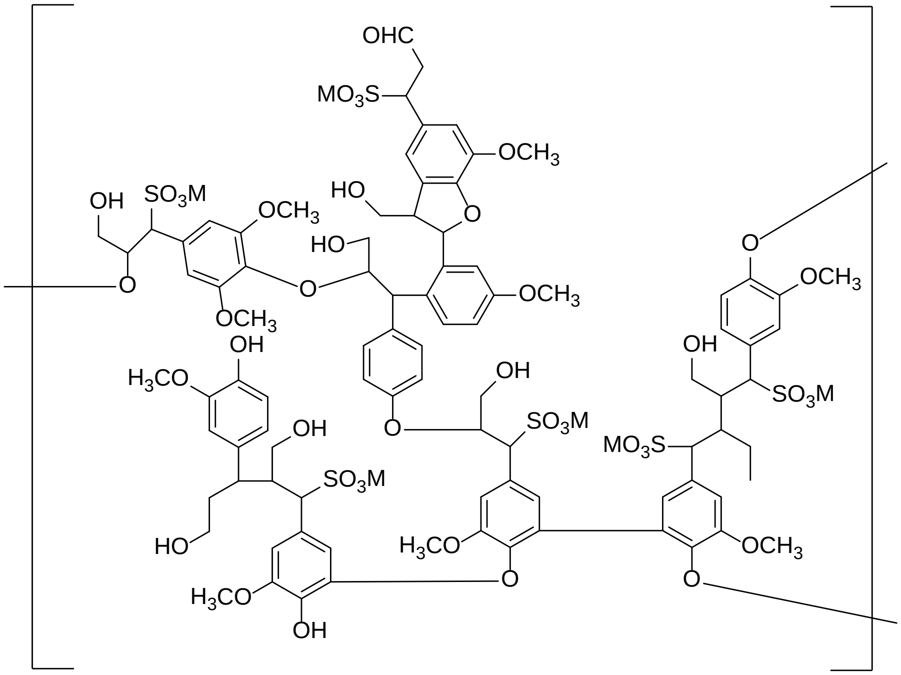


Figure 2.4. Model structure for lignosulfonate lignin [54].

The disadvantage of this type of lignin is associated with its high molar mass and high sulfur content. Sulfite lignin contains up to 8% sulfur, and is unsuitable for catalytic valorization. Moreover, it can be considered an impure material, in which 25-30 wt. % is carbohydrate, ash and other impurities. Due to their amphiphilic behavior lignosulfonates can be used in the production of binders, surfactants, lubricants and emulsifiers [21, 54].

1.4.1.3 Kraft lignin.

Kraft pulping is the most common pulping technique employed in the pulping industry. The wood is cooked at high pH, and considerable amounts of aqueous sodium hydroxide and sodium sulfide [54]. The Kraft pulping process can be divided into three phases, initial, bulk and final or residual phases. In the initial phase, the delignification takes place at temperatures of about 150 ^{0}C, and it is controlled by diffusion. The bulk phase includes a period of heating from about 150 – 170 ^{0}C, and the cooking treatment at 170 ^{0}C. The rate of delignification in this phase is controlled by chemical reaction; the majority of the lignin is removed in this phase. The residual or final phase marks the end of the heating process. The selectivity in this phase is poor and further pulping should result in significant degradation of carbohydrates [58]. This treatment results in lignin depolymerization and release as soluble fragments, allowing the cellulose fibers to be recovered. Lignin precipitates on lowering pH of the obtained “black liquor” [21].

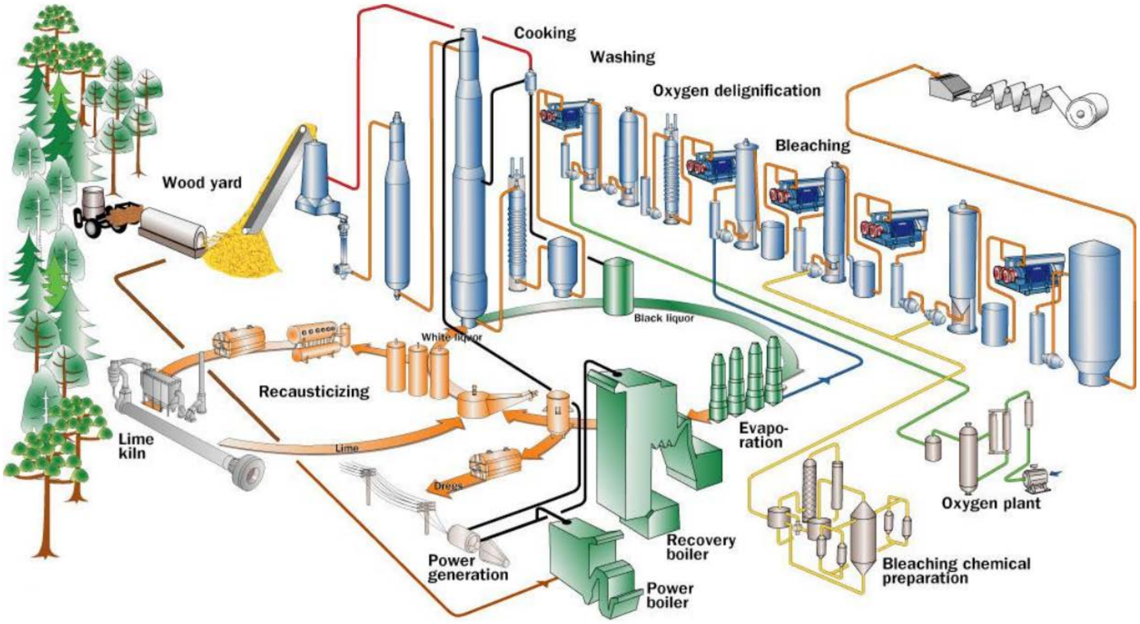


Figure 2.5. Overview of a kraft process – Innventia (Sweden) [59].

The β-O-4 linkages breaks during this process. The phenolic groups, leading to the addition of HS^- onto α-carbon, are converted into quinone methide groups. The benzylthiolate anion formed undergoes a rearrangement forming an epilsulfide. This epilsulfide can lose a sulfur atom and generate a double bond, which can form a C-C bond through several types of reaction [21].

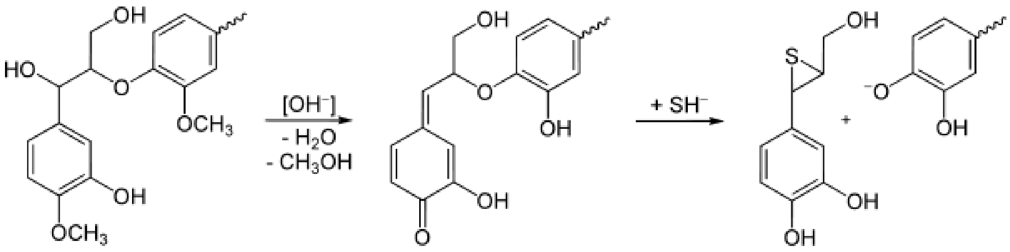


Figure 2.6. Cleavage of β-O-4 linkages in Kraft lignin [21].

Kraft lignin is readily available and low in price, but it is not an ideal feedstock for lignin valorization. During the pulping process, sulfur is introduced into the structure making up around 1-2 wt. % of the lignin produced. This sulfur may poison the catalyst used in the upgrading process. Furthermore, the presence of C-C linkages formed during pulping makes it difficult to depolymerize this kind of lignin into monomers. For that reason, a sulfur tolerant and a highly C-C bond cleavage-active system for upgrade kraft lignin is required.

1.4.1.4 Soda pulping process.

The soda process is employed for pulp production from annual crops, such as flax, bagasse and straws [56]. This process, unlike the Kraft process, is sulfur-free, and the reactant, NaOH, is exclusively active towards the cleavage of α-O-4 bonds. The efficiency of the process can be improved by the addition of an anthrahydroquinone catalyst, producing H_2O_2 in situ. The great disadvantage of this process is that it is limited to annual plants, and the products contained significant amount of colloidal silica, that can destroy some catalysts [21, 38, 56].

1.4.1.5 Organosolv process.

The organosolv process is based on the treatment of wood of bagasse with various organic solvents, such as methanol or ethanol, at temperatures ranging from 180 – 200 ^{o}C [21, 38]. The organosolv process accomplishes the production of high-quality cellulose and water-insoluble lignin [21, 38]. The major organosolv processes are the following:

- Lignol process, ethanol/water pulping process [60].
- ASAM, Alkaline Sulfite Anthraquinone Methanol pulping [61].
- Organocell, methanol pulping followed by anthraquinone/NaOH pulping [62].
- Acetosolv, an acetic acid /HCl pulping [63].
- Milox, formic acid/hydrogen peroxide delignification [64].
- Avidel, formic/acetic acid pulping [65].

These processes have been demonstrated on a pilot scale, but they are not commercial yet. The most successful process is the Lignol Process, based on the Alcell Process, in which wood is extracted with a mixture of ethanol and water. The lignocellulosic biomass is boiled in a mixture of ethanol/water (1:1, v/v) at 200 ^{o}C and autogenous pressure of about 35 bar [66]. The Alcell process is no longer operational, but it is the most well-known organosolv process, involving dissolutions of lignin in either ethanol or ethanol/water mixtures. Lignol Energy Corporation modified the pretreatment developed in the Repap Alcell pilot plant and started with an organosolv pilot plant to produce high purity and potential high value lignin [60]. The French company CIMV has developed a biorefinery based on the organosolv process where the cellulose, hemicellulose and lignin are obtained separately and can be used in various products [67].

The principal advantage of the organosolv process is that separate streams of cellulose, hemicellulose and lignin are formed, allowing the valorization of all the main lignocellulosic components. The process is considered environmentally friendly, because it does not require harsh conditions or sulfides, as in lignosulfonate or Kraft lignin. Therefore, lignin obtained from the organosolv process has a very low sulfur content and higher purity than other technical lignin materials produced from other pretreatment methods. The principal disadvantage of the organosolv process is the high cost of solvent recovery. Organosolv lignin is highly soluble in organic solvents [21, 60-67]

In this thesis, an organosolv process has been developed for producing high quality lignin from hardwood (birch and beech) and will be described in *Chapter 3*. The high purity organosolv lignin obtained from ethanol/water fractions of beech hardwood was studied for the production of aromatic chemicals, as will be described in *Chapter 4*.

1.4.1.6 Other lignin types

Several other methods for pretreatment and isolation of lignin are available. The ammonia fiber explosion process (AFEX) has been applied to lignocellulosic pretreatment. Biomass is treated with liquid anhydrous ammonia at moderate temperatures, of around 60-100 ^{0}C and high pressure (17- 20 bar) over a 5 min period. The AFEX process cannot offer a well-defined lignin stream [54, 68]. The diluted acid process involves the hydrolysis of cellulose using diluted sulfuric acid as a catalyst, but suffer low yields and also corrosion of equipment in the acidic environment [54].

Recently, the use of ionic liquids (ILs) for wood depolymerization has achieved great interest. The current high price of the solvents used, however, make the ILs based process unattractive for operation on an industrial scale [69-71].

1.4.2 Potential applications for lignin.

Lignin is a versatile feedstock that can be used in many different applications, such as a green alternative to many petroleum-derived substances, including fuels, resins, rubber additives, thermoplastics blends, food and pharmaceutical products. It is also known to be one of the few possible renewable source for the production of simple aromatic chemicals, such as benzene, toluene and xylene (BTX) [72-77].

The lignin structure, properties and purity depends on the delignification process. The delignification processes is discussed in *Chapter 3*.

The main applications of lignin can be classified into three groups (Table 1.3):

Table 1.3. Main applications for lignin [76].

Group	Volume	Value	Application example
Power – fuel –syngas	High	Low	Energy production
Macromolecules	Medium	Medium	Adhesives, carbon fibers polymers
Aromatics	Low	High	Aromatics, Vanillin, Phenol, BTX

The challenge resides in the diversity and complexity of the lignin material. The production of high value chemicals such as aromatics and carbon fibers are seen as the most rewarding and challenging goal in lignin valorization [74 -77]

1.4.2.1 Lignin for macromolecules.

In 2014, lignin was mostly used for manufacturing macromolecules, exceeding 65% of global market volume [77]. In macromolecules, lignin can find an application as dispersant, binder, and emulsifier in several industries, but in many cases these uses of lignin mainly lead to low-value products. However, there are other applications with higher earnings, like lignin uses for resins and plastics [73]. Lignin has a certain similarity to phenol-formaldehyde (PF) resins, used for varnishes, circuit boards, wood adhesives, etc. It maybe possible to use lignin in place of phenol used in the petrochemical industry. Lignin, can substitute the phenol from the petrochemical industry to produce PF resins, which are formed by polycondensation of phenols in the presence of formaldehyde [75].

Additionally, the expansion in the use of carbon fibers (CF) in construction and automotive industries as a lightweight material is increasing the importance of macromolecules [77]. Carbon fibers are mainly used in the automotive industry, but they also have other applications in the aerospace industry (aircrafts), wind-energy mills and sport equipment (bicycles, tennis rackets, etc.)[76]. Today, the use of CF is limited by the cost of the conventional carbon fiber precursor Poly-Acrylic-Nitrile (PAN), which compromises 80% of the cost of the CF. Pyrolysis is used to convert PAN to carbon fibers. This process is slow and energy consuming, hence, an expensive process. The use of lignin as an alternative precursor shows a significant reduction in the cost of CF and reduction of CO_2 emission during carbon fiber production. Lignin is readily available, inexpensive as a feedstock and structurally rich in phenyl propane groups with high carbon content (60%). Many researchers are working to improve the viability of lignin-based precursor technology, with significant benefits in this area of application expected [76, 78].

1.4.2.2 Lignin for production of aromatic chemicals.

Lignin is by far the most abundant renewable resource on earth available as feedstock for the industrial production of aromatic compounds, being the obvious replacement for fossil fuels in this purpose. The main aromatic compounds currently used in industry are phenol and BTX (Benzene, toluene and xylene) [44, 76-77].

BTX compromises 60% by volume of the aromatics produced industrially, representing almost 24% of the global petrochemical market value. Potentially these simple aromatic compounds can be obtained from lignin, and their application would be similar to the ones, that are being obtained from petroleum. However, for lignin to be used of BTX, the complete removal of oxygen functional groups by decarboxylation, decarbonylation, dehydroxylation, etc. Progress on lignin depolymerization techniques is also required in order to improve yield and selectivity. For this reason, lignin-based BTX is still in development [44, 76].

Phenols are extremely interesting building blocks for new synthetic bioplastics, as described previously in *1.4.1.1 Lignin macromolecules*. However, lignin can be used to produce phenol. Phenol is considered a commodity chemical and is directly affected by the price of oil. Lignin prices are stable, and are likely to decrease as yields improve and technologies advance. The interest in lignin-based phenol is the same as seen before in the lignin-based BTX building block production. However, this use is not yet commercially available [57].

Vanillin production has been commercial since 1937, with around 80% of its production from lignin-containing waste produced by the sulfite process in the pulp paper industry. However, in 1980 subsequent developments in the wood pulp industry made its lignin wastes less attractive as a raw material for vanillin synthesis. Today, Borregaard (1.3.1 Biorefineries), is the only company that converts lignin into vanillin, covering only, 20% of the total production of synthetic vanillin. The remaining 80% is currently synthesized in a two-step process from the petrochemical precursors guaiacol and glyoxylic acid which come from petrochemical industry [35, 76, 80].

Smolarski's studies show that an economically viable lignin valorisation route is needed, and more research to optimize the process for the production of lignin-based aromatic chemicals is required. The Organosolv technology can approach the high lignin purities required for these processes. However, large capital investments should be made for further studies and developments to achieve industrial scale production. It is expected that in the next five years, lignin could totally replace phenol in the production of polymers. Lignin-based vanillin production could also gain some momentum depending on the price of oil and demand for vanillin. The next five years are expected to confirm these trends, but also to give momentum to new technologies for the depolymerization of lignin into phenol and BTX [76].

1.4.2.3 Lignin upgrading process.

The lignin polymer can be converted from a low quality, low-price product into a high quality, high-value feedstock for fuels, electricity, or bulk and specialty chemicals using a wide range of chemicals transformations (Figure 2.4) [81]. Different fragmentation reactions can depolymerize lignin; it can be converted into syngas using lignin gasification at high temperature or under supercritical conditions [82-84], and can also be depolymerized into small units using enzymatic [85-86], mechanical [87-88], or catalytic processes. In this PhD thesis, the focus is on the isolation and catalytic depolymerization of lignin for the production of fine or bulk chemicals, therefore the enzymatic and mechanical processes are out of scope. The fragmentation reactions will be divided into four classes: lignin pyrolysis, hydrolysis reactions, catalytic hydrogenolysis reactions, and catalytic oxidation reactions.

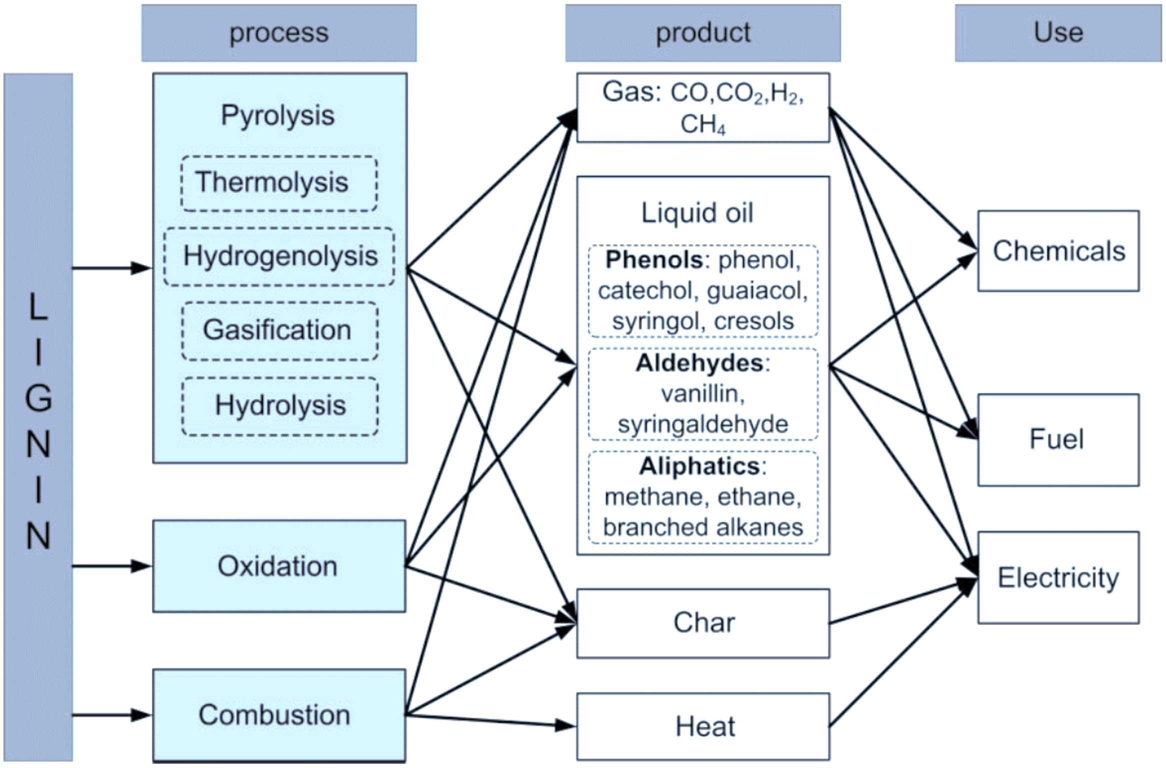


Figure 2.4. Main Thermochemical lignin conversion processes and their potential products [81]

Pyrolysis.

Pyrolysis can be defined as a thermochemical route to break down lignin anaerobically into low molecular weight compounds [89]. In biomass pyrolysis, a decomposition of the organic components occurs at temperatures between 200 to 500 ˚C, and then at 700-800 ˚C in absence of air/oxygen biomass is converted further into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal.

Depending on the operating conditions (temperature, solid residence time, biomass particle size, etc.) pyrolysis can be classified into three main categories: conventional or slow, fast and flash pyrolysis [90].

Table 1.4. Types of pyrolysis and operation parameters [68].

Pyrolysis process	Solid residence time (s)	Particle size (mm)	Temperature (˚C)	Product yield (%)		
				Oil	Char	Gas
SLOW	450 -550	5 – 50	250-650	30	35	35
FAST	0.5 – 10	<1	550-950	50	20	30
FLASH	<0.5	<0.2	750-1000	75	12	13

Lignin pyrolysis is a challenging process and produces relatively low yields of valuable products. Several studies have focused on gas products for lignin pyrolysis. Carbon monoxide and carbon dioxide are the most abundant components in the gas phase during lignin pyrolysis. In addition, methane has also been reported with yields < 5 wt. % [91-96]. Caballero et al. demonstrated an increase in methane, carbon monoxide, and carbon dioxide yield when the reactor temperatures increased from 500 to 900 ˚C [92-93]. In addition, Ferdous et al. indicated a generation of 25-mol % yield of Hydrogen in the gas phase. The H_2 content increases significantly when the thermal conversion temperature increases [94, 96]. H_2 and CO are the major components of synthesis gas (syngas), which is the feedstock used in Fischer-Tropsch synthesis.

More than 400 organic chemicals can be found amongst the bio-oils produced during biomass pyrolysis. These compounds can be classified in five different groups: 1. Hydroxyaldehydes, 2. Hydroxyquetones, 3. Sugars and dehydrosugars, 4. Carboxylic acids and 5. Phenolic compounds [97]. Evans et al. has found that the pyrolysis of the carbohydrate fraction can produce compounds from the first four groups mentioned above. Furthermore, bio-oils composed of phenolic compounds, are the mayor products of lignin pyrolysis. In particular, products such as coniferyl alcohol, sinapyl alcohol, vanillin, eugenol, guaiacol, vinylguaiacol, creosol, and catechol can be detected in the bio oils from lignin pyrolysis among others. The most abundant of these are lignin building blocks, coniferyl and sinapyl alcohol, which are former in early stages of lignin pyrolysis [98-99].

Catalysts significantly improve the selectivity of the pyrolytic process and the quality of the pyrolytic oil produced from lignocellulosic biomass [100]. Olazar et al. have used H-ZSM-5 in the catalytic pyrolysis of pine sawdust, achieving the production of aromatic and aliphatic hydrocarbons in a conical spouted-bed reactor [101]. Carlson et al. have studied the catalytic pyrolysis of bio-derived carbohydrates over different solid acid catalysts getting 30 -50 % yield of arenes with ZSM-5 catalysts. However, the process required more detailed studies into the effect of catalyst loading, deactivation and regeneration [102].

Presently, bio-oil samples are under investigation as a feedstock for extracting high-value chemicals, which could be substituted for phenol in several applications as discussed in section *1.4.1 Potential applications for lignin*. Pyrolysis technologies can increase the profitability of lignocellulosic biorefineries if the challenge of the cost-effective separation of the oligomeric fraction from the monomeric fraction can be solved. Thus, further investigation is needed into the liquid and solid char products [103].

Solvolysis.

Solvolysis involves the fragmentation of lignin molecules into lower molecular weight products and occurs at moderate temperatures in acidic or a basic condition. If this process uses water as the solvent, it may also be referred to as hydrolysis [104]. Karagöz et al. have used alkaline hydrolysis to treat pine sawdust to form phenolic compounds. The oil obtained consisted of a mixture of oxygenated lignin products, produced with Rb_2CO_3 and Cs_2CO_3 catalysts. The base catalysts prevent the formation of char and promote the formation of catechol and 2-methoxy-phenol [105]. Miller et al. have developed a two-stage process for the conversion of lignin and lignin model compounds. The first stage involves base-catalyzed depolymerization using supercritical methanol or ethanol at 250-290 ^{o}C, and in the second step, the lignin intermediate is hydroprocessed. Only 7% of the ether-insoluble material was left in the KOH/methanol solution after 10-15 minutes. The strong bases favored the reaction. A combination of bases, such as NaOH and $Ca(OH)_2$ gave positive synergistic effects. In contrast if $Ca(OH)_2$ is combined with LiOH or CsOH, negative synergistic effects occur, producing a relative decrease in insolubles [106]. Nenkova et al. carried out an aqueous alkaline depolymerization of hydrolysed lignin model compound with 5% NaOH solution at 180 ^{o}C. They were able to repeat this with poplar wood sawdust- The isolated products from extraction with toluene included several high-value chemicals commonly obtained from lignin oxidation, such as 2-methoxyphenol, 4-hydroxy-3- methoxybenzaldehyde, 2,6-dimethoxyphenol, and 1-(4-hydroxy-3-methoxyphenyl) ethanone [107].

Hydrolysis in supercritical water is reported as an alternative approach for lignin depolymerization. Supercritical water has several advantages, for example, it is not necessary to dry the feedstock, oxidations and hydrolysis reactions can be achieved without a catalyst, and it is thermally stable as well as miscible with gases, hydrocarbons and aromatic substances. Lignin model compounds, such as guaiacol and catechol have been used to produce phenol under supercritical conditions [108-109].

Hydrogenolysis.

Hydrogenolysis, which can be defined as pyrolysis performed in the presence of hydrogen, is probably the most promising method for producing phenols from lignin. Hydrogenolysis leads to higher net conversion, higher yields of phenols, and less char formation than pyrolysis. Even higher conversion and oil yields may be achieved by using pretreatment methods such as microwave and ultrasound irradiation before hydrogenolysis. In addition, the reaction temperature used is in the range of 160-250 °C, and the reaction is carried out in water or a polar organic solvent, such as methanol or ethanol. Hydrogenolysis is performed either by treating lignin in an active hydrogen-donating solvent, such as tetralin, sodium formate solution and formic acid or in gaseous hydrogen [81].

Although hydrogenolysis can be carried out without a catalyst, catalysis is the key to the hydrogenolysis process [110]. Hydrogenolysis is catalyzed mainly by transition metal catalysts. These catalysts can dissociate gaseous H_2 into hydrogen atoms, and hydrogenate the lignin fragment, reducing the extend of recondensation [38]. Augustine et al. have investigated the hydrogenation of a lignin model compound, 4-methyl-1-cyclohexene, over Pt/SiO_2 catalyst. The data show that the solvent plays an important role in these reactions. The polarity of the solvent was a key factor in the interaction between solvent and reactant [111]. Tagaki et al. reported the influence of the solvent on the hydrogenation of aromatic lignin model compounds catalyzed by Ru/Al_2O_3 and Pt/Al_2O_3. Their studies show that polar solvents (acetone, THF, dioxane and diethyl ether) suppressed the hydrogenation. Furthermore, they also demonstrated that decreasing the relative permittivity of the solvent, increase the hydrogenation reactivity [88]. Wang et al. demonstrated the effect of solvents with different properties on the hydrogenolysis of diphenyl ether with Raney nickel as catalyst. Catalytic activity was influenced by Lewis basicity. Non-basic solvents enhanced the catalytic activity, producing mainly saturated alkanes, alcohols and ether at 90 °C [113]. Zhang et al. investigated the influence of bimetallic catalysts of the formed $Ni_{85}M_{15}$ (M=Ru, Rh and Pd) in the hydrogenolysis of lignin model compounds and Organosolv lignin under mild reaction conditions in water. They showed that single-component Ni and noble metal catalysts were active for this reaction, but the combination of the two presented prominent effects overcome the limitations of a single component catalyst [114].

Oxidation.

Lignin oxidation reactions tend to form complex aromatic compounds with additional functionality, which serve as a platform for subsequent reactions or produce fine chemicals themselves. The oxidation products of lignin range from aromatic aldehydes to carboxyl acids based on the severity of the reaction conditions [115]. Among them, vanillin is an important product of commercial interest as described in section *1.4.1.2 Lignin for production of aromatic chemicals*.

Many studies have been carried out on lignin valorization using oxidation reactions, over the last few years. Several strategies for the catalytic oxidation of lignin and lignin models were reported including the use of heterogeneous catalysis, bio-catalysis, biomimetic catalysis and organometallic catalysis [38, 116-118]. The focus in this PhD thesis is heterogeneous catalysis for lignin valorization.

Heterogeneous oxidation catalysts play an important role in the pulp and paper industry in the removal lignin and other compounds from wood pulps. There are many examples of lignin heterogeneous catalysis [38, 115-118]. Crestini et al. have worked on the oxidation of phenolic and non-phenolic, monomeric, and dimeric lignin model compounds in addition to sugar cane lignin and softwood Kraft lignin for treatment of Kraft pulp using heterogeneous methylrhenium trioxide catalysts. Vanillin and veratryl alcohol were oxidized to the corresponding acids, aldehydes and quinones, achieving yields up to 49% [119-120]. Methylrhenium trioxide was also used by Hermann et al. for vanillin production from the oxidation of isoeugenol and transferulic acid in presence of H_2O_2. The catalyst could cleave C-C double bonds with reasonable yields depending on the reaction conditions and starting material [121].

Various oxide-based catalysts led to a significant conversion of raw lignin in aqueous or alcoholic media in the presence of oxygen under pressure [122-124]. Sales et al. investigated the applicability of Pd/Al_2O_3 catalyst, prepared by incipient wet impregnation, in the oxidative conversion of alkaline lignin extracted from sugar cane bagasse in batch slurry and continuous fluidized-bed reactors. Aldehyde compounds were more susceptible to oxidation producing syringaldehyde and p-hydroxybenzaldehyde. After 2 hours at 120 ^oC, 0.56 g of vanillin (< 2 wt. %) and 0.50 g of syringaldehyde were produced from 30 g of lignin [122]. Zhang et al. tested the wet aerobic oxidation of lignin into aldehydes with perovskite-type oxide catalyst prepared using a sol-gel method. The catalytic activity was shown to increase with increasing Cu content, due to the anion vacancies generated by incorporation of Cu into the $LaCoO_3$ catalysts which increased the amount of adsorbed oxygen surface active site species. The catalyst could be recycled for use in five successive runs without significant activity loss [123]. Suresh Bhargava et al. described the catalytic wet oxidation of ferulic acid, using single metal (Cu), bimetallic (Cu-Ni, Cu-Co and Cu-Mn), and multimetallic (Cu-Ni-Ce, Cu-Co-Mn, Cu-Fe-Mn) alumina supported catalysts. Cu-Ni-Ce/Al_2O_3 catalyst was the most active, while Cu-Mn/Al_2O_3 presented the highest stability of the nine catalysts studied [124].

Heterogeneous catalysts exhibit several advantageous properties not only in terms of easier separation and recyclability, but also when the oxidation reactions are conducted in the presence of molecular O_2 or aqueous H_2O_2. Innovative research into heterogeneous catalytic system that can provide more selective and efficient catalysts under mild conditions in the presence of O_2, air and H_2O_2 has to be encouraged. Furthermore, oxidation is not the only way to valorize lignin, but constitutes a relevant route for eco-efficient processes, involving several principles of Green Chemistry such as catalysis, energy efficiency, waste limitation and use of clean processes.

1.5 Aim and outline of this thesis.

Finding a process for biomass valorization that could be directly adapted to the current biorefineries represents a challenge. At present, only a small proportion of lignin is used as an energy source for power generation or in the production of value-added products. It is obvious, that new systems for the valorisation of lignin are needed to assist the implementation of the current concept of biorefinery, in a profitable and sustainable way.

The aim of this thesis is to develop new sustainable catalytic technology that allows the lignin contained in second-generation biomass to be valorized into fuels or chemicals. The focus will be on the oxidative cleavage strategy used to break lignin bonds and degrade it into smaller units. For that, fundamental insight is needed to develop new catalytic systems designed specifically for lignin. In order to achieve the degradation strategy, the catalysts will first be optimized for a number of small relevant model substrates and then applied to Organosolv lignin.

Due to complexity and variability of lignin, model compounds are needed in order to study lignin valorization. *Chapter 2.* outlines these model compounds, and focuses on the development of a catalytic system for the oxidation of β-O-4 lignin model compounds, specifically, veratryl alcohol and guaiacyl glycerol-β-guaiacyl ether.

Lignin pretreatment is an important initial step in a biorefinery operation, separating the principal components of biomass and related materials. *Chapter 3*, describes the methods of biomass pretreatment, with an emphasis on the Organosolv process, the method that was selected in this research work to obtain lignin from wood.

Chapter 4 describes the results of a study to screen the reaction conditions and catalytic systems for the oxidation of lignin with molecular oxygen. An efficient two-step valorization route consisting of a first step oxidative cleavage followed by a second stage hydrogenolysis has also been studied.

Concluding remarks and key findings of this PhD thesis are summarized in *Chapter 5.*

2

Chapter 2

Catalytic aerobic oxidation of β-O-4 lignin model compounds

Abstract.

Lignin is a complex polymeric molecule with a high degree of variability, thus making it difficult to design an effective catalytic system for its valorization. For a better understanding of lignin chemical transformations, and to simplify the plethora of products obtained therefrom, a wide number of model compounds have been used. These model compounds contain linkages that resemble those found in the lignin polymer, with the β-O-4 moiety the most common among them, and thus their reactivity provides insight into the degradation and reaction of the polymer structure as a whole [38].

One of the viable methods for the valorisation of lignin and lignin model compounds is oxidative depolymerisation using environmentally friendly oxidants like O_2 or H_2O_2. Oxidative depolymerisation involves the cleavage of ether bonds, such as β-O-4 and other linkages present in lignin and its model compounds, giving aldehydes or carboxylic acids as products, depending on the applied reaction conditions [115].

The aim of this chapter is to describe an efficient catalytic system for the aerobic oxidation of β-O-4 lignin model compounds to simple aromatic chemicals.

2.1 Introduction.

The catalytic conversion of lignin into bulk chemicals is a possible scenario for the use of this abundant feedstock. For this purpose, the chemical transformation of lignin or lignin model compounds, have become increasingly important in the last decade because of their potential application as supplements or replacements for fossil fuel derived products [23, 38]. Different strategies have been followed, such as lignin pyrolysis [89-103], lignin hydrolysis [107-109, 125] and catalytic hydrogenolysis reactions [113-114, 126], for the production of value-added chemicals. One approach that carries considerable potential is the use of catalytic oxidation, since lignin contains many hydroxyl groups that are susceptible to oxidation and oxidative depolymerization [115]. Catalytic oxidation of lignin gives various attractive advantages, such as the production of a wider range of aromatic compounds with additional functionalities coupled with easy product separation [127].

The complexity and variability of lignin has prompted the use of simpler and lower molecular weight model compounds to study lignin oxidation reactions. These model compounds serve several proposes in the study of lignin valorization. They are formed from the linkages and functional groups found in the lignin polymer, and appear frequently after lignin depolymerization in the degradation streams. The study of the reactivity of lignin model compounds provides insights into the reactivity of the lignin molecule itself, helping in the development of methods for lignin valorisation to obtain high-value chemicals, which are of great importance in a profitable biorefinery development. In addition, model compounds often contain only one type of linkage present in lignin, reducing the analytical challenges and simplifying the catalytic performance in the lignin reaction pathway [38, 104]. There are many different lignin model compounds grouped by type, usually differing only by the number and type of functional groups present. It is worthwhile to choose a model that represent the most abundant interunit linkage in lignin. As stated in *Chapter 1. Section 1.4 Lignin.*, the β-O-4 ether bond comprises above 50% of the monomer linkages in lignin and is significantly weaker than other bonds [129].

The oxidative depolymerization of β-O-4 lignin model compounds has been intensively discussed in the literature, as it is easier to analyze the reactions of small and well-defined molecules. This section is divided in two parts, according to the two different model compounds (Figure 2.1) chosen for the studies in this PhD thesis: veratryl alcohol (VA) and guaiacyl-glycerol-β- guaiacyl ether (GGGE)

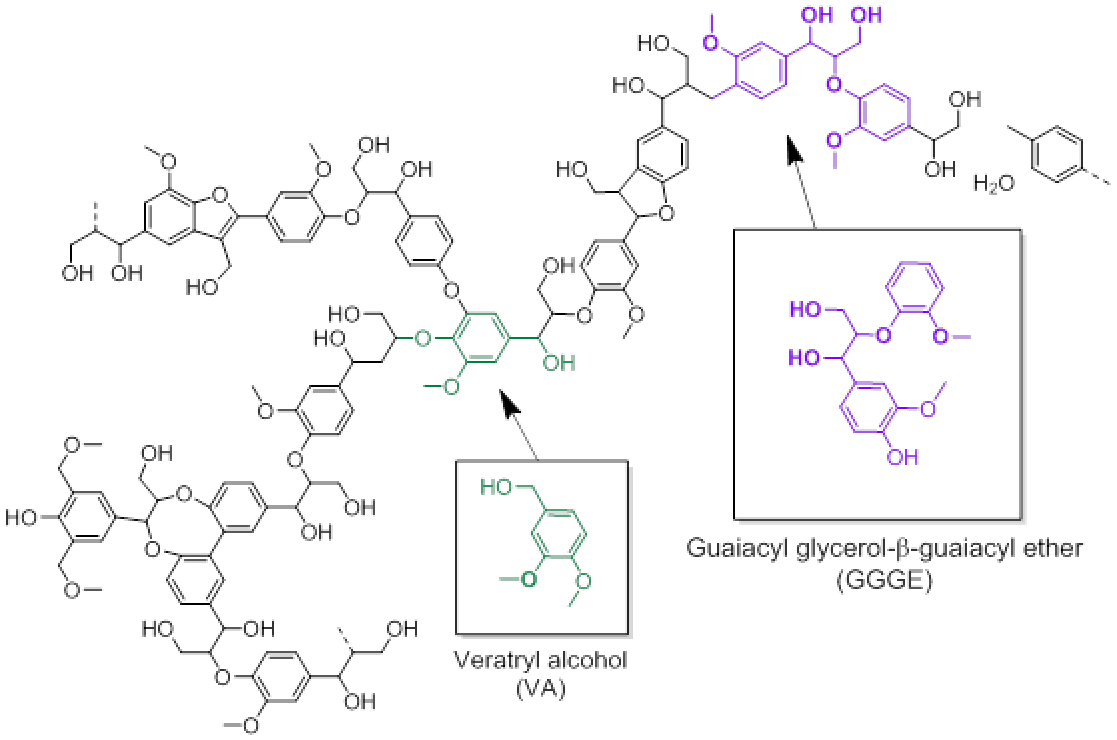
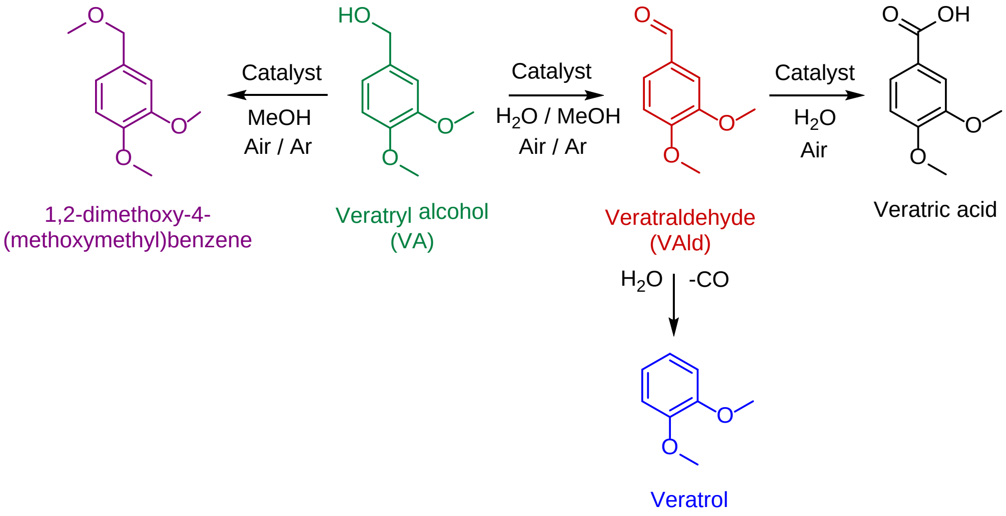


Figure 2.1. Schematic representation of lignin fragment and the corresponding selection of β-O-4 lignin model compo

2.2 Veratryl alcohol.

As a derivative of coniferyl alcohol, veratryl alcohol or 3, 4-dimethoxybenzyl alcohol, has been extensively studied in order to understand the chemistry of lignin and explore efficient transformation routes. One of the directions followed is the oxidation of veratryl alcohol to its corresponding aldehyde, veratraldehyde(3, 4-dimethoxybenzaldehyde (VAld)) (Scheme 2.1), which is a useful flavorant and odorant, well-known commercially because its pleasant woody fragrance. Veratraldehyde formation has been reported using enzymatic and homogeneous catalytic systems.



Scheme 2.1. Catalytic oxidation of veratryl alcohol (VA) to veratraldehyde (VAld) and other products.

In 1987, Kirk and Farrell reported the catalytic enzymatic oxidation of VA to VAld as part of a study into the microbial degradation of lignin [131]. Later, Diaz-González et al. carried out extensive studies into the enzymatic oxidation of VA using laccase in the presence of phenolic compounds as enhances. The yield of VAld was poor, consistently less than 20% [132]. With optimized reaction conditions, Larson et al. developed an improved laccase mediated oxidation and gained a yield of 94% isolated VAld [133]. However, while the enzymatic reactions have demonstrated efficient conversion of lignin model compounds, they also present a number of drawbacks, which limit their use, such as poor thermal stability, the requirement of a narrow range pH, and the need of an enzyme replacement to maintain good activity, due to enzymatic deactivation [85, 131-133].

As an alternative to the enzymatic transformation of VA to VAld, various homogeneous catalysts have been tested including porphyrins, Schiff-bases, polyoxometalates and other metal salts in the presence of stoichiometric oxidants (H_2O_2, t-BuOOH, NaClO, PhIO, $KHSO_5$, etc.) [134-136]. Zucca et al. reached good yields (up to 90%) of VAld, using M-phorphyrin (M= Mn, Fe or Co) based catalysts at room temperature in presence of H_2O_2 [136]. By contrast, lower yields of VAld were achieved using of Co-sulphosalen ($\leq$7%) and Co-salen complexes (43%) [137-138]. Several other catalyst systems based on Co, Cu or Ru salts have also been reported to provide VAld yields in the range 73-84% [139-140]. Although many homogeneous catalytic systems have been reported with good yields, there are inherent limitations in the recovery and recycling of the used catalysts.

