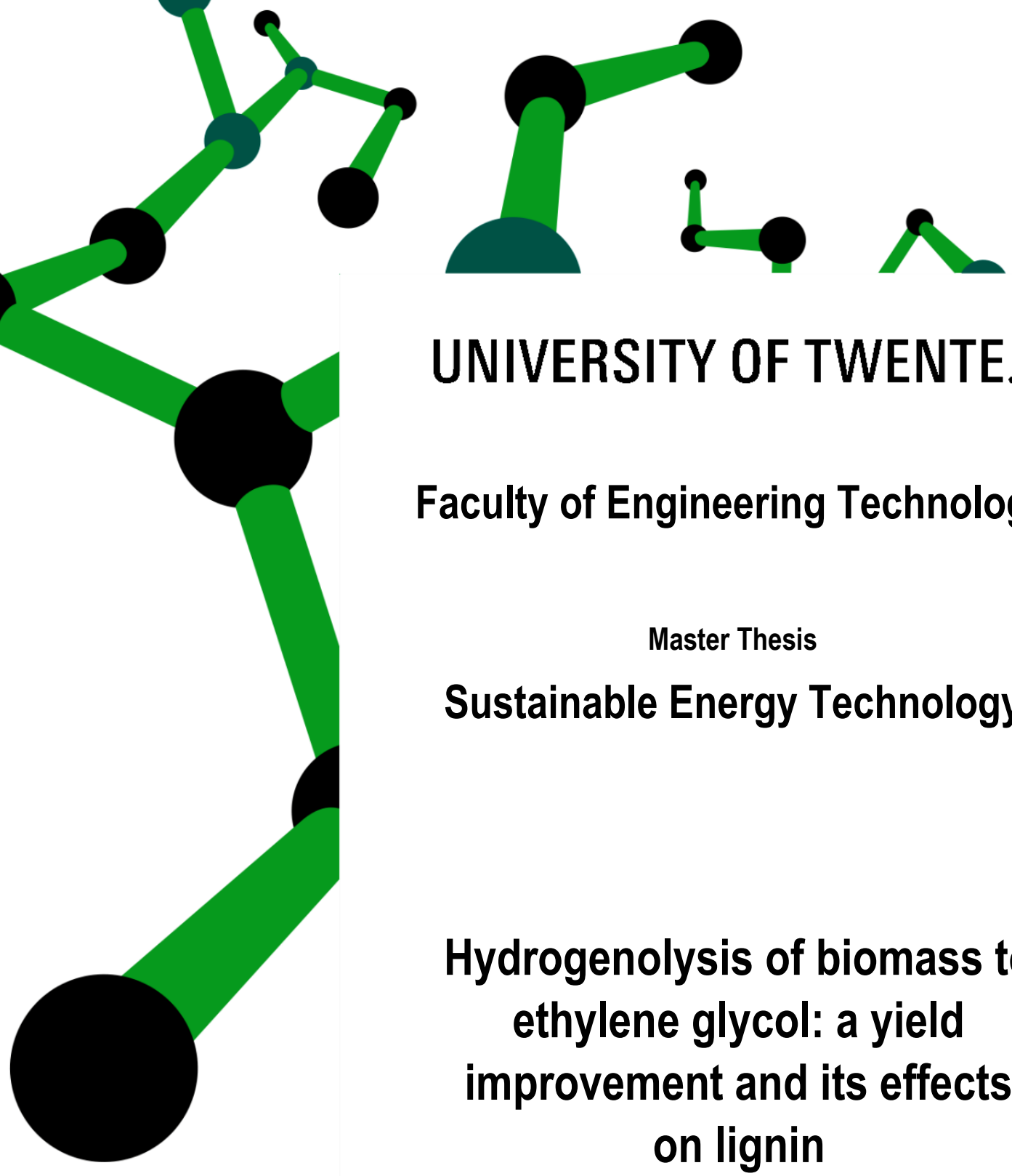

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Faculty of Engineering Technology

Master Thesis

Sustainable Energy Technology

Hydrogenolysis of biomass to ethylene glycol: a yield improvement and its effects on lignin

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August 29th, 2024.

(Confidential)

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Abstract

The production of ethylene glycol (EG) from biomass is possible through biomass hydrogenolysis. Yields of around 25 wt.% were obtained in previous research, but the low value and low biomass feed (only 5%) make them unsuitable for industrial scale. By studying the effects caused by the catalyst and biomass load, temperature, hydrogen pressure, and pH, more suitable conditions to increase the EG yield were found, which led to a yield of 34 wt.% with a biomass feed of 10 wt.%. It translates to almost three times the mass of EG of the first experiment (from 0.12 to 0.37 g) with a slight increase of resources (from 245°C to 260°C and from a catalyst ratio of 0.3 to 0.93). Moreover, since biomass contains lignin and its selective and controlled conversion is achievable under similar conditions to biomass hydrogenolysis, we investigated if lignin upgrading was possible simultaneously. The results showed that lignin upgrading is constrained by its slow kinetics, the competition for resources with the EG production (especially for hydrogen and the catalysts), and its structure. It was proved that the most influential factor in lignin upgrading is temperature and that an extended reaction (five hours) does not improve lignin upgrading compared to a two-hour reaction. Hence, under the most optimal conditions for EG production, only 41% of lignin was extracted and 16 wt.% converted to 4-propyl guaiacol and guaiacol (9.4 wt.% and 5.9 wt.%, respectively), being these results, the probable limits of pinewood lignin upgrading. Although the results are low, we demonstrated that a one-pot conversion under optimal conditions for EG production is the best way to upgrade pinewood biomass.

(Confidential)

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To my family, who supported me from Mexico all those days I have been far away…

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And to myself for giving such wonderful step … What an experience

No fue fácil, pero ahora siento más pasión y emoción por lo que hago. Ph.D. voy por ti.

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List of abbreviations

1,4-BDO	*1,4-butanediol*
4-MethG	*4-methyl guaiacol*
4-EthG	*4-ethyguaiacol*
4-PropG	*4-propyl guaiacol*
EG	*Ethylene glycol*
GA	*Glycolaldehyde*
GC-MS	*Gas chromatography – mass spectroscopy*
GPC	*Gas permeation chromatography*
HAc	*Acetic acid*
HPLC	*High performance liquid chromatography*
HVAc	*Homovanillic acid*
H_xWO_3	*Bronze tungstate*
PG	*Polyethylene glycol*
Raney Ni	*Raney nickel*
Ra/BM	*Raney nickel / Biomass ratio (w/w)*
RCF	*Reductive catalytic fractionation*
UV-Vis	*Ultraviolet – visible light spectrometry*
WOx	*Sodium polytungstate catalyst*
WOx/BM	*Sodium polytungstate / Biomass ratio (w/w)*
WOx/Ni	*Sodium polytungstate / Active nickel ratio (w/w)*

Introduction

Ethylene glycol (EG) is the smallest diol produced via ethylene oxide hydration, a product of petroleum cracking. It is one of the major large-scale products of industrial synthesis and is used in the production of anti-freezing, resins, polyester, and polyethylene terephthalate (PET) [1]–[3]. With the growing demand for these products, especially for the last one that consumes more than 58% of the global production [2], the EG production capacity is expected to reach 60 million tons by 2025 [4]. The depletion of fossil fuels and the climate change crisis have highlighted the urgent necessity for sustainable practices across all sectors. The production of EG is one of such process that demands attention due to its significant demand and contribution to greenhouse gas (GHG) emissions. A study by Yang et. al. [3] calculated that 7.29 tons CO_2 eq. are released into the atmosphere per ton of produced EG.

In recent years, more sustainable pathways to produce EG have been proposed. Some include using (bio)ethanol, sorbitol, glycerol, and cellulose [2]. The first two became very promising, and the technology is already commercialized. However, those two feedstocks still have high petroleum shares that may require less refinement process but are still insufficient to decrease the GHG emissions. Only cellulose can reduce them.