In contrast to homogeneous catalysts, solid catalyst can be recovered easily from liquid reaction mixtures; they can be good candidates for recycling if metal leaching is insignificant and can be used at elevated temperatures. Fan et al. has reported yields up to 95% of VAld at 130 ^{o}C, combining a Ru-imidazole/CuO ionic liquid catalyst system. However, the recyclability of the catalyst system was not documented [141]. Yamaguchi et al. showed that RuOx supported on γ-Alumina works effective and can be reused in the aerobic oxidation of alcohols in presence of sulfur, nitrogen and carbon-carbon double bonds [142]. Many studies have demonstrated that Ru-based catalysts play an important role in hydrogenation and hydrogenolysis reactions [141-145]. For this reason, Ru-based catalysts are of interesting to investigate in the context of lignin valorization.

RuO_X catalysts supported on silica (Ru/SiO_2) and alumina (Ru/Al_2O_3) have been prepared, characterized and examined for the oxidation of VA to VAld with air in aqueous media. Analogous M/Al_2O_3 catalysts (M = MnO_X, CoO_X, CuO_X and AgO_X) were also prepared and applied to the VA oxidation reaction. Important reaction parameters such as temperature, time and solvent effect were optimized using the Ru/Al_2O_3 catalyst in order to limit the formation of by-products such as veratrol (Scheme 2.1). The recyclability of the catalyst was further examined by performing consecutive reaction runs in order to demonstrate the viability of the system.

2.2.1 Experimental.

2.2.1.1 Materials.

All chemicals were used as received without further purification unless otherwise specified. Veratryl alcohol (> 96%, VA), veratraldehyde (99%, VAld), veratrol (99%), manganese(II)acetate tetra-hydrate (> 99%), cobalt(II)nitrate hexahydrate (p.a.), copper(II)acetate monohydrate (p.a.), iron(III)nitrate nonahydrate (p.a.), silver(I)nitrate (p.a.), ruthenium(IV)oxide hydrate (> 99.9%), ruthenium(III)acetylacetonate (> 97%), ruthenium(III) chloride hydrate (>99%), Zirconium(IV) oxide (99%), magnesium aluminate, spinel (99%), Acetonitrile (99.8%) Methanol (99%) and silica gel 60 were purchased from Sigma Aldrich. γ-Aluminium oxide (> 99%) was provided by Saint Gobain as a generous gift. Compressed air (~21% oxygen), oxygen (>99.99%) and argon (> 99.99%) was purchased from Air Liquide, Denmark.

2.2.1.2 Catalyst preparation.

The supported catalysts were prepared by wet impregnation. Appropriate amounts of ruthenium or other metal (manganese, cobalt, copper and silver) precursors were dissolved in water and either alumina, zirconia, spinel or silica was slowly added to the aqueous solution of metal precursor and stirred for 3 h. The slurry was then dried at 80 ^{o}C overnight in order to remove the water. Finally, the dried catalysts were calcined at 450 ^{o}C for 6 h in static air to get metal oxide (1, 3, 5 wt. % with respect to metal) supported catalysts. The catalysts were stored in a desiccator and not pre-activated before use.

2.2.1.3 Catalyst characterization

The synthesized catalyst were characterized by nitrogen physisorption and TEM. Nitrogen physisorption analysis was performed with Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer at 77K. The samples were outgassed under vacuum at 200 ^{o}C prior to measurement and the total surface area was calculated according to the Brunauer Emmett Teller surface area (BET) method. TEM was performed on a FEI Tecnai T20 G2 microscope operated at 200 kV. All the specimens were dispersed in ethanol and left dry on the TEM grids at room temperature prior to analyses.

2.2.1.4 Standard oxidation procedure.

Catalytic experiments were performed in an autoclave (Microclave 50 ml reactor, Autoclave Engineers) charged with an appropriate amount of veratryl alcohol, catalyst (100 mg) and water or methanol (10 ml) as solvent. The reactor was pressurized with air (5 bars) or argon (20 bars) and heated to the desired reaction temperature. Mechanical stirring of the reactor (300 rpm) was started when a temperature 20 °C below the set-point was reached. After the reaction, the autoclave was quenched in cold water and filtered. Aliquots of the reaction mixture were analysed to GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 µm × 0.25 µm) to quantify the conversion and product yield. The conversions of VA and yields of VAld were calculated in relation to a series of individual standard solutions. The products were identified by GC-MS.

2.2.2 Results and discussion.

The conversion and yield of a number of prepared catalysts for the aerobic oxidation of VA to VAld are compiled in Table 2.1. As expected, blank experiments without catalysts, using alumina and silica alone gave very poor yields of VAld, confirming that the oxidation reaction did not occur in absence of the active metal catalyst. An improvement in catalytic activity was observed when Mn/Al_2O_3 was used as a catalyst, giving a 17% yield of VAld. However, the selectivity towards VAld was low (25%), as the conversion of VA reached 69%.

Table 2.1.Testing with different catalysts in water as solvent.

Catalyst	BET surface area (m^2/g)	Conversion (%) veratryl alcohol	Product yield (%)	
			Veratraldehyde	Veratrol
Ru/Al_2O_3 (1)[a]	166	93	67	3
Ru/Al_2O_3 (2)[b]	152	77	37	<1
Ru/SiO_2[a]	422	96	46	<1
Mn/Al_2O_3	152	69	17	<1
Al_2O_3	204	46	3	0
SiO_2	472	59	3	0
-	-	34	2	0

Reaction conditions: 100 mg VA, 100 mg catalyst (5 wt% with respect to metal), 10ml water, 160 °C, 5 bar Air, 5 h.

[a] Catalyst prepared using ruthenium(IV) oxide hydrate precursor.

[b] Catalyst prepared using ruthenium(III) acetylacetonate precursor.

When Ru/Al_2O_3 (2) catalyst made with ruthenium (III) acetylacetonate, was applied, the yield of VAld increased significantly from 17 to 37%. The VAld yield favorably improved to 67%, when Ru/Al_2O_3 (1) made from ruthenium (IV) oxide hydrate was used. Both Ru/Al_2O_3 catalysts were subjected to surface area measurement and microscopic studies. As shown in Table 2.1, the surface area of Ru/Al_2O_3 (1) and Ru/Al_2O_3 (2) did not show significant differences. However, TEM studies showed a substantial change in the particle size of the Ru/Al_2O_3 catalysts, as shown in Figure 2.2. The TEM images showed that the RuO_x particle size for Ru/Al_2O_3 (1) ranged between 20-30 nm, and Ru/Al_2O_3 (2) contained particles ranging from 100-200 nm, 5-10 times larger than Ru/Al_2O_3 (1). As can be seen, the size of the particles apparently plays a very important role in the conversion of VA to VAld, and the choice of Ru precursor has a big impact on the particle size produced.

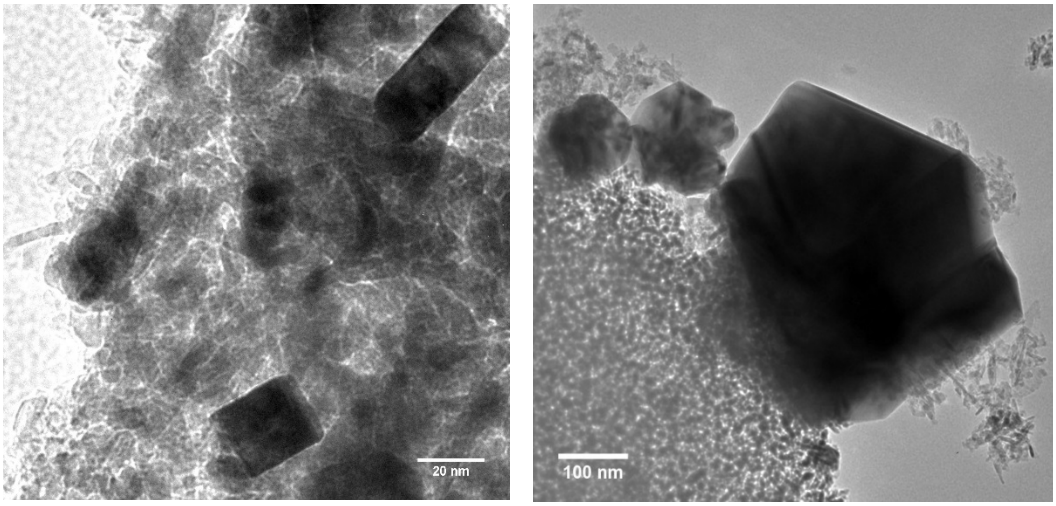


Figure 2.2. High-resolution TEM images of (left) 5 wt. % Ru/Al_2O_3 (1) and (right) 5 wt. % Ru/Al_2O_3 (2).

When the support was changed from alumina to silica, the yield decrease from 67 to 46% from Ru/Al_2O_3 (1) to Ru/SiO_2 after 5 h. Large differences were also measured in surface areas of the two catalysts.

In the case of by-product, veratrol (Scheme 2.1) in reaction with VA and Ru catalysts, very poor yields, less than 3% were found, even at temperatures below 160°C as shown in Figure 2.3, where the yield of all products decreased with temperature. Previous reports in the literature showed that Ru-based catalysts are efficient for decarbonylation of aromatic and aliphatic aldehydes [146-147]. The pH of the reaction mixture was measured before and after the reaction. Here a change from pH 7-8 before reaction to pH 5-6 after reaction was found. This change in the pH values indicate the formation of veratric acid, which was observed in previous studies [148]. Veratric acid could not be detected by our GC, GC-MS and HPLC equipment, so in order to evaluate how veratric acid and veratrol formation occurred during the reaction in water, the reaction time was prolonged to 20 h. Results are summarized in Table 2.2, and in the accompanying time-course study on Figure 2.4.

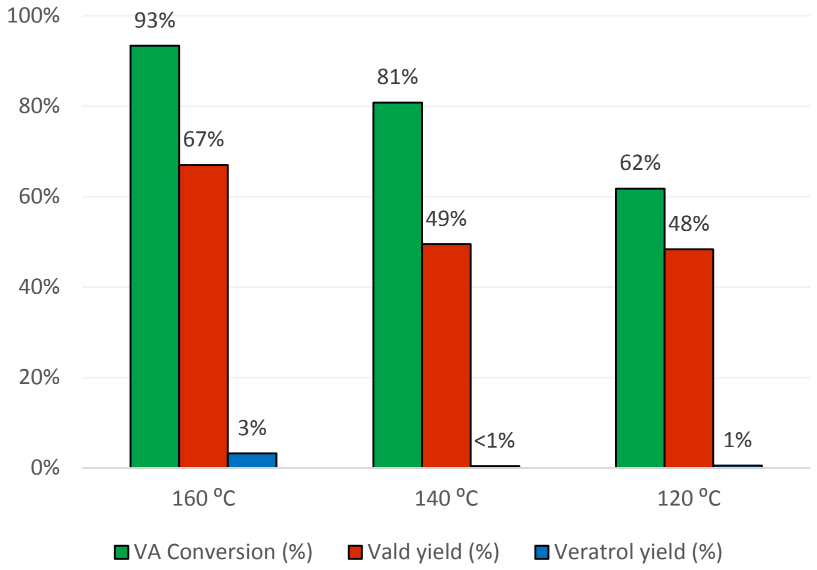


Figure 2.3. Temperature study for VA conversion into VAld with Ru/Al_2O_3 (1) in water, 5h (Each set of data are from individual experiments).

A 69% yield of VAld, along with 21 % yield of veratrol and full conversion of VA, were achieved using Ru/Al_2O_3 (1), with the VAld yield practically the same as that obtained after 5 h of reaction. In the case of Ru/SiO_2, the VAld yield was around 69% with less than 1% for veratrol, along with quantitative VA conversion after 5h. The other metal supported alumina catalysts gave lower VAld yields, from 5 to 26%

with less than 6% yield of veratrol. The time-course study (Figure 2.4) showed an excellent 89% VAld yield after about 8 h reaction, at which point the veratrol yield was less than 2%. Prolonged time reactions showed an increase in veratrol yield at the expense of VAld yield, corroborating the idea that veratrol is formed by decarbonylation of VAld. A separate experiment using VAld as substrate, resulted in a very low yield of veratrol (<2%) after 5 h, in line with the time course-study result.

Table 2.2. Testing with different catalysts in water as solvent.

Catalyst	**BET surface area (m^2/g)**	**Conversion (%) veratryl alcohol**	**Product yield (%)**	
			Veratraldehyde	**Veratrol**
Ru/Al_2O_3 (1)[a]	166	>99	69	21
Ru/SiO_2[a]	422	99	69	<1
Mn/Al_2O_3	152	81	23	6
Ag/Al_2O_3	164	34	26	<1
Co/Al_2O_3	160	61	13	4
Cu/Al_2O_3	158	>99	5	1

Reaction conditions: 170 mg VA, 170 mg catalyst (5 wt.% with respect to metal), 10ml water, 160 °C, 20 bar Ar, 20 h.
[a] Catalyst prepared using ruthenium(IV) oxide hydrate precursor.

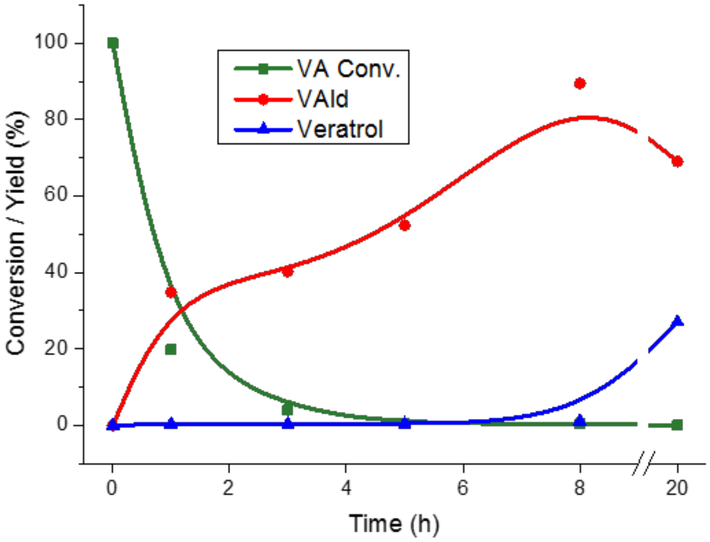


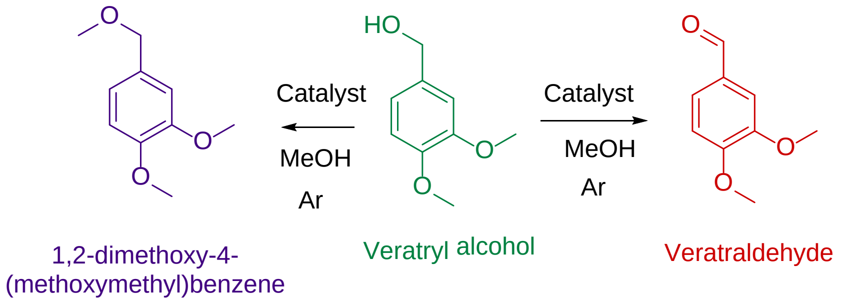
Figure 2.4. Time course study for VA conversion into VAld with Ru/Al_2O_3 (1) at 160 °C in water (each set of data are from individual experiments).

When water was replaced with methanol as solvent, a drastic reduction in the yield of VAld with Ru/Al_2O_3 (1) was observed at 160 ^oC and 20 bar Ar, decreasing from 69% to 22% due to the formation of the by-product 1, 2-dimethxy-4-(methoxymethyl)benzene (VA-ether) (Scheme 2.2.)(Table 2.3). The highest yield of VA-ether (67%) was obtained over Ru/SiO_2. Accordingly, the VAld yield was reduced to 10% with the latter catalyst, almost 5 times lower than the corresponding yield in water with 5 bar of Air and 20 h reaction (Table 2.2. and 2.3). The presence of O_2 in the reaction, promoted the conversion of VA to VAld, instead of dehydrogenation, which was favored under Ar atmosphere. In addition, when the reaction was performed in methanol under 5 bar air, no improvement in VAld yield (15%) was observed, confirming that water was the preferred solvent for the aerobic oxidation of VA to VAld.

Table 2.3. Testing with different catalysts in methanol as solvent and argon

Catalyst	**BET surface area (m^2/g)**	**Conversion (%) veratryl alcohol**	**Product yield (%)**		
			Veratraldehyde	**Veratrol**	**VA-Ether**
Ru/Al_2O_3 (1)[a]	166	90	22	17	36
Ru/SiO_2[a]	422	96	10	<1	67
Mn/Al_2O_3	152	47	24	<1	22
Ag/Al_2O_3	164	89	2	22	34
Co/Al_2O_3	160	56	7	6	16
Cu/Al_2O_3	158	56	13	8	37

Reaction conditions: 170 mg VA, 170 mg catalyst (5 wt.% with respect to metal), 10ml methanol, 160 ^oC, 20 bar Ar, 20 h.
[a] Catalyst prepared using ruthenium(IV) oxide hydrate precursor.



Scheme 2.2. The conversion of veratryl alcohol to its corresponding ether (VA-ether).

To determine the viability of the catalytic system, the catalyst Ru/Al_2O_3 (1) was subjected to recyclability studies in the VA oxidation reaction (Figure 2.5). After each reaction run, the catalyst was collected by filtration, and thoroughly washed with water. Subsequently, the before recovered catalyst was dried overnight at 80 °C and finally calcined at 450 °C over 6 h for being used in the later reaction. Unfortunately, the conversion of VA decreased after three reaction cycles from 93% to 65%, and the yield of VAld, also reduced from 67% to 34%, meaning the VAld selectivity slayed above 50%. The reduction in the catalytic activity could be a consequence of the loss of the catalyst during the separation or due to an increase in the particle size of ruthenium during the additional calcinations, as earlier observed in supported Ru catalysts [149].

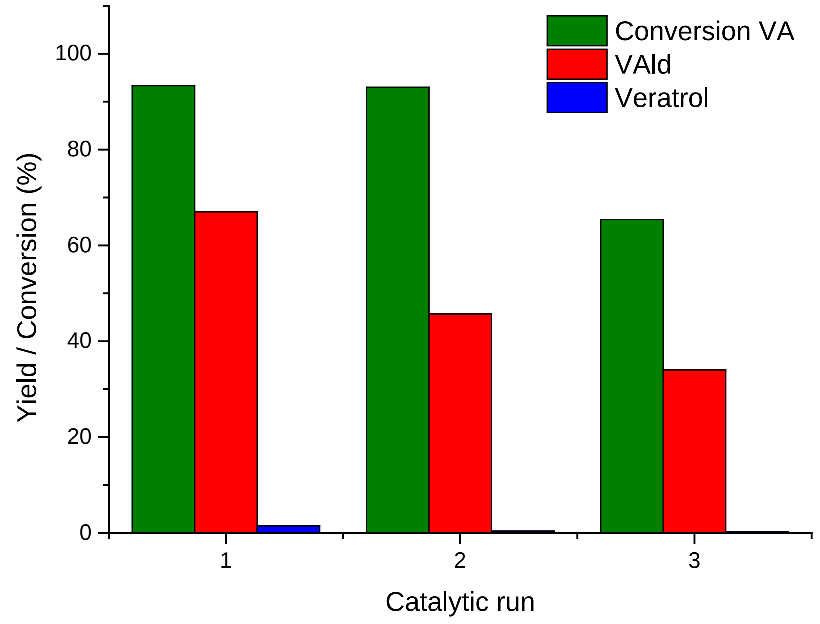


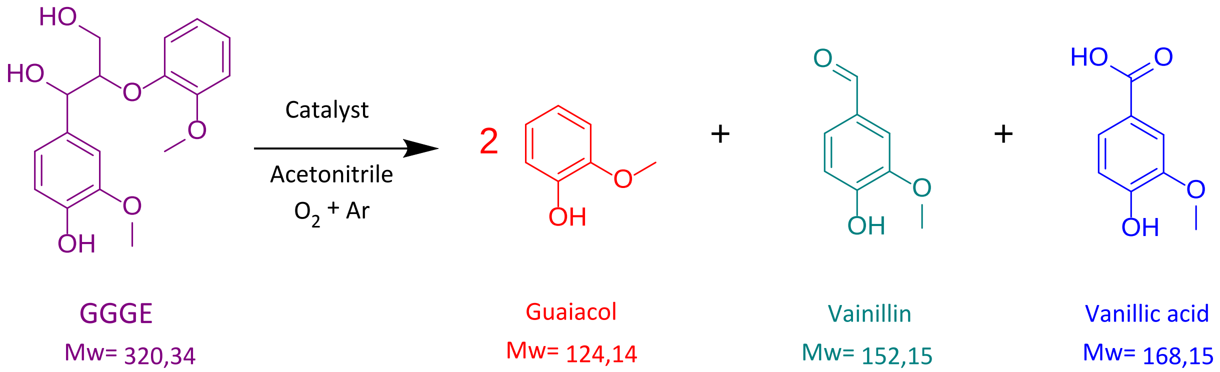
Figure 2.5. Reuse of Ru/Al_2O_3 (1) catalyst for three consecutive VA oxidation reactions (r**eaction** conditions: VA to catalyst mass ratio = 1.04, 10 ml of water, 5 h, 160 °C).

After the consecutive reactions, the Ru/Al_2O_3 (1) catalyst was subjected to surface area measurements. There was an increase in the BET surface area of about 20%, from an original 166 m^2/g to about 201 m^2/g, which is more akin to the surface area of the alumina support alone, 204 m^2/g. The combination of loss of activity, and the increase in surface area may indicate the possibility of Ru leaching from the support to the reaction solution. However, Ru leaching from this type of catalyst under similar conditions has previously been considered a minor problem [149-150].

2.3 Guaiacyl glycerol-β-guaiacyl ether.

The vast majority of the methods focused on the oxidation of lignin and associated model compounds employ harsh conditions, afford products with low yield or selectivity, or use simple model compounds, such as veratryl alcohol. The use of dimeric lignin model compounds containing β-O-4 linkages, which represent the most common substructures in lignin, helps to gain a better understanding of the reactivity and selectivity of some motifs found in lignin, as well as how specific bonds, such β-O-4, can be broken [38]. Recent studies have begun to make progress in the catalytic aerobic oxidation of more realistic lignin model compounds, such as guaiacyl glycerol-β-guaiacyl ether (GGGE). Vanadium catalysts have emerged as being attractive for the homogeneous catalytic depolymerization of GGGE [151-154]. Son et al. have applied a vanadium-catalyst for the non-oxidative C-O bond cleavage of dimeric lignin model compounds with conversion over 80% [151]. Recently, alternative vanadium complexes were investigated for the oxidative C-C bond cleavage of lignin model compounds, showing promising aerobic reactivity. The vanadium catalysts promoted a multistep reaction that can afford C-C and C-O cleavage products [152-153]. Beyond these applications, Zhang et al. have used similar vanadium based catalysts to evaluate the ability of different complexes to mediate the oxidative C-C bond cleavage of a dimeric β-O-4 lignin model compound [154]. In order to reduce the complexity and number of steps in the aforementioned studies, Rahimi et al., have developed an organocatalytic method using 4-acetamido-TEMPO as catalyst, for a chemoselective aerobic oxidation of secondary benzylic alcohols in GGGE. The treatment of benzylic ketones with H_2O_2 afforded 88% yield of veratric acid together with a 42% yield of guaiacol [155-156]. However, despite the advances achieved in homogeneous catalysis in the selective cleavage of C-C and C-O bonds, recyclability and separation of catalysts and products, remain as issues to be solved in this field of catalysis.

The oxidative depolymerization of GGGE has been useful for developing an insight into lignin depolymerization. Based on the previous studies of the catalytic aerobic oxidation of veratryl alcohol, a simpler β-O-4 lignin model compound, this part of the research has been focused on establishing a catalytic system for the selective oxidation of the dimeric β-O-4 lignin model compound, GGGE, for the production of high-value chemicals (guaiacol, vanillin, vanillic acid). Scheme 2.3 represents the reaction pathway followed. Different catalysts have been prepared and characterized. The efficiency of RuO_x supported on γ-alumina (Ru/Al_2O_3), silica (Ru/SiO_2), zirconia (Ru/ZrO_2), spinel (Ru/Spinel) and HY(6) (Ru/HY(6)) for the oxidation of GGGE to guaiacol, vanillin and vanillic acid using a mixture of 20% oxygen in argon and acetonitrile have been examined. Analogous M/Al_2O_3 catalysts (M =MnO_x, AgO_x, CoO_x, CuO_x and FeO_x) have also been prepared and applied to the oxidation reaction. Important parameters such as catalyst loading, temperature and time have been optimized in order to increase the selectivity to the desirable products (Schema 2.3). The recyclability of the catalyst was further examined by performing consecutive reaction runs to demonstrate the viability of the system.



Scheme 2.3. Aerobic catalytic oxidation of guaiacyl glycerol-β-guaiacyl ether (GGGE) to guaiacol, vanillic acid, vanillin and other products.

2.3.1 Experimental.

2.3.1.1 Materials.

All chemicals were used as received, and without further purification unless otherwise specified. Guaiacyl glycerol-β-guaiacyl ether (>99%) was prepared from acetovanillone through a multiple step synthesis route, using a reported procedure [106]. Vanillin (99%), vanillic acid (99%), manganese(II)acetate tetra-hydrate (> 99%), cobalt(II)nitrate hexahydrate (p.a.), copper(II)acetate monohydrate (p.a.), iron(III)nitrate nonahydrate (p.a.), silver(I)nitrate (p.a.), ruthenium(IV)oxide hydrate (> 99.9%), ruthenium(III)acetylacetonate (> 97%), ruthenium(III) chloride hydrate (>99%), Zirconium(IV) oxide (99%), magnesium aluminate, spinel (99%), Acetonitrile (99.8%) Methanol (99%) and silica gel 60 were purchased from Sigma Aldrich. γ-Aluminium oxide (> 99%) was provided by Saint Gobain as a generous gift. Compressed air (~21% oxygen), oxygen (>99.99%) and argon (> 99.99%) was purchased from Air Liquide, Denmark.

2.3.1.2 Catalyst preparation.

The supported catalysts were prepared by wet impregnation. Appropriate amounts of ruthenium or other metal (manganese, cobalt, copper and silver) precursors were dissolved in water and either alumina, zirconia, spinel or silica was slowly added to the aqueous solution of metal precursor and stirred for 3 h. The slurry was then dried at 80 °C overnight in order to remove the water. Finally, the dried catalysts were calcined at 450 °C for 6 h in static air to get metal oxide (5, 3 or 1 wt. % with respect to metal) supported catalysts. The catalysts were stored in a desiccator and not pre-activated before use.

2.3.1.3 Catalyst characterization

The synthesized catalyst were characterized by nitrogen physisorption and TEM. Nitrogen physisorption analysis was performed with Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer at 77K. The samples were outgassed under vacuum at 200 ^{0}C prior to measurement and the total surface area was calculated according to the Brunauer Emmett Teller surface area (BET) method. TEM was performed on a FEI Tecnai T20 G2 microscope operated at 200 kV. All the specimens were dispersed in ethanol and left dry on the TEM grids at room temperature prior to analyses.

2.3.1.4 Standard oxidation procedure.

The catalytic aerobic oxidation of GGGE was typically conducted in an autoclave (Microclave 50 ml reactor, Autoclave Engineers) charged with an appropriate amount of guaiacyl glycerol-β-guaiacyl ether (GGGE), catalyst (40 mg) and acetonitrile (10 ml) as solvent. The reactor was pressurized to 5 bar with a mixture of 20% oxygen and argon, and heated to the desired reaction temperature. Mechanical stirring of the reactor (300 rpm) was started when a temperature 20 ^{o}C below the set-point was reached. After the reaction, the autoclave was cooled down in cold water and filtered. An aliquot of the reaction mixture was analysed by HPLC analysis performed using an Agilent® 1200 series instrument equipped with an Agilent C-18 column (15 cm length) in order to quantify the yield and conversion. The eluent was in all cases a 60 vol. % aqueous acetonitrile solution. The conversions of GGGE and yields of products were calculated in relation to a series of individual standard solutions. The products were identified by GC-MS.

2.3.2 Results and discussion.

Different metal oxide catalysts were tested for the aerobic oxidation of GGGE in acetonitrile, and results are show in Table 2.4. Initially, blank experiments were carried out using no catalyst or alumina support in place of the catalyst. Poor yields of guaiacol (<15%) and very poor yields of vanillin (<1%) and vanillic acid (<1%) were obtained. The results confirmed that a catalytically active metal was needed to oxidize GGGE.

Table 2.4. Oxidation of GGGE over various supported catalyst in acetonitrile.

Catalyst	**BET surface area (m^2/g)**	**Conversion (%) GGGE**	**Product yield (%)**		
			Guaiacol	**Vanillin**	**Vanillic acid**
Ru/Al_2O_3 (A)[a]	148	>99	28	11	11
Ag/Al_2O_3	164	>99	27	10	8
Fe/Al_2O_3	154	92	23	7	4
Mn/Al_2O_3	152	>99	21	8	8
Cu/Al_2O_3	158	>99	9	3	<1
Co/Al_2O_3	160	>99	18	1	<1
Al_2O_3	204	73	15	<1	<1
Blank	-	70	11	<1	<1

Reaction conditions: 10 ml (0.017 M GGGE in acetonitrile), 12 mol % catalyst/substrate, 160 ˚C, 5 bar (20% Oxygen + Ar), 20 h.
[a] Catalyst prepared using ruthenium(III) chloride hydrate precursor.

The yield of guaiacol increased from 15 to 18 % when the Co/Al_2O_3 catalyst was applied in the reaction. Encouragingly, the guaiacol, vanillin and vanillic acid yields were improved even further to 21, 8 and 8 %, respectively, for the Mn/Al_2O_3 catalyst. In comparison, the activity of the Mn/Al_2O_3 catalyst was much lower than Ag/Al_2O_3, resulting in yields of 27% guaiacol, 10% vanillin and 8 % vanillic acid.

When Ru/Al_2O_3 (A) catalyst made with ruthenium (III) chloride hydrate was applied, the yields of guaiacol and vanillin increased by 1% in each case in relation to the yield obtained with the Ag/Al_2O_3 catalyst. In addition, the vanillic acid yield favorably improved until 11%.

It is well documented in the literature that the metal loading present in a metal oxide based catalyst can have a significant effect on the structural, physical and catalytic properties of the catalyst being developed [157-159]. Ru/Al_2O_3 catalysts with varying Ru loadings were synthesized and examined for the conversion of GGGE to guaiacol, vanillin and vanillic acid, results are show in Table 2.5.

The highest yield of guaiacol (28%), vanillin (11%) and vanillic acid (11%) were reached with a 5 wt. % (with respect to the metal), Ru/Al_2O_3 (A) made with ruthenium(III) chloride hydrate. The catalysts with 3 wt. % and 1 wt. % respect to the metal gave the lowest yields of guaiacol at 20% and 18%, respectively. For both catalysts the yield of vanillin was 8% and vanillic acid 6%. Hence, as expected, the yields of products increased with increasing Ruthenium loading.

Table 2.5. Oxidation of GGGE over different loadings for the Ru/Al_2O_3 (A) catalyst in acetonitrile.

Catalyst	**BET surface area (m^2/g)**	**Conversion (%) GGGE**	**Product yield (%)**		
			Guaiacol	**Vanillin**	**Vanillic acid**
5 Ru/Al_2O_3(A)[a]	148	>99	28	11	11
3 Ru/Al_2O_3 (A)[b]	160	>99	20	8	6
1 Ru/Al_2O_3 (A)[c]	157	>99	18	8	6

Reaction conditions: 10 ml (0.017 M GGGE in acetonitrile), 40 mg catalyst, 160 ˚C, 5 bar (20% Oxygen + Ar), 20 h.

[a] Catalyst prepared using ruthenium(III) chloride hydrate precursor. 5 wt. % with respect to metal

[b] Catalyst prepared using ruthenium(III) chloride hydrate precursor. 3 wt. % with respect to metal

[c] Catalyst prepared using ruthenium(III) chloride hydrate precursor. 1 wt. % with respect to metal

BET surface area of the synthesized catalysts remained constant at approximately 160 m^2g^{-1} for the catalyst below 5 wt. % (Table 2.5). A higher ruthenium loading used in Ru/Al_2O_3 (A), led to a decrease in the BET surface area to 148 m^2g^{-1}, possibly due to the increased acidity of $RuCl_3$ solution during catalyst synthesis, which may have changed the Al_2O_3 support. Alternatively, RuO_x particles may block the Al_2O_3 pores and therefore reduce the observed BET surface area of the catalyst.

TEM images of the fresh and used Ru/Al_2O_3 catalysts with 1, 3 and 5 wt. % ruthenium loading are presented in Figure 2.6. The catalysts with 5 wt. % ruthenium loading revealed the presence of Ru containing nanoparticles. The nanoparticles observed had characteristic straight edges; they were trapeze or rod shaped and appeared to be darker than the surrounding Al_2O_3 support (as be expected for elements with high atomic masses observed by TEM) suggesting the presence of Ru. The observed nanoparticles were 7-60 nm in length. However, there may be many smaller particles or amorphous Ru containing regions that could not be measured. In comparison to the 5wt. % catalyst, Ru/Al_2O_3 (A), the catalysts with lower Ru loadings appeared to contain larger nanoparticles with more variation length at 20-100 nm for 1 wt. % Ru/Al_2O_3 (A) and 50-100 nm for 3 wt. % Ru/Al_2O_3 (A). It is therefore likely that each nanoparticle contains more than one crystallite. The same three Ru/Al_2O_3 catalysts, were also analyzed by TEM after reaction, showing approximately the same sized RuO_x nanoparticles as those observed in the corresponding fresh Ru/Al_2O_3 catalysts, suggesting that no appreciable change in the RuO_x particle size had ocurred following one catalytic run using GGGE (Figure 2.6). The nanoparticles observed in the ruthenium catalysts appear to be similar to RuO_x nanoparticles observed in literature [160].

The discovery that the Al_2O_3 support was active for the conversion of GGGE under the reaction conditions inspired the synthesis and catalytic testing of a number of catalysts varying the support material, including SiO_2, Spinel, ZrO_2 and HY(6), see Table 2.6. Although by no means an exhaustive study, none of the alternative catalysts synthesized yielded any significant improvement in activity or selectivity for the conversion of GGGE into guaiacol, vanillin and vanillic acid. Therefore, it was decided to continue with Ru/Al_2O_3 catalyst for further studies, as these gave the highest yields.

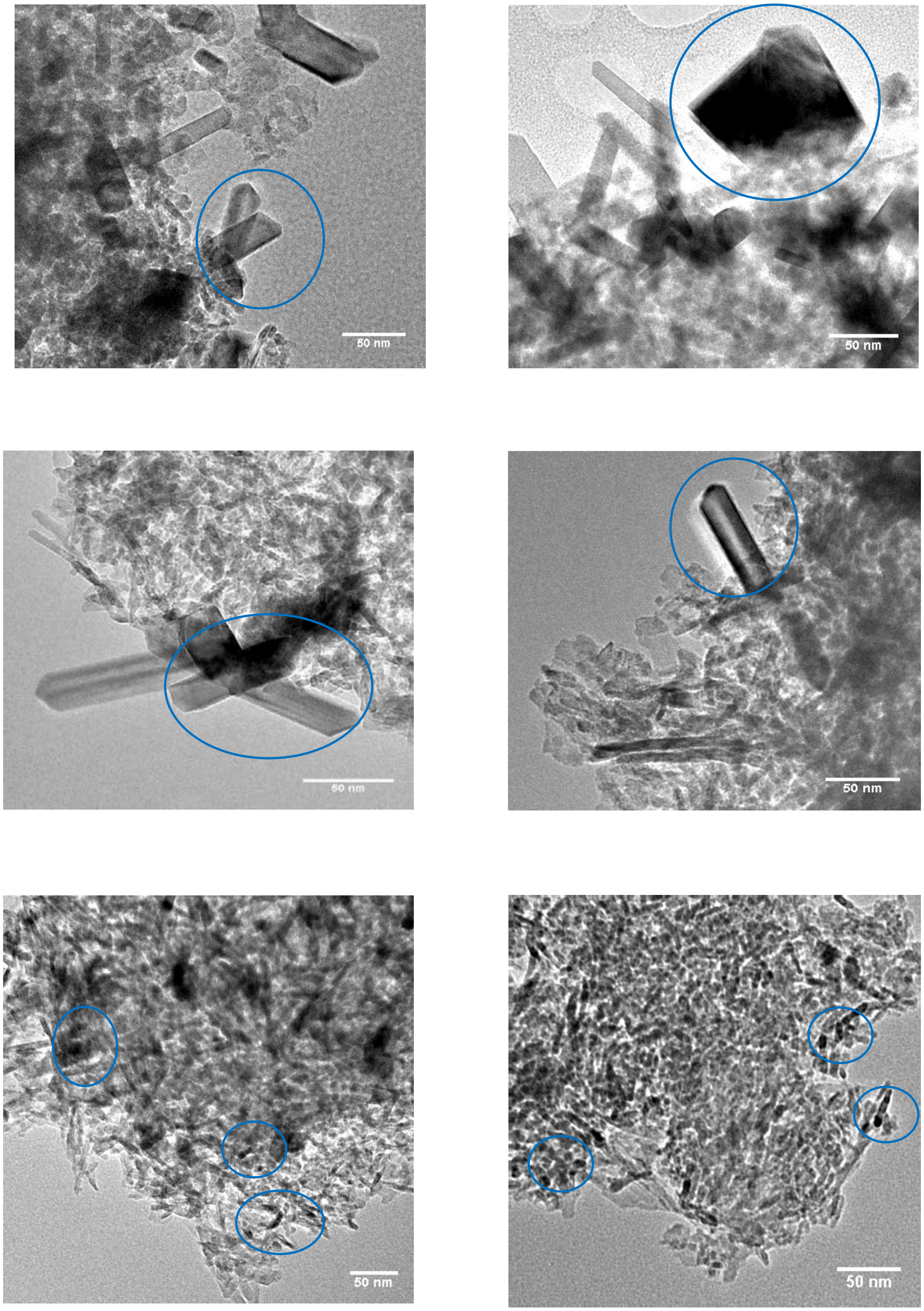


Figure 2.6. High-resolution TEM catalysts images of (up-left) Ru/Al_2O_3 (A1) fresh, (up-right) Ru/Al_2O_3 (A1) used, (medium-left) Ru/Al_2O_3 (A3) fresh, (medium-right) Ru/Al_2O_3 (A3) used, (down-left) Ru/Al_2O_3 (A) fresh, (up-right) Ru/Al_2O_3 (A) used.

Table 2.6. Oxidation of GGGE over different loadings for the Ru/Al_2O_3 (A) catalyst in acetonitrile.

Catalyst	**Conversion (%)** **GGGE**	**Product yield (%)**		
		Guaiacol	**Vanillin**	**Vanillic acid**
Ru/Al_2O_3 (A)	>99	28	11	11
Ru/SiO_2	>99	22	7	10
Ru/Spinel	>99	20	12	8
Ru/HY (6)	>99	15	8	9
Ru/ZrO_2	>99	20	9	8

Reaction conditions: 10 ml (0.017 M GGGE in acetonitrile), 40 mg catalyst (5 wt. % with respect to metal), 160 ˚C, 5 bar (20% Oxygen + Ar), 20 h.
Catalysts prepared using ruthenium(III) chloride hydrate precursor.

Three different precursors were also used for the preparation of Ru/Al_2O_3 catalysts results are shown in Table 2.7. The lowest product yield was obtained by Ru/Al_2O_3 (B) made using ruthenium (III) acetylacetonate as the Ru precursor. An improvement was observed when ruthenium (III) chloride hydrate was used as precursor for the production of the catalyst Ru/Al_2O_3 (A). The yield of guaiacol increase from 24% to 28% when we use Ru/Al_2O_3 (A) instead of Ru/Al_2O_3 (B) and in the case of vanillin and vanillic acid, yields goes from 9% and 3% respectively with Ru/Al_2O_3 (B), to 11% of vanillin and 11% of vanillic acid when Ru/Al_2O_3 (A) was applied. Surprising results were achieved when Ru/Al_2O_3 (C) (made with ruthenium (IV) oxide hydrate) was tested; the yield of guaiacol was improved even further to 34%, and vanillin to 13%. The yield of vanillic acid remained at 11%.

Table 2.7. Oxidation of GGGE over ruthenium catalysts made with different precursors.

Catalyst	**BET surface area (m^2/g)**	**Conversion (%) GGGE**	**Product yield (%)**		
			Guaiacol	**Vanillin**	**Vanillic acid**
Ru/Al_2O_3 (A)[a]	148	>99	28	11	11
Ru/Al_2O_3 (B)[b]	152	>99	24	9	3
Ru/Al_2O_3 (C)[c]	166	>99	34	13	11

<u>Reaction conditions</u>: 10 ml (0.017 M GGGE in acetonitrile), 40 mg catalyst (5 wt. % with respect to metal), 160 ˚C, 5 bar (20% Oxygen + Ar), 20 h.

[a] Catalyst prepared using ruthenium(III) chloride hydrate precursor.

[b] Catalyst prepared using ruthenium(III) acetylacetonate precursor.

[c] Catalyst prepared using ruthenium(IV) oxide hydrate precursor.

In order to understand the discrepancy in activity between the Ru/Al_2O_3 catalysts synthesized with the three different precursors, the catalysts were subjected to surface area measurement and microscopes studies. As shown in Table 2.5 BET surface area of the Ru/Al_2O_3 (A) made with ruthenium(III) chloride hydrate precursor gave approximately 148 m^2g^{-1}, Ru/Al_2O_3 (B) made with ruthenium(III) acetylacetonate precursor displayed 152 m^2g^{-1}, and 166 m^2g^{-1} in the case of Ru/Al_2O_3 (C) made with ruthenium(IV) oxide hydrate. It can be concluded that no significant differences in the surface area of these three catalyst were found. However, a considerable change in the particle sizes of the Ru/Al_2O_3 catalysts was observed from TEM images (Figure 2.7). The microscopic studies showed that Ru/Al_2O_3 (C) contained RuO_x particle between 7 to 60 nm, whereas Ru/Al_2O_3 (A) had less variation in the RuO_x particle size, with particles ranging from 40-60 nm. In the case of Ru/Al_2O_3 (B), the particle size was 5-10 fold larger than Ru/Al_2O_3 (B), ranging from 100-200 nm. This suggested that RuO_x particle size played a significant role in determining the conversion of GGGE to guaiacol, vanillin and vanillic acid, demonstrating the importance of choosing a suitable metal precursor when preparing active Ru/Al_2O_3 catalysts.

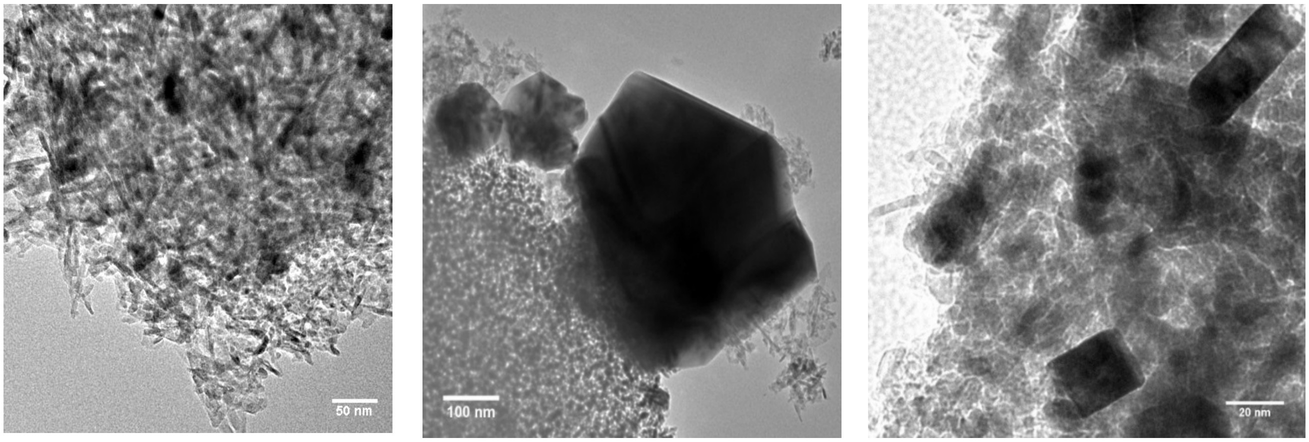
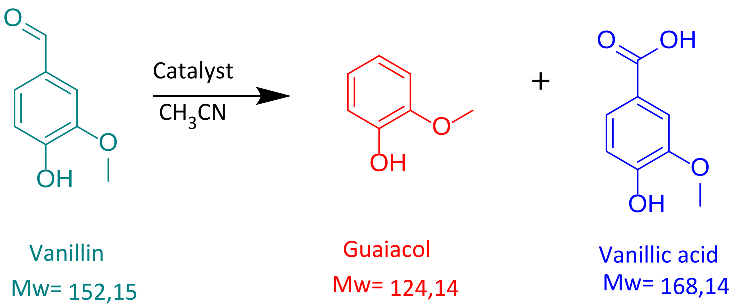


Figure 2.7. High-resolution TEM catalysts images of (left) Ru/Al_2O_3 (A), (middle) Ru/Al_2O_3 (B), and (right) Ru/Al_2O_3 (C).

It is important to emphasize that when determining the mass balance of the reaction, it has been assumed that two molecules of guaiacol are formed per molecule of GGGE used (Scheme 2.3). One of these guaiacol molecules could be formed from vanillin decarbonylation in the reaction, as has been previously reported in the literature [161-162]. In order to verify the possibility of guaiacol production from vanillin a separate experiment was carried out using vanillin as the reagent (Scheme 2.4). Three of the best metal oxide catalyst previously synthesized and tested were used in this study, Ru/Al_2O_3, Mn/Al_2O_3 and Ag/Al_2O_3. Results are shown in Table 2.8.



Scheme 2.4. Aerobic catalytic oxidation of vanillin into guaiacol.

Table 2.8. Vanillin conversion into Guaiacol for Ru/Al_2O_3 (C), Ag/ Al_2O_3 and Mn/Al_2O_3 catalysts.

Catalyst	BET surface area (m^2/g)	Conversion (%) Vanillin	Product yield (%)	
			Guaiacol	Vanillic acid
Ru/Al_2O_3 (C)[a]	166	58	3	6
Mn/Al_2O_3	157	25	<1	<1
Ag/Al_2O_3	164	30	1	<1

Reaction conditions: 30 mg vanillin in acetonitrile, 12 mol % catalyst/substrate, 160 ˚C, 5 bar (20% Oxygen + Ar), 20 h.

[a] Catalyst prepared using ruthenium(IV) oxide hydrate precursor.

The aerobic oxidation of vanillin resulted in poor yields of guaiacol for the three catalysts tested after 20 h of reaction. Ru/Al_2O_3 (C) gave the highest yield to products, with a vanillin conversion of 58 %, however only 3% was converted to guaiacol. Due to the production of guaiacol in the reaction, it was confirmed that the decarbonylation could be achieved with the corresponding ruthenium catalyst.

The influence of the pressure on the catalytic conversion of GGGE using Ru/Al_2O_3 (C) has been analyzed in different atmospheres, and solvents (Table 2.9). The first three experiments (1-3) have been tested in pressure tubes, using water as solvent at 140 ^oC over a 20 hour reaction period. Results showed that in air, argon and oxygen atmospheres, without any added pressure, the catalytic conversion of GGGE to guaiacol, vanillin and vanillic acid was inefficient. The highest yield was produced with an air atmosphere in water, and yielded 22 % of guaiacol and almost no vanillin or vanillic acid. In addition, it was found that without pressure and water as the solvent, no conversion to vanillin or vanillic acid took place, and a very poor yield of guaiacol was achieved. Experiments 4 to 6 were conducted in an autoclave, with acetonitrile as solvent at 160 ^oC. It has been reported in the literature that guaiacol can be formed from the hydrolysis of β-O-4 lignin model compounds similar to GGGE [163]. Therefore, experiment 4 was carried out under 20 bar of argon to examine the product formation in the absence of oxygen. A poor yield of guaiacol (24%), a very poor yield of vanillin (3%) and no production of vanillic acid was obtained. Accordingly, the presence of oxygen was shown to be a requirement for the production of vanillin and vanillic acid, and also improved the guaiacol yield. Consequently, experiment 5 was carried out in air, and experiment 6 in a mixture of 20% oxygen in argon. Results did not show significant differences between these two experiments, as the amount of oxygen in both was approximately equal. In addition, a 34% guaiacol yield, a 13% vanillin yield and a 11% guaiacol yield were achieved with 20% oxygen and argon.

Table 2.9. GGGE conversion over different atmosphere pressure.

Experiment	**Media**	**Solvent**	**Atmosphere**	**Conversion (%)** **GGGE**	**Product yield (%)**		
					Guaiacol	**Vanillin**	**Vanillic acid**
1	Press. tube	H_2O	Air	>99	22	1	<1
2	Press. tube	H_2O	Ar	>99	12	<1	<1
3	Press. tube	H_2O	O_2	>99	15	<1	<1
4	Autoclave	CH_3CN	20 bar Ar	>99	24	3	<1
5	Autoclave	CH_3CN	5 bar Air	>99	32	11	11
6	Autoclave	CH_3CN	5 bar (20% O_2)	>99	34	13	11

Reaction conditions: Ru/Al_2O_3 (C) made with ruthenium(IV) oxide hydrate precursor. 12 mol % catalyst/substrate

$^{1, 2, 3}$ 3 g GGGE , 140 ˚C, 20 h.

$^{4, 5, 6}$ 10 ml (0.017 M GGGE), 160 ˚C, 20 h.

The effects of reaction temperature on the formation of guaiacol, vanillin and vanillic acid was studied in the range 120 to 200 ^{o}C, and the results are shown in Figure 2.8. The conversion of GGGE increased gradually in the range of 120 – 160 ^{o}C, to full conversion. In the temperature range from 120 to 160 ^{o}C, the effect on yield is significant. The maximum product yield was obtained at 160 ^{o}C. When the temperature increased to 180 ˚C and 200 ˚C, full conversion of GGGE was observed, but the yield of products decreased significantly due to the possible deactivation of the Ru/Al_2O_3 (C) catalyst at higher temperatures. The temperature affects the yield in two opposite ways. On the one hand, the conversion of GGGE increased with increasing temperature, which was favorable for enhancing the yield of the products. On the other hand, elevating the temperature above 160 °C also promoted the deactivation of the catalyst and could also promote the occurrence of side reactions. The competition of these two factors resulted in the maximum yield of guaiacol (34 %), vanillin (13%) and vanillic acid (11%) being achieved at 160 °C.

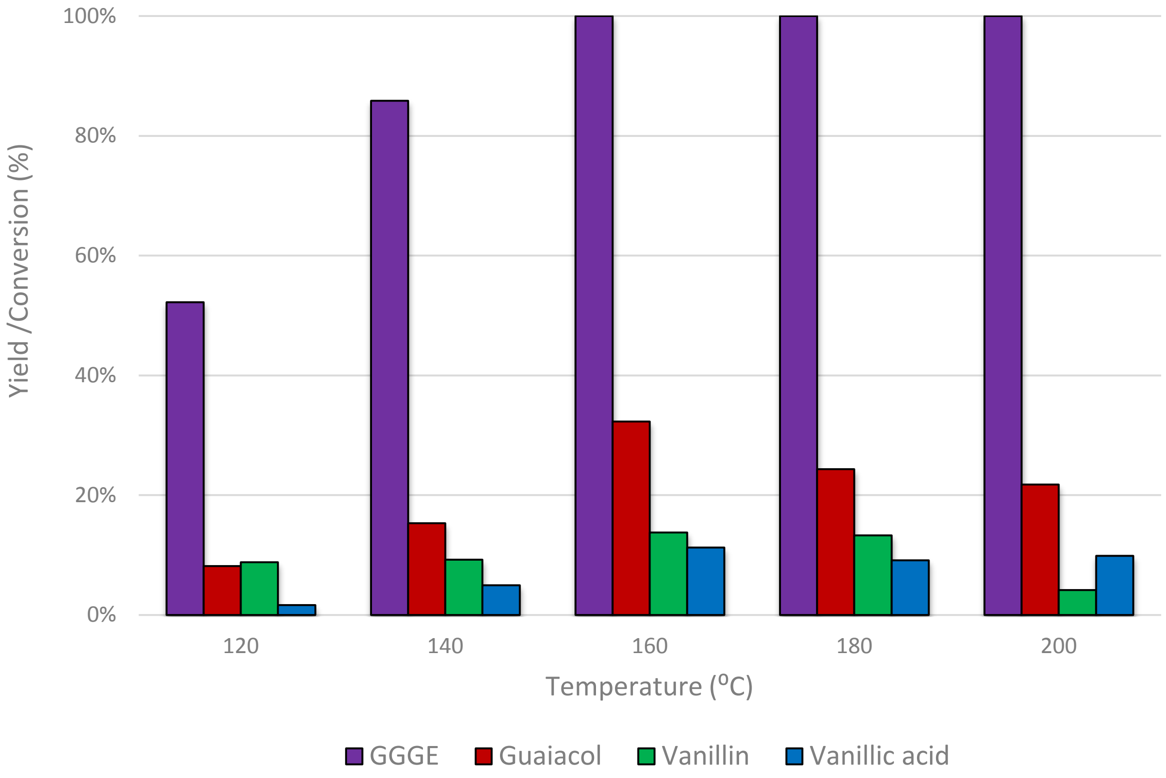


Figure 2.8. Temperature study for GGGE conversion into with Ru/Al_2O_3 (C).
Reaction conditions: 10 ml 0.017 M GGGE solution in CH_3CN; 40 mg catalyst (5 wt. % metal), 20 h, 5 bar (20 % O_2 + Argon). Each set of data on the time axis is from individual experiments.

In order to examine in more details the way in which guaiacol, vanillin and vanillic acid formation develop during the reaction with Ru/Al_2O_3 (C) in acetonitrile, the reaction time was prolonged to 30 h, and the results are summarized in the time-course study on Figure 2.9. The results showed that good yields of guaiacol (34%), vanillin (13%) and vanillic acid (11%) were reached after about 20 h of reaction. The time-course study further revealed that at least 4 hours were needed for the production of vanillic acid to be observed. Furthermore, If the reaction time was increased to 30h, the yield of products declined dramatically, in the case of guaiacol to 21% vanillin to 11% and vanillic acid to 7 %, possibly, due to the occurrence of side reactions and the formation of byproducts, such as quinone and acetic acid, which are decomposition products, detected in the analysis by NMR after reaction. However, due to the low amount of these products comprehensive analysis could not been obtained and reliable quantification of the yields of these products could therefore not be carried out.

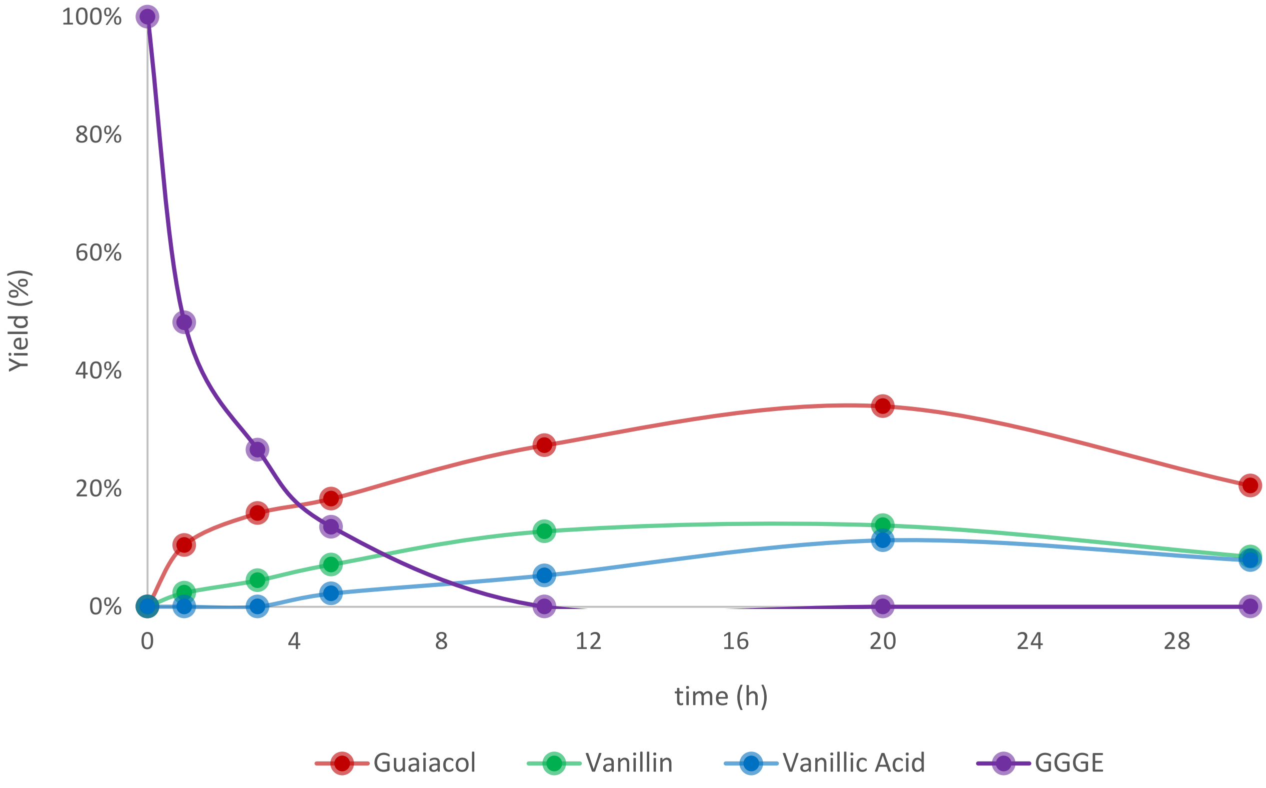


Figure 2.9. Time-course study for GGGE conversion into with Ru/Al_2O_3(C).
Reaction conditions: 10 ml 0.017 M GGGE solution in CH3CN; 40 mg catalyst (5 wt. % metal), 160°C, 5 bar (20% oxygen + argon). Each set of data on the time axis is from individual experiments.

Catalyst recyclability is important for the viability of a catalyst system. Accordingly, the Ru/Al_2O_3 (C) catalyst was subjected to reuse studies in the GGGE oxidation reaction (Figure 2.10). After each run, the catalyst was recovered by filtration, thoroughly washed with acetonitrile, dried overnight at 60 ˚C, and finally calcined at 450 ˚C for 6 h before being used in the next reaction.

The results shown in Figure 2.10 indicate a slight loss of catalyst performance after the fifth reaction run, resulting in a decrease in the guaiacol yield from 34 to 30%, with vanillin yield reduction from 13 to 7% and vanillic acid from 11 to 6%. Part of the loss of catalytic activity could be due to loss of catalyst during the separation or due to the increase in the Ru particle size during the additional calcinations, as previous observed for supported Ru catalysts [149].

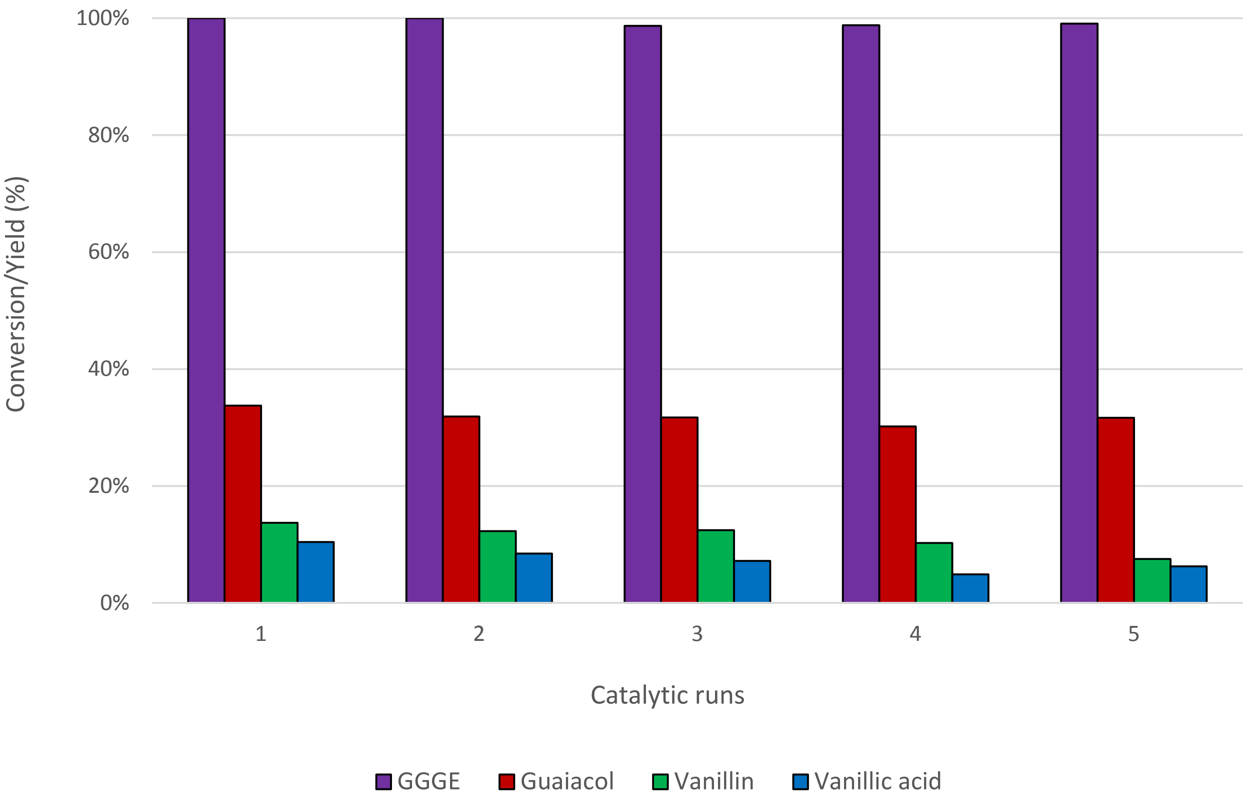


Figure 2.10. Reuse of Ru/Al_2O_3 (C) catalyst for five consecutive GGGE oxidation reaction in acetonitrile. Reaction conditions: GGBGE to catalyst mass ratio: 1.30, solvent: acetonitrile, 160 ºC, 20 h, 5 bar (20% O_2 + Ar).

The used Ru/Al_2O_3 (C) catalyst was subjected to TEM studies, and the results are displayed in Figure 2.11. As expected, the Ru/Al_2O_3 (C) contain relative larger nanoparticles, with defined straight edges, after five consecutive runs. Hence, the used catalyst appeared to contain larger nanoparticles and with less variation in length than the ones found in the fresh one. RuO_x particle sizes for the fresh catalyst ranged from 7-60 nm, and after five runs from 30 to 100 nm. The differences in RuO_x particles may have affected the catalyst activity for the GGGE conversion, in the same way as was observed for the Ru/Al_2O_3 catalysts made from different precursors.

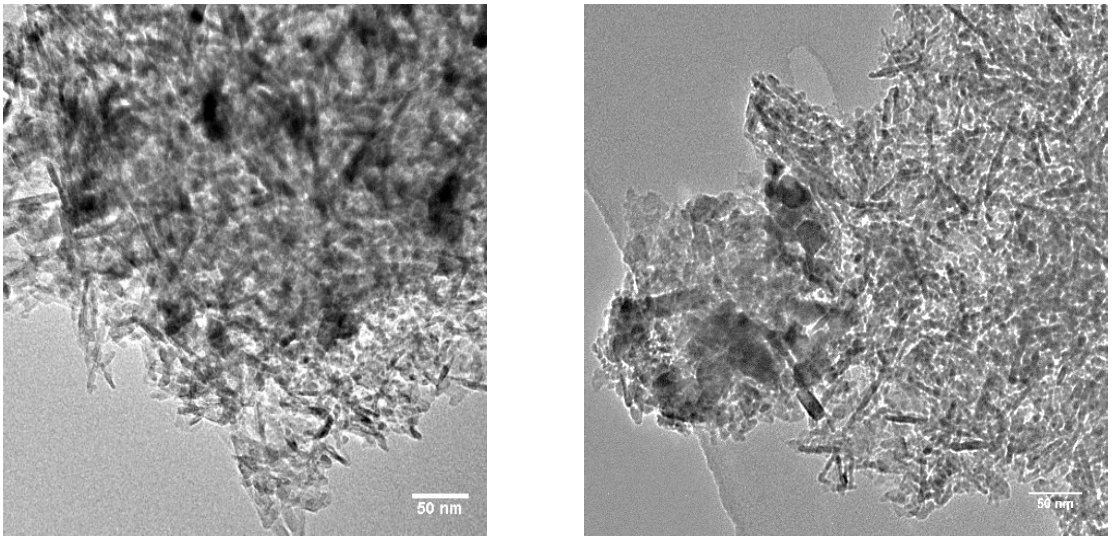


Figure 2.11. High-resolution TEM catalysts images of (left) Ru/Al_2O_3 (C) fresh, and (right) Ru/Al_2O_3 (C) after 5 uses.

2.4 Summary

Two different β-O-4 lignin model compounds (VA and GGGE) were tested in an oxidation reaction and attempted converted into high-value chemicals, such as VAld (useful flavorant and odorant), guaiacol (precursor to various flavorants, such as eugenol and vanillin, and medically used as expectorant, antiseptic and local anesthetic), vanillin (flavoring agent, vanilla, in foods, beverages and pharmaceuticals) and vanillic acid (food additive).

Different catalysts containing transition metals (Mn, Co, Cu, Ag and Ru) supported on Al_2O_3 and SiO_2 have been tested in the oxidative transformation of veratryl alcohol (VA) in a batch reactor. The Ru/Al_2O_3 catalyst prepared with ruthenium (IV) oxide hydrate showed superior catalytic activity, yielding 89% VAld in water at 160 ^{o}C with 5 bar air pressure after an 8-hour reaction. Prolonged reaction times led to the formation of the by-product, veratrol, from the decarbonylation of VAld. When the reaction was completed with methanol as solvent under 20 bar of argon, the VA-ether prevailed, yielding 36% and indicating that methanol helped to prevent the oxidation of the hydroxyl group in VA. The Ru/Al_2O_3 catalyst, prepared with ruthenium (IV) oxide hydrate was reused in three consecutive runs in water, but a decrease in VAld yield was obtained after the third cycle, possibly due to leaching of Ru from the support. The unsatisfying recyclability is a major drawback as a water-tolerant and stable supported catalyst is needed for the implementation of the Ru/Al_2O_3 catalyst in more complex lignin model compounds and lignin valorization.

The catalytic oxidative transformation of guaiacyl glycerol-β-guaiacyl ether (GGGE), a dimeric β-O-4 lignin model compound, to produce simpler aromatic compounds (guaiacol, vanillin and vanillic acid) using metal supported catalysts was further examined in a bath reactor with acetonitrile as solvent. The Ru/Al_2O_3 catalyst, prepared using ruthenium (IV) oxide hydrate gave the highest yields of guaiacol (34%), vanillin (13%) and vanillic acid (11%) with full conversion of GGGE in acetonitrile at 160 ^{o}C under 5 bar of 20% oxygen in argon. Analogous catalysts prepared with ruthenium (III) chloride hydrate and ruthenium (III) acetylacetonate gave lower product yields, which could be correlated to the RuO_x particle size measured by

TEM. A large variation in the RuO_x particle size was observed for the catalysts prepared with ruthenium (III) chloride hydrate, whilst large particles were found in the Ru/Al_2O_3 catalysts made with ruthenium (III) acetylacetonate. Different loadings of Ru/Al_2O_3 catalyst were examined and the yield of products increased with ruthenium loading. Catalyst containing other transition metals (Ag, Fe, Mn, Co and Cu) supported on alumina, and ruthenium catalysts based on alternative supports (silica, spinel, HY (6) and zirconia) gave significantly lower activities compared to Ru/Al_2O_3 catalysts when using identical reaction conditions. The Ru/Al_2O_3 catalyst, prepared with ruthenium (IV) oxide hydrate was used in five consecutive reaction runs in order to test its recyclability, demonstrating that the catalyst is easy to regenerate and recycle.

Future work concerning catalyst optimization may involve the development of Ru/Al_2O_3 catalysts that display higher activity and selectivity, and a process which results in less Ru loss during the reaction.

Chapter 3

3

Organosolv process for wood depolymerization

Abstract.

This chapter describes the use of an environmentally friendly process, the organosolv process, for treating lignocellulosic biomass in the presence of a solvent and using reaction conditions under which at least part of the lignin is separated from the biomass. The solvent (ethanol-water) ratio, and the use of different catalysts and temperatures have been studied in order to optimize the organosolv process for the delignification of birch and beech sawdust (hardwood) and subsequent production of high-quality lignin for further upgrading.

3.1 Introduction.

The organosolv process, as described in *Chapter 1*, is a chemical process that can be used to separate lignin and other useful materials from biomass. The organosolv process typically involves the use of organic solvents at high temperature and pressure, in order to separate the fibers contained in lignocellulosic materials. In general terms, the organosolv process involves boiling the raw material in a solution or bleach, in order to solubilize a great part of lignin, causing fibers to disintegrate, and be released in a suspended form. In addition, the organosolv process has a low environmental impact as the recovery of solvents is simple, and the process is operated in the absence of sulfur compounds, in contrast to other processes such as kraft lignin or lignosulfonates [60-67].

The solvents used are varied: ethanol, methanol, other aliphatic alcohols, aromatic alcohols, ketones, carboxylic acids, or amides. The use of methanol and ethanol are of great interest because of their lower cost, high volatility and the attractive properties obtained in the resulting lignin.

Organosolv processes can be classified as acidic or basic, depending on the pH of the reaction medium [164].

Acidic media.

The simplest organosolv processes are carried out at neutral pH. High temperatures cause hemicellulose degradation into organic acids (mainly acetic acid) that acidify the medium to a pH between 3 and 4. These processes are autocatalyzed. The acidic environment causes breakdown of the polysaccharides and lignin monomers. However, these autocatalyzed processes offer good delignification only for hardwood pulps and herbaceous angiosperms [165].

Some methods typically focus on the addition of strong inorganic acids such as H_2SO_4 or HCl, as catalyst. This increases the acidity of the system, leading to a reduction in the temperature and pressure required to obtain good delignification. The recovery of the solvents in the process is simple (Figure 3.1) [165-166].

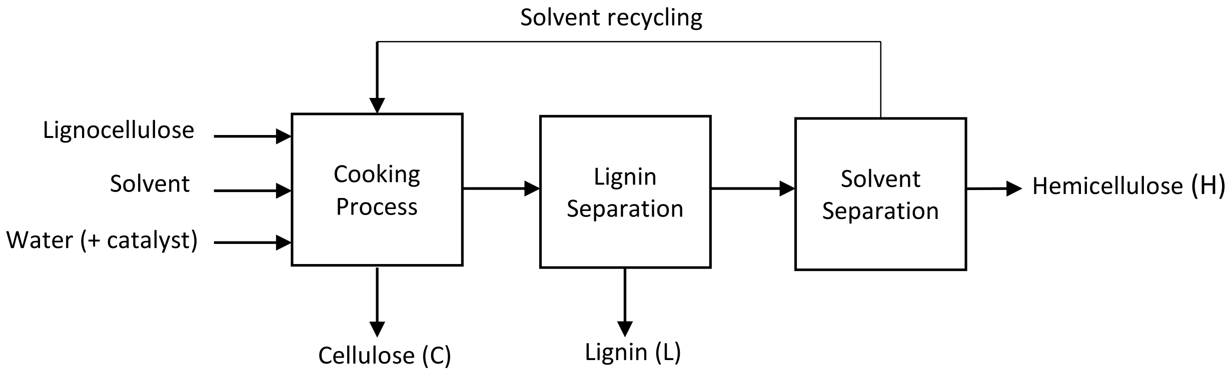


Figure 3.1. Fractionation of lignocellulosic biomass by organosolv process [166]

The best-known autocatalyzed process is the Alcell Process, which uses a 50% v/v ethanol/water mixture. The operating temperature is around 195 – 200 ^{o}C, with a process time of 60 min and a liquid/solid ratio of 6:1 to 7:1. The Alcell process is especially applicable for hardwood, but also to bagasse and straw [60, 166].

Lignin exhibits better solubility in pure solvents (alcohol), but organic solvent-water mixtures provide higher delignification. This is because some water is needed to force the acidification of the medium released by dissociation of the acid. Acidification of the medium will be more pronounced the larger the ratio of water with respect to the acid.

Excess acidity can cause hydrolysis of the polysaccharides and thus a loss of selectivity, yield and viscosity, besides giving rise to condensation and subsequent precipitation of the dissolved lignin pulp, causing the so called redeposition [164-166].

Alkaline media.

These processes can be considered as variants of the conventional alkaline processes (lignosulphonate, Kraft, soda pulping) in which different proportions of organic solvents have been introduced [166]

One example of an alkaline organosolv-process is the Organocell process, which uses methanol (5-30 vol. %) and soda (17-20 vol. %) in a first step, followed by a second step using anthraquinone (0,1 vol. %). This process, unlike the Alcell process, is applicable to softwood. Typically, the reaction requires temperatures between 155 and 170 ^{o}C, with a process time of 60-120 min and a liquid/solid ratio of about 4:1 [62].

The main advantage of alkaline over acidic processes is that they are effective for the treatment of softwoods as well as hardwoods, but solvent recovery is more complex since the alkali used must be retrieved [166].

This section of the thesis focuses on the optimization of an acidic organosolv process, similar to the Alcell process. As part of the process optimization, different inorganic acids have been tried as catalysts, as well as different ethanol-water ratios, liquid-solid ratios and reaction temperatures. The aim of the process optimization was to optimize the degree of delignification and produce a better quality lignin product, based on the ratio of binding of β-O-4 and phenylcoumaran to resinol.

3.2 Experimental.

3.2.1 Materials.

All chemicals were purchased from Sigma-Aldrich as received, and without further purification unless otherwise specified. Birch sawdust was provided by Dalian Institute of Chemical Physics (DICP), China, as a generous gift. Beech sawdust was acquired from Dansk Træmel. Compressed nitrogen (>99.99%) and argon (> 99.99%) were purchased from Air Liquide, Denmark.

3.2.2 Characterization techniques.

NMR spectroscopy

^{1}H-^{13}C HSQC NMR spectra were recorded on an 800 MHz Bruker (Fällanden, Switzerland) Avance spectrometer. Sensitivity enhanced ^{1}H-^{13}C HSQC spectra were acquired with narrow spectral width in the indirect dimension using the standard Bruker pulse sequence.

Lignin (40 mg) or reaction mixture was dissolved in 0.5 mL of DMSO-d6. The spectra were interpreted according to values published in the excellent report by Wen et al. [167]. The signal intensity before and after treatment of the lignin material were normalized relative to the signal the of protons in the aromatic region (δF1 = 100-125 ppm, δF2 = 7.5- 6.0 ppm) as the intensity of the aromatic protons was expected to remain unchanged during the cleavage reaction. Analysis was performed according to Bolm et al. [168], with minor modifications. For the quantification of the bond types present in the material, the following signals were used: Aα, Aβ, Aγ, Bα, Bβ, Bγ, Cα, Cβ, and Cγ (Figure 3.2)

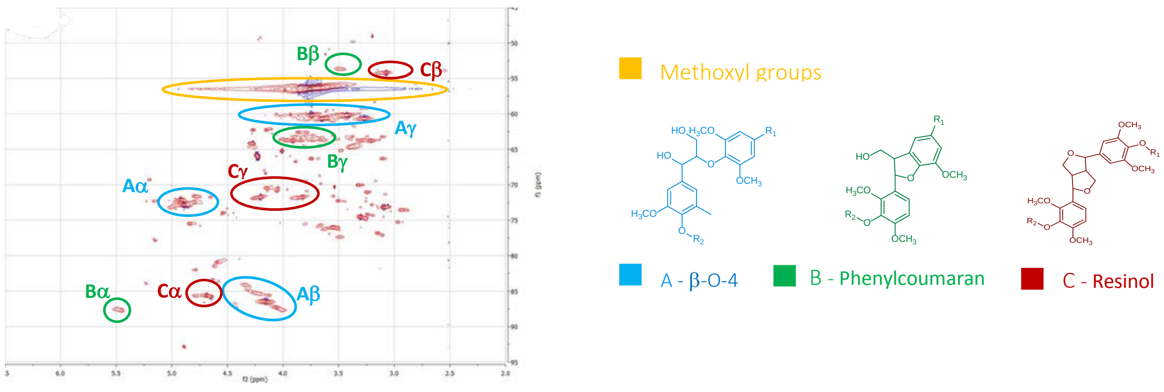


Figure 3.2. 2-D NMR spectrum (HSQC experiment) for organosolv lignin (A1). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure.

3.2.3 Modified Organosolv process procedure

The raw materials were dried at 60 ^{o}C under vacuum for 48 h. The desired amount of wood was then dispersed in the solvent and charged to an autoclave (Microclave 50 ml reactor, Autoclave Engineers). The reactor was pressurized with argon (20 bar) or nitrogen (20 bar). The mixture was then heated to the required temperature (over 30 min heating program) and maintained at that temperature for 200 minutes with mechanical stirring (300 rpm). After the reaction, the autoclave was quenched in cold water and cooled down to room temperature. The suspension obtained was filtered and the solid washed three times with a 20 mL portion of the solvent used in the reaction.

The reaction filtrate was stirred slowly, and twice the volume of water was added to the solution, causing the precipitation of light yellow floccules. The precipitate was centrifuged and dried at 60 ^{o}C under vacuum for 24 hours. All the components were weighed and analyzed.

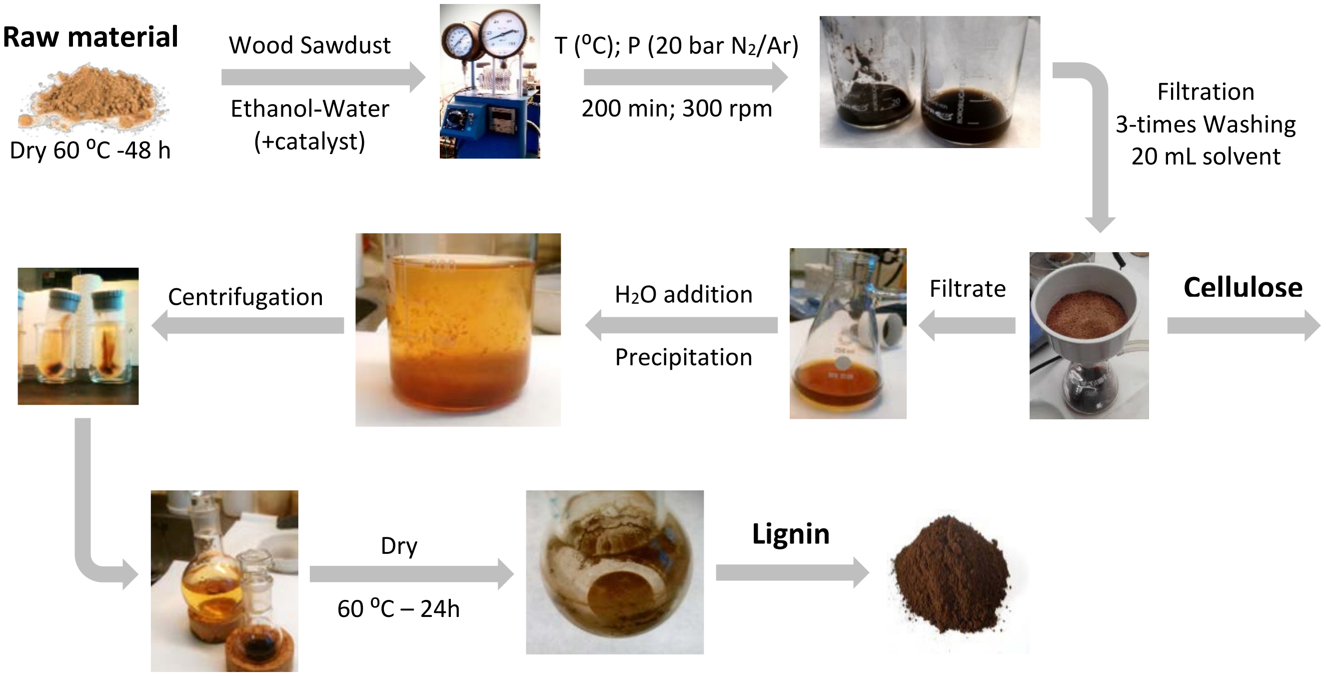


Figure 3.3. Scheme of the organosolv procedure followed.

3.3 Results and discussion.

Two different kinds of wood, birch (A1) and beech (A2) sawdust were subjected to the organosolv process, in the absence of a catalyst, using 30 mL solvent (50% ethanol, 50% water) at 180 ^{o}C., with a solid/liquid ratio of 1/16. Results are shown in Table 3.1. The amount of each of the main components of lignocellulosic biomass obtained after wood depolymerization was measured by weight, and the percentages of cellulose, hemicellulose and lignin were calculated with respect to the weight of wood used. Figure 3.4 shows 2D-NMR spectra of the organosolv lignin extracted from birch sawdust (A1) and beech sawdust (B1). The spectra showed that the carbohydrate content was very low. Birch sawdust (A1) gave 56 wt. % cellulose, 22 wt. % hemicellulose and 8 wt. % lignin. When beech sawdust (B1) was used, the percentage of lignin acquired decreased significantly to 3%. However, literature reports state that the maximum lignin percentage contained in beech wood is 21% and around 30% in birch wood [169]. Despite the major differences obtained in lignin yield from the delignification of these two types of wood, it was decided to continue using beech wood for this thesis, as it comes from Denmark, and is therefore easier to obtain.

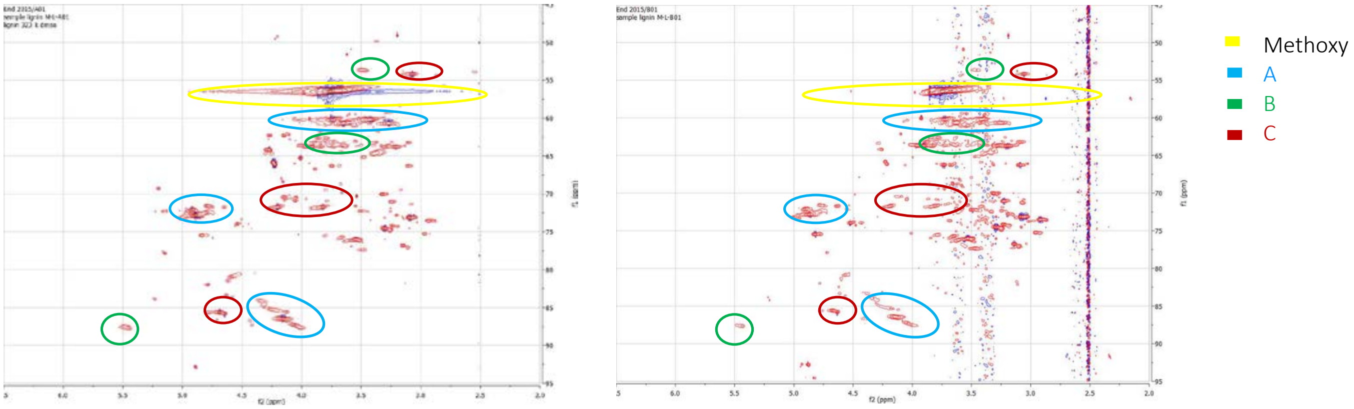


Figure 3.4. 2-D NMR spectrum (HSQC experiment) for A1 organosolv lignin (left) and B1 organosolv lignin (right). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure.

Table 3.1. Results of different organosolv procedures. Changing in ethanol-water ratio, and catalyst.