Cellulose comes from biomass. It is the only natural feedstock from which EG can be produced, and the most recent research has notably shown that the production of EG is even possible without prior extraction of cellulose from biomass. Therefore, the use of raw biomass has become the most promising and sustainable option to produce the diol and reduce its GHG emissions to half the petroleum-based production (without considering the CO_2 absorbed during plant growth) [3].

Unfortunately, the sustainable option comes with a low EG production and low biomass feeds that hinder its scaling up, so an increase of both aspects is necessary to bring this process to the next Technology Readiness Level (TRL). Here is where most of this work focuses on. Furthermore, the use of raw biomass comes with another advantage: the use of lignin.

Lignin is the only natural source of aromatics, and it can be converted to several high-value-added products that serve as chemical platforms of fuels, polymers and other products. Therefore, if cellulose and lignin are converted in a one-pot procedure, a more industrially appealing process can be developed. Hence, apart from increasing the EG production and biomass feed, this work studied to what extent lignin can be converted during biomass hydrogenolysis and which are its high-value-added derivatives.

Outline

In this thesis, chapter 1 presents the concepts and previous research necessary to comprehend this work. At the end of this chapter, we present the problem statement, the main research question, and the sub-questions that guided this work. Chapter 2 describes the used materials and the methodology followed in every experiment. Chapter 3 presents and discusses the results. This chapter was divided into subsections for the main hydrolysis products and lignin to stress the findings on each of them. Also, a small chapter regarding sustainability beyond EG yields and lignin conversion improvements was included to remind the reader of the importance of considering more than technical aspects when launching a new technology. Finally, Chapter 4 presents the conclusion of this work.

1. Background

1.1 Cellulose and biomass

Biomass is the scientific term used to designate all the products, wastes, and residues of biological origin [5]. Among them, plants biomass is the most interesting feedstock to produce chemicals and fuels. It is composed by cellulose (37 – 60 wt.%), hemicellulose (20 – 36 wt.%), and lignin (10 – 30 wt.%) [6] (Figure 1). Cellulose is the most studied and used component of biomass, and agro-industrial and woody wastes (lignocellulosic feedstocks) are its primary sources.

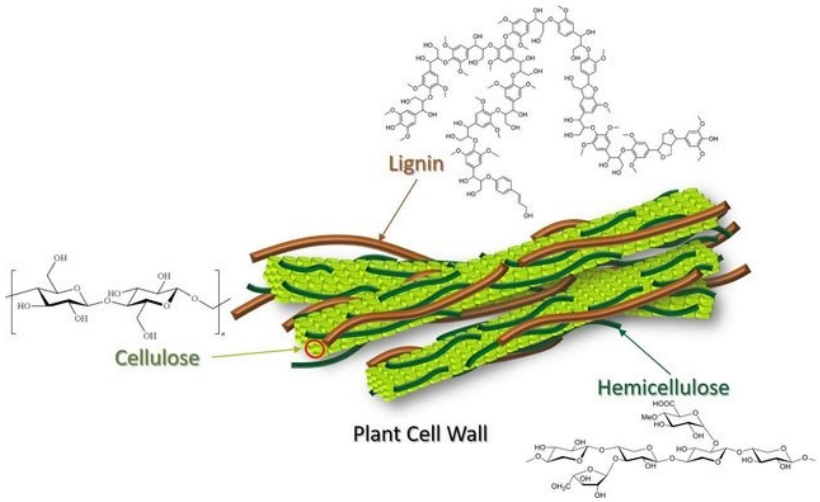

Figure 1. Biomass composition [6].

It is a non-branched linear polymer constituted by cellobiose molecules (glucose dimer) connected by β-(1-4) glycosidic bonds [6]. In woody biomass, cellulose has around 10,000 glucose monomer units [7]. The production of the sugar is what grants cellulose with interesting applications (such as the production of EG), and it is why research significantly focuses on its conversion, but to obtain glucose, a breaking-down process (called hydrogenolysis) is required. In it, a molecule of water reacts with a molecule of cellulose to form glucose (Eq. 1). The reaction seems simple. However, due to a parallel and flat alignment of the cellulose chains, it has a highly crystalline and thermally stable structure [6]–[8] hard to break through mild chemical and biological treatments, so severe conditions are needed. Dilute acids at temperatures around 220°C [7] and critical water [6] are among the best conditions for hydrolysis.

(Eq. 1) $$(C_6H_{10}O_5)_n + n\,H_2O \rightarrow n\,C_6H_{12}O_6$$

The use of pure cellulose offers the advantage of high conversion yields with high selectivity [9]. However, to obtain pure cellulose, biomass must undergo pre-treatments to separate cellulose from the other two components of biomass. The process is well-known as cellulose is the paper industry basis. However, the purification process is time-consuming, involves highly acidic or alkaline conditions, and produces cellulose with arbitrary crystallinity values [10] that affect the conversion yield. Hence, the direct use of raw biomass can avoid all these problems. Nonetheless, one must be careful when choosing a lignocellulosic feedstock since the cellulose content varies with every kind of

biomass (Table 1) and only the rich-in-cellulose ones are suitable for conversion processes.

Table 1. Composition of some kind of biomass [11].

Biomass	Composition [wt.%]		
	Cellulose	Hemicellulose	Lignin
Corn straw	43.1	31.8	11.0
Sugar cane	51.8	27.6	10.7
Bagasse	45.9	28.0	20.7
Pine	*47.0*	*21.7*	*27.6*
Poplar wood	49.7	24.1	23.6
Wood chips	44.4	23.0	30.6
Birch	47.0	25.9	22.0
Straw pellets	30.0	28.9	23.0

The use of raw biomass comes with another advantage: the conversion of hemicellulose, the other rich-in-sugars component of biomass.

Hemicellulose is an amorphous and branched polymer with shorter chains constituted by hexoses (glucose, galactose) and pentoses (xylose, arabinose) [8]. Its amorphous nature makes it easier to transform (hydrolysis with dilute acids at 100 – 200 °C [7]), but when cellulose is extracted, hemicellulose degrades. Even in extractions at lower temperatures, it degrades to volatiles, such as CO_2, CO, and some hydrocarbons [8], so its isolation is almost impossible considering that temperature aids cleaving its highly cross-linking bonds with cellulose and lignin [11]. Therefore, only an in-situ conversion makes its use possible, leading to a higher content of sugars and so a higher products yield (such as that of EG).

As cellulose and hemicellulose are the rich-in-sugar components of biomass, we will refer to them as *"holocellulose*" in the following chapters.

1.2 Biomass hydrogenolysis for EG production

Cellulose from raw biomass undergoes three main steps to produce EG (Figure 2). First, the hydrolysis of cellulose to produce a sugar monomer, followed by a retro-aldol condensation that breaks it down into glycolaldehyde (GA), and finally, a hydrogenation that results in EG. For every mol of a hexose, 3 moles of EG are produced, while for every mole of a pentose (from hemicellulose for example), 1 mole of EG and 1 mole of propylene glycol (PG) are obtained [12]. PG is a three-carbon diol with a lower market demand than EG (450 tons/year in the USA [13]), but also important for pharmaceutical, food, cosmetics, and other industries. More sustainable production pathways are also under research since its actual production comes from the hydration of propylene oxide [13], another petroleum-derived product. Therefore, its obtention as a side product does not represent a drawback of hydrogenolysis. PG can also come from the glucose isomer: fructose (Figure 2), after undergoing a retro-aldol condensation that produces dihydroxyacetone (DHA), which is later hydrogenated. Two moles of the glycol are produced per every mol of fructose.