Experiment	Type of wood	Solvent EtOH/H_2O (vol. %/vol. %)	Catalyst	Total wt. % from wood			Ratio of binding A : C : B
				Cellulose	Hemicellulose	Lignin	
A1	Birch	50/50	-	56	22	8	3.62 : 1 : 0.85
B1	Beech	50/50	-	60	29	3	3.06 : 1 : 0.90
B2	Beech	50/50	H_2SO_4	53	30	7	3.22 : 1 : 0.83
B3	Beech	60/40	H_2SO_4	57	27	8	3.43 : 1 : 0.79
B4	Beech	80/20	H_2SO_4	79	18	1	2.01 : 1 : 0.49
B5	Beech	60/40	Acetic Acid	60	30	3	3.26 : 1 : 0.85

Reaction conditions: 5 g of Dry wood, 30 ml solvent. The mixture was heating to 180 ˚C (30 min heating program) and maintained for 200 min at 300 rpm, 20 bar Argon

Catalyst 0,0005M H_2SO_4; 0.5 mM acetic acid.

Ratio of binding: A:C:B represents β-O-4 : Resinol : Phenylcoumaran

Experiments B1 and B2 were conducted using beech sawdust with 30 mL solvent (50 vol. % ethanol, 50 vol. % water) at 180 ^{o}C, and a solid/liquid ratio of 1/16 (Table 3.1). H_2SO_4 was added during experiment B2 in order to increase the acidity of the system and facilitate the delignification process. As expected, when H_2SO_4 was present in the system, the percentage of lignin increased from 3 to 7 wt. %. Analysis of the NMR spectra (Figure 3.5.) showed that the carbohydrate component was consistently very low. NMR analysis also provided information regarding the amount of binding in lignin, as the proportion of β-O-4 groups was higher for experiment B2 (3.22) than B1 (3.06).

The β-O-4 ratio of binding is of great importance for subsequent lignin upgrading processes, as shown in *Chapter 2 of this thesis* in which β-O-4 lignin model compounds have been used. The use of H_2SO_4, as catalyst in the organosolv process demonstrated a significant improvement in the delignification of beech wood. For this reason, it was decided to continue to use H_2SO_4 as catalyst in the organosolv process, and vary the ethanol-water ratio in order to improve the delignification process for the beech sawdust. Three different ratio (vol. %/vol. %) of ethanol-water were tested, 50/50 (B2), 60/40 (B3) and 80/20 (B4), and the 2D-NMR spectra from organosolv lignin extracted over H_2SO_4 are showed in Figure 3.5. The carbohydrate content was very low, as can be seen in the correspondent 2D-NMR spectra. The lowest amount of lignin (1%) was obtained by using 80 vol. % ethanol. The cellulose content in experiment B4 was 79%. As seen previously in *Chapter 1* of this thesis, the maximum cellulose content in woody plants is around 50 to 60 %. Results shown in Table 3.1 suggest that not all the lignin has been extracted meaning an amount of the lignin fraction has been retained in the cellulose component, suggesting that the ratio of solvent used (80 vol. % ethanol) was not adequate for complete lignin extraction. The amount of lignin extracted increased significantly to 8 wt. % when 60 vol. % ethanol was applied, and no great difference was observed when 50 vol. % ethanol was used (7% lignin). When the NMR spectra for experiments B2 and B3 (Figure 3.5) were compared, the ratio of β-O-4 binding increased from 3.22 for B2 to 3.44 for B3. The use of acetic acid instead of sulfuric acid was tested with 30 mL solvent (60 vol. % ethanol, 40 vol. % water) at 180 ^{o}C, and a solid/liquid ratio of 1/16; results are shown in experiment B5 (Table 3.1 and Figure 3.5). Acetic acid (B5), had a lower delignification power than sulfuric acid (B3). Only 3 wt. % of lignin was obtained, a small amount compared to the 8% achieved when using H_2SO_4. The β-O-4 binding ratio in experiment B5 (3.26) showed no improvement over that of experiment B3 (3.43), demonstrating that H_2SO_4 was a better option for the delignification of beech sawdust.

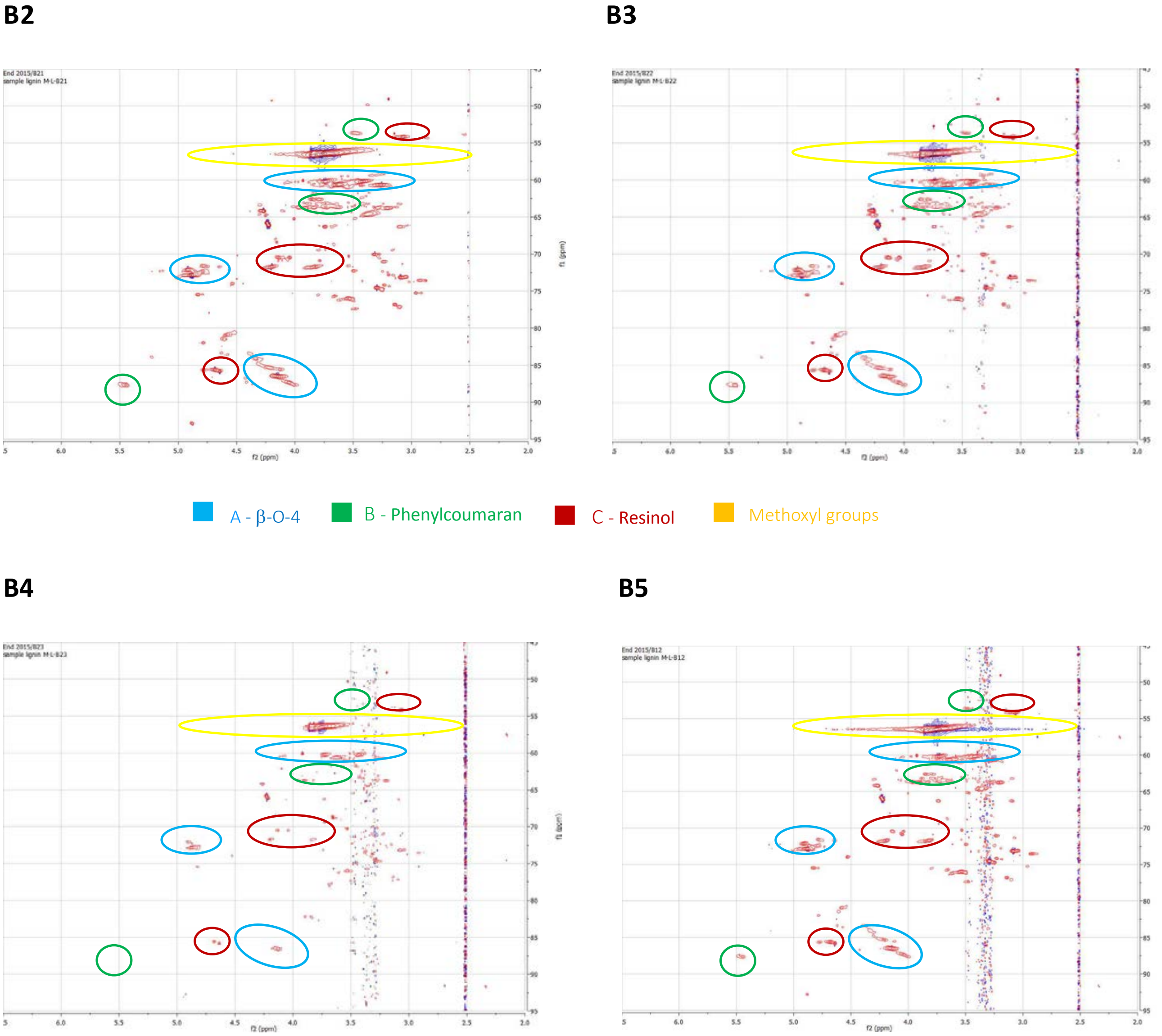


Figure 3.5. 2-D NMR spectrum (HSQC experiment) for organosolv lignin over H_2SO_4: B2 (top-left), B3 (top-right) and B4 (bottom-left), and for organosolv lignin over Acetic acid B5 (bottom-right). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

The process was scaled up from 5 to 50 g of beech wood. Table 3.2 shows the results of the larger scale experiments using 0.5 mM H_2SO_4 as catalyst, with 60 vol. % ethanol, 40 vol. % water as solvent with a 200 min reaction period under 20 bar of nitrogen. The ratio of solid/liquid and the temperature were varied in order to study their effect on the organosolv treatment. Figure 3.7 shows 2D-NMR spectra from organosolv lignin extracted in the scaled up process. The spectra showed that the carbohydrate content was very low.

Experiment C2 and C3 can be used to compare the effect of the solid/liquid ratio (m/v) on the lignin yield. Experiment C2, which used 1/6 solid/liquid ratio (m/v) produced 17 wt. % of lignin after the organosolv process. In experiment C3, only 14 wt. % of lignin was obtained when a 1/12 ratio solid/liquid (m/v) was used. Nonetheless, when the ratio of binding in experiments C2 and C3 were compared, it was discovered that C3 showed a higher ratio of β-O-4 binding (3.24) than C2 (3.03). Hence, the ratio of solid/liquid (m/v) was kept at 1/12, and temperature was varied from 160 to 200 ^{o}C; Table 3.2, experiments C1, C2 and C3.

In experiment C1 a temperature of 200 ^{o}C was used for the organosolv treatment. 13 wt. % of lignin was obtained from this reaction, with a β-O-4 ratio of 2.90 and a phenylcoumaran ratio of 0.62, attained from the NMR spectrum (appendix). When the temperature was reduced to 180 ^{o}C (C3), the amount of lignin increased to 14 wt. %, and the ratio of β-O-4 binding improved to 3.24, while the ratio of phenylcoumaran decreased to 0.49. Experiment C4 was carried out at 160 ^{o}C, and resulted in a low yield of lignin of only 9%. However, when the ratio of binding was analyzed (appendix), it was found that a significant improvement in the β-O-4 binding ratio was achieved (3.68), with a decrease in the ratio of phenylcoumaran to 0.38.

Lignin C2 gave the highest amount of lignin (17 wt. %) and lignin C4 presented the highest β-O-4 ratio of binding of all the lignin polymers obtained from the organosolv treatment developed. Therefore these lignin materials were selected for use in further studies of lignin depolymerization (*Chapter 4*).

Table 3.2. Scale-up organosolv process. Optimization of temperature and solid/liquid ratio.

Experiment	**Temperature (°C)**	**Solid/Liquid Ratio (m/v)**	**Lignin (wt. %)**	**Ratio of binding** **A : C : B**
C1	200	1/12	13	2.90 : 1 : 0.62
C2	180	1/6	17	3.03 : 1 : 0.79
C3	180	1/12	14	3.24 : 1 : 0.49
C4	160	1/12	9	3.68 : 1 : 0.38

Reaction conditions: 50 g of Dry beech wood with ethanol-water 60/40 v/v. The mixture was heating to T ˚C (30 minutes heating program) and maintained for 200 min at 300 rpm, 20 bar Nitrogen Catalyst 0.5 mM H_2SO_4

Ratio of binding: A:C:B represents β-O-4 : Resinol : Phenylcoumaran

The lignin materials obtained in the larger scale organosolv experiments had different colors and textures, as can be seen in Figure 3.6. However, no link could be made between the appearance of the lignin material obtained and the reaction conditions used.

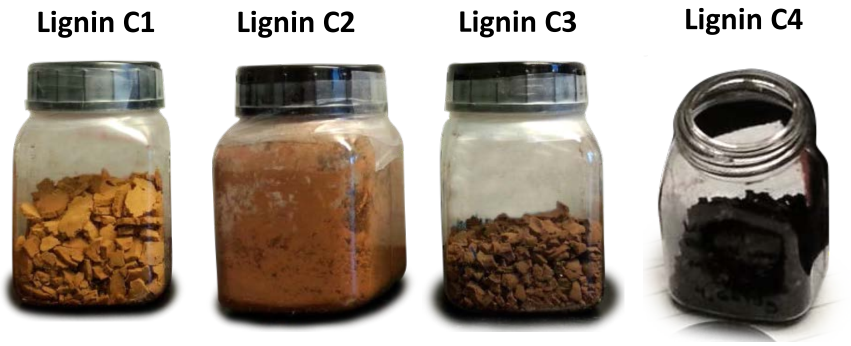


Figure 3.6. Organosolv lignin obtained from C1 to C4.

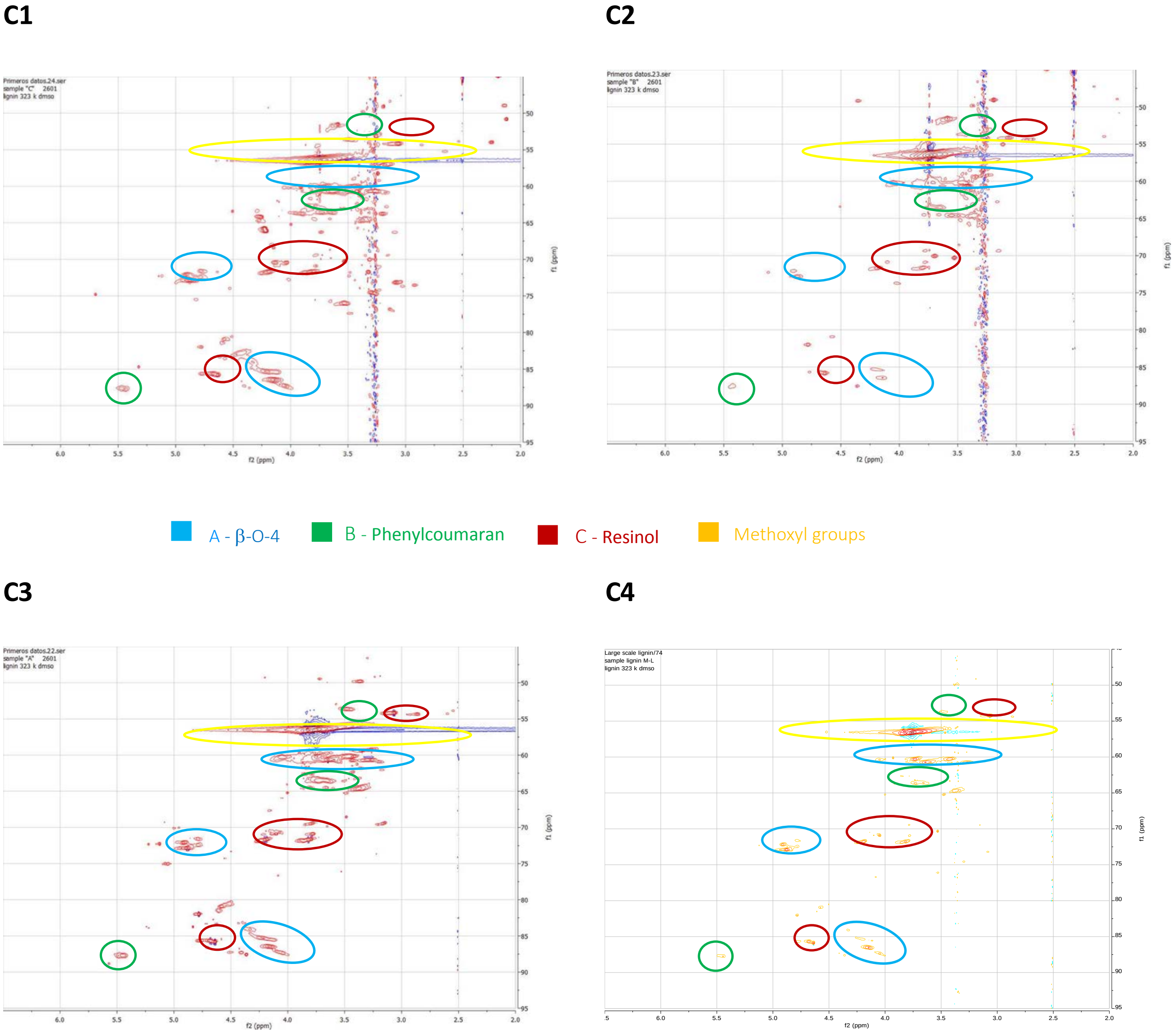


Figure 3.7. 2-D NMR spectrum (HSQC experiment) for the organosolv lignin obtained in the scale-up processes: C1 (top-left), C2 (top-right), C3 (bottom-left) and C4 (bottom-right).

The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

3.4 Summary

Two different kinds of wood have been used in the organosolv treatment. Birch sawdust gave the highest amount of lignin and a better ratio of β-O-4 binding than beech sawdust. However, beech sawdust was chosen for use in further experiments due to its higher availability in Denmark. Different organosolv pretreatment parameters have been tested for beech sawdust in the process, including catalyst, ratio of ethanol-water, temperature and ratio of solid-liquid.

The highest amount of lignin (17% wt. %) was obtained in an organosolv process using 0.5 mM H_2SO_4 as catalyst, with 60 vol. % ethanol, 40 vol. % water as solvent, a reaction time of 200 min and a pressure of 20 bar of nitrogen, with a solid/ liquid ratio of 1/6 at 180 ^{o}C. The β-O-4 ratio of binding was improved to 3.68 when the temperature was changed to 160 ^{o}C, and the solid/liquid ratio to 1/12.

Chapter 4

4

Organosolv lignin oxidation and hydrogenolysis

Abstract.

This chapter describes a catalytic process for the valorization of lignin (C2 and C4 organosolv lignin as described in chapter 3) using a mixture of methanol (80 vol. %) and water. A two-step catalytic system was tested for the organosolv lignin produced: catalytic oxidation, followed by hydrogenolysis. A catalytic system was found for lignin hydrogenolysis and the influence of the temperature and reaction time was studied for the catalytic oxidation of lignin.

4.1 Introduction.

Currently, over 98% of lignin is burned as a source of energy [170]. While the small scale production of low-value lignin products exists (epoxy resins, polyurethane foams, circuit boards, dispersants, car brakes, etc.), the absence of high-value commercial products is mainly due to the large heterogeneity of the lignin molecular structure and the lack of efficient methods for its valorisation. Nevertheless, lignin is regarded as the only renewable source for the production of high-volume aromatic compounds for the chemical industry [72-81]. Considering that over 70 million tons of lignin are produced annually, accrued as a byproduct in the manufacture of pulp, the fact that lignin does not compete in the production of food is highly advantageous, as it does not cause detrimental social or ecological consequences. Furthermore, the declining oil resources have made the conversion of lignin into high-volume and low-molecular weight aromatic compounds a subject of worldwide scientific interest [54].

Heterogeneous catalytic oxidation reactions can help in the production of the more complex platform aromatic compounds with additional functionalities, coupled with easy product separation. Moreover, hydrogenolysis of lignin is one of the most promising methods for lignin depolymerization, producing high yields of phenols. However, the majority of academic research work is focused on the oxidation and hydrogenolysis of model compounds, so more studies should be conducted using native lignin. Obtaining useful chemicals from lignin is challenging due to its high level of complexity compared to the simplest model compounds previously studied (see *Chapter 1* and *2*).

Establishing a process for lignin valorization that could be directly adapted to the biorefineries currently in operation represents a real challenge. Thus, this chapter intends to explore alternative technologies, that have not been previously applied to catalytic lignin valorisation. In this respect, a two step catalytic process has been developed, involving the oxidative depolymerization of lignin followed by hydrogenolysis of the oxidation products obtained.

Ni supported on silica (Ni/SiO_2), mordenite (Ni/HMOR) and magnesia (Ni/MgO) have been prepared and tested in the hydrogenolysis of organosolv lignin (*Chapter 3*) with H_2 in a mixture of methanol (80%) and water.

The efficiency of RuO_x supported on γ-alumina (Ru/Al_2O_3), silica (Ru/SiO_2), zirconia (Ru/ZrO_2), spinel (Ru/Spinel), mordenite (Ru/HMOR) and HY(6) (Ru/HY(6)) has been tested for organosolv lignin oxidation. Analogous M/Al_2O_3 catalysts (M = MnO_X, and FeO_X) were also prepared and applied in the oxidation reaction. After the lignin oxidation reaction, catalytic hydrogenolysis was carried out. Important reaction parameters for the oxidative depolymerization of lignin, such as temperature and reaction time were optimized.

4.2 Experimental

4.2.1 Materials.

All chemicals were purchased from Sigma Aldrich, and used as received, without further purification unless otherwise specified. Lignin C2 and C4 were prepared from beech sawdust using the organosolv procedure described in *Chapter 3*. γ-Aluminium oxide (> 99%) was provided by Saint Gobain as a generous gift. Compressed oxygen (>99.99%) and argon (> 99.99%) was purchased from Air Liquide, Denmark.

4.2.2 Catalyst preparation.

Excess solution impregnation was used to prepare the supported catalysts. Appropriate amounts of ruthenium or other metal (manganese, and iron) precursors were dissolved in water and either alumina, zirconia, spinel, magnesia, HY(6), HMOR or silica was slowly added to the aqueous solution of metal precursor and stirred for 3 h. The slurry was then dried at 80 ^oC overnight in order to remove the water. Finally, the dried catalysts were calcined at 450 ^oC for 6 h in static air to produce metal oxide (5 wt. % with respect to metal) supported catalysts. The catalysts were stored in a desiccator and were not pre-activated before use.

4.2.3 Oxidation and hydrogenolysis of lignin

In a typical catalytic reaction, methanol (80 vol. %) in water was added into a 50 mL autoclave (Parr 4843) with an appropriate amount of lignin and catalyst (50 mg). Afterwards, the reactor was flushed three times with the reactant gas mixture: oxygen/argon (20 bar) or hydrogen (30 bar). Mechanical stirring of the reactor (1000 rpm) was started when the temperature reached 20 ^oC below the set-point. After the desired reaction time, the autoclave was rapidly cooled, depressurized and the products analyzed by GC-FID (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 µm × 0.25 µm) and by NMR spectroscopy (See 4.2.5 Characterization techniques). The products were identified by GC-MS.

4.2.4 Oxidation followed by hydrogenolysis.

Catalytic oxidation experiments were performed in an autoclave (Parr 4843, 50 mL reactor autoclave) charged with an appropriate amount of lignin, catalyst (100 mg) and mixture of methanol (80%) in water as solvent (20 mL). The reactor was pressurized with oxygen (8 bar) and heated to the desired reaction temperature. Mechanical stirring of the reactor (1000 rpm) was started when the temperature reached 140 ^{0}C. After the reaction (5 h), the autoclave was rapidly cooled and depressurized. 10 mL of the product solution was then set aside for hydrogenolysis and the rest separated for analyses.

The 10 mL portion of the oxidation product solution was added into a 50 mL autoclave (Parr 4843) with an appropriate amount of catalyst (50 mg). Afterwards, the reactor was flushed three times with hydrogen (20 bar). Mechanical stirring of the reactor (1000 rpm) was started when the temperature reached 160 ^{0}C. After 5 h, the autoclave was rapidly cooled, depressurized and the products analyzed by GC-FID (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 µm × 0.25 µm) and by NMR spectroscopy (following the procedure in 4.2.5 Characterization techniques). The products were identified by GC-MS.

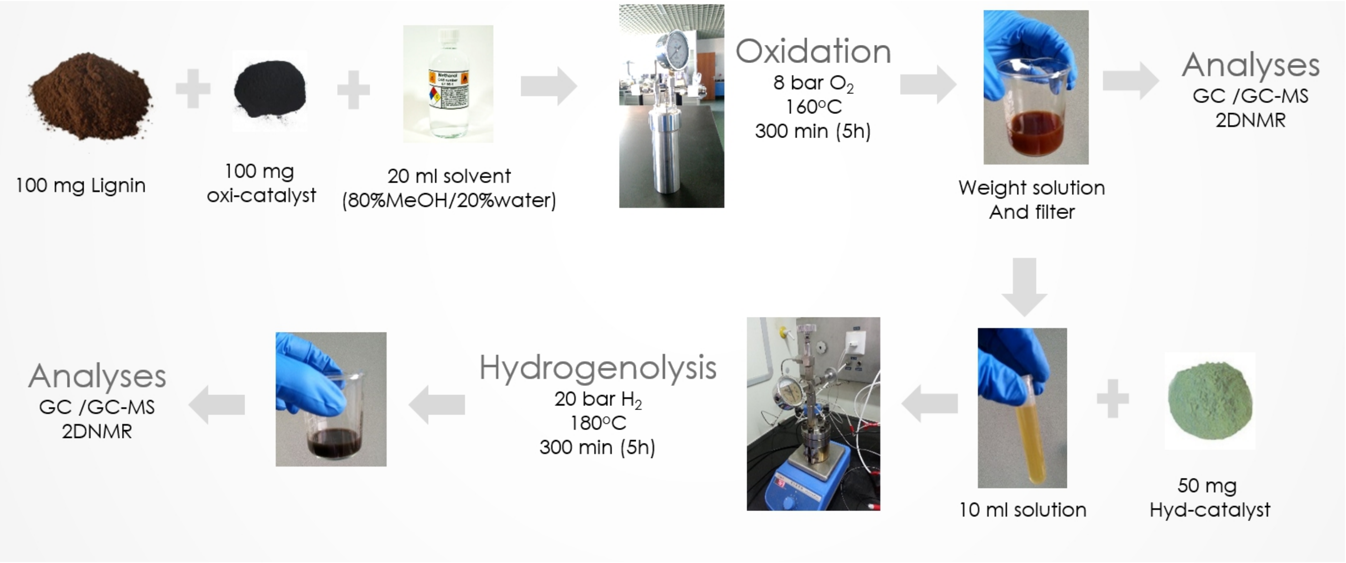


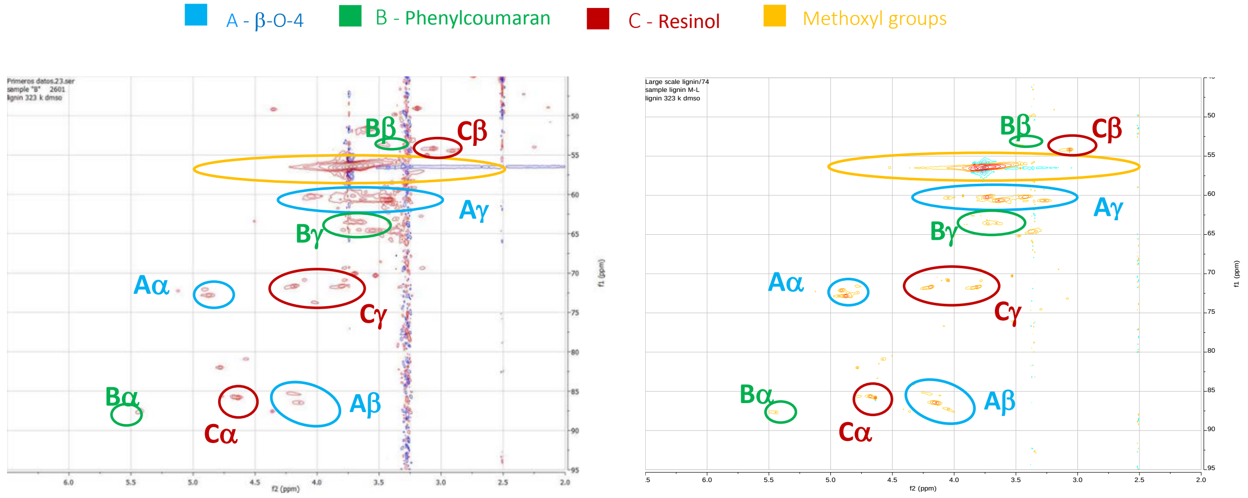
Figure 4.1. Scheme for oxidation followed by hydrogenolysis experiments.

4.2.5 Characterization techniques.

NMR spectroscopy

^{1}H-^{13}C HSQC NMR spectra were recorded on an 800 MHz Bruker (Fällanden, Switzerland) Avance spectrometer. Sensitivity enhanced ^{1}H-^{13}C HSQC spectra were acquired with narrow spectral width in the indirect dimension using the standard Bruker pulse sequence.

After lignin oxidation or hydrogenolysis, the reaction mixture was dissolved in 0.5 mL of DMSO-d6. NMR spectra were interpreted using assignments made by Wen et al. [167]. The signal intensity before and after treatment of the lignin material were normalized relative to the signal of the protons in the aromatic region (δF1 = 100-125 ppm, δF2 = 7.5- 6.0 ppm) as the intensity of this signal is expected to remain unchanged during the cleavage reaction. Analysis was performed according to Bolm et al. [168], with minor modifications. For the quantification of bond types present in the material, the following signals were used: AA, Aβ, Aγ, Bα, Bβ, Bχ, Cα, Cβ, and Cγ (Figure 4.1). All NMR-spectra are shown in the Appendix A.



C2 - ratio of binding: 3,03 : 1 : 0,79

C4 - ratio of binding: 3,68 : 1 : 0,62

Figure 4.1. 2-D NMR spectra (HSQC experiment) for organosolv lignin obtained in *Chapter 3*, C2 (left), C4 (right). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure.

4.3 Results and discussion

Several promising studies have been reported on the use of the hydrogenolysis process for the depolymerization of native lignin into monomeric phenols using alcoholic solvents and nickel-based catalysts [113, 126, 130, 171-173]. In addition, organosolv lignin can be solubilized in an 80% methanol/ water solution at 60 °C. Hence, the catalytic hydrogenolysis reactions were performed by dissolution of the organosolv lignin (*Chapter3*), in a mixture of methanol (80%) and water over three different nickel-based catalysts, the results of which are shown in Table 4.1.

When the Ni/MgO catalyst was used in the hydrogenolysis of C2 organosolv lignin (ratio of binding 3.03:1:0.79), a decrease in the β-O-4 (from 3.03 to 2.07) and phenylcoumaran (from 0.79 to 0.69) interunit was observed, which was poor in comparison to other catalysts tested. After Ni/SiO_2 was applied in the hydrogenolysis of organosolv lignin C2, the ratio of binding motifs β-O-4: resinol: phenylcoumaran was 1.89:1:0.68, indicating that 38% of the β-O-4 linkages and 14% of the phenylcoumaran had been cleaved. Encouragingly, 42% of the β-O-4 binding motifs present in the untreated organosolv lignin C2 were cleaved during the hydrogenolysis over Ni/HMOR catalyst, and the 2D-NMR spectra can be seen in Figure 4.2. As one of the aims was to perform the cleavage of the β-O-4 bond (Chapter 2), the hydrogenolysis catalyst, Ni/HMOR, that cleaved the highest amount of β-O-4 linkages, was chosen for further studies.

Table 4.1. Hydrogenolysis of organosolv lignin over various nickel supported catalysts

Experiment	Catalyst	Ratio of binding A : C : B
H1	Ni/SiO_2	1.89 : 1 : 0.68
H2	Ni/MgO	2.07 : 1 : 0.69
H3	Ni/HMOR	1.76 : 1 : 0.74

Reaction conditions:
Hydrogenolysis: 100 mg lignin, 100 mg catalyst, 20 ml solvent (80 vol. % MeOH and water), 30 bar H_2, 180°C, 5 h
Native lignin C2 *(Chapter 3)* **–** Ratio of binding (A : C : B) 3.03 : 1 : 0.79
Ratio of binding: A : C : B represents β-O-4 : Resinol : Phenylcoumaran

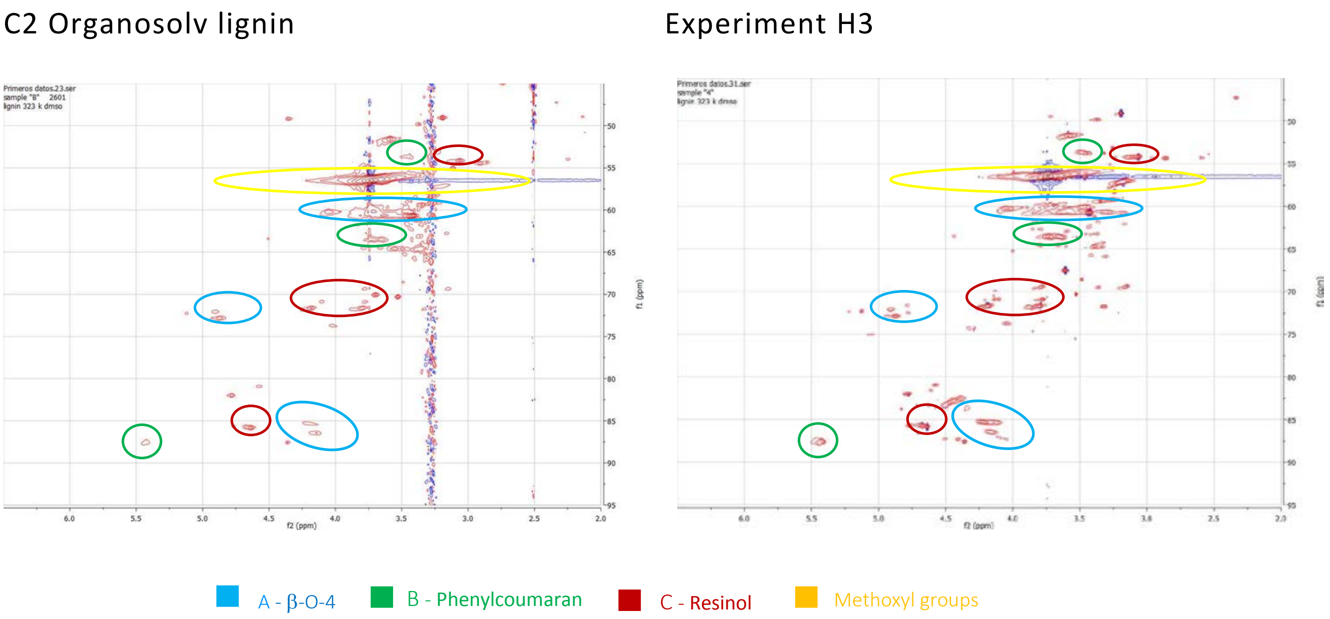


Figure 4.2. 2-D NMR spectrum (HSQC experiment) for organosolv lignin C2 before (left) and after hydrogenolysis over Ni/HMOR, experiment H3 (right).
The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

With a successful ether bond cleavage method established for β-O-4 model compounds (Chapter 2), it was decided to test the depolymerization method on organosolv lignin. This method consisted of a first step, involving the oxidative depolymerization of organosolv lignin C2, and a second stage in which the oxidized reaction products were subjected to hydrogenolysis in the presence of the previously described Ni/HMOR catalyst (Table 4.1), that worked best for the β-O-4 linkage cleavage in catalytic hydrogenolysis of organosolv lignin.

Different metal oxide catalysts were tested for the first step (oxidation of organosolv lignin), and results can be seen in Table 4.2. Initially, an experiment was carried out using silica stead of a catalyst (L11), which resulted in very poor degradation of β-O-4 binding motif as expected, decreasing from 3.03 to 2.49 (18%) after the first step, and to 1.87 after the second step. In addition, the phenylcoumaran interunit degraded by 11% after the first step and 26% after the second (Table 4.2). These results revealed that lignin depolymerization occurred to a very limited degree in the absence of a catalytically active metal.

When manganese- and nickel-based catalysts (L08 to L10) were applied to the oxidative organosolv lignin depolymerization and further hydrogenolysis, it was discovered that the tandem Mn/Al_2O_3 and Ni/HMOR (L10) produced the highest amount of lignin degradation. After oxidation over Mn/Al_2O_3, the ratio was 1.43:1:0.35, and after hydrogenolysis with Ni/HMOR, the ratio decreased further to 1.40:1:0.33. Favorably, 36% of the β-O-4 binding motifs present in the C2 organosolv lignin were cleaved during the oxidation process over Fe/Al_2O_3 (L07) and over 55% after the second step, hydrogenolysis with Ni/HMOR.

Due to the favorable results obtained in the cleavage of the β-O-4 model compounds (Chapter 2), it was decided to test ruthenium-based catalysts to enhance the catalytic oxidation of organosolv lignin (L01 to L06), and the results are shown in Table 4.2 of the ruthenium based catalysts tested two stand out: Ru/Al_2O_3 (L06) and Ru/SiO_2 (L01).

After the organosolv lignin oxidation over Ru/Al_2O_3 (L06), the β-O-4 binding motif was degraded from a binding ratio of 3.03 to 1.45 (52 %) after the first step, and to 1.33 (56 %) after the second step (Figure 4.4). Furthermore, the phenylcoumaran interunit degraded from 0.79 to 0.53 (33 %) after the first step, and to 0.32 (59 %) after the second step. Encouragingly, 56 % of the β-O-4 binding motifs present in the C2 organosolv lignin were cleaved during the oxidation process over Ru/SiO_2 (L01) and around 57% after the second step, hydrogenolysis with Ni/HMOR, as can be seen in the 2D-NMR spectra showed in Figure 4.3. Nevertheless, the phenylcoumaran interunit practically did not degrade after the first step, and 46% degradation was achieved after the hydrogenolysis reaction over Ni/HMOR.

Table 4.2. Two steps oxidation and hydrogenolysis of organosolv lignin over various supported catalyst.