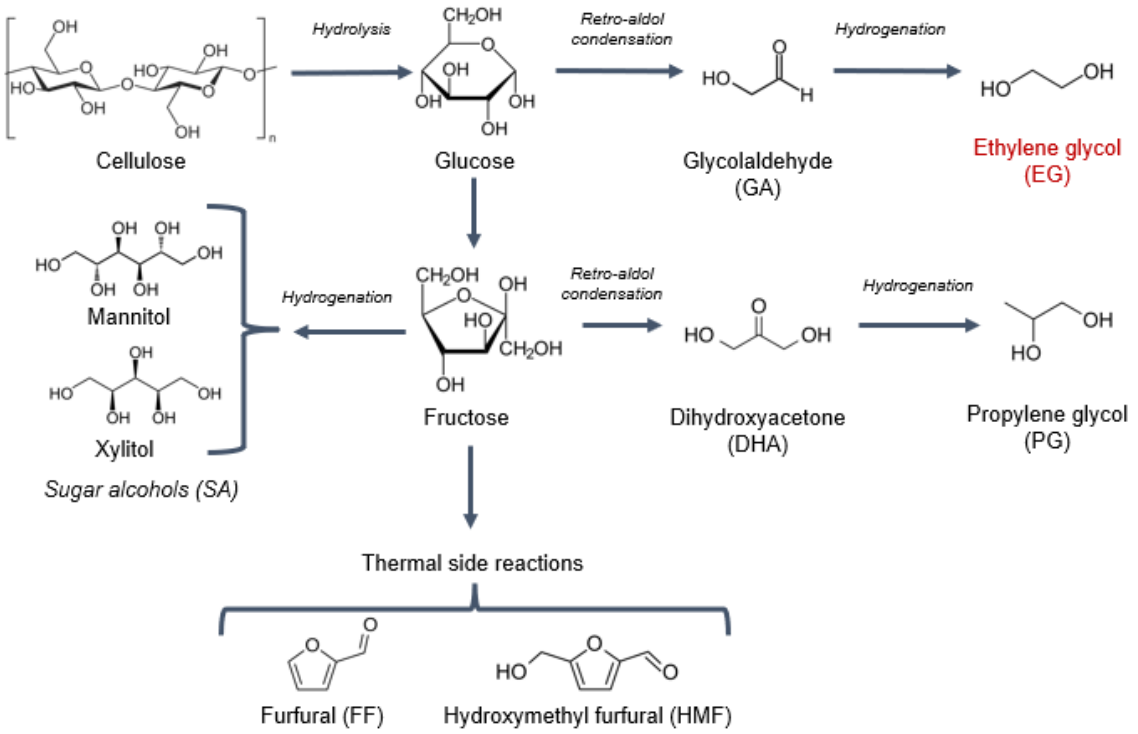

Figure 2. Reaction pathway of EG from cellulose.

Other byproducts of the reaction are sugar alcohols (SA: mannitol, xylitol, or sorbitol) and humins. The first can come from the reduction of fructose and (sometimes) glucose [14], and the second from thermal side reactions that produce hydroxymethyl furfural (HMF) and furfural (FF), which later condense into humins [12]. Depending on the reaction conditions, the selectivity changes. However, producing any of them requires four main components: a solvent, catalysts, temperature, and hydrogen.

1.3 Solvent

A liquid medium is required to perform effective mass and heat transfer. Since it is a one-pot reaction that starts with a solid feedstock, the catalyst and the rest of the elements need to penetrate biomass first to start holocellulose breaking down. Once the polymer chains break, they must be removed (or extracted) to facilitate hydrolysis and the following conversion of the small glucose units into EG. Hence, good mixing within the liquid is necessary to allow catalyst-reactant interactions and product removal. This is a critical stage because a weak mass transfer in hydrolysis will lead to low product yields or long reaction times.

In addition, a good mass transfer allows a good heat transfer. Holocellulose requires high temperatures to break down, but hemicellulose degrades faster than cellulose [7]. If there are hot spots, degradation will happen extremely fast in the absence of liquid, leading to the production of char or incondensable gases [11] that affect the carbon economy of the reaction. Therefore, a uniform liquid distribution is also essential for an increase in the process efficiency.

Since the solvent carries the active species within the biomass fibbers, water must be one of its main components because it is necessary for the hydrolysis of cellulose. If it is

accompanied by an acid, the cleavage of the glycosidic bonds is enhanced [7], so water and an acid need to be present in the solvent. With its inclusion, the energy demand also lowers as the mixture is more homogeneous and has a lower density.