Experiment	OXIDATION		HYDROGENOLYSIS	
	Oxidation Catalyst	Ratio of binding A : C: B	Hydrogenolysis Catalyst	Ratio of binding A : C : B
L01	Ru/SiO_2	1.34 : 1 : 0.78	Ni/HMOR	1.32 : 1 : 0.43
L02	Ru/ZrO_2	1.53 : 1 : 0.49	Ni/HMOR	1.52 : 1 : 0.43
L03	Ru/Spinel	1.87 : 1 : 0.48	Ni/HMOR	1.79 : 1 : 0.46
L04	Ru/MOR	1.55 : 1 : 0.38	Ni/HMOR	1.41 : 1 : 0.38
L05	Ru/HY(6)	1.68 : 1 : 0.37	Ni/HMOR	1.47 : 1 : 0.36
L06	Ru/Al_2O_3	1.45 : 1 : 0.53	Ni/HMOR	1.33 : 1 : 0.32
L07	Fe/Al_2O_3	1.95 : 1 : 0.38	Ni/HMOR	1.36 : 1 : 0.38
L08	Mn/MOR	1.56 : 1 : 0.46	Ni/HMOR	1.55 : 1 : 0.45
L09	Mn/SiO_2	1.57 : 1 : 0.40	Ni/HMOR	1.43 : 1 : 0.38
L10	Mn/Al_2O_3	1.43 : 1 : 0.35	Ni/HMOR	1.40 : 1 : 0.33
L11	SiO_2	2.49 : 1 : 0.70	SiO_2	1.87 : 1 : 0.58

Reaction conditions:

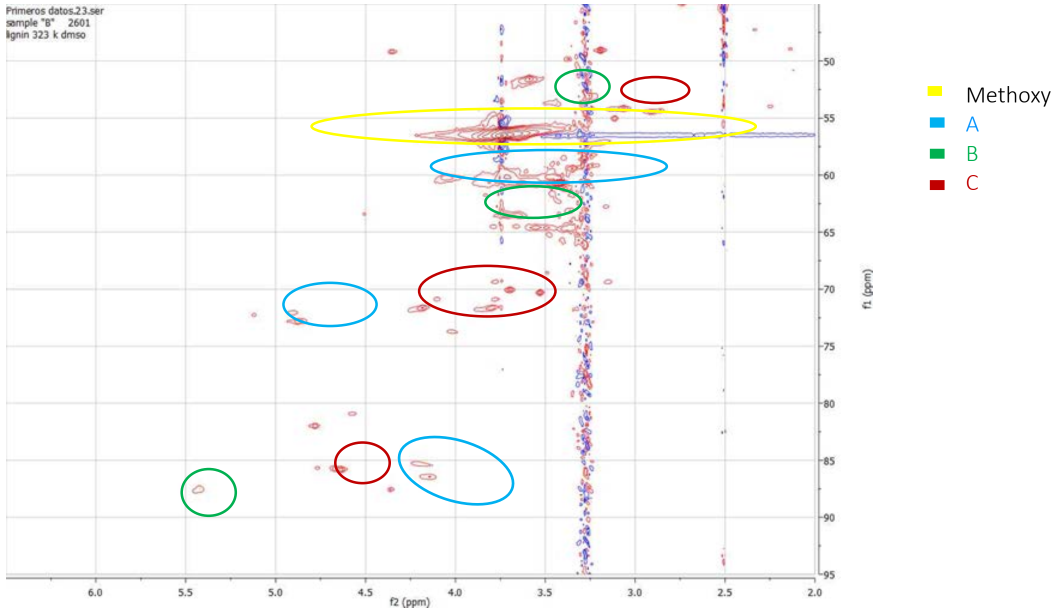
Oxidation: 100 mg lignin, 100 mg catalyst, 20 ml solvent (80 vol. % MeOH and water), 8 bar O_2, 160°C, 5 h

Hydrogenolysis: 10 ml oxidation solution, 50 mg catalyst, 20 bar H_2, 180°C, 5 h

Native lignin C2 *(Chapter 3)* **–** Ratio of binding (A:C:B) 3.03 : 1 : 0.79

Ratio of binding (A:C:B) represents β-O-4:Resinol:Phenylcoumaran

C2 Organosolv lignin



Experiment L01 Oxidation

Experiment L01 Hydrogenolysis

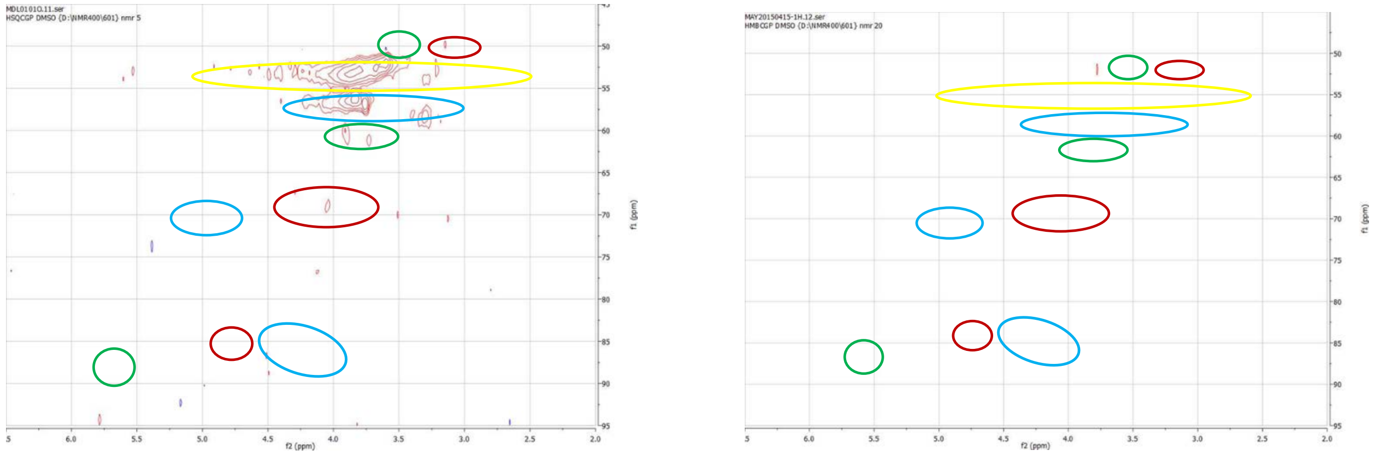
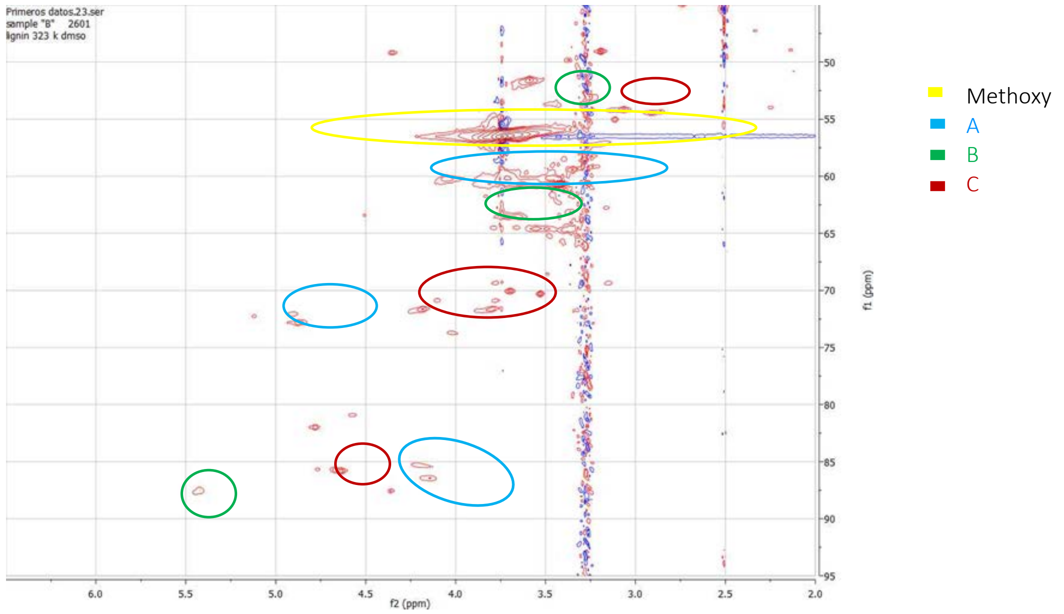


Figure 4.3. 2-D NMR spectrum (HSQC experiment) for organosolv lignin C2 before (top) and after oxidation over Ru/SiO$_2$ (left) and hydrogenolysis over Ni/HMOR, experiment L01 (right). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

C2 Organosolv lignin



Experiment L06 Oxidation

Experiment L06 Hydrogenolysis

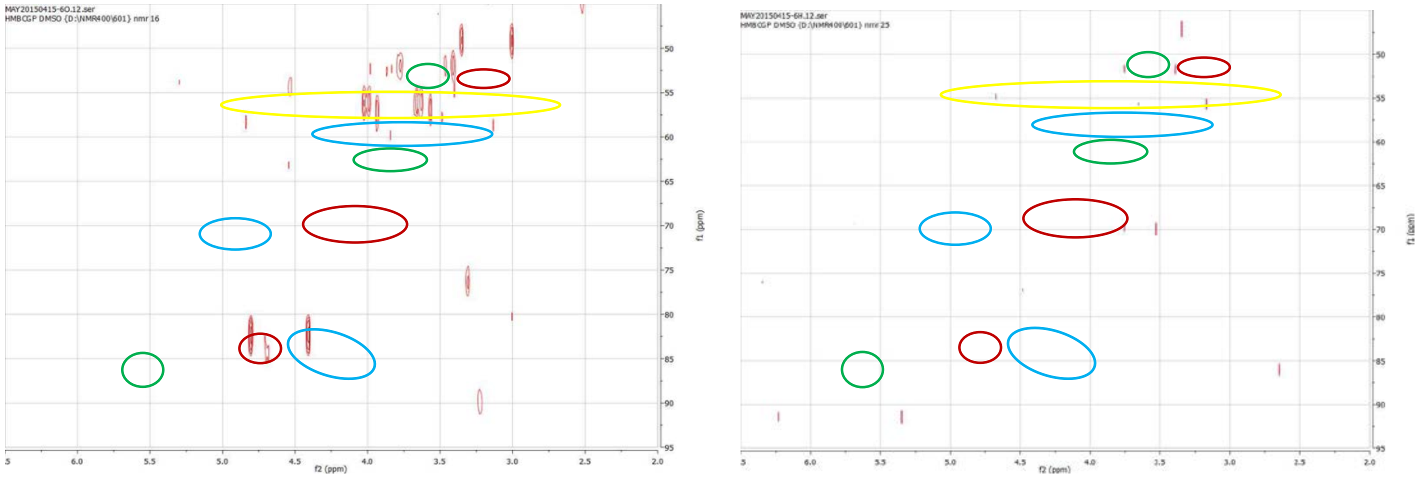


Figure 4.4. 2-D NMR spectrum (HSQC experiment) for organosolv lignin C2 before (top) and after oxidation over Ru/Al_2O_3 (left) and hydrogenolysis over Ni/HMOR, experiment L06 (right). The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

The effect of reaction temperature on the oxidative lignin depolymerization followed by hydrogenolysis was studied in the range of 160 to 200 ^{o}C, with a pressure of 20 bar of 20% oxygen in argon for the first step (oxidation), with a fixed temperature of 180 ^{o}C with 30 bar H_2 for the second step (hydrogenolysis). As seen in the previous studies, Ru/Al_2O_3 gave the highest degradation of β-O-4 and phenylcoumaran binding motifs, and was therefore selected for testing in the temperature variation study. Organosolv lignin C4, which had a ratio of binding motifs β-O-4 : resinol : phenylcoumaran of 3.68 : 1.00 : 0.62 (Table 4.3), was used as the lignin reagent.

Table 4.3. Temperature study for two-step lignin depolymerization over Ru/Al_2O_3 catalyst.

Experiment	Oxidation Temperature (^{o}C)	Ratio of binding A : C : B
T1	160	1.79 : 1 : 0.24
T2	180	1.43 : 1 : 0.26
T3	200	1.14 : 1 : 0.38

Reaction conditions: Catalyst: Ru/Al_2O_3 (5 wt. % respect to the metal)

Oxidation: 50 mg lignin, 50 mg catalyst, 10 ml solvent (80 vol. % MeOH and water), 20 bar (20 % O_2 + Ar), 5 h.

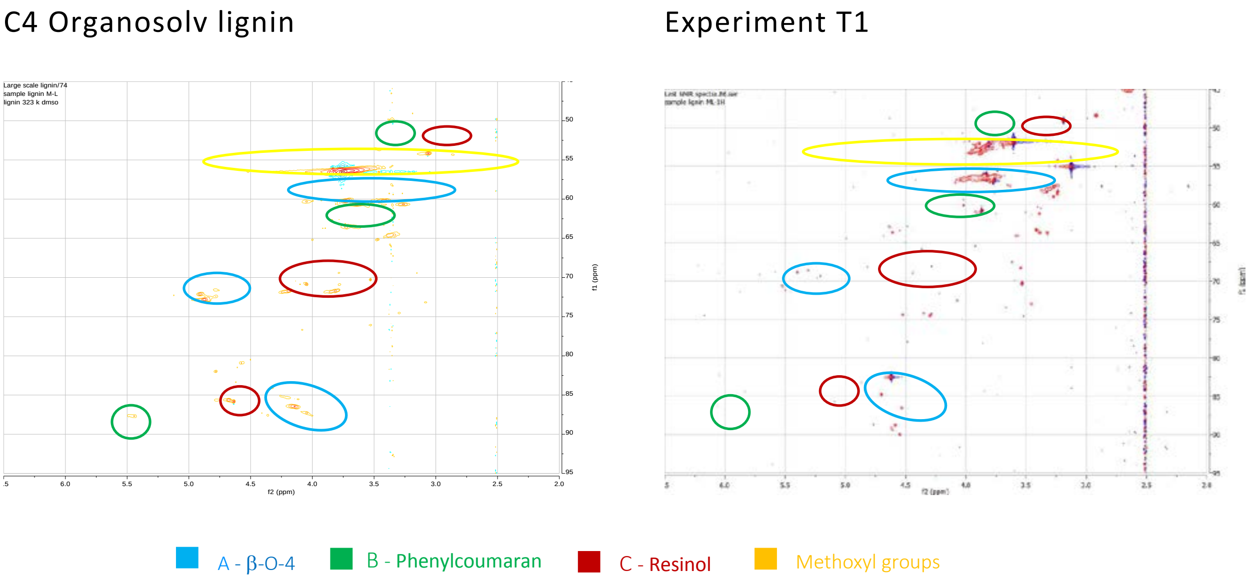
Hydrogenolysis: 10 ml oxidation solution, 50 mg catalyst, 30 bar H_2, 180^{o}C, 5 h

Native lignin C4 *(Chapter 3)* **–** Ratio of binding (A:C:B) 3.68 : 1 : 0.62

Ratio of binding: A:C:B represents β-O-4 : Resinol : Phenylcoumaran

It has been demonstrated that an increase in the temperature of the oxidation step, caused an increase in the degradation of the β-O-4 interunit after the two steps. After oxidation at 200 ^{o}C (T3) with methanol (80%) in water as solvent, under a pressure of 20 bar (20 % O_2 + Ar) followed by hydrogenolysis at 180 ^{o}C with a pressure of 30 bar H_2 using Ru/Al_2O_3 as catalyst, the original ratio of the organosolv lignin C4 (3.68:1:0.62) changed to 1.14:1:0.38. Hence, 69% of the β-O-4 bonds, and 39% of the phenylcoumaran linkages present in the untreated organosolv lignin C4 were cleaved during the process. However, most phenylcoumaran degradation occurred at the lower oxidation temperature (160 ^oC), with the binding ratio decreasing from 0.62 to 0.24. Figure 4.5 shows 2D-NMR spectra from organosolv lignin C4 and further oxidation and hydrogenolysis over Ru/Al_2O_3 catalyst at 160 ^oC.

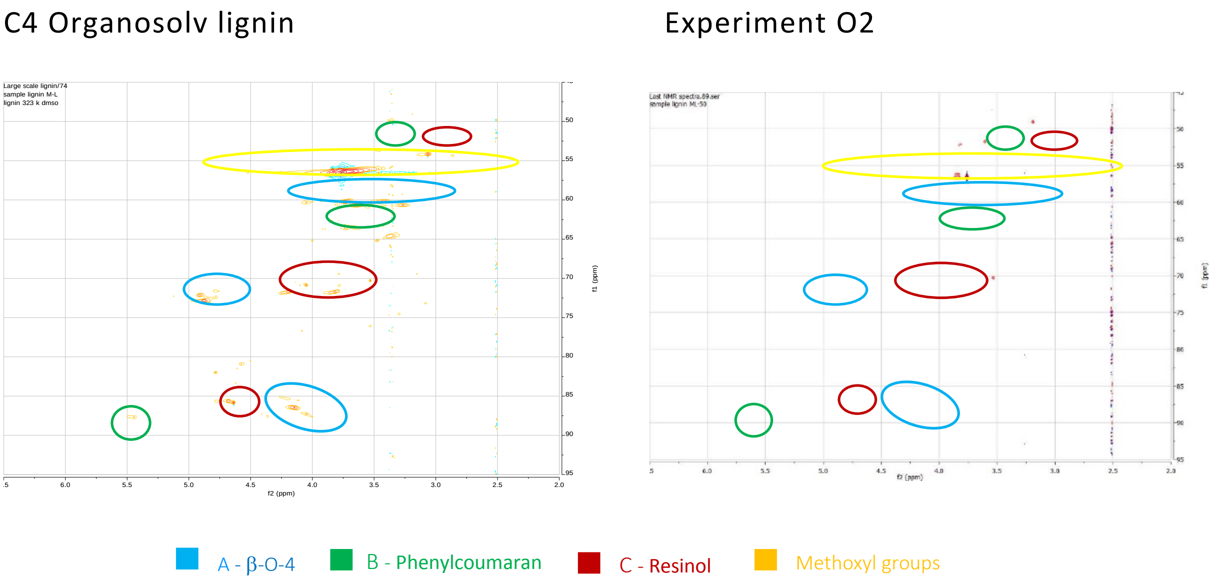
The influence of the oxidation time on the binding ratio was also studied over Ru/SiO_2, which gave the highest degradation in the β-O-4 interunit in previous studies, and Ni/SiO_2, which showed promising results in previous lignin hydrogenolysis runs at 160 ^oC and 20 bar of 20% O_2 in argon. Results are shown in Table 4.4.


C4 Organosolv lignin

Experiment T1

Figure 4.5. 2-D NMR spectrum (HSQC experiment) for organosolv lignin C4 before (left) and after oxidation and hydrogenolysis over Ru/Al_2O_3 (right).
The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

Originally, a blank experiment (O5) showed very poor degradation of the organosolv lignin binding groups, with a decrease in the binding ratio from 3.68 to 3.45 (6%) for the β-O-4 interunit, and from 0.62 to 0.60 (3%) for the phenylcoumaran interunit. Thus, it was demonstrated that an active metal catalyst was needed to perform the catalytic aerobic oxidation of organosolv lignin. When Ru/SiO_2 (O1, O2) and Ni/SiO_2 (O3, O4) catalysts were compared, it was clear that Ru/SiO_2 showed higher activity in the oxidative degradation of organosolv lignin (Table 4.4). Focusing on the Ru/SiO_2 catalyst, it has been shown that after a 5-hour reaction (O1) at 160 ^{0}C with 80% methanol in water as solvent, the ratio was 1.98: 1: 0.36, indicating that 46% of the β-O-4 linkages had been cleaved. When the reaction time was increased to 20 hours (O2) the ratio of binding motifs (β-O-4: resinol: phenylcoumaran) was 0.89: 1: 0.22 revealing that an increase in reaction time resulted in an increase in the degradation of the organosolv lignin bonds, as can be seeing in the 2D-NMR spectra showed in Figure 4.6.


C4 Organosolv lignin

Experiment O2

Figure 4.6. 2-D NMR spectrum (HSQC experiment) for organosolv lignin C4 before (left) and after oxidation over Ru/SiO_2 (right) after 20 h.
The lignin structures identified are: (**A**) β-O-4′ substructure; (**B**) β-5′, α-O-4′ phenylcoumaran substructure; (**C**) β-β′ resinol substructure

Table 4.4. Influence of time-reaction and catalyst in the oxidative depolymerization of lignin

Experiment	Catalyst	Ratio of binding A : C : B
O1[a]	Ru/SiO_2	1.98 : 1 : 0.36
O2[b]	Ru/SiO_2	0.89 : 1 : 0.22
O3[a]	Ni/SiO_2	2.53 : 1 : 0.45
O4[b]	Ni/SiO_2	0.99 : 1 : 0.18
O5[a]	Blank	3.45 : 1 : 0,60

Reaction conditions:
50 mg lignin, 50 mg catalyst, 10 ml solvent (80% MeOH /20% water), 20 bar (20 % O_2 + Ar), 160 ^{o}C **-** [a] 5 h. [b] 20 h.
Native lignin C4 *(Chapter 3)* **–** Ratio of binding (A : C : B) 3.68 : 1 : 0.62
Ratio of binding: A : C : B represents β-O-4 : Resinol : Phenylcoumaran

Encouraged by the finding that the linkages of both lignin C2 and C4 were cleaved, the reaction samples were analysed by GC-MS, in order to identify the possible products obtained. Compounds such as vanillin, guaiacol, catechol were identified, but with a very poor yields (<1%). Unfortunately, the analysis did not reveal more information regarding the other compounds formed; in order to identify these an alternative method is required to characterize the reaction products obtained, such as size exclusion chromatography (SEC), which was not available for the project.

4.4 Summary

The oxidative depolymerization of organosolv lignin followed by a catalytic hydrogenolysis, has been developed as a two-step depolymerization process for lignin degradation. Different catalysts have been tested with the highest degradation degree achieved with the tandem Ru/SiO_2 – Ni/HMOR, with 57 % of the β-O-4 binding motifs, and 46% of the phenylcoumaran interunit present in organosolv lignin cleaved. The effect of the oxidation reaction temperature was also studied for the two-step process, and it was revealed that at a higher temperature, the lignin binding motifs degraded further.

In order to improve the oxidation step, the reaction time was studied over the Ru/SiO2 catalyst. When the reaction time was prolonged to 20 hours an increase in the degradation of the organosolv lignin linkages ocurred. 76 % of the β-O-4 binding motifs, and 64 % of the phenylcoumaran interunit present in organosolv lignin were cleaved in this case.

Although GC, GC-MS and HPLC analyses were carried out in order to identify more of the products obtained, no further identifications could be made. Alternative methods, such as size exclusion chromatography are required to investigate this further.

Chapter 5

Conclusion

5

The results presented in this thesis contributed to study the potential of lignin to become the renewable aromatic resource for chemical industry in the future. While the need for energy and raw materials is increasing, the depletion of fossil fuels and the severity of the environmental challenge are growing; consequently, there is an urgent need for an alternative renewable resource, which is as efficient and effective as possible. Biomass, which formally is CO_2 neutral, displays great potential as a resource for energy and chemical production.

Lignocellulosic biomass consists mainly of three components, cellulose (carbohydrate polymers), hemicellulose, and lignin (aromatic polymers). The conversion of lignocellulosic biomass are envisaged to take place in biorefineries, which are analogous to petrochemical refineries. However, all the components of lignocellulosic biomass must be valorized in order to make a biorefinery profitable. Whilst several commercial processes have been developed for the valorization of cellulose and hemicellulose fractions, the lignin fraction has received less cattention, and processes for its valorization are still under development.

Lignin is a complex amorphous polymer with many chemical functionalities and a structure that varies from plant to plant. The pretreatment method used for the extraction of lignin is also known to affect the structure of the polymers produced. However, despite the complex structure of lignin, the phenyl propane units of which it is composed make it a potentially rich source of phenolic compounds for chemical production.

Lignin depolymerization with selective bond cleavage is an important challenge for converting it into value-added chemicals. The catalytic transformation of lignin can be carried out by pyrolysis, solvolysis, hydrogenolysis and oxidation reactions. In general, oxidation reactions using homogeneous, heterogeneous or enzymatic catalysts, result in the production of more complex platform aromatic compounds with additional functionalities.

Due to the complexity and variability of the lignin structure, model compounds, which include the most common and most reactive bonds found in lignin, can be applied to investigate the behavior of lignin in the oxidation reaction. The most abundant of these bonds is the β-O-4 linkage, the reactivity of which has been investigated in this thesis. In **Chapter 2** of this thesis, two compounds (veratryl alcohol (VA) and guaiacyl glycerol-β-guaiacyl ether (GGGE)) were chosen and tested in oxidative depolymerization reactions. Different supported transition metal heterogeneous catalysts were applied and a Ru/Al_2O_3 catalyst prepared with ruthenium (IV) oxide hydrate showed superior catalytic activity for all the model compounds tested. An 89 % yield of veratraldehyde (VAld) was obtained from the oxidation of VA in water at 160 ^oC with 5 bar air pressure after an 8-hour reaction. Veratrol, a by-product from the decarbonylation of VAld, was formed when the reaction time was prolonged to 20 h. When the solvent was changed to methanol, using 20 bar of argon, the VA-ether was formed yielding 36%, indicating that methanol protected the hydroxyl group present in VA from being oxidised. A recyclability test was performed on the Ru/Al_2O_3 catalyst in the oxidative transformation of VA. After three consecutive runs, the VAld yield decreased, possibly due to Ru leaching from the support, therefore further investigation is required to improve the stability of the Ru catalyst or reduce the severity of the conditions used to extract and recycle the catalyst.

When the Ru/Al_2O_3 catalyst prepared with ruthenium (IV) oxide hydrate was used in the oxidative transformation of GGGE, 34 % yield of guaiacol, 13 % of vanillin and 11% of vanillic acid were obtained after 20 h in acetonitrile at 160 ^oC under 5 bar of 20% oxygen in argon. The Ru/Al_2O_3 catalyst was easy to regenerate and recycle. It was found to be stable over five consecutive runs in acetonitrile.

In **Chapter 3**, Birch and beech sawdust were subjected to the organosolv treatment for lignin extraction. Although the highest amount of lignin was extracted from birch sawdust, giving a better ratio of the β-O-4 interunit, beech sawdust was elected for further studies due to its wider availability and local origins.

The addition of a catalyst was tested to increase the acidity of the media used in the organosolv process. Additionally, the ratio of ethanol-water as well as the temperature and the solid-liquid ratio used in the process were tested and optimized for the organosolv pulping treatment. 17 wt. % of lignin was obtained after 200 minutes of reaction using 0,5 mM H_2SO_4 as catalyst, with a solvent consisting of 60 vol. % ethanol, 40 vol. % water, and a pressure of 20 bar of nitrogen, with a solid/ liquid ratio of 1/6 at 180 ^oC. However, the β-O-4 ratio of binding was improved to 3.68 when the temperature was decreased to 160 ^oC, and the solid/liquid ratio changed to 1/12. All the catalytic depolymerization methods were designed to perform the cleavage of the β-O-4 bond, so it was rational to choose the lignin batch with highest proportion of β-O-4 interunits for further analyses.

Chapter 4 is dedicated to the study of a two-step conversion route from lignin to aromatics. The first step consisted of the oxidative depolymerization of lignin at 160 ^oC, over 5 h with 8 bar of oxygen. A second step followed, wherein the oxidation products were subjected to catalytic hydrogenolysis at 180 ^oC for 5 h under a pressure of 30 bar H_2. Different catalysts were tested using the two-step conversion procedure. The tandem Ru/SiO_2 – Ni/HMOR, gave the highest degree of degradation of the organosolv lignin binding motifs, with 57 % of the β-O-4 binding motifs, and 46% of the phenylcoumaran interunits cleaved. In addition, it was showed that increasing the temperature used in the first step increased the degree of degradation of the lignin motifs. Prolonged reaction times, up to 20 h for the oxidation step, produced an increase in the degradation of the organosolv lignin linkages, resulting in the cleavage of 76 % of the β-O-4 binding motifs, and 64 % of the phenylcoumaran interunits, using Ru/SiO_2 as catalyst at 160 ^oC, and 20 bar of 20% oxygen in argon with 80 vol. % methanol in water as solvent. Unfortunately, additional methods are required to characterize the reaction products, in order to identify more of the products obtained from the reactions.

The similarities between the functionalities present in lignin and its reaction products make characterization of reaction mixtures challenging. Additionally, the elucidation of the reactions and side reactions taking place becomes almost impossible due to the complexity of the system. Mechanistic insight into the reaction, such as the role of the solvent, catalyst and reactant are important in order to understand and improve the catalytic system for lignin upgrading.

Reactions involving model compounds are not always directly applicable to a complex system with native lignin, so lignin polymers must be studied to discover the real changes taking place in this complex molecule. More research and new developments are required in this field.

Heterogeneous catalysis provides great advantages, not only in terms of easy separation and recyclability, but also providing the ability to use molecular oxygen as oxidant, as was demonstrated by the results shown in this thesis. It is clear, that oxidation is not the only option for the depolymerization of lignin, but it is a relevant route as an eco-efficient process involving several principles of green and sustainable chemistry, such as the use of catalysts, energy efficiency and the use of clean processes.

It is important to continue the development of lignin valorization strategies. In this respect, a number of potential options exist. For example, the functionalization of lignin can lead to the development of new polymeric materials and depolymerization coupled with selective oxidation reactions can provide routes to the production of fine chemicals. With a combination of strategies and reaction processes, the complete replacement of fossil fuel based aromatic chemicals with sustainable lignin based products can possibly be realized.

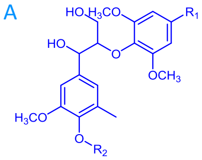
A

Appendix A

Organosolv lignin 2-D NMR spectra (HSQC experiment)

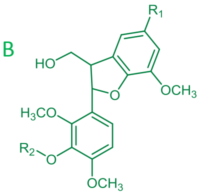
Ratio of binding: A: C : B

A



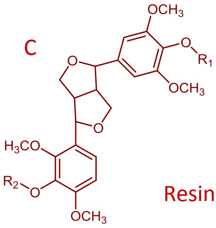
β-O-4

B



Phenylcoumaran

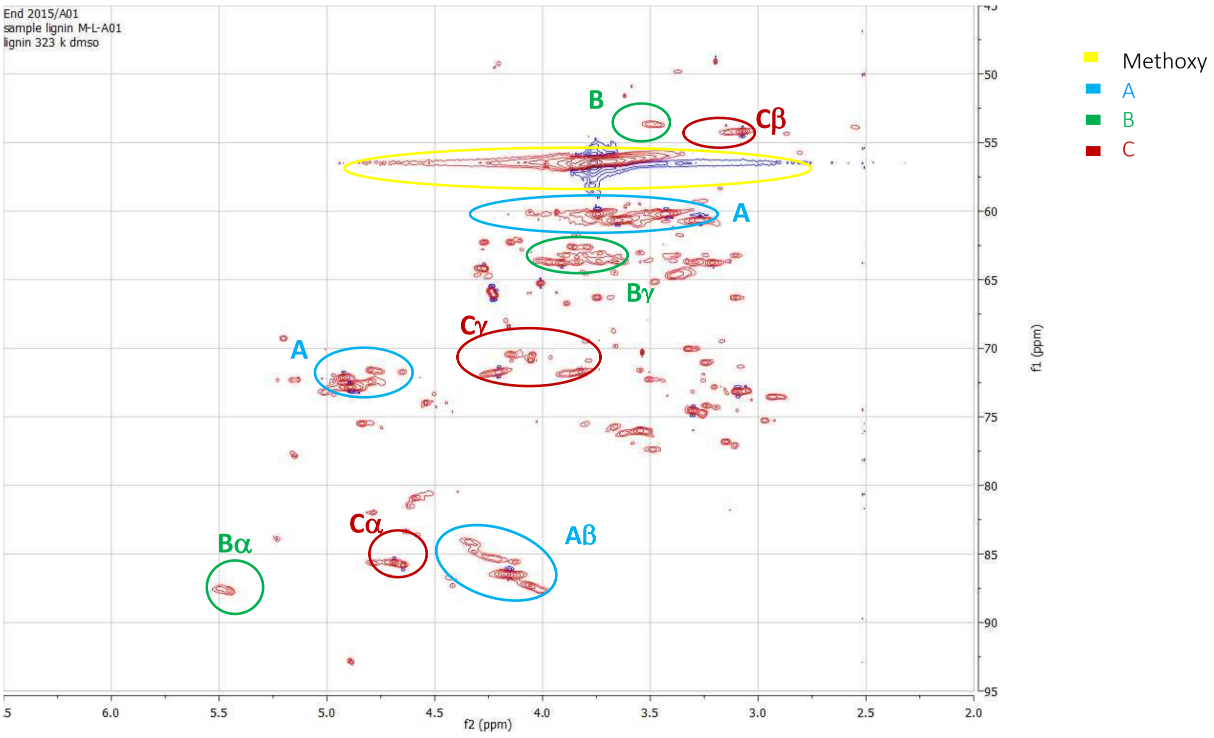
C



Resinol

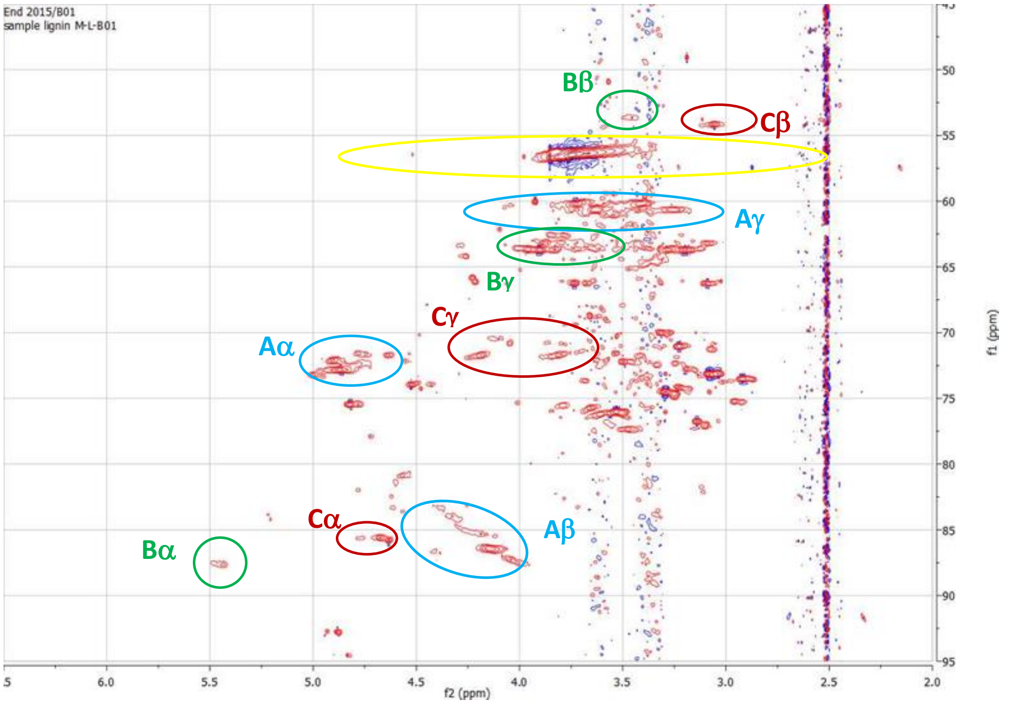
Experiment A1

Ratio of binding: 3,62 : 1 : 0,85



Experiment B1

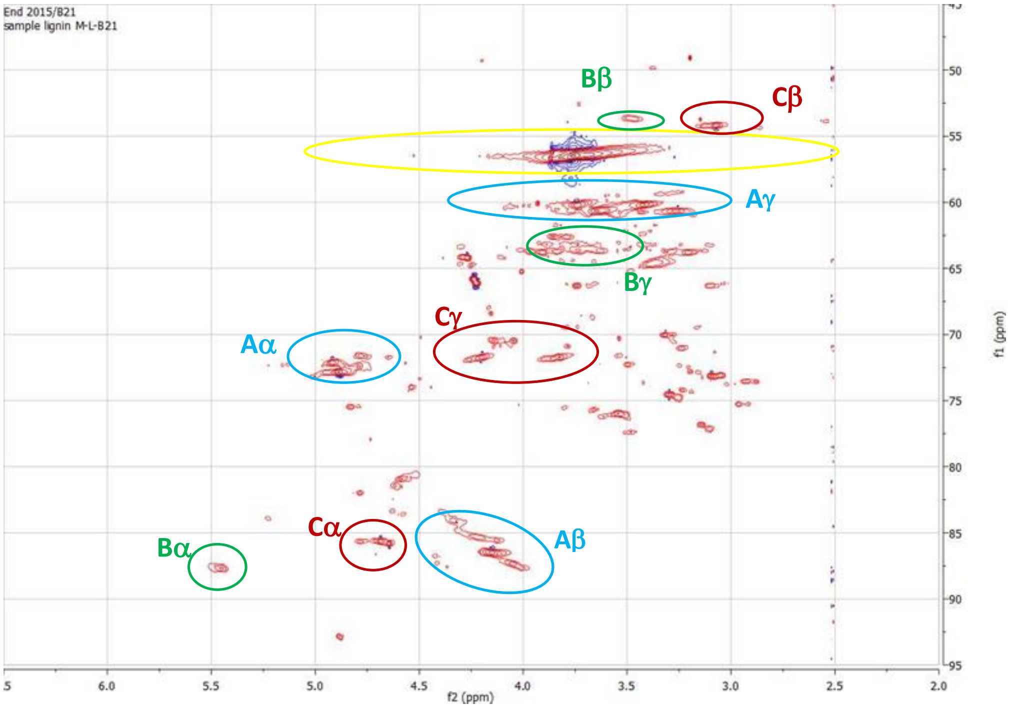
Ratio of binding: 3,06 : 1 : 0,90



🟨 Methoxy
🟦 A
🟩 B
🟥 C

Experiment B2

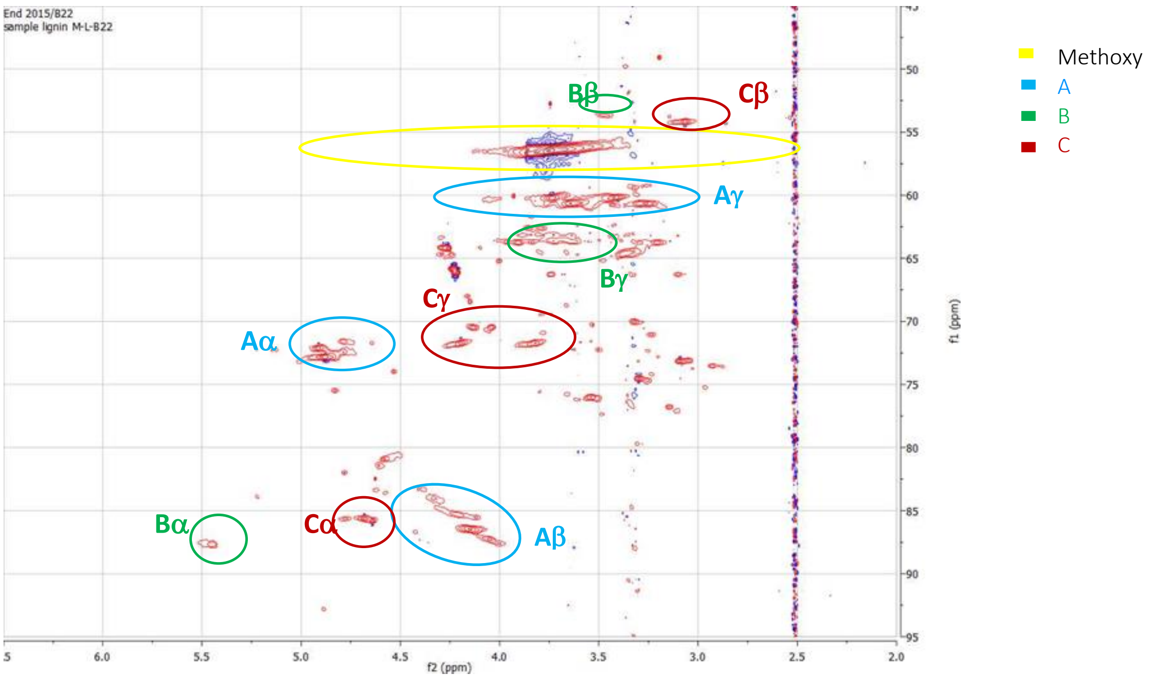
Ratio of binding: 3,22 : 1 : 0,83



🟨 Methoxy
🟦 A
🟩 B
🟥 C

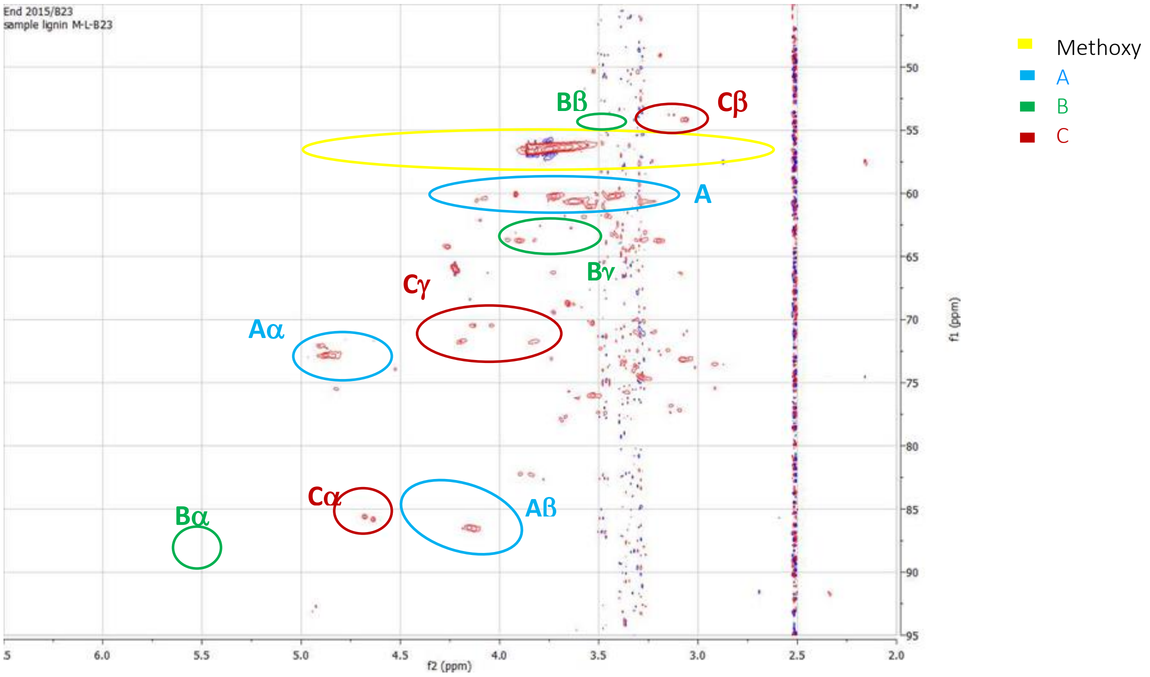
Experiment B3

Ratio of binding: 3,43 : 1 : 0,79



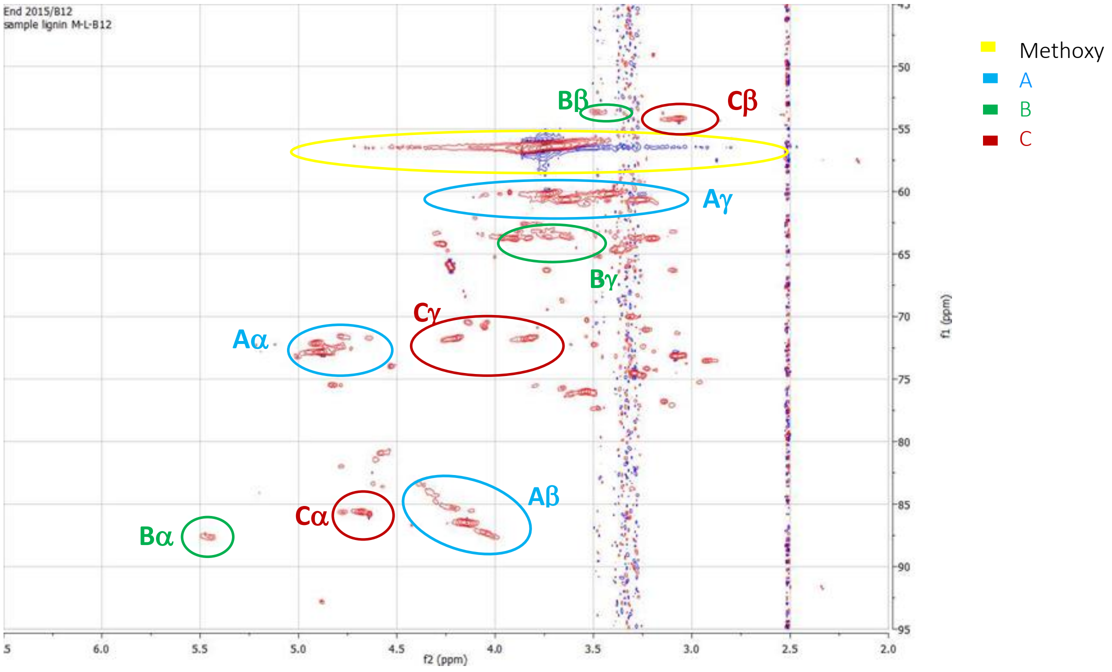
Experiment B4

Ratio of binding: 2,01 : 1 : 0,49



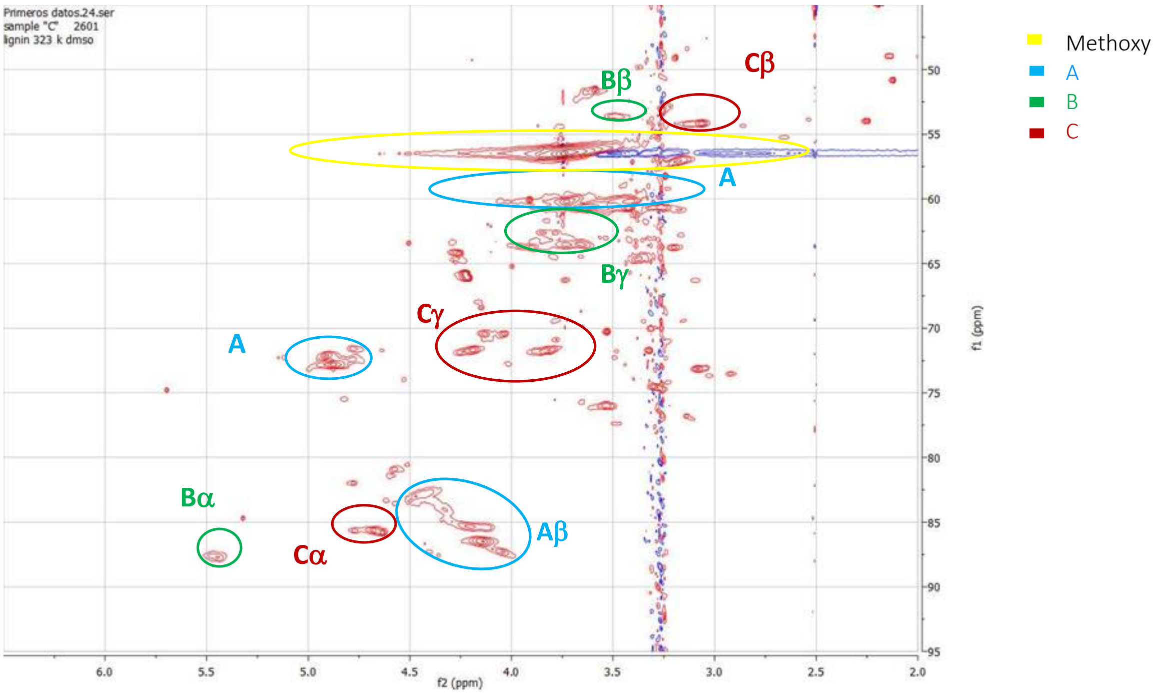
Experiment B5

Ratio of binding: 3,26 : 1 : 0,85



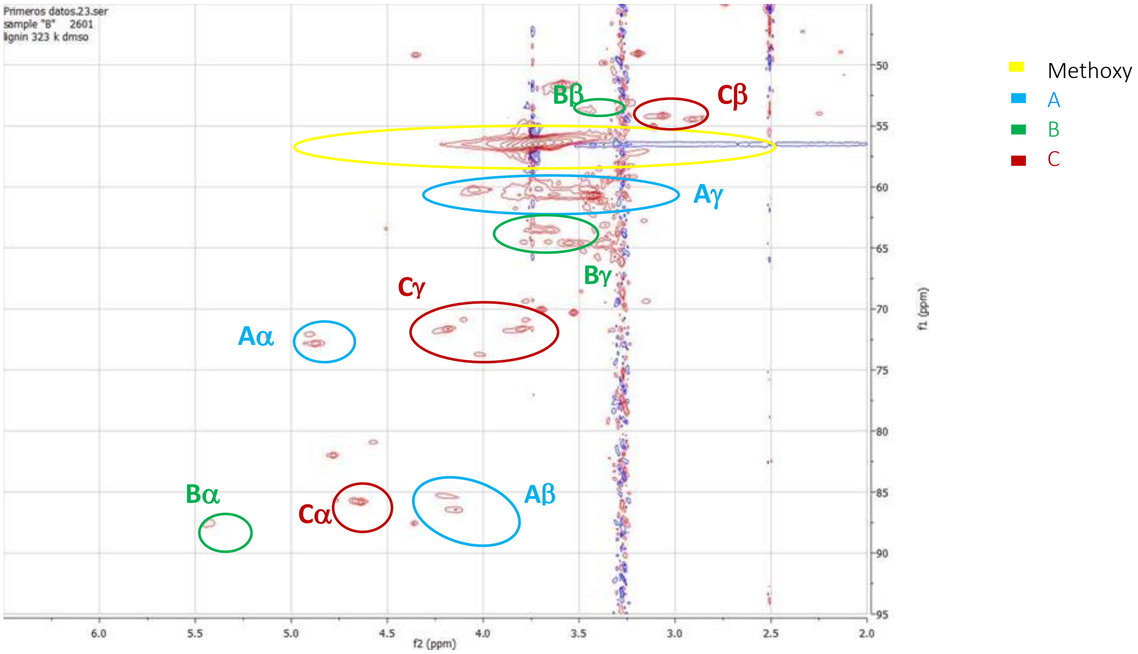
Experiment C1

Ratio of binding: 2,90 : 1 : 0,38

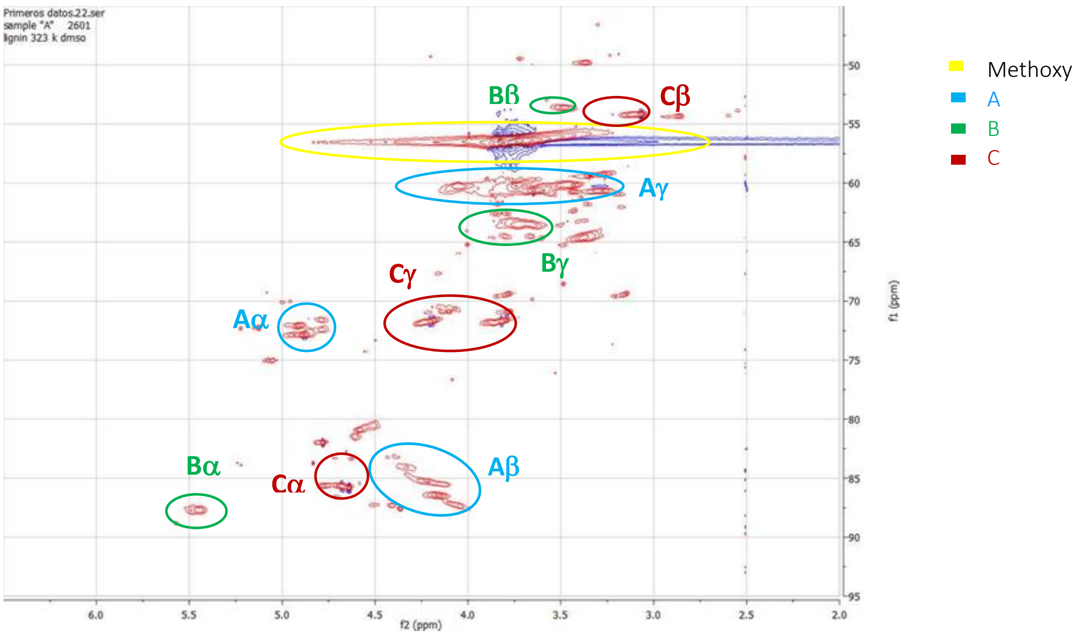


Experiment C2

Ratio of binding: 3,03 : 1 : 0,79

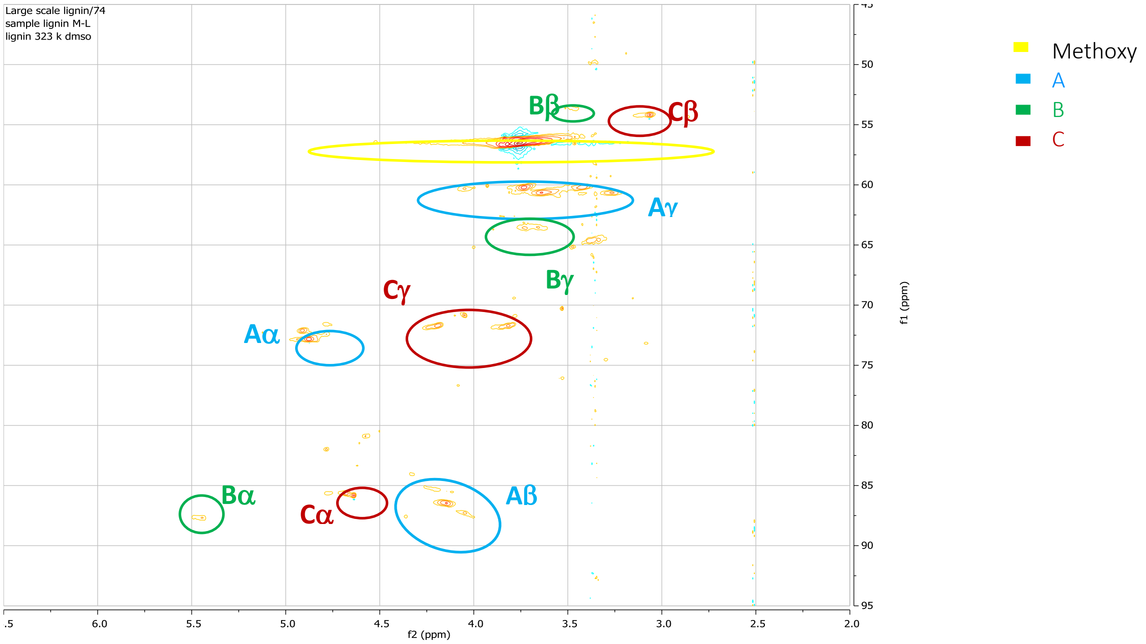


Experiment C3



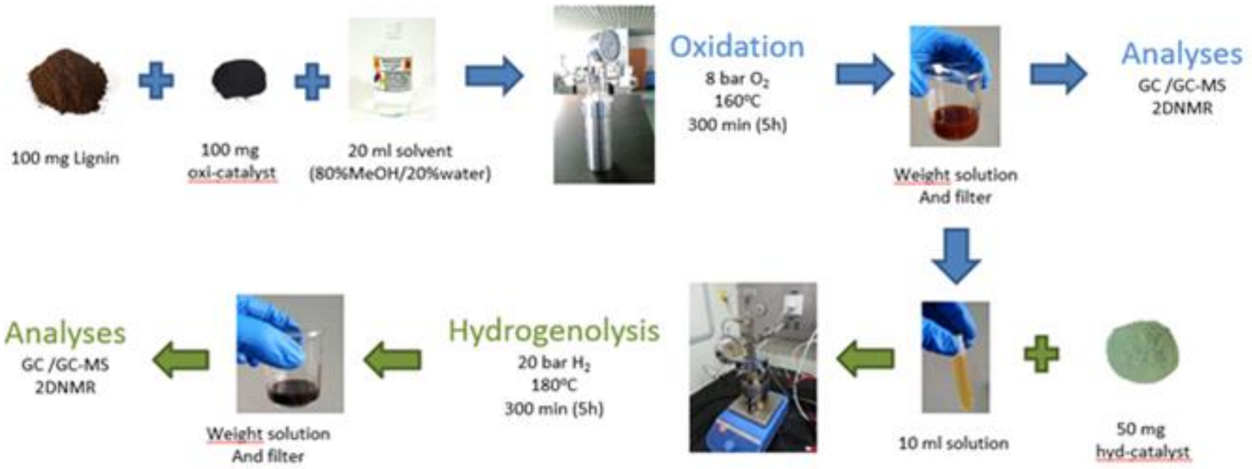
Experiment C4

Ratio of binding: 3,68 : 1 : 0,62



Lignin oxidation followed by hydrogenolysis 2-D NMR spectra (HSQC experiment)

Scheme process for lignin oxidation and hydrogenolysis

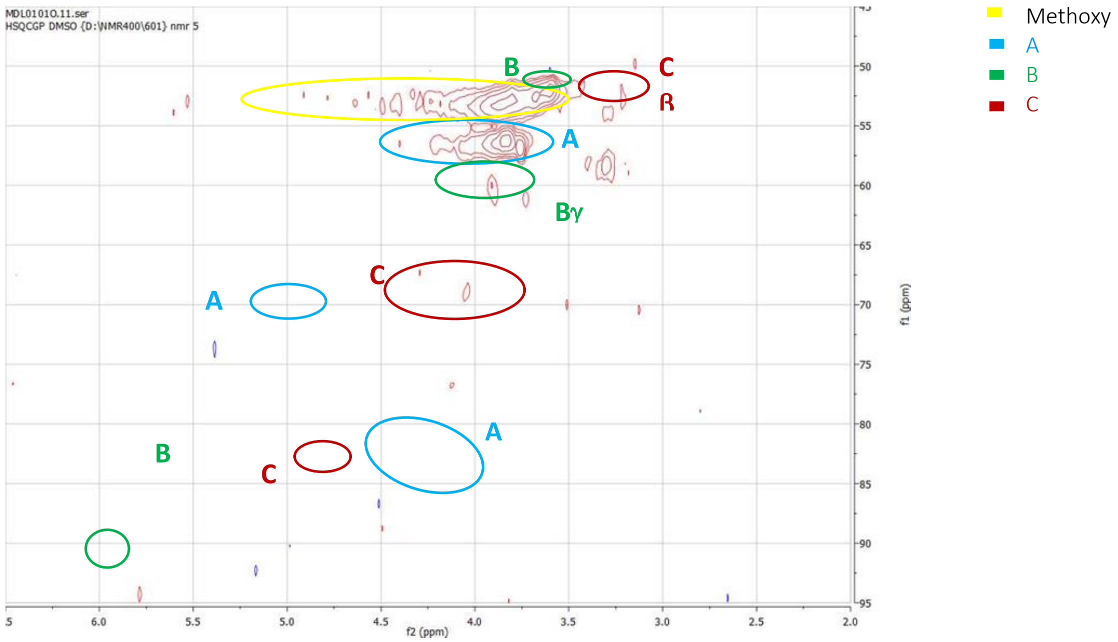


NATIVE LIGNIN C2

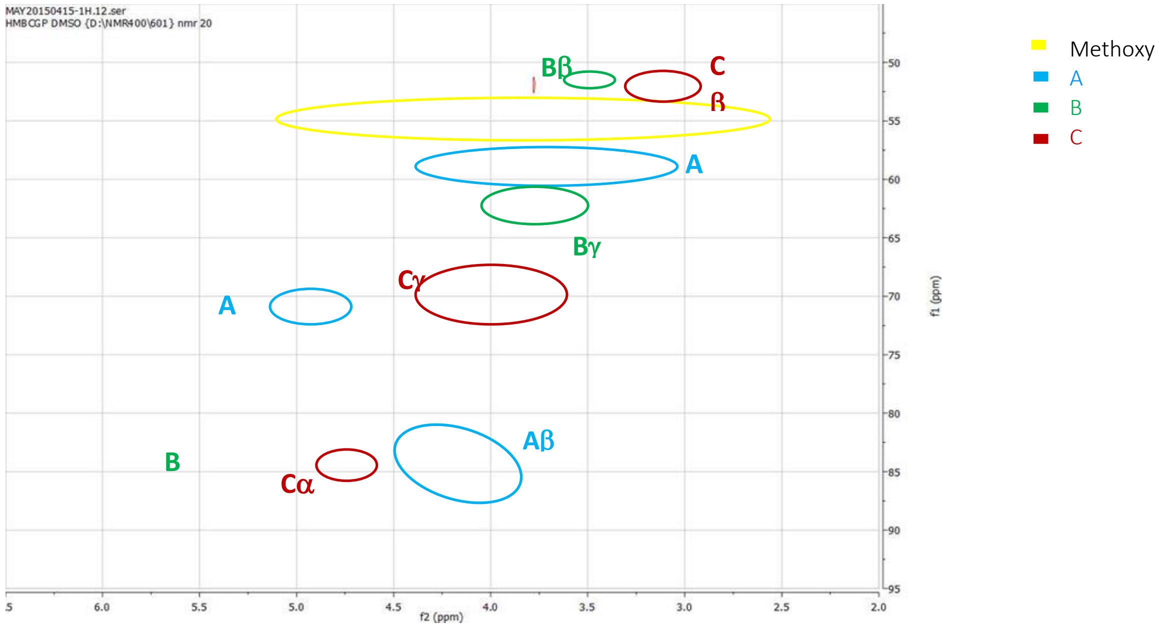
Ratio of binding: 3,03 : 1 : 0,79

Experiment L01

Oxidation



Hydrogenolysis

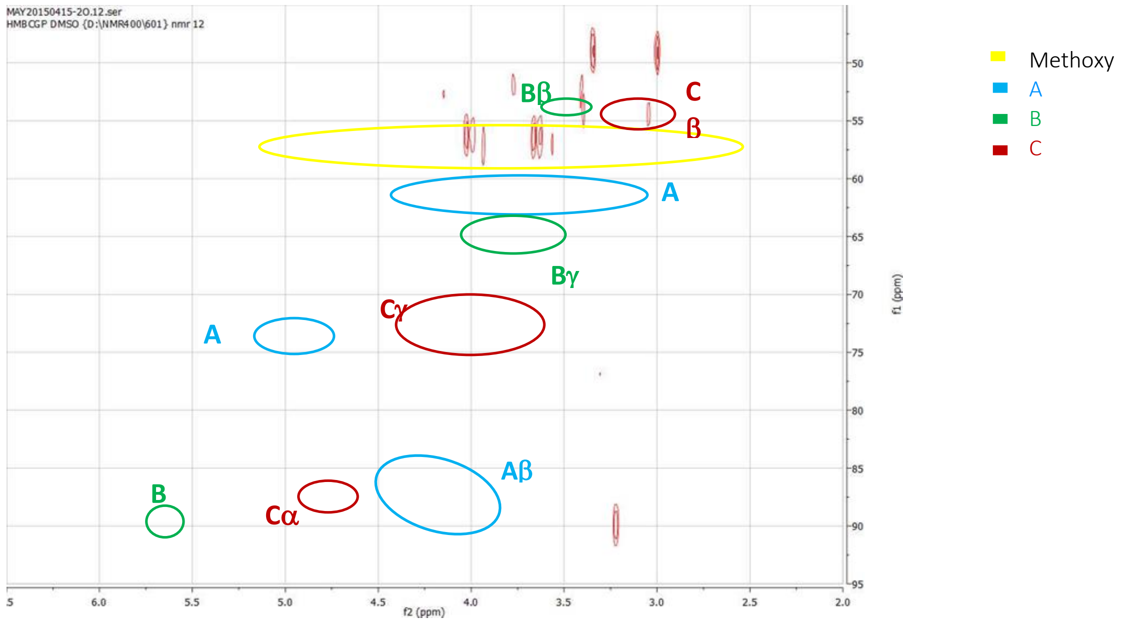


AFTER OXIDATION
Ratio of binding: 1,34 : 1 : 0,78

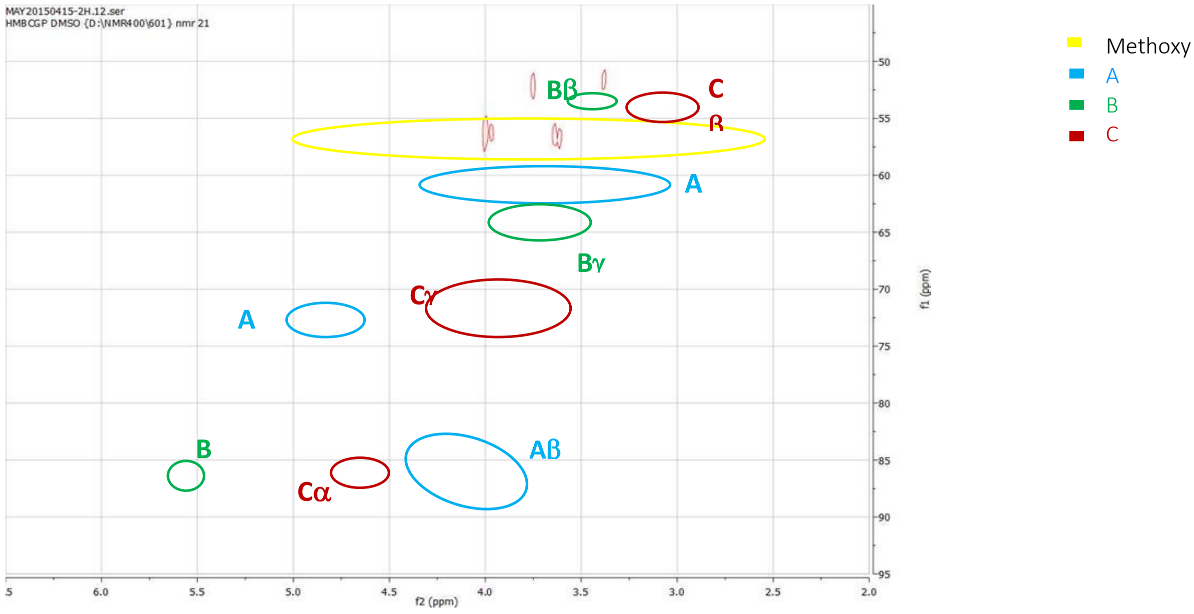
AFTER HYDROGENOLYSIS
Ratio of binding: 1,32 : 1 : 0,43

Experiment L02

Oxidation



Hydrogenolysis



AFTER OXIDATION

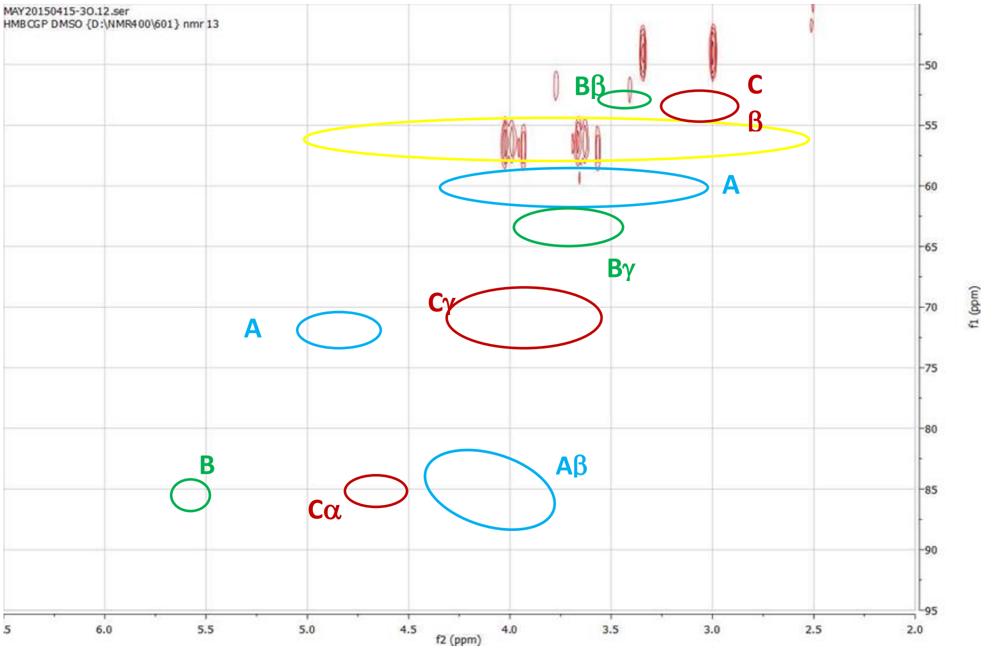
Ratio of binding: 1,53 : 1 : 0,49

AFTER HYDROGENOLYSIS

Ratio of binding: 1,52 : 1 : 0,43

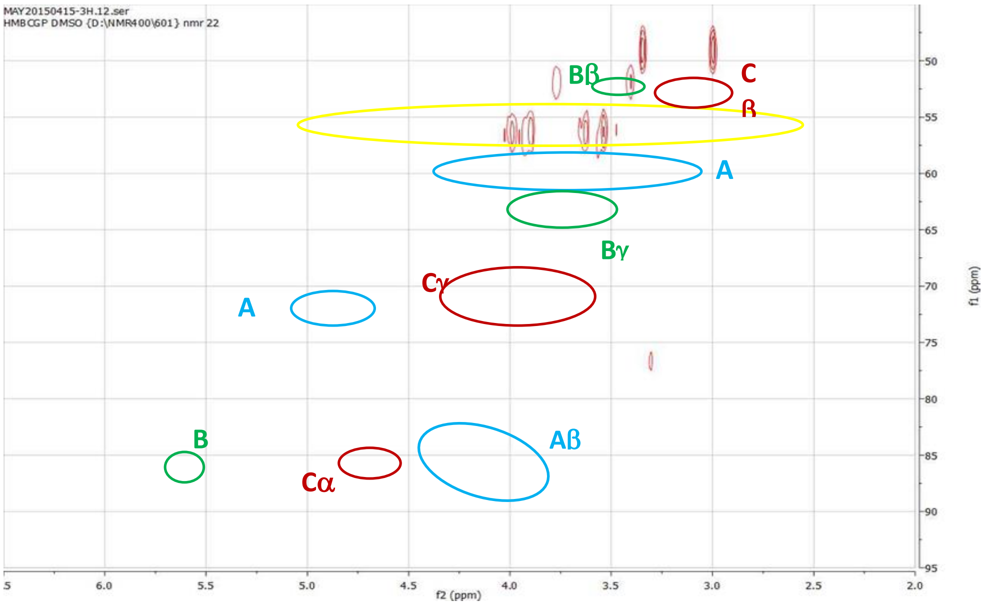
Experiment L03

Oxidation



🟨 Methoxy
🟦 A
🟩 B
🟥 C

Hydrogenolysis



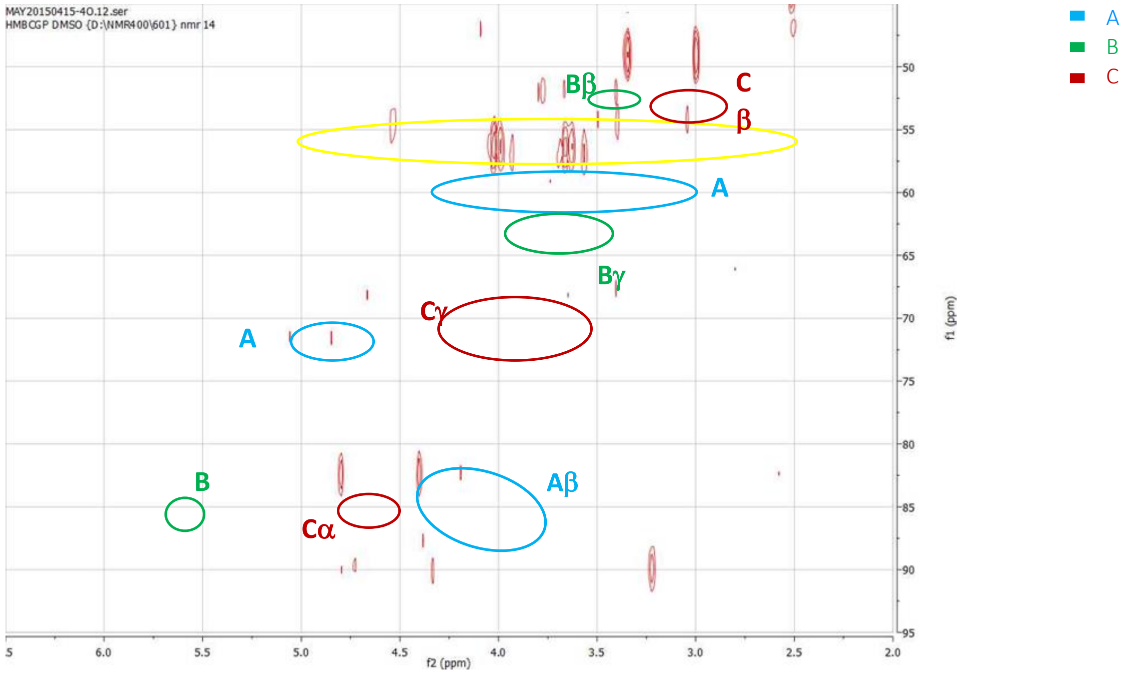
🟨 Methoxy
🟦 A
🟩 B
🟥 C

AFTER OXIDATION
Ratio of binding: 1,87 : 1 : 0,48

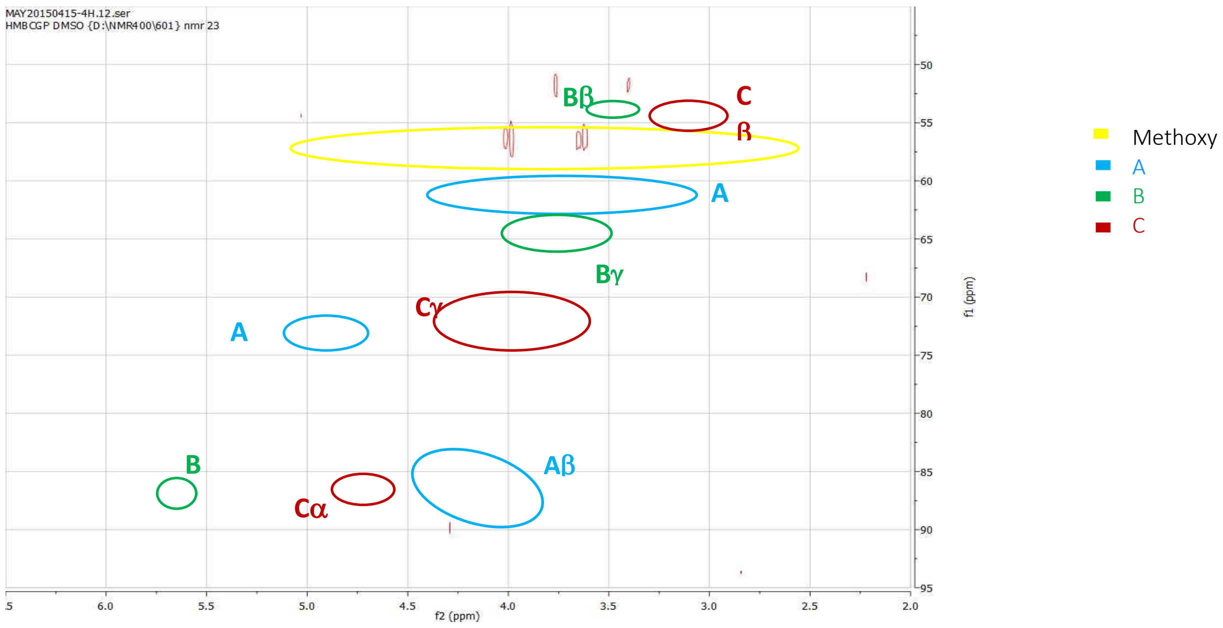
AFTER HYDROGENOLYSIS
Ratio of binding: 1,79 : 1 : 0,46

Experiment L04

Oxidation



Hydrogenolysis

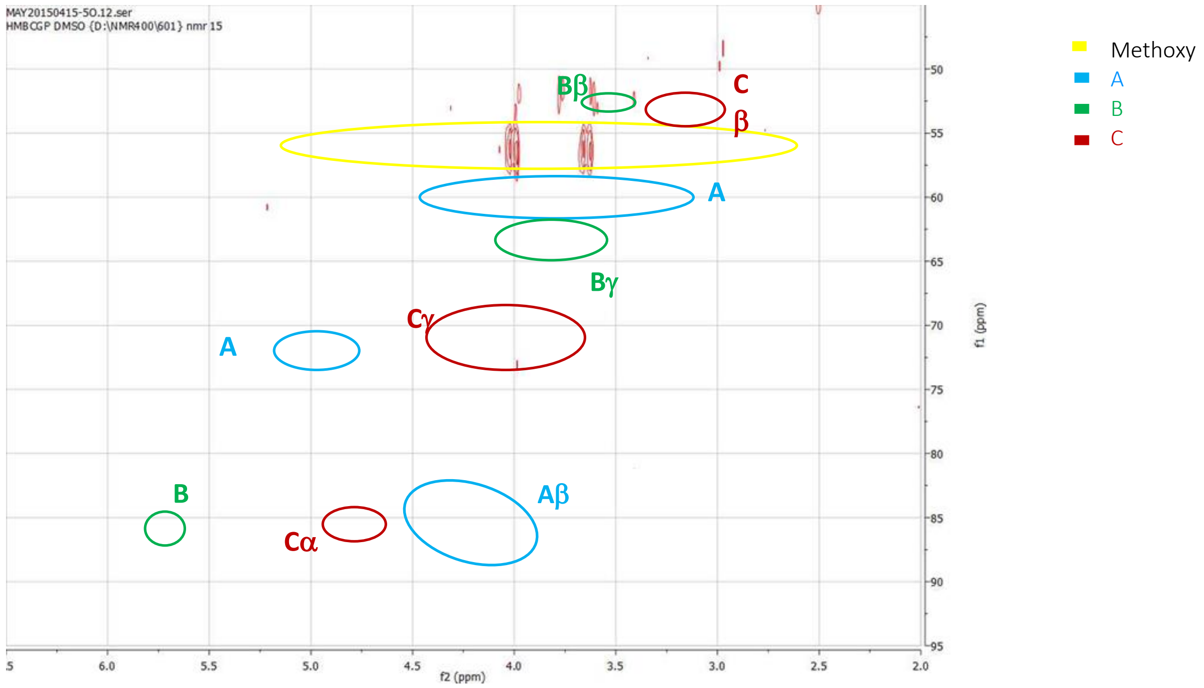


AFTER OXIDATION
Ratio of binding: 1,55 : 1 : 0,38

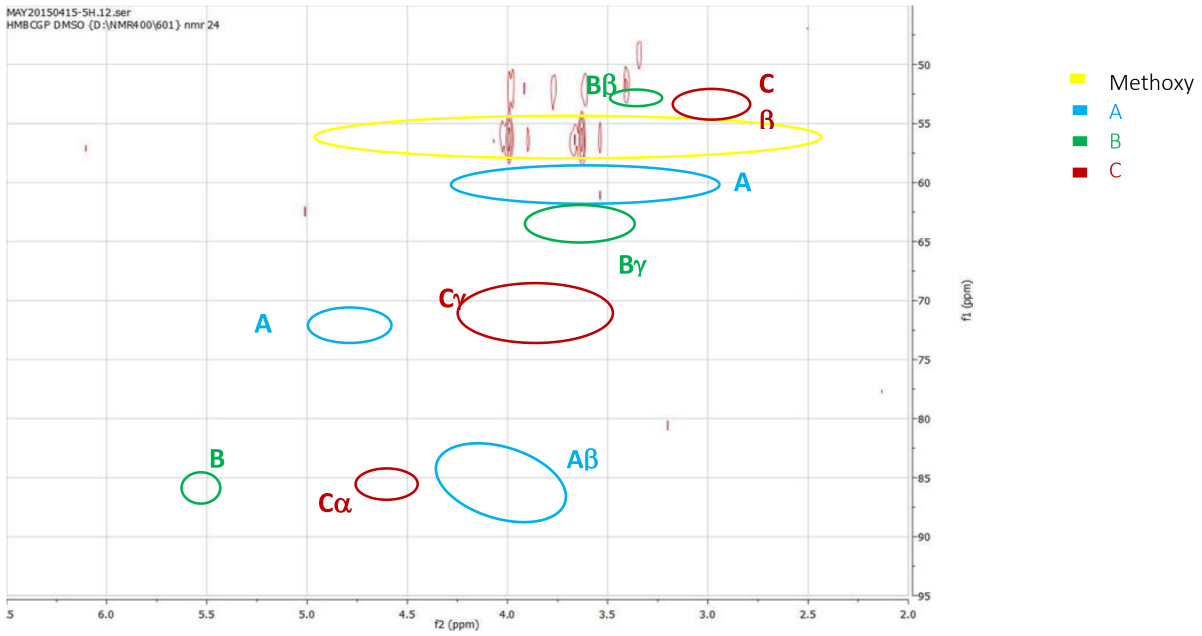
AFTER HYDROGENOLYSIS
Ratio of binding: 1,41 : 1 : 0,38

Experiment L05

Oxidation



Hydrogenolysis

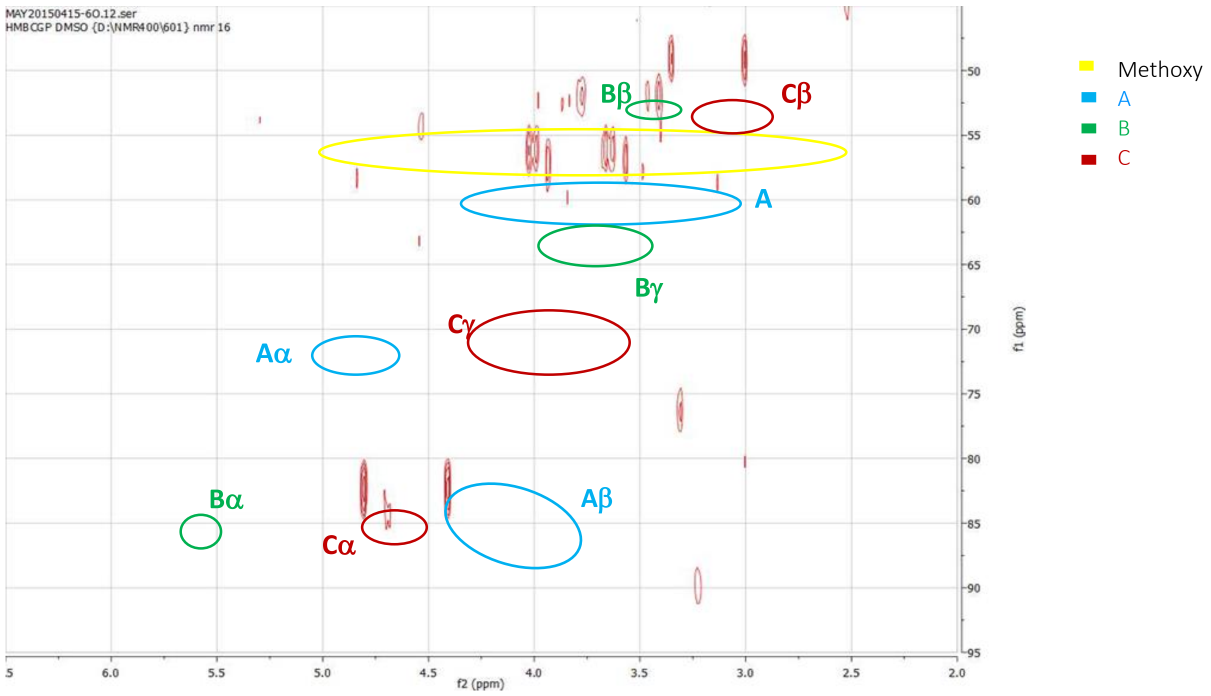


AFTER OXIDATION
Ratio of binding: 1,68 : 1 : 0,37

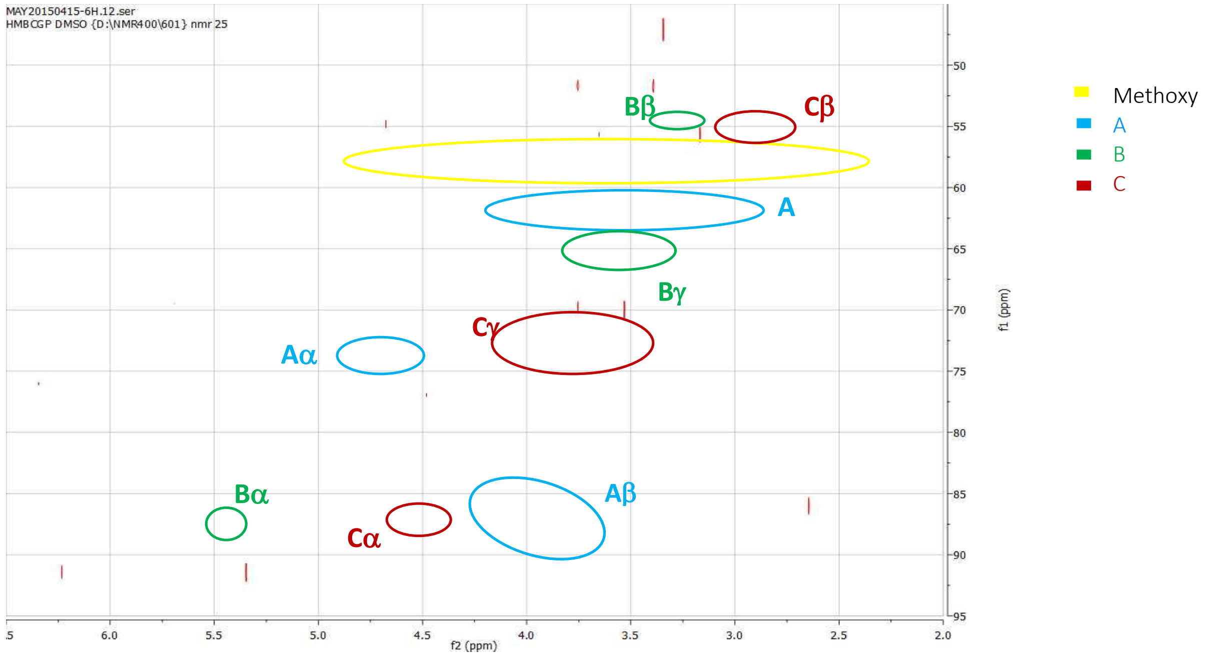
AFTER HYDROGENOLYSIS
Ratio of binding: 1,47 : 1 : 0,36

Experiment L06

Oxidation



Hydrogenolysis

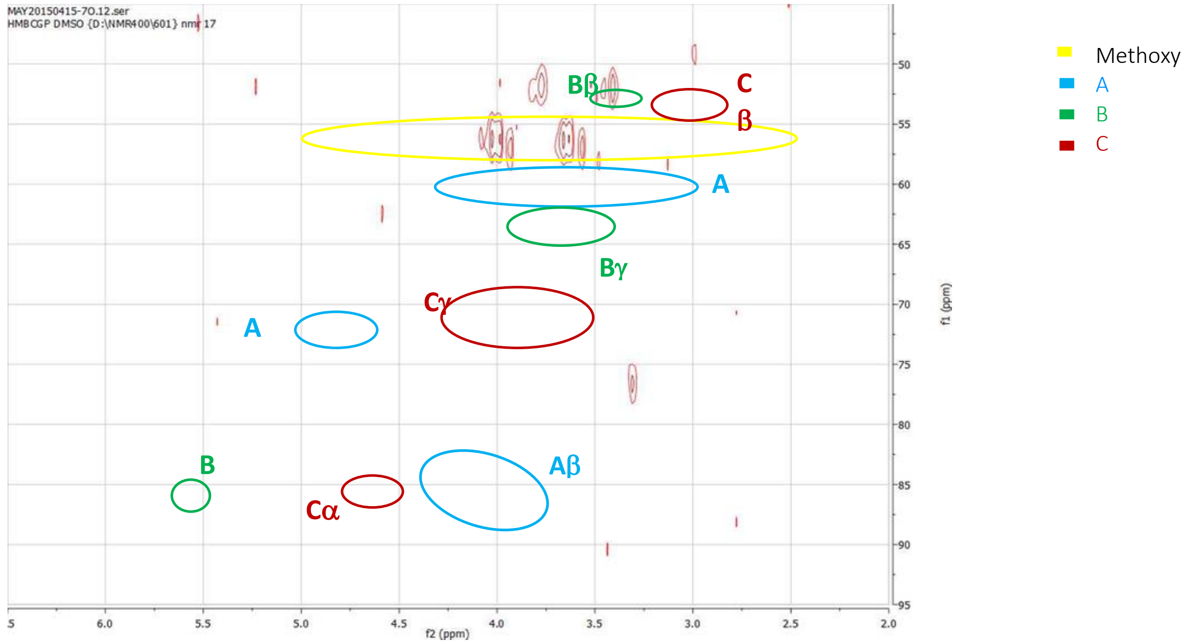


AFTER OXIDATION
Ratio of binding: 1,45 : 1 : 0,53

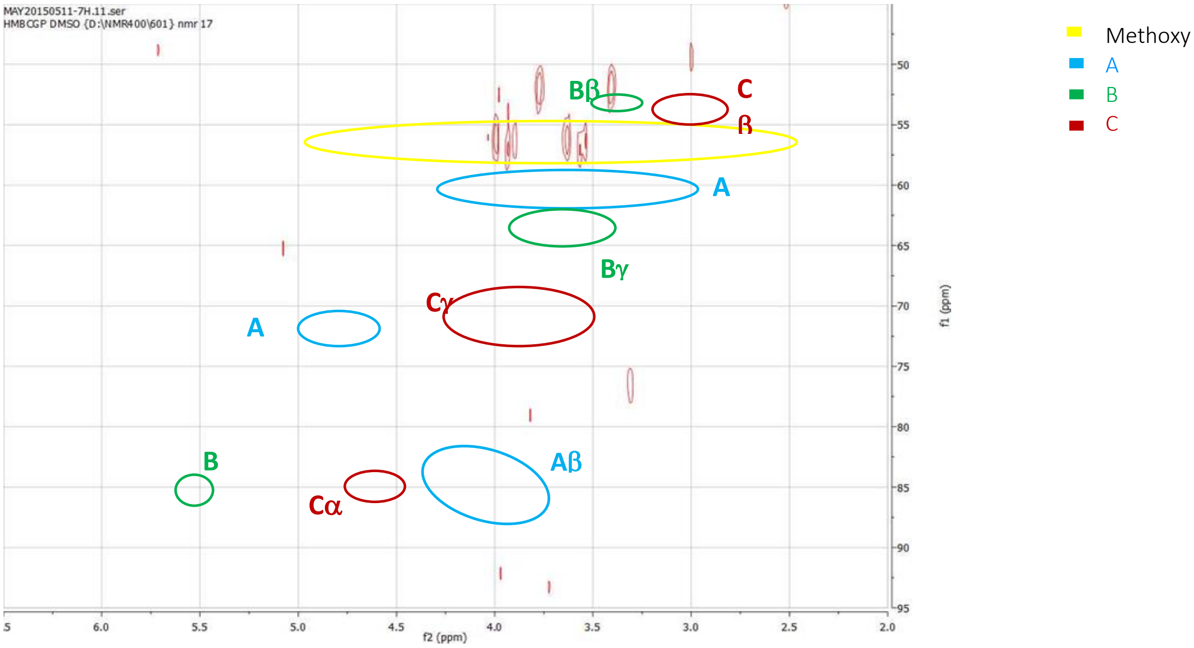
AFTER HYDROGENOLYSIS
Ratio of binding: 1,33 : 1 : 0,32