1.4 Catalysts

High selectivity towards EG requires two catalysts: one for the retro-aldol condensation and one for the hydrogenation reaction. For the retro-aldol condensation, which cleaves β-C-C bonds, bases such as NaOH or CaO are traditionally used [15], [16]. Nonetheless, their low selectivity towards C_2 and C_3 compounds and high catalytic reactivity with intermediates [16] make them unsuitable for EG production. In recent years, tungstate-based catalysts have demonstrated good selectivity towards C_2 and C_3 compounds from glucose, especially for glycolaldehyde [9], [15], [16]. Depending on their nature, they can catalyse the retro-aldol condensation and the subsequent hydrogenation, leading to moderate EG yields using pure cellulose (≈ 30%) [15]. Nonetheless, when the tungstate catalyst can only perform a retro-aldol condensation, the incorporation of a hydrogenating catalyst leads to higher yields.

Copper (Cu), ruthenium (Ru), and nickel (Ni) are the primary metal hydrogenating catalysts due to their high and controlled selectivity [2], [9]. Particularly, the last two have performed better in the production of GA. However, Ni gained more attention due to its high availability and low cost. It can be incorporated into the reaction in different ways, but when it does it as a Raney-type catalyst, it is durable in one-pot conversions to EG [17] and sorbitol [18] despite the highly energetic conditions. Still, one must be careful when choosing the reaction conditions as it is also prone to leaching in the aqueous phase [18].

1.5 Hydrogen

The final step of biomass hydrogenolysis for EG requires hydrogen. Its supply needs to be fast so that unstable intermediates or side products (such as GA) do not condense into complex structures challenging to upgrade. It can be provided in different ways, such as in the gas phase or through a liquid hydrogen donor.

Its supply in the gas phase offers the advantage of immediate availability. However, it must overcome a liquid–gas mass transfer limitation before the hydrogenating process starts. On the other hand, by incorporating a liquid hydrogen donor, the system avoids the liquid–gas mass transfer limitation, and a more cost-effective process is enhanced as hydrogen gas is expensive. Small alcohols, such as methanol or ethanol, have been demonstrated to be good hydrogen donors (better than water) due to their reactive nature. In the presence of Raney Ni, diols with terminal -OH groups perform outstandingly better than the primary alcohols [18].

Although including a liquid hydrogen donor offers multiple advantages over hydrogen gas, the last should not be totally excluded when using Raney Ni because it requires high hydrogen pressures to promote significant hydrogenation (40 – 80 bar) [14]. Nonetheless, the use of diols as hydrogen donors is recent, and its excellent capacity in combination with Raney Ni could allow the supply of less hydrogen gas, making the process more affordable. Still, more research is needed to confirm this.

1.6 Temperature

SA and EG are produced when using a hydrogenating catalyst, especially in the presence of Raney Ni and high H_2 pressure, so it is necessary to give adequate conditions to the system to produce one compound over the other. Temperature is probably the most critical factor in this sense because mild temperatures (90 – 150°C) [14], [18] support the direct hydrogenation of glucose and fructose, while above 230°C [12] do it for GA. Also, high temperatures enable faster holocellulose hydrolysis, which can enhance higher EG yields in short reaction times.

Although high temperatures do not guarantee suppression of SA production, it has been demonstrated that GA hydrogenation is much faster than that of glucose and fructose [17]. Hence, the use of high temperatures can result in fast conversions, high EG yields, and high selectivity. However, one must be careful with choosing high temperatures as they can produce humins or the polymers degradation to tars and char [11] that will only retain mass and will not generate any valuable compound.

1.7 Recent research

In recent years, the Sustainable Process Technology Group (SPT) of the University of Twente has investigated the potential of biomass hydrogenolysis using pinewood biomass. The most recent results show that 5 wt.% biomass with Raney Ni and sodium polytungstate (WOx) at 245°C and 60 bar H_2 in a two-hour reaction achieved yields of ≈25 wt.% EG, ≈ 4 wt.% PG, and ≈9 wt.% SA [19].