Experiment L07

Oxidation



Hydrogenolysis

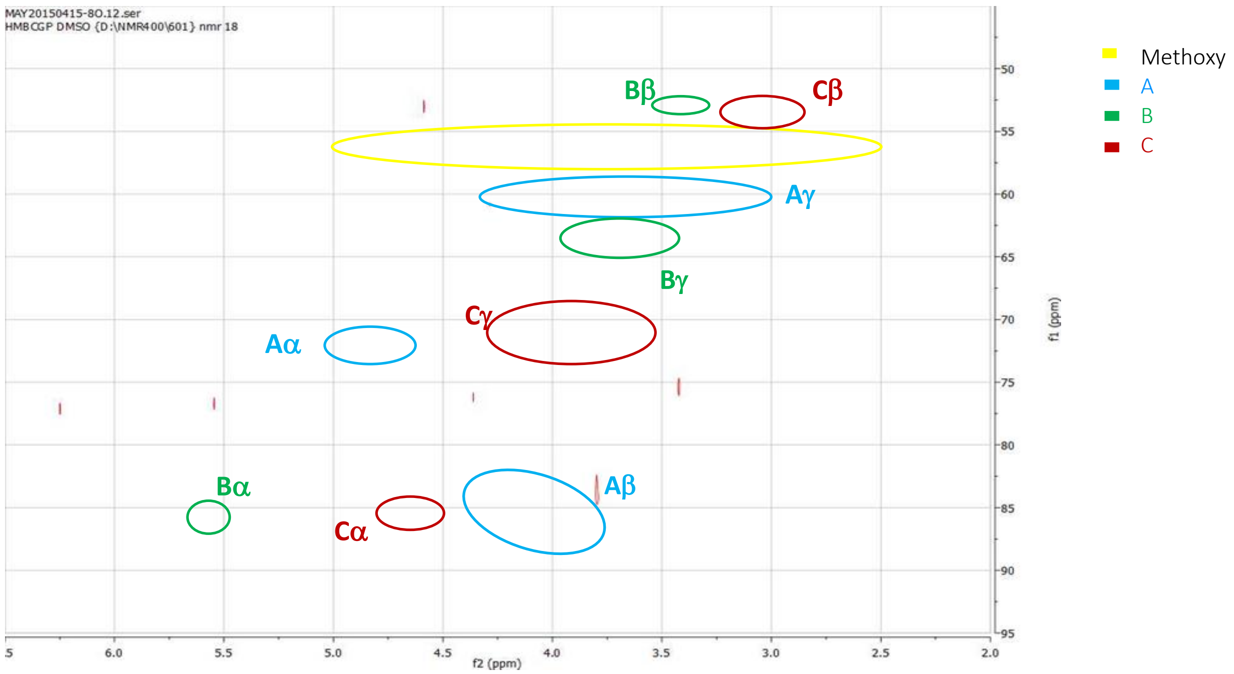


AFTER OXIDATION
Ratio of binding: 1,95 : 1 : 0,38

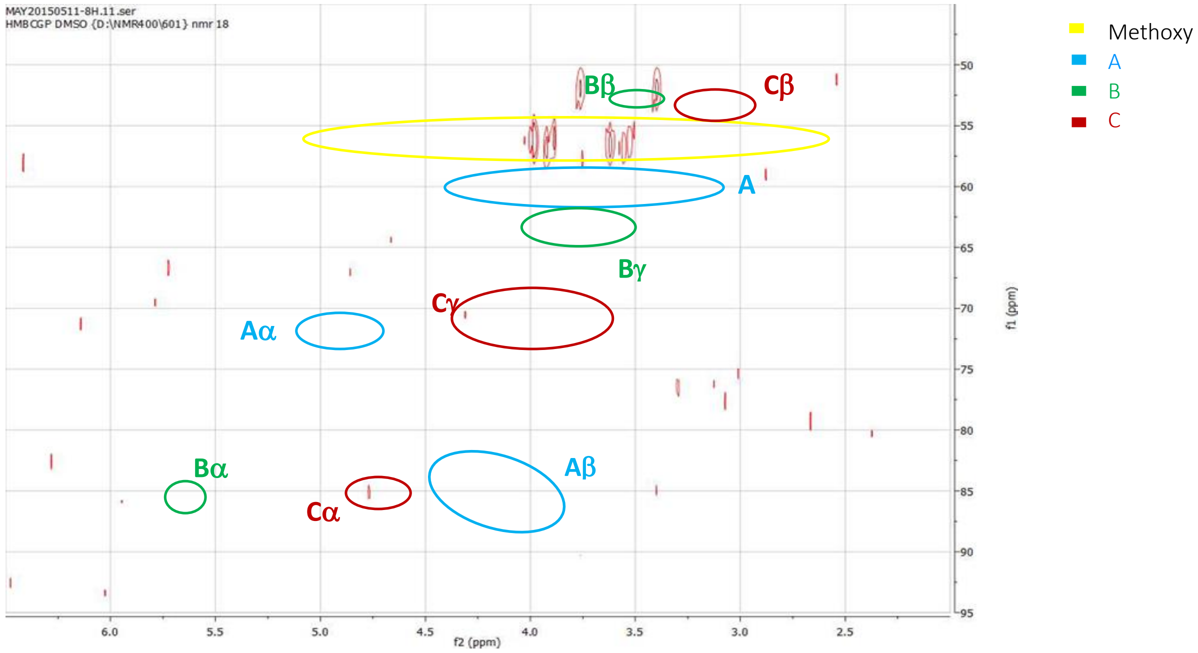
AFTER HYDROGENOLYSIS
Ratio of binding: 1,36 : 1 : 0,38

Experiment L08

Oxidation



Hydrogenolysis



AFTER OXIDATION

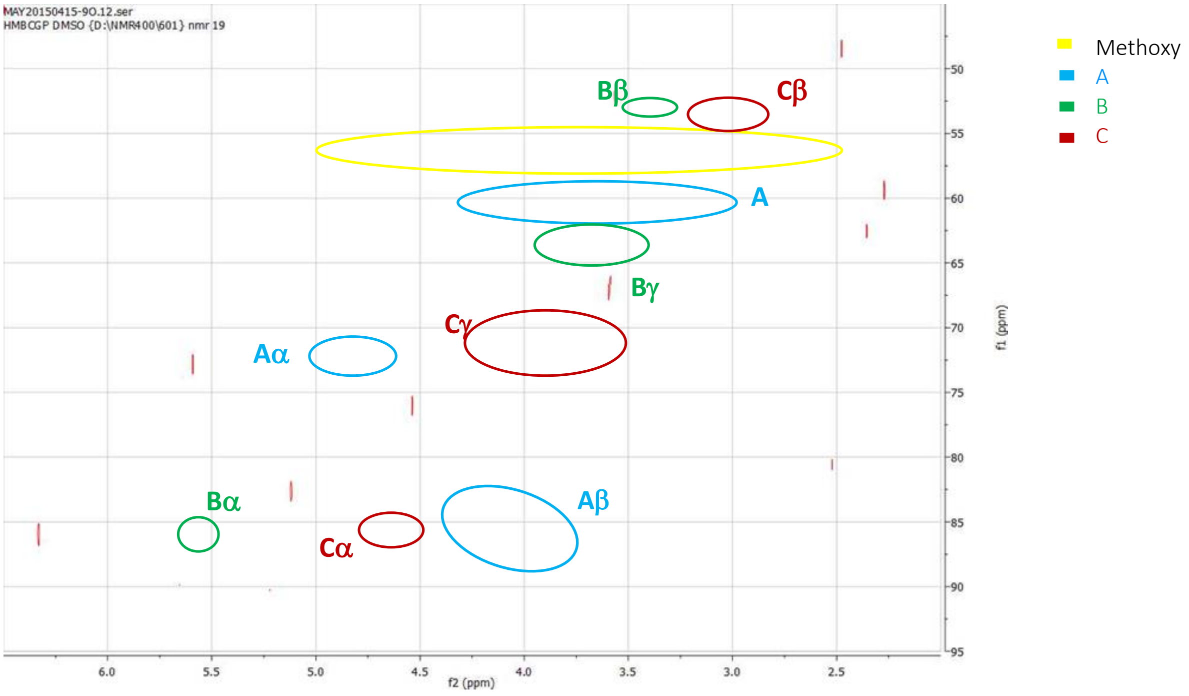
Ratio of binding: 1,56 : 1 : 0,46

AFTER HYDROGENOLYSIS

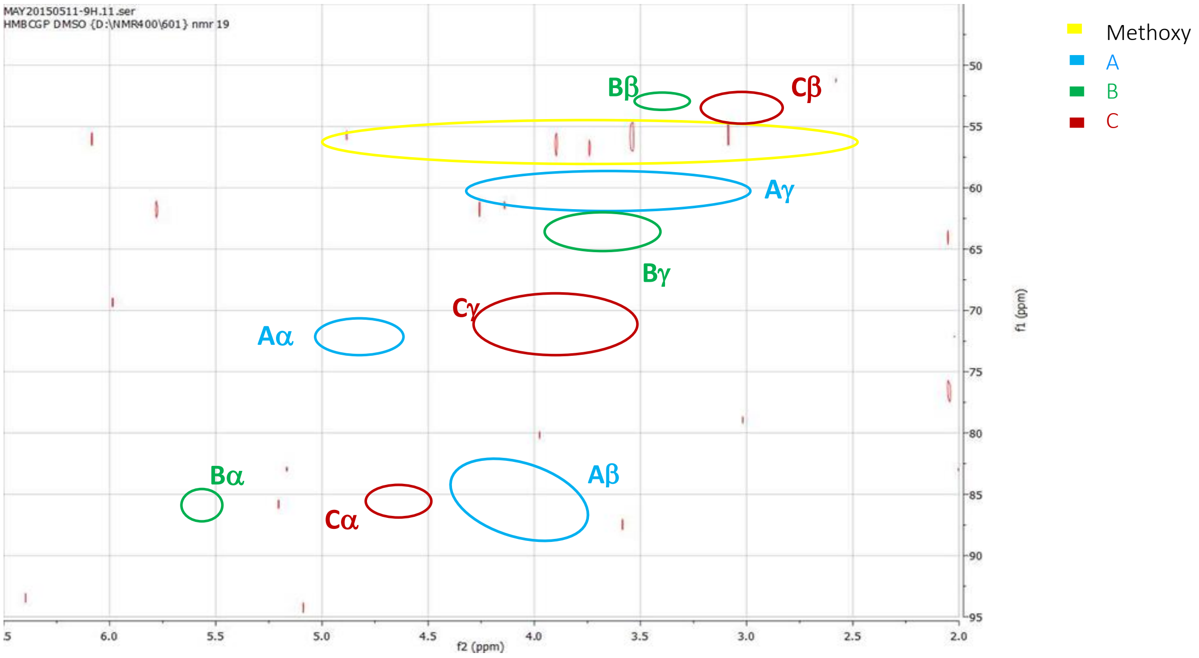
Ratio of binding: 1,55 : 1 : 0,45

Experiment L09

Oxidation



Hydrogenolysis

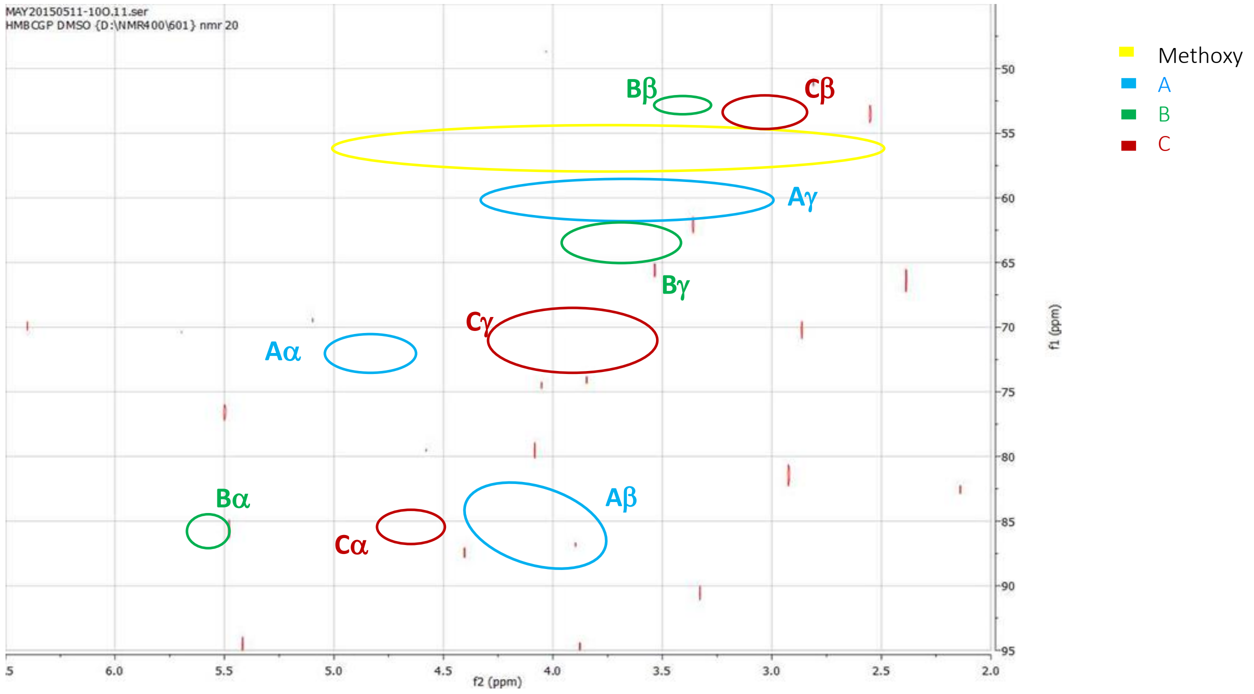


AFTER OXIDATION
Ratio of binding: 1,57 : 1 : 0,40

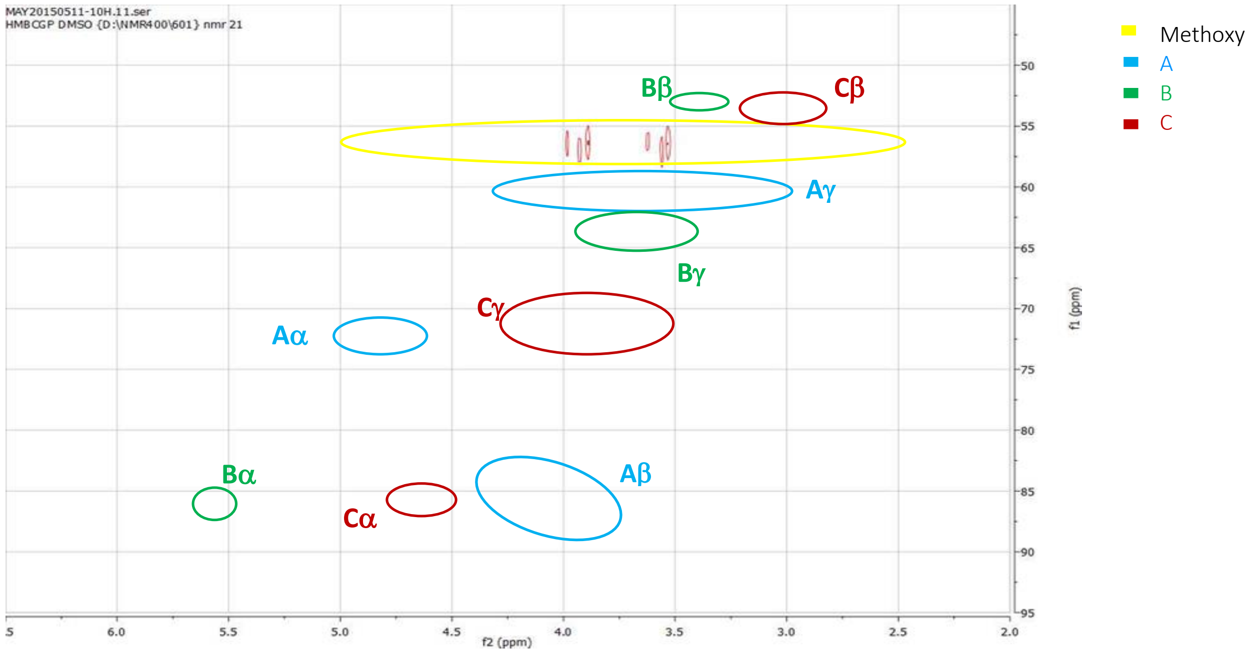
AFTER HYDROGENOLYSIS
Ratio of binding: 1,43 : 1 : 0,38

Experiment L10

Oxidation



Hydrogenolysis

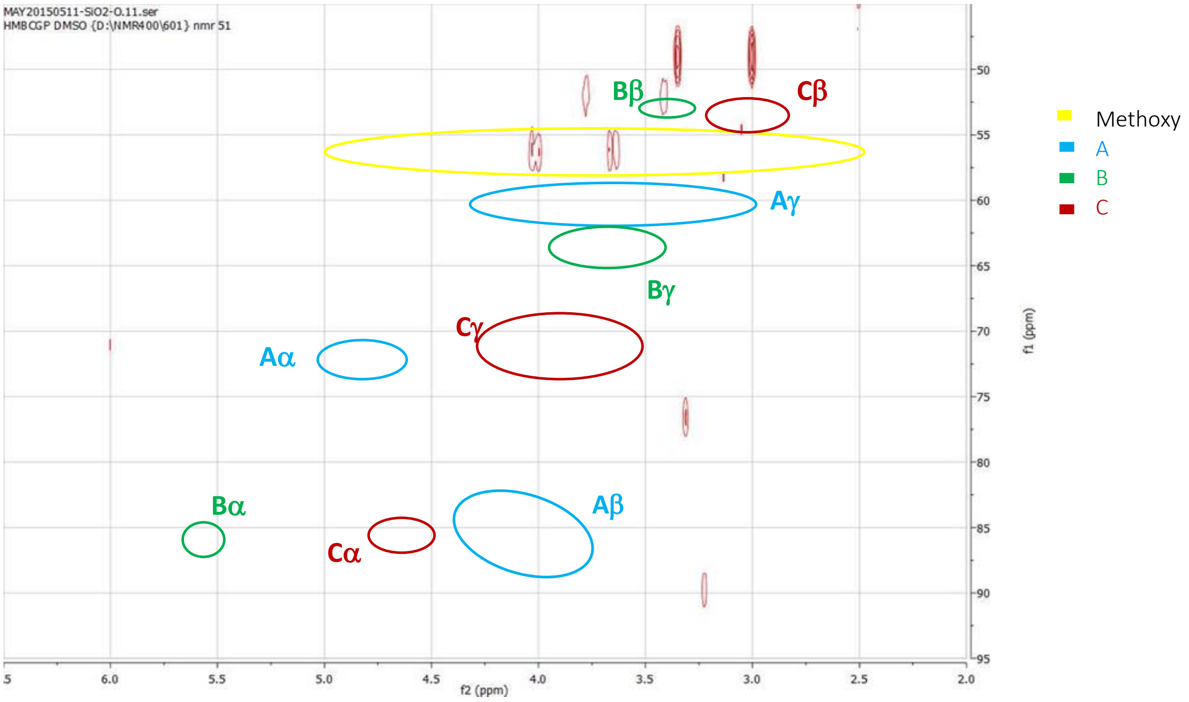


AFTER OXIDATION
Ratio of binding: 1,43 : 1 : 0,35

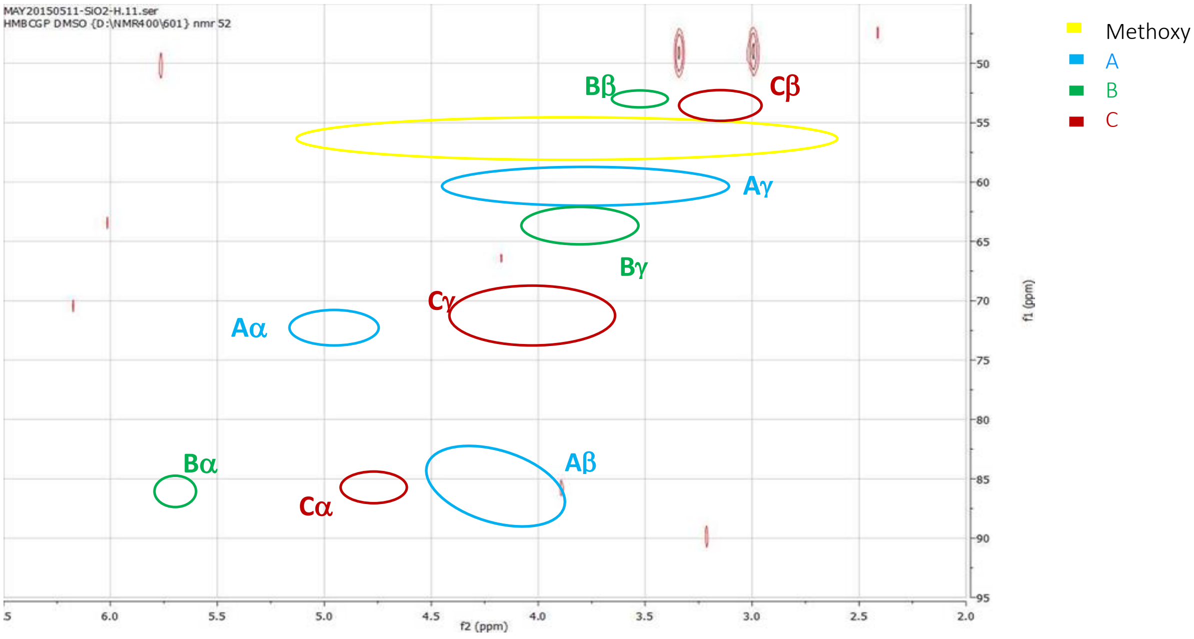
AFTER HYDROGENOLYSIS
Ratio of binding: 1,40 : 1 : 0,33

Experiment L11

Oxidation



Hydrogenolysis

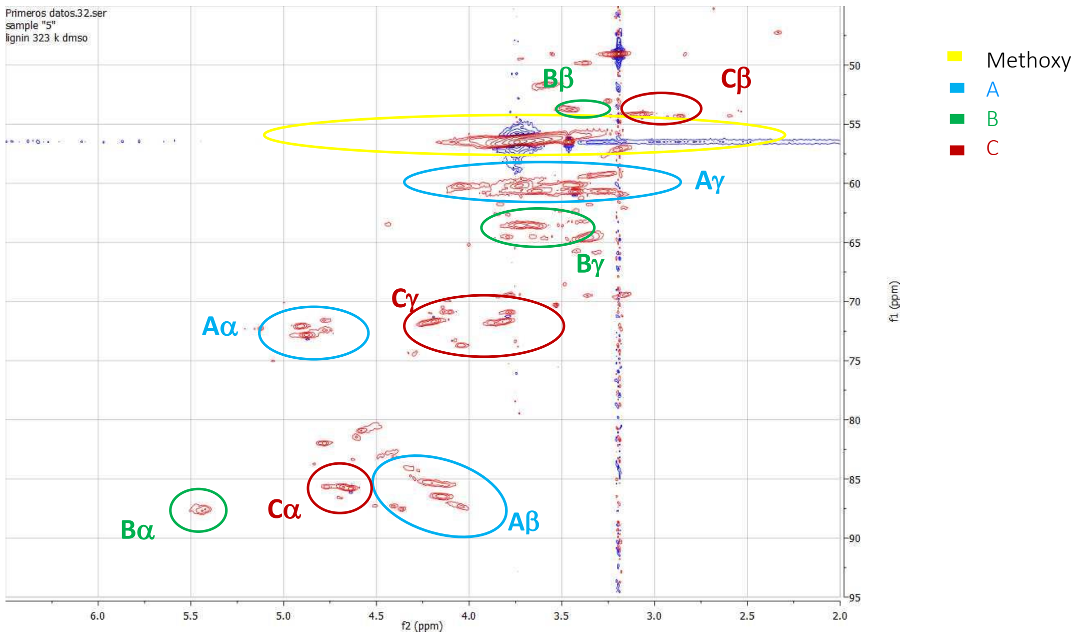


AFTER OXIDATION
Ratio of binding: 2,49 : 1 : 0,70

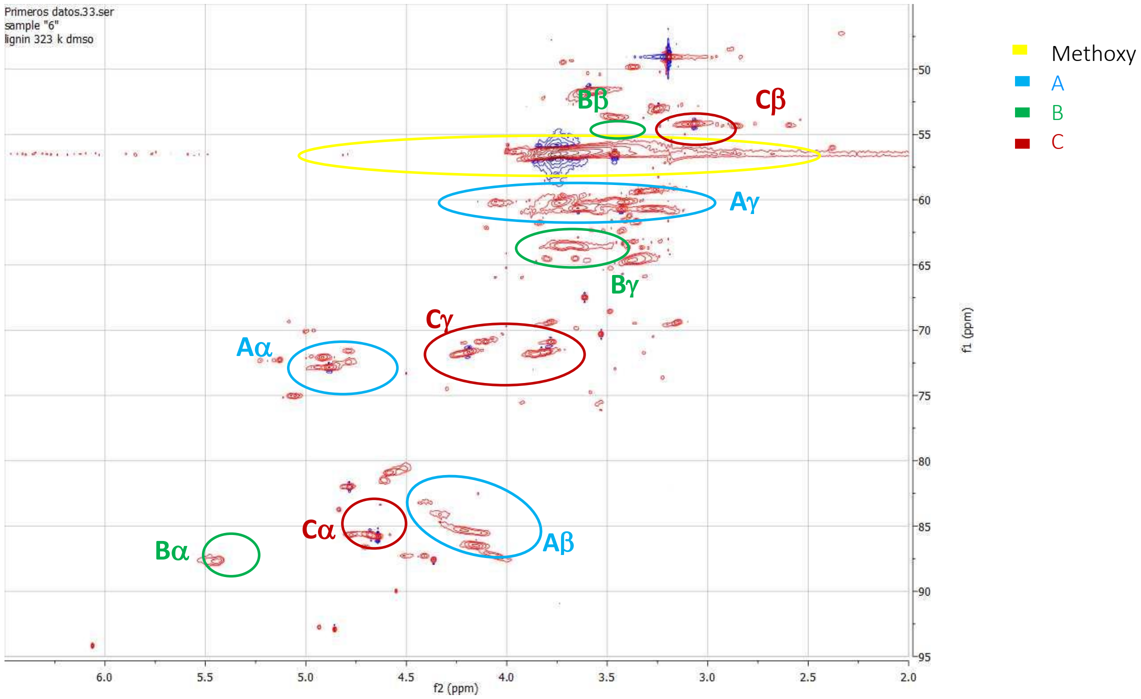
AFTER HYDROGENOLYSIS
Ratio of binding: 1,87 : 1 : 0,48

Hydrogenolysis

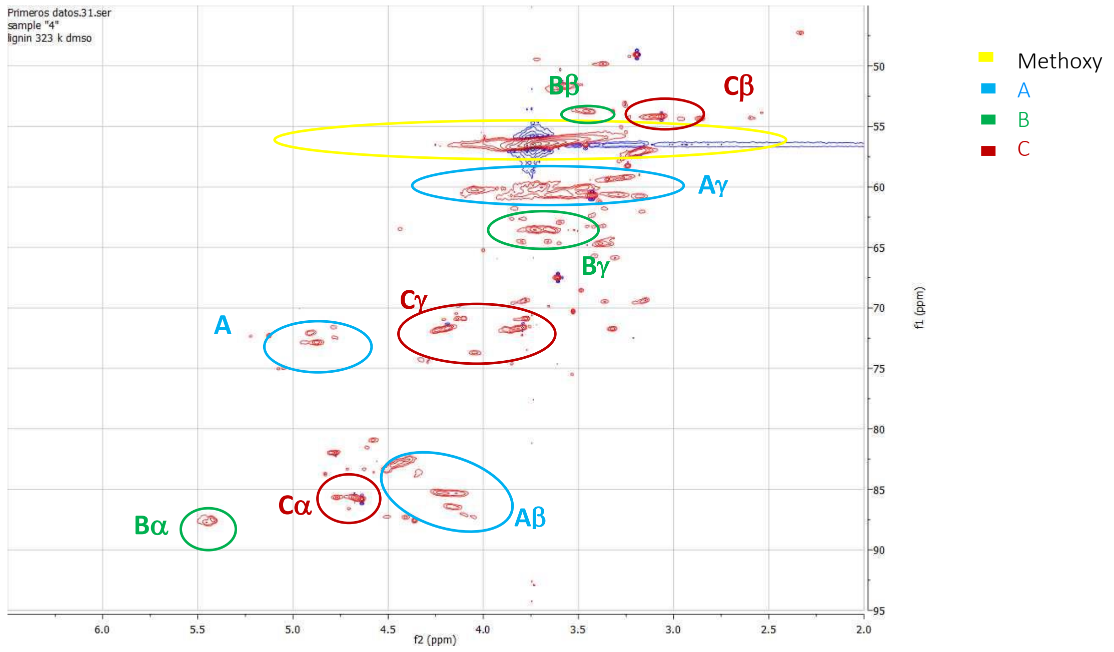
H1



H2

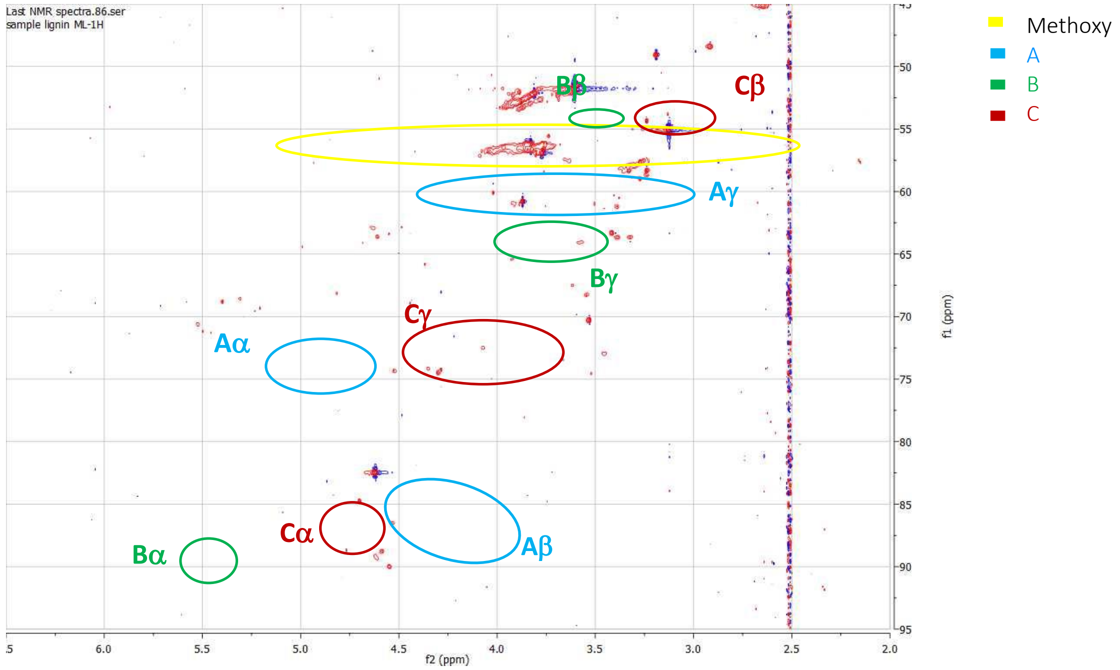


H3

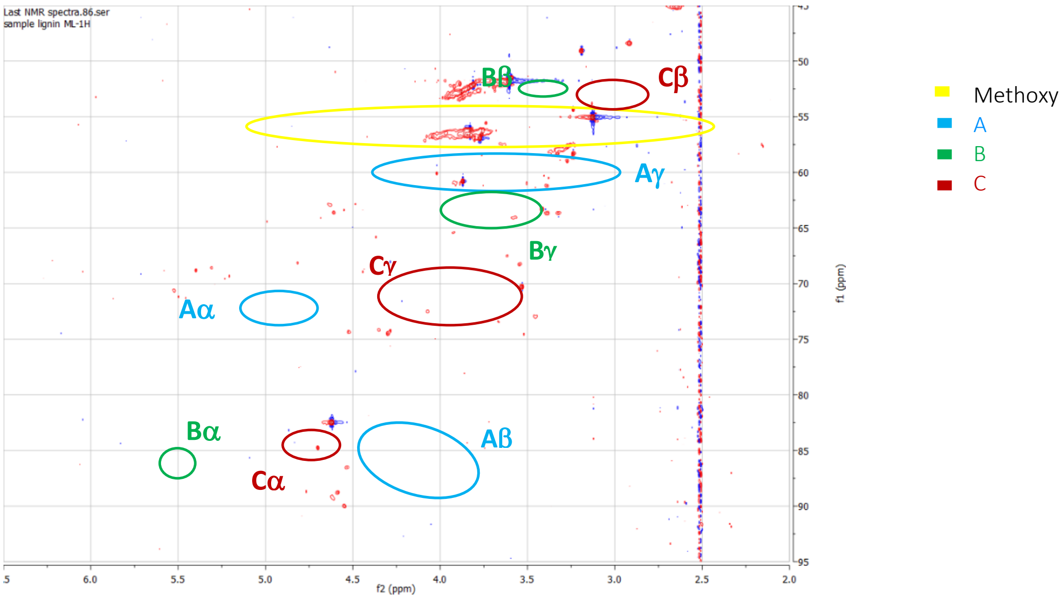


Temperature study

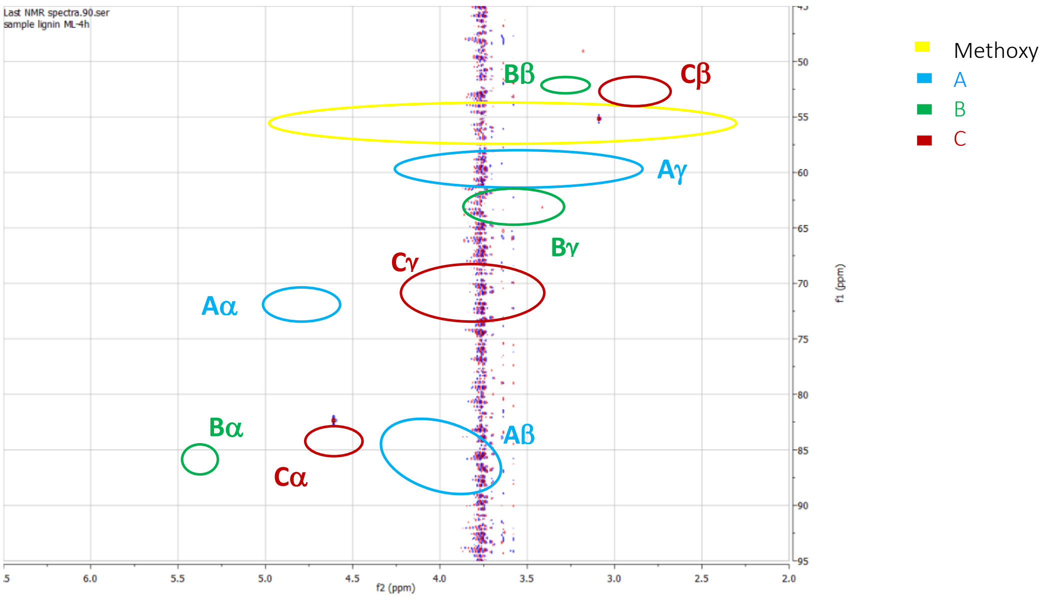
T1



T2

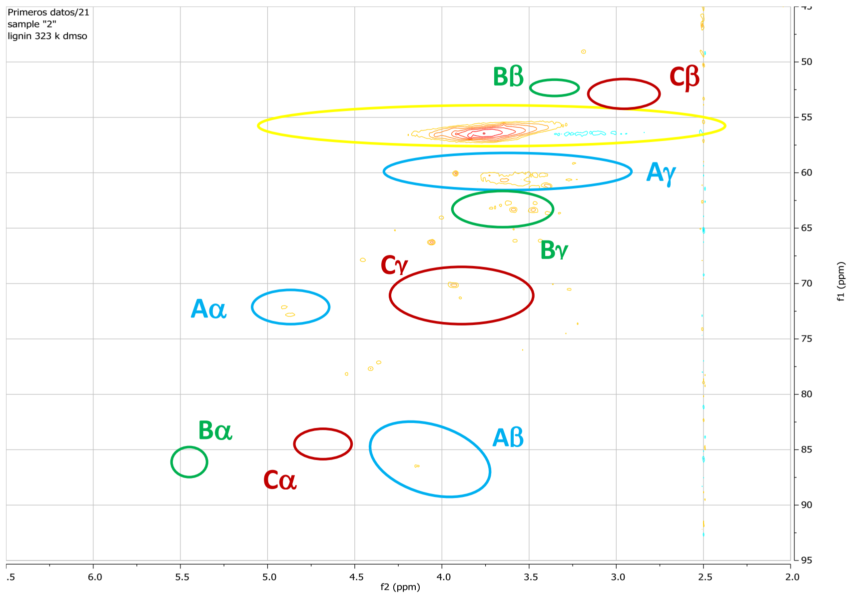

Last NMR spectra.86.ser
sample lignin ML-1H
Bβ
Cβ
Aγ
Bγ
Cγ
Aα
Bα
Cα
Aβ
f2 (ppm)
f1 (ppm)
.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
45
50
55
60
65
70
75
80
85
90
95
Methoxy
A
B
C

T3


Last NMR spectra.90.ser
sample lignin ML-4h
Bβ
Cβ
Aγ
Bγ
Cγ
Aα
Bα
Cα
Aβ
f2 (ppm)
f1 (ppm)
.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
45
50
55
60
65
70
75
80
85
90
95
Methoxy
A
B
C