Although the glycol yield is low compared to that of pure cellulose or other pure feedstocks (>70 wt.%), the result is significant because it proves that raw biomass is suitable for this purpose. It is noteworthy to mention that contrary to pure feedstocks, lignocellulosic biomass has many different compounds that can undergo chemical reactions simultaneously. Hence, by showing that more than 20 wt.% of raw holocellulose was converted into EG, it was demonstrated that it really serves as a sustainable feedstock to produce the glycol and that more research is needed to improve its performance.

In this sense, one of the purposes of this work is to increase EG production while maintaining its good selectivity. However, there is another component that requires attention: lignin. It is the richest natural source of aromatics, and its upgrading can lead to high-value-added products for the chemical industry. Hence, if the process converts more than one layer, it will acquire a higher efficiency and affordability.

1.8 Lignin

Lignin is the second most abundant polymer in biomass (15 – 30 wt.% dry basis) and is responsible for around 40% of the biomass energy content [20]. It is composed of three major monolignols: para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, commonly referred to as p-hydroxyphenyl (H-units), guaiacyl (G-units), and syringyl (S-units), respectively (Figure 3). Every biomass has a different content of monolignols [21], [22]. However, (independently of the composition) lignin is difficult to convert thanks to its amorphous and highly branched structure, low and varying solubility [23], high

heterogeneity, and high bond stability, which grants rigidity and resistance against insects and pathogens to the plant [24].

For many years, several techniques have been proposed to convert it because it is the only natural source of aromatics (phenols, carboxylic acids, ketones, aldehydes, alcohols [25]) capable of helping us cut ties with petroleum (Figure 5). None of those techniques have succeeded yet, but the exhaustive research around it is helping us understand better the steps necessary to convert it.

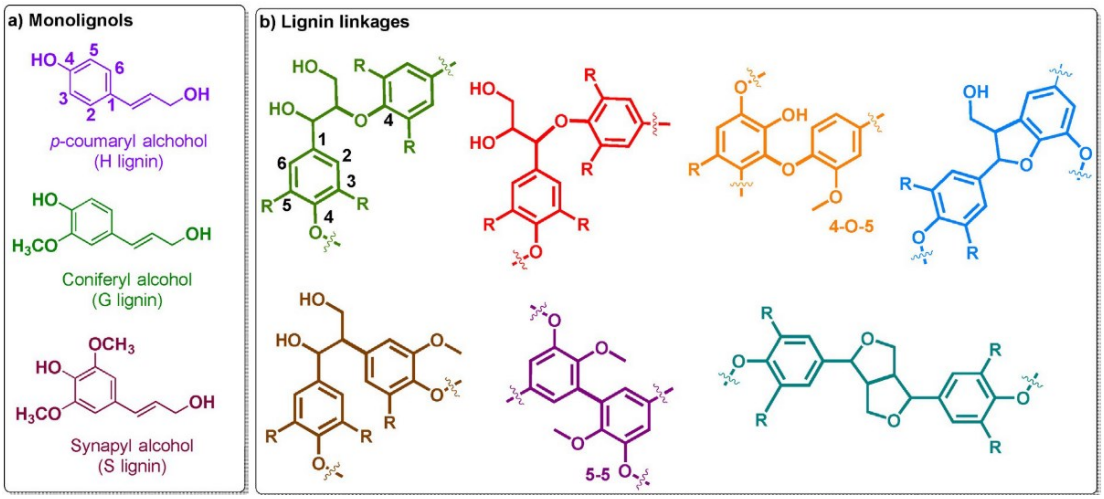

Figure 3. Lignin basic structures (monolignols) and the common unit C-O linkages (β-O-4, α-O-4, 4-O-5) and C-C linkages (β-5, β-1, 5-5, β-β) [26].

One of them is a controlled cleavage of the C–O (β-O-4, α-O-4, 4-O-5) and C–C (β-5, β-1, 5-5, β-β) linkages of lignin, were the first are easier to break (bond strength: α-O-4 < β-O-4 < 4-O-5 << C-C [20], [27]). By doing this, the condensation of reactive fragments that may have stronger C-C bonds than the original structures is avoided.