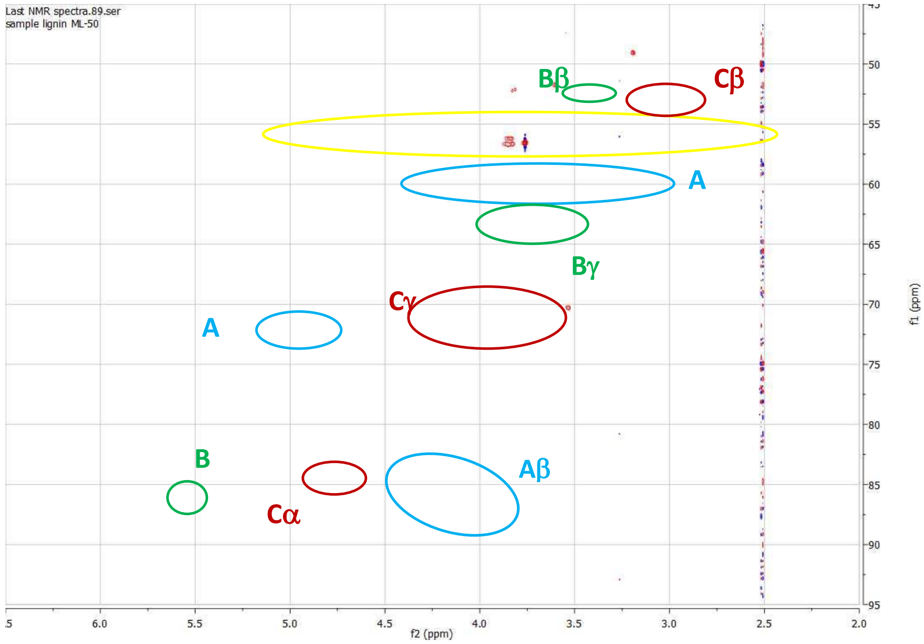
Oxidation

O1

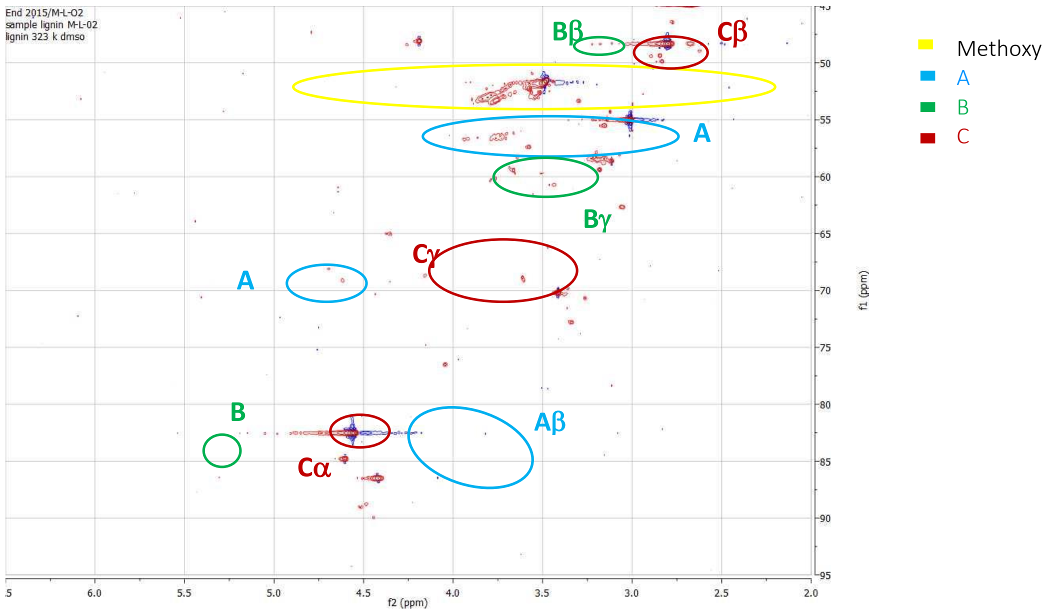


🟨 Methoxy
🟦 A
🟩 B
🟥 C

O2



O3


End 2015/M-L-O2
sample lignin M-L-02
lignin 323 k dmso
Bβ
Cβ
A
Bγ
Cγ
A
B
Aβ
Cα
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
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50
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80
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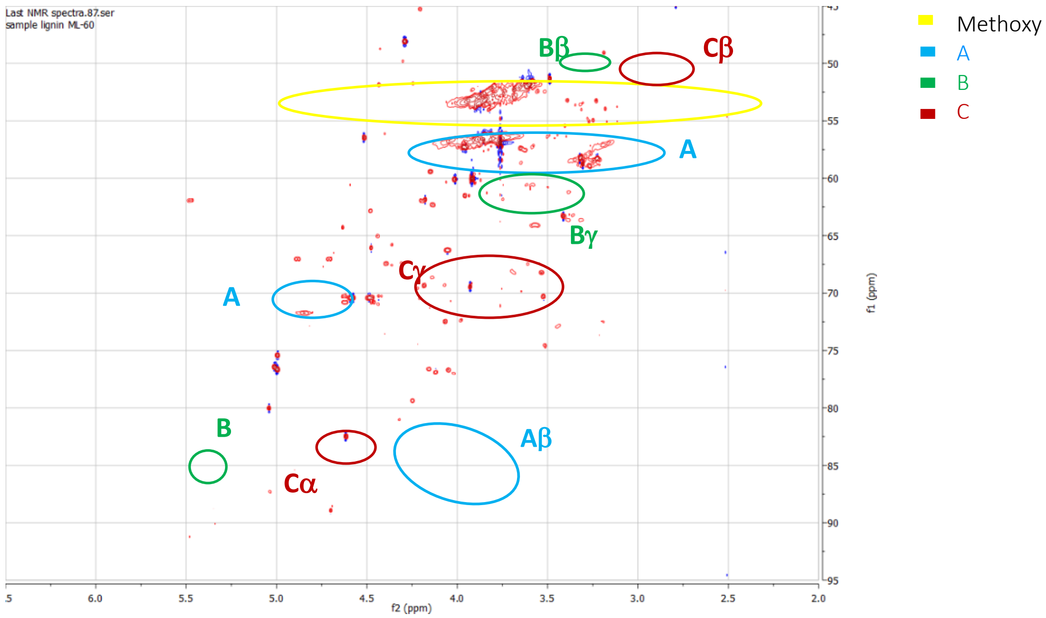
90
95
Methoxy
A
B
C

O4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Bβ
Cβ
A
Bγ
Cγ
A
B
Aβ
Cα
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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80
85
90
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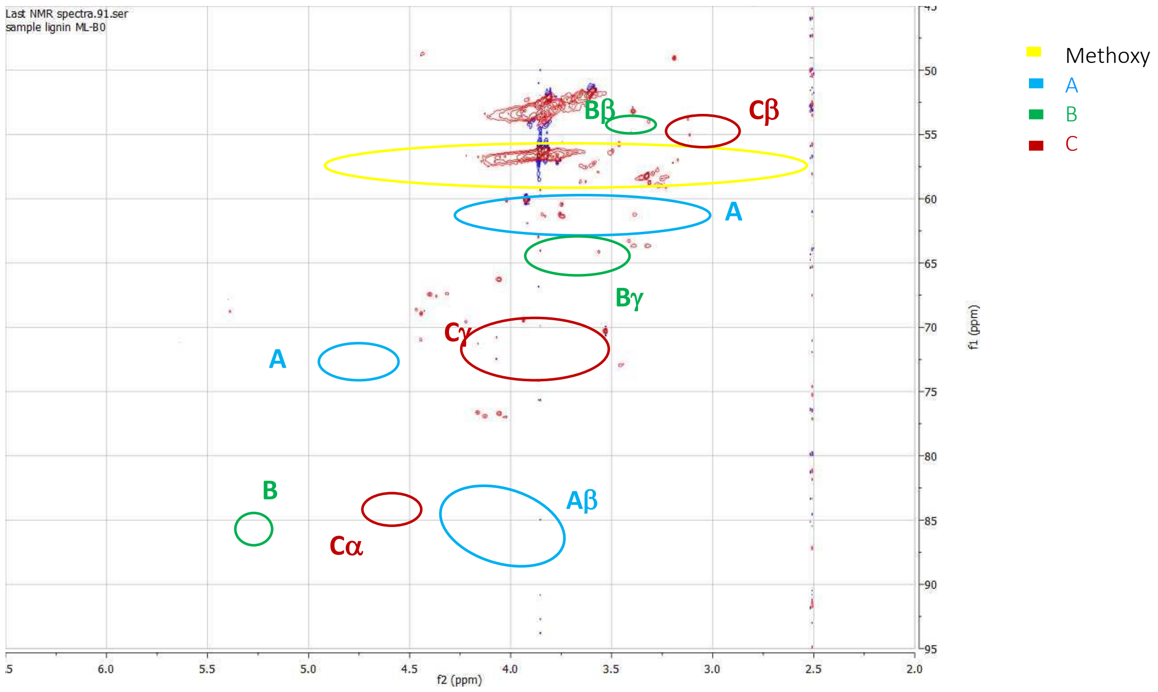
Methoxy
A
B
C

O5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sample lignin ML-B0
Bβ
Cβ
A
Bγ
Cγ
A
B
Aβ
Cα
45
50
55
60
65
70
75
80
85
90
95
f1 (ppm)
.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
🟨 Methoxy
🟦 A
🟩 B
🟥 C

B

Appendix B

Publications

Project related articles.

M. Melián-Rodríguez, S. Saravanamurugan, S. Kegnæs, A. Riisager, Aerobic Oxidation of Veratryl Alcohol to Veratraldehyde with Heterogeneous Ruthenium Catalysts, Top. Catal. 58 (2015) 1036–1042.

M. Melián-Rodríguez, S. Saravanamurugan, S. Meier, S. Kegnæs, A. Riisager, Heterogeneous catalysts for the selective oxidation of guaiacyl glycerol-β-guaiacyl ether- a lignin model compound (2016). In preparation.

M. Melián-Rodríguez, J. Chen, S. Saravanamurugan, F. Lu, S. Kegnæs, A. Riisager, Study of the influence of organosolv lignin treatment in hydrogenolysis and oxidation reactions (2016). In preparation.

Other articles.

M. Paniagua, S. Saravanamurugan, M. Melián-Rodríguez, J.A. Melero, A. Riisager, Xylose Isomerization with Zeolites in a Two-Step Alcohol-Water Process, ChemSusChem. 8 (2015) 1088–1094.

C. Álvarez-Galván, M. Melián-Rodríguez, L. Ruiz-Matas, B. Roldan-Cuenya, R. M. Navarro, J.L.G. Fierro, Ni-Rh catalysts for hydrogen production by partial oxidation of methane. Influence of support type (2016). In preparation.

Conferences, presentations and courses attended

Oral Presentation

2015 **COST Action Lignoval**, Litvinov, Czech Republic.
Selective aerobic oxidation of b-O-4 lignin model compounds into Guaiacol and other simple aromatic compounds.

2015 **DTU Chemistry Ph.D. Symposium**, Kongens Lyngby, Denmark.
Heterogeneous catalysts for the conversion of lignin and lignin model compounds.

2015 **COST Action Lignoval**, Belgrade, Serbia.
Aerobic oxidation of β-O-4 lignin model compounds with solid catalysts.

2014 **DTU Chemistry Ph.D. Symposium**, Kongens Lyngby, Denmark.
Aerobic oxidation of veratryl alcohol to veratraldehyde with heterogeneous ruthenium catalysts.

Poster Presentation

2015 **12th European Congress on Catalysis**, Kazan, Russian Federation.
Catalytic oxidation of veratryl alcohol – a β-O-4 lignin model compound - to veratraldehyde.

2014 **Summer School on Catalysis of Biomass**, Liblice, Czech Republic.
Lignin valorization using heterogeneous catalytic oxidation.

2014 **16th Nordic Symposium on Catalysis**, Oslo, Norway.
Heterogeneous catalysis in oxidation of lignin model compounds.

2014 **4th International Congress in Green Process Engineering**, Sevilla, Spain.
Lignin Valorization by Heterogeneous Catalytic Oxidation.

2013 **DTU Chemistry Ph.D. Symposium**, Søro, Denmark.
Heterogeneous catalysis for lignin conversion.

2013 **2nd International Congress on Catalysis for Biorefineries**, Dalian, China.
Conversion of lignin into chemicals with heterogeneous catalysis: Current and future technologies.

References

1. Ragauskas. A. J. The Path Forward for Biofuels and Biomaterials. *Science (80).* **311.** 484–489 (2006).
2. Europe 2020 - http://ec.europa.eu/europe2020/index_en.htm (January 2016)
3. European Commission. A resource-efficient Europe – Flagship initiative under the Europe 2020 Strategy. 1–17 (2011).
4. Serrano-Ruiz. J. C. & Dumesic. J. A. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. *Energy Environ. Sci.* **4.** 83–99 (2011).
5. United Nations - www.un.org (January 2016)
6. BP statistical Review of World Energy 2015 - www.bp.com (January 2016)
7. Food and Agriculture Organization of the United Nations - www.fao.org (January 2016)
8. U.S. Energy information Administration (EIA) - www.eia.gov/ (January 2016)
9. IPPC Panel. *Climate Change 2014: Synthesis Report*. (2014).
10. International Energy Agency (IEA) – www.iea.org (January 2016)
11. The World Bank – www.worldbank.org - Foster. V. & Bedrosyan. D. Understanding CO2 Emissions from the Global Energy Sector. *Live wire* **5.** 1–12 (2014).
12. Manley. J. B.. Anastas. P. T. & Cue. B. W. Frontiers in Green Chemistry: meeting the grand challenges for sustainability in R&D and manufacturing. *J. Clean. Prod.* **16.** 743–750 (2008).
13. Marteel-parrish. A. E. & Abraham. M. A. Green Chemistry and Engineering: A Pathway to sustainability. 235–262 (2014).
14. Brundtland. G. C. Report of the World Commission on Environment and Development: Our Common Future (The Brundtland Report). *Med. Confl. Surviv.* **4.** 300 (1987).
15. Sheldon. R. A. E factors. green chemistry and catalysis: an odyssey. *Chem. Commun.* 3352–3365 (2008).
16. Sheldon. R. A. The E Factor: fifteen years on. *Green Chem.* **9.** 1273 (2007).
17. Sheldon. R. A. Fundamentals of green chemistry: efficiency in reaction design. *Chem. Soc. Rev.* **41.** 1437 (2012).
18. Anastas. P. T.. Kirchhoff. M. M. & Williamson. T. C. Catalysis as a foundational pillar of green chemistry. *Appl. Catal. A Gen.* **221.** 3–13 (2001).
19. Rothenberg. G. *Catalysis: Concepts and Green Applications*. Willey – VH. (2008).
20. Sheldon. R.. Arends. I. & Hanefeld. U. *Industrial Catalysis: A practical approach. Second Edition*. *Willey-VHC* (2006).
21. Knözinger. H. & Kochloefl. K. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH (2003).

22. Ertl. G. *et al. Handbook of heterogeneous catalysis*. Wiley-VCH (2008).

23. Corma Canos. A.. Iborra. S. & Velty. A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **107.** 2411–2502 (2007).

24. Baskar. C. *et al. Biomass conversion: the interface of biotechnology. chemistry and materials science*. Springer (2012).

25. PFaltzgraff. L. A. & Clark. J. H. Green chemistry. biorefineries and second-generation strategies for re-use of waste: an overview. *Adv. Biorefineries Biomass Waste Supply Chain Exploit.* 3–33 (2014).

26. Eisentraut. A. & Brown. A. Technology Roadmap Bioenergy for Heat and Power. *IEA Publ.* 1–41 (2012).

27. Regalbuto. J. An NSF perspective on next generation hydrocarbon biorefineries. *Comput. Chem. Eng.* **34.** 1393–1396 (2010).

28. Rinaldi. R. & Schüth. F. Design of solid catalysts for the conversion of biomass. *Energy Environ. Sci.* **2.** 610 (2009).

29. Rubin. E. M. Genomics of cellulosic biofuels. *Nature* **454.** 841–845 (2008).

30. Kamm. B. & Kamm. M. Principles of biorefineries. *Appl. Microbiol. Biotechnol.* **64.** 137–145 (2004).

31. Clark. J. H.. Deswarte. F. E. I. & Farmer. T. J. The integration of green chemistry into future biorefineries. *Biofuels. Bioprod. Biorefining* **3.** 72–90 (2009).

32. Murat Sen. S.. Henao. C. A.. Braden. D. J.. Dumesic. J. A. & Maravelias. C. T. Catalytic conversion of lignocellulosic biomass to fuels: Process development and technoeconomic evaluation. *Chem. Eng. Sci.* **67.** 57–67 (2012).

33. Huber. G. W.. Iborra. S. & Corma. A. Synthesis of Transportation Fuels from Biomass : Chemistry. Catalysts. and Engineering. **2.** 4044–4098 (2006).

34. Goyal. H. B.. Seal. D. & Saxena. R. C. Bio-fuels from thermochemical conversion of renewable resources: A review. *Renew. Sustain. Energy Rev.* **12.** 504–517 (2008).

35. Borregaard – www.borregaard.com (January 2016)

36. Patil. P. T.. Armbruster. U.. Richter. M. & Martin. A. Heterogeneously catalyzed hydroprocessing of organosolv lignin in sub- and supercritical solvents. *Energy and Fuels* **25.** 4713–4722 (2011).

37. Gosselink. R. J. a *et al.* Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals. *Bioresour. Technol.* **106.** 173–177 (2012).

38. Zakzeski. J.. Bruijnincx. P. C. a. Jongerius. A. L. & Weckhuysen. B. M. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* **110.** 3552–99 (2010).

39. Chundawat. S. P. S.. Beckham. G. T.. Himmel. M. E. & Dale. B. E. Deconstruction of lignocellulosic biomass to fuels and chemicals. *Annu. Rev. Chem. Biomol. Eng.* **2.** 121–45 (2011).

40. Pauly. M. & Keegstra. K. Cell-wall carbohydrates and their modification as a resource for biofuels. *Plant J.* **54.** 559–568 (2008).
41. Langan. P. *et al.* Common processes drive the thermochemical pretreatment of lignocellulosic biomass. *Green Chem.* **16.** 63 (2014).
42. Thomas Splettstoesser - SciStyle – Scientific Ilustration & Animation. www.scistyle.com/Lignocellulose.
43. Gregorio Rodríguez Pérez - GRPstudio – www.grpstudio.com (January 2016)
44. Van Haveren. J.. Scott. E. L. & Sanders. J. Bulk chemicals from biomass. *Biofuels. Bioprod. Biorefining* **2.** 41–57 (2008).
45. Sjöström. E. *Wood chemistry: Fundamentals and applications*. Academic. (1993).
46. Lin. S. Y. & Dence. C. W. *Methods in Lignin Chemistry*. Springer Science & Business Media. (1992).
47. Belgacem. M. N. & Gandini. A. Monomers. polymers and composites from renewable resources. Elsevier (2008)
48. Adler. E. Lignin Chemistry - Past. Present and Future. *Wood Sci. Technol.* **11.** 169–218 (1977).
49. Evstigneev. E. I. Factors affecting lignin solubility. *Russ. J. Appl. Chem.* **84.** 1040–1045 (2011).
50. Kilpeläinen. I. *et al.* Dissolution of wood in ionic liquids. *J. Agric. Food Chem.* **55.** 9142–9148 (2007).
51. Delmas. M. Vegetal refining and agrichemistry. *Chem. Eng. Technol.* **31.** 792–797 (2008).
52. da Costa Sousa. L.. Chundawat. S. P.. Balan. V. & Dale. B. E. 'Cradle-to-grave' assessment of existing lignocellulose pretreatment technologies. *Curr. Opin. Biotechnol.* **20.** 339–347 (2009).
53. Tejado. A.. Peña. C.. Labidi. J.. Echeverria. J. M. & Mondragon. I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresour. Technol.* **98.** 1655–1663 (2007).
54. Holladay. J. E.. Bozell. J. J.. Johnson. D. & White. J. F. *Top Value Added Chemicals from Biomass. Pacific Northwesr National Laboratory. Richland. WA* (2007).
55. Avellar. B. C. & Glassier. W. G. Steam-assisted biomass fraction. I. Process considerations and economic evaluation. *Biomass and Bioenergy* **14.** 205–218 (1998).
56. Vishtal. A. & Kraslawski. A. Challenges in industrial applications of technical lignins. *BioResources* **6.** 3547–3568 (2011).
57. Lora. J. H. Industrial commercial lignins: Sources. properties and applications. *Monomers. Polym. Compos. from Renew. Resour.* 225–241 (2008).
58. Chakar. F. S. & Ragauskas. A. J. Review of current and future softwood kraft lignin process chemistry. *Ind. Crops Prod.* **20.** 131–141 (2004).
59. Axegård. P. Biorefinery – Simultaneous production of fibers. Energy and chemicals. (2011).

60. Hallberg. C. *et al.* Continuos counter-current organosolv processing of lignocellulosic feedstock. (2008).

61. Sarwar Jahan. M.. Nasima Chowdhury. D. A.. Russel. M. A. N.. Mun. S. P. & Quaiyyum. M. A. Alkaline Aulfite – Antraquinone – Methanol (ASAM) Pulping of corn stalks. *Cellul. Chem. Technol.* **40.** 531–536 (2006).

62. Meier. D.. Berns. J.. Faix. O.. Balfanz. U. & Baldauf. W. Hydrocracking of organocell lignin for phenol production. *Biomass and Bioenergy* **7.** 99–105 (1994).

63. Vázquez. G.. Antorrena. G.. González. J.. Freire. S. & López. S. Acetosolv pulping of pine wood. Kinetic modelling of lignin solubilization and condensation. *Bioresour. Technol.* **59.** 121–127 (1997).

64. Ligero. P.. Vega. A. & Villaverde. J. J. Delignification of Miscanthus x Giganteus by the Milox process. *Bioresour. Technol.* **101.** 3188–3193 (2010).

65. Kham. L.. Le Bigot. Y.. Delmas. M. & Avignon. G. Delignification of wheat straw using a mixture of carboxylic acids and peroxoacids. *Ind. Crops Prod.* **21.** 9–15 (2005).

66. Pye. E. K. & Lora. J. H. The AlcellTM process : a proven alternative to kraft pulping. *Tappi J.* **74.** 113–118 (1991).

67. CIMV The biorefinery concept - www.cimv.fr (February 2016)

68. Kim. T. H.. Kim. J. S.. Sunwoo. C. & Lee. Y. Y. Pretreatment of corn stover by aqueous ammonia. *Bioresour. Technol.* **90.** 39–47 (2003).

69. Tan. S. S. Y. *et al.* Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. *Green Chem.* **11.** 437–592 (2009).

70. Sun. N. *et al.* Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chem.* **11.** 646 (2009).

71. Fasching. M.. Schröder. P.. Wollboldt. R. P.. Weber. H. K. & Sixta. H. A new and facile method for isolation of lignin from wood based on complete wood dissolution. *Holzforschung* **62.** 15–23 (2008).

72. Hatakeyama. T. & Hatakeyama. H. Lignin Structure. Properties. and Application. *Biopolym. Lignin. Proteins. Bioact. Nanocomposites* **232.** 1–63 (2010).

73. Clements. L. D. & Van Dyne. D. L. *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions*. *Willey-VHC* (2006).

74. Gosselink. R. J. a.. de Jong. E.. Guran. B. & Abächerli. a. Co-ordination network for lignin—standardisation. production and applications adapted to market requirements (EUROLIGNIN). *Ind. Crops Prod.* **20.** 121–129 (2004).

75. Stewart. D. Lignin as a base material for materials applications: Chemistry. application and economics. *Ind. Crops Prod.* **27.** 202–207 (2008).

76. Smolarski. N. High-Value Opportunities for Lignin: Unlocking its Potential Lignin potential. Frost & Sullivan. 1–15 (2012).

77. Lignin Market Analysis By Product (Ligno-sulphonates. Kraft Lignin. Organosolv Lignin. High Purity Lignin) By Application (Macromolecules. Aromatics) And Segment Forecasts To 2022. Gran View Research - www.grandviewresearch.com (January 2016)

78. Mainka. H. *et al.* Lignin – an alternative precursor for sustainable and cost-effective automotive carbon fiber. *J. Mater. Res. Technol.* **4.** 283–296 (2015).

79. Kleinert. M. & Barth. T. Phenols from lignin. *Chem. Eng. Technol.* **31.** 736–745 (2008).

80. Kamlet. J.. Easton & Conn. Manufacturing of vanillin and its homologues. U.S. Patent Office. (1953).

81. Pandey. M. P. & Kim. C. S. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol.* **34.** 29–41 (2011).

82. Wang. H. *et al.* Study on the catalytic gasification of alkali lignin over Ru/C nanotubes in supercritical water. *J. Fuel Chem. Technol.* **43.** 1195–1201 (2015).

83. Voitkevich. O. V. Kabo. G. J.. Blokhin. A. V. Paulechka. Y. U. & Shishonok. M. V. Thermodynamic Properties of Plant Biomass Components. Heat Capacity. Combustion Energy. and Gasi fi cation Equilibria of Lignin. 8–14 (2012).

84. Elliott. D. C. Catalytic hydrothermal gasification of biomass. *Biofuels. Bioprod. Biorefining* **2.** 254–265 (2008).

85. Pollegioni. L.. Tonin. F. & Rosini. E. Lignin-degrading enzymes. *FEBS J.* **282.** 1190–1213 (2015).

86. Tomek. K. J. *et al.* Removal and upgrading of lignocellulosic fermentation inhibitors by in situ biocatalysis and liquid-liquid extraction. *Biotechnol. Bioeng.* **112.** 627–632 (2015).

87. Pucciariello. R. *et al.* Lignin/Poly(ε-Caprolactone) blends with tuneable mechanical properties prepared by high energy ball-milling. *J. Polym. Environ.* **18.** 326–334 (2010).

88. Bolm. C.. Kleine. T. & Buendia. J. Mechanochemical degradation of lignin and wood by solvent-free grinding in a reactive medium. *Green Chem.* **15.** 160–166 (2012).

89. De Wild. P.. Van der Laan. R.. Kloekhorst. A. & Heeres. E. Lignin valorisation for chemicals and (Transportation) Fuels via (Catalytic) Pyrolysis and hydrodeoxygenation. *Environ. Prog. Sustain. Energy* **28.** 404–409 (2009).

90. Jahirul. M. I.. Rasul. M. G.. Chowdhury. A. A. & Ashwath. N. Biofuels production through biomass pyrolysis- A technological review. *Energies* **5.** 4952–5001 (2012).

91. Jegers. H. E. & Klein. M. T. Primary and Secondary Lignin Pyrolysis Reaction Pathways. *Ind. Eng. Chem. Process Des. Dev.* **24.** 173–183 (1985).

92. Caballero. J. A.. Font. R. & Marcilla. A. Study of the primary pyrolysis of Kraft lignin at high heating rates: Yields and kinetics. *J. Anal. Appl. Pyrolysis* **36.** 159–178 (1996).

93. Caballero. J. A.. Font. R. & Marcilla. A. Pyrolysis of Kraft lignin: yields and correlations. *J. Anal. Appl. Pyrolysis* **39.** 161–183 (1997).

94. Ferdous. D.. Dalai. A. K.. Bej. S. K. & Thring. R. W. Pyrolysis of lignins: Experimental and kinetics studies. *Energy and Fuels* **16.** 1405–1412 (2002).

95. Jiang. G.. Nowakowski. D. J. & Bridgwater. A. V. Effect of the Temperature on the Composition of Lignin Pyrolysis Products. *Energy & Fuels* **24.** 4470–4475 (2010).

96. Ferdous. D.. Dalai. A. K.. Bej. S. K.. Thring. R. W. & Bakhshi. N. N. Production of H_2 and medium Btu gas via pyrolysis of lignins in a fixed-bed reactor. *Fuel Process. Technol.* **70.** 9–26 (2001).

97. Mohan. D.. Pittman. C. U. & Steele. P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy and Fuels* **20.** 848–889 (2006).

98. Evans. R. J. & Milne. T. a. Molecular characterization of pyrolysis of biomass. 1. Fundamentals. *Energy & Fuels* **1.** 123–138 (1987).

99. Evans. R. J.. Milne. T. A. & Soltys. M. N. Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels. III. Primary pyrolysis of lignin. *J. Anal. Appl. Pyrolysis* **9.** 207–236 (1986).

100. Samolada. M. C.. Papafotica. a. & Vasalos. I. a. Catalyst Evaluation for Catalytic Biomass Pyrolysis. *Energy & Fuels* **14.** 1161–1167 (2000).

101. Olazar. M.. Aguado. R.. Bilbao. J. & Barona. A. Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst. *AIChE J.* **46.** 1025–1033 (2000).

102. Carlson. T. R.. Vispute. T. P. & Huber. G. W. Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem* **1.** 397–400 (2008).

103. De Wild. P. J.. Huijgen. J. J. & Gosselink. R. J. A. Lignin pyrolysis for profitable lignocellulosic biorefineries. *Biofuels. Bioprod. Biorefining* **8.** 645–657 (2014).

104. Goldstein. I. S. *Organic chemicals from biomass*. CRC Press (1981).

105. Karagöz. S.. Bhaskar. T.. Muto. A. & Sakata. Y. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel* **83.** 2293–2299 (2004).

106. Miller. J. E.. Evans. L.. Littlewolf. A. & Trudell. D. E. Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Fuel* **78.** 1363–1366 (1999).

107. Nenkova. S.. Vasileva. T. & Stanulov. K. Production of phenol compounds by alkaline treatment of technical hydrolysis lignin and wood biomass. *Chem. Nat. Compd.* **44.** 182–185 (2008).

108. Wahyudiono. Kanetake. T.. Sasaki. M. & Goto. M. Decomposition of a Lignin Model Compound under Hydrothermal Conditions. *Chem. Eng. Technol.* **30.** 1113–1122 (2007).

109. Wahyudiono. Sasaki. M. & Goto. M. Conversion of biomass model compound under hydrothermal conditions using batch reactor. *Fuel* **88.** 1656–1664 (2009).

110. Kleinert. M. & Barth. T. Towards a lignincellulosic biorefinery: Direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy and Fuels* **22.** 1371–1379 (2008).

111. Augustine. R. L. & Techasauvapak. P. Heterogeneous catalysis in organic synthesis. Part 9. Specific site solvent effects in catalytic hydrogenations. *J. Mol. Catal.* **87.** 95–105 (1994).

112. Takagi. H.. Isoda. T.. Kusakabe. K. & Morooka. S. Effects of solvents on the hydrogenation of mono-aromatic compounds using noble-metal catalysts. *Energy and Fuels* **13.** 1191–1196 (1999).

113. Wang. X. & Rinaldi. R. Solvent effects on the hydrogenolysis of diphenyl ether with raney nickel and their implications for the conversion of lignin. *ChemSusChem* **5.** 1455–1466 (2012).

114. Zhang. J. *et al.* A series of NiM (M = Ru. Rh. and Pd) bimetallic catalysts for effective lignin hydrogenolysis in water. *ACS Catal.* **4.** 1574–1583 (2014).

115. Xiang. Q. & Lee. Y. Y. Oxidative cracking of precipitated hardwood lignin by hydrogen peroxide. *Appl. Biochem. Biotechnol.* **84-86.** 153–162 (2000).

116. Lange. H.. Decina. S. & Crestini. C. Oxidative upgrade of lignin - Recent routes reviewed. *Eur. Polym. J.* **49.** 1151–1173 (2013).

117. Crestini. C.. Crucianelli. M.. Orlandi. M. & Saladino. R. Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers. *Catal. Today* **156.** 8–22 (2010).

118. Ma. R.. Xu. Y. & Zhang. X. Catalytic oxidation of biorefinery lignin to value-added chemicals to support sustainable biofuel production. *ChemSusChem* **8.** 24–51 (2015).

119. Crestini. C.. Pro. P.. Neri. V. & Saladino. R. Methyltrioxorhenium: A new catalyst for the activation of hydrogen peroxide to the oxidation of lignin and lignin model compounds. *Bioorganic Med. Chem.* **13.** 2569–2578 (2005).

120. Crestini. C.. Caponi. M. C.. Argyropoulos. D. S. & Saladino. R. Immobilized methyltrioxo rhenium (MTO)/H2O2 systems for the oxidation of lignin and lignin model compounds. *Bioorganic Med. Chem.* **14.** 5292–5302 (2006).

121. Herrmann. W. A.. Weskamp. T.. Zoller. J. P. & Fischer. R. W. Methyltrioxorhenium: Oxidative cleavage of CC-double bonds and its application in a highly efficient synthesis of vanillin from biological waste. *J. Mol. Catal. A Chem.* **153.** 49–52 (2000).

122. Sales. F. G.. Maranhão. L. C. A.. Filho. N. M. L. & Abreu. C. A. M. Experimental evaluation and continuous catalytic process for fine aldehyde production from lignin. *Chem. Eng. Sci.* **62.** 5386–5391 (2007).

123. Zhang. J.. Deng. H. & Lin. L. Wet aerobic oxidation of lignin into aromatic aldehydes catalysed by a perovskite-type oxide: LaFe1-xCuxO3 (x=0. 0.1. 0.2). *Molecules* **14.** 2747–2757 (2009).

124. Bhargava. S.. Jani. H.. Tardio. J.. Akolekar. D. & Hoang. M. Catalytic Wet Oxidation of Ferulic Acid (A Model Lignin Compound) Using Heterogeneous Copper Catalysts. *Ind. Eng. Chem. Res.* **46.** 8652–8656 (2007).

125. Roberts. V. M. *et al.* Towards quantitative catalytic lignin depolymerization. *Chem. - A Eur. J.* **17.** 5939–5948 (2011).

126. Molinari. V.. Clavel. G.. Graglia. M.. Antonietti. M. & Esposito. D. Mild Continuous Hydrogenolysis of Kraft Lignin over Titanium Nitride-Nickel Catalyst. *ACS Catal.* (2016). doi:10.1021/acscatal.5b01926

127. Collinson. S. R. & Thielemans. W. The catalytic oxidation of biomass to new materials focusing on starch. cellulose and lignin. *Coord. Chem. Rev.* **254.** 1854–1870 (2010).

128. Kleinert. M. & Barth. T. Phenols from lignin. *Chem. Eng. Technol.* **31.** 736–745 (2008).

129. Younker. J. M.. Beste. A. & Buchanan. A. C. Computational study of bond dissociation enthalpies for substituted β-O-4 lignin model compounds. *ChemPhysChem* **12.** 3556–3565 (2011).

130. Song. Q.. Wang. F. & Xu. J. Hydrogenolysis of lignosulfonate into phenols over heterogeneous nickel catalysts. *Chem. Commun.* **48.** 7019 (2012).

131. Kirk. T. K. & Farrell. R. L. Enzymatic ‘combustion’: The microbial degradation of lignin. *Ann. Rev. Microbiol.* **41.** 465–505 (1987).

132. Díaz-González. M.. Vidal. T. & Tzanov. T. Phenolic compounds as enhancers in enzymatic and electrochemical oxidation of veratryl alcohol and lignins. *Appl. Microbiol. Biotechnol.* **89.** 1693–700 (2011).

133. Larson. T. M.. Anderson. A. M. & Rich. J. O. Combinatorial evaluation of laccase-mediator system in the oxidation of veratryl alcohol. *Biotechnol. Lett.* **35.** 225–31 (2013).

134. Zucca. P.. Sollai. F.. Garau. A.. Rescigno. A. & Sanjust. E. Fe(III)-5.10.15.20-tetrakis(pentafluorophenyl)porphine supported on pyridyl-functionalized. crosslinked poly(vinyl alcohol) as a biomimetic versatile-peroxidase-like catalyst. *J. Mol. Catal. A Chem.* **306.** 89–96 (2009).

135. Kumar. A.. Jain. N. & Chauhan. S. M. S. Biomimetic oxidation of veratryl alcohol with H2O2 catalyzed by iron(III) porphyrins and horseradish peroxidase in ionic liquid. *Synlett* 411–414 (2007).
136. Zucca. P.. Mocci. G.. Rescigno. A. & Sanjust. E. 5.10.15.20-Tetrakis(4-sulfonato-phenyl)porphine-Mn(III) immobilized on imidazole-activated silica as a novel lignin-peroxidase-like biomimetic catalyst. *J. Mol. Catal. A Chem.* **278.** 220–227 (2007).
137. Sena-Martins. G.. Almeida-Vara. E. & Duarte. J. C. Eco-friendly new products from enzymatically modified industrial lignins. *Ind. Crops Prod.* **27.** 189–195 (2008).
138. Sippola. V.. Krause. O. & Vuorinen. T. Oxidation of Lignin Model Compounds with Cobalt-sulphosalen Catalyst in the Presence and Absence of Carbohydrate Model Compound. *J. Wood Chem. Technol.* **24.** 323–340 (2004).
139. Kervinen. K.. Korpi. H.. Leskelä. M. & Repo. T. Oxidation of veratryl alcohol by molecular oxygen in aqueous solution catalyzed by cobalt salen-type complexes: The effect of reaction conditions. *J. Mol. Catal. A Chem.* **203.** 9–19 (2003).
140. Ambrose. K.. Hurisso. B. B. & Singer. R. D. Recyclable Ionic Liquid Tagged Co(Salen) Catalysts for the Oxidation of Lignin Model Compounds. *Can. J. Chem.* **91.** 1258–1261 (2013).
141. Fan. H. *et al.* One-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol catalyzed by the Ru@ZIF-8 + CuO/basic ionic liquid system. *Green Chem.* **16.** 600 (2014).
142. Yamaguchi. K. & Mizuno. N. Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen. **34.** 4538–4542 (2002).
143. Gorbanev. Y. Y.. Kegnæs. S. & Riisager. A. Effect of Support in Heterogeneous Ruthenium Catalysts Used for the Selective Aerobic Oxidation of HMF in Water. *Top. Catal.* **54.** 1318–1324 (2011).
144. Nie. J.. Xie. J. & Liu. H. Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2.5-diformylfuran on supported Ru catalysts. *J. Catal.* **301.** 83–91 (2013).
145. Ruppert. A. M.. Weinberg. K. & Palkovits. R. Hydrogenolysis goes bio: From carbohydrates and sugar alcohols to platform chemicals. *Angew. Chemie - Int. Ed.* **51.** 2564–2601 (2012).
146. James. R. Catalytic Decarbonylation. *J. Chem. Soc. Chem. Commun.* **939.** 939–940 (1980).
147. Liana Allen. C. & Williams. J. M. J. Ruthenium-catalyzed alkene synthesis by the decarbonylative coupling of aldehydes with alkynes. *Angew. Chemie - Int. Ed.* **49.** 1724–1725 (2010).
148. Jha. A.. Chandole. T.. Pandya. R.. Roh. H.-S. & Rode. C. V. Solvothermal synthesis of mesoporous manganese oxide with enhanced catalytic activity for veratryl alcohol oxidation. *RSC Adv.* **4.** 19450 (2014).

149. Gorbanev. Y.. Kegnæs. S.. Hanning. C. W.. Hansen. T. W. & Riisager. A. Acetic Acid Formation by Selective Aerobic Oxidation of Aqueous Ethanol over Heterogeneous Ruthenium Catalysts. *A C S Catal.* **2.** 604–612 (2012).

150. Gorbanev. Y. Y.. Kegnæs. S. & Riisager. A. Selective aerobic oxidation of 5-hydroxymethylfurfural in water over solid ruthenium hydroxide catalysts with magnesium-based supports. *Catal. Letters* **141.** 1752–1760 (2011).

151. Son. S. & Toste. F. D. Non-Oxidative Vanadium-Catalyzed C À O Bond Cleavage : Application to Degradation of Lignin Model Compounds **. *Angew. Chem. Int. Ed.* **49.** 3791 (2010).

152. Hanson. S. K.. Baker. R. T.. Gordon. J. C.. Scott. B. L. & Thorn. D. L. Aerobic oxidation of lignin models using a base metal vanadium catalyst. *Inorg. Chem.* **49.** 5611–5618 (2010).

153. Hanson. S. K.. Wu. R. & Silks. L. A. P. C-C or C-O bond cleavage in a phenolic lignin model compound: Selectivity depends on vanadium catalyst. *Angew. Chemie - Int. Ed.* **51.** 3410–3413 (2012).

154. Zhang. G.. Scott. B. L.. Wu. R.. Silks. L. A. P. & Hanson. S. K. Aerobic oxidation reactions catalyzed by vanadium complexes of bis(phenolate) ligands. *Inorg. Chem.* **51.** 7354–7361 (2012).

155. Rahimi. A.. Azarpira. A.. Kim. H.. Ralph. J. & Stahl. S. S. Chemoselective metal-free aerobic alcohol oxidation in lignin. *J. Am. Chem. Soc.* **135.** 6415–8 (2013).

156. Stahl. S. S. & Madison. A. R. Selective Aerobic alcohol oxidation method for conversion of lignin into simple aromatic compounds. Patent: US 8969534 B2 (2015).

157. Chang. Y. feng. McCarty. J. G. & Wachsman. E. D. Effect of ruthenium-loading on the catalytic activity of Ru-NaZSM-5 zeolites for nitrous oxide decomposition. *Appl. Catal. B. Environ.* **6.** 21–33 (1995).

158. Harvey. T. G. & Pratt. K. C. The effect of ruthenium loading on Ru-zeolite/NiMo HDN catalysts. *Appl. Catal. A Gen.* **146.** 317–321 (1996).

159. Betancourt. P.. Rives. a. Hubaut. R.. Scott. C. . & Goldwasser. J. A study of the ruthenium–alumina system. *Appl. Catal. A Gen.* **170.** 307–314 (1998).

160. Cruz. J. & Baglio. V. Preparation and Characterization of RuO2 Catalysts for Oxygen Evolution in a Solid Polymer Electrolyte. *Int. J. Mol. Sci.* **6.** 6607–6619 (2011).

161. Bahceci. K. S.. Gokmen. V. & Acar. J. Formation of guaiacol from vanillin by Alicyclobacillus acidoterrestris in apple juice: A model study. *Eur. Food Res. Technol.* **220.** 196–199 (2005).

162. Peng. C.. Zhang. G.. Yue. J. & Xu. G. Pyrolysis of lignin for phenols with alkaline additive. *Fuel Process. Technol.* **124.** 212–221 (2014).

163. Zakzeski. J. & Weckhuysen. B. M. Lignin solubilization and aqueous phase reforming for the production of aromatic chemicals and hydrogen. *ChemSusChem* **4.** 369–378 (2011).
164. Sannigrahi. P. & Ragauskas. A. J. Fundamentals of Biomass Pretreatment by Fractionation. *Aqueous Pretreat. Plant Biomass Biol. Chem. Convers. to Fuels Chem.* 201–222 (2013). doi:10.1002/9780470975831.ch10
165. Santos. A.. Rodriguez. F.. Gilarranz. M. A.. Moreno. D. & Garcia-Ochoa. F. Kinetic modeling of kraft delignification of Eucalyptus globulus. *Ind. Eng. Chem. Res.* **36.** 4114–4125 (1997).
166. Rodríguez. A.. Rosal. A. & Jiménez. L. Biorefinery of agricultural residues by fractionation of their components through hydrothermal and organosolv processes. *Afinidad Rev. química teórica y Apl.* **67.** 14–20 (2010).
167. Wen. J.-L. *et al.* Recent Advances in Characterization of Lignin Polymer by Solution-State Nuclear Magnetic Resonance (NMR) Methodology. *Materials (Basel).* **6.** 359–391 (2013).
168. Bolm. C.. Kleine. T. & Buendia. J. Mechanochemical degradation of lignin and wood by solvent-free grinding in a reactive medium. *Green Chem.* **15.** 160–166 (2012).
169. Brauns. F. E. & Brauns. D. A. *The Chemistry of Lignin: Covering the Literature for the Years 1949–1958*. (Elsevier. 2013).
170. Lora, J. H. & Glasser, W. G. Recent Industrial Applications of Lignin A Sustainable. **10,** (2002).
171. Song, Q. *et al.* Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation–hydrogenolysis process. *Energy Environ. Sci.* **6,** 994 (2013).
172. Lee, Y. W. Lignin and related compounds. *Can. J. Chem.* 4–6 (1970).
173. Gao, F., Webb, J. D. & Hartwig, J. F. Chemo- and Regioselective Hydrogenolysis of Diaryl Ether C-O Bonds by a Robust Heterogeneous Ni/C Catalyst: Applications to the Cleavage of Complex Lignin-Related Fragments. *Angew. Chemie - Int. Ed.* 1474–1478 (2015).