At temperatures between 80 – 180°C, selective cleavage of the C-O bonds is achieved, especially of the β-O-4 bond, which is the most abundant bond in lignin (45 – 60% [20], [28]). These conditions offer the advantage of homogeneous and high-quality mixtures with intact aromatic rings easy to convert into higher value-added products. However, as the mild temperatures will fail to break C-C bonds, the resultant mixture will require a post-treatment to finish the upgrading.

If higher temperatures are used, such as in pyrolysis (400 – 700 °C [20]), the extraction rates will be high but with low selectivity and high re-polymerization rates in secondary reactions.

These two examples show us that a high lignin extraction with high quality is very challenging to obtain simultaneously. Nonetheless, recent “lignin-first” techniques have demonstrated that both things could be possible with the addition of two elements: hydrogen and a catalyst [29]. One of the most promising procedures is the Reductive Catalytic Fractionation.

1.9 Reductive catalytic fractionation (RCF)

Reductive Catalytic Fractionation (RCF) aims to fully delignify biomass (≈99.9%) and selectively convert it (>75%) in a one-pot procedure without conversion of holocellulose [29]. It consists of three steps: first a solvothermal extraction, then a depolymerization of the extracted lignin, and finally a derivatives stabilization (Figure 4) [29].

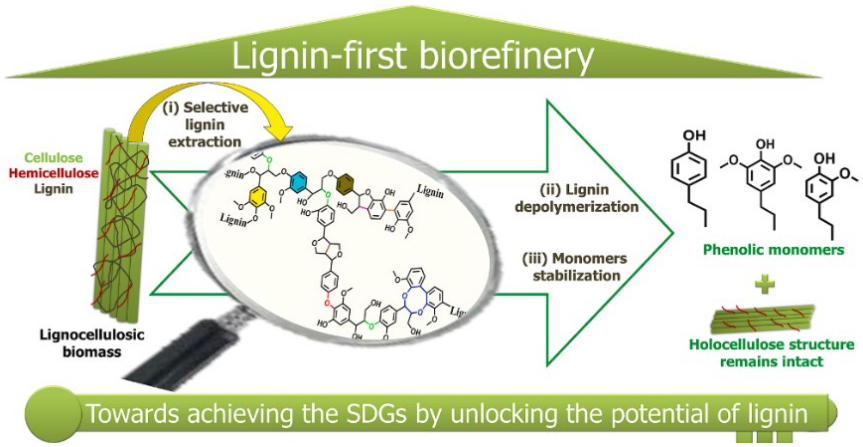

Figure 4. Reductive Catalytic Fractionation (RCF) as a lignin-first biorefinery strategy [29].

This novel technique follows logical steps to upgrade lignin that are nothing different from what one could expect. However, the way and the elements it uses are of relevance. For example, for the solvothermal extraction, the use of a protic polar solvent (MeOH, EtOH, PropOH [30]) that cleaves lignin–holocellulose bonds guarantees that lignin and holocellulose maintain intact most of their structure. Also, the alcohol can protect the recently cleaved bonds from undesired linking [28] by linking itself to the reactive bond, and a mixture of water and alcohol in a 1:1 ratio can increase the extraction [29].

The second step consists of breaking the extracted lignin into the monolignols that compose it. For this purpose, hydrogen is vital because the C-O bond cleavage generates very reactive carbocations that can form recalcitrant C-C bonds, more difficult to break [29]. Hydrogen can be supplied as a gas or through a hydrogen donor solvent (MeOH, EtOH, PrOH) [27]. The advantage of the last is the low pressure at which the process performs, which results in a lower reactor capital cost. However, as the hydrogen donor solvent also extracts lignin, it could result in a competition for the resource. Hence, hydrogen gas is more recommended unless further research demonstrates high conversion yields using internal hydrogen donors.

Ideally, during the first and second steps, only the lignin–holocellulose and lignin monolignols C-O and C-C bonds are broken, but in reality, it partially happens, and many other cleavages simultaneously occur. This can produce undesirable reactive compounds that easily re-polymerize and lower the monomer yield. This is why RCF incorporates a catalyst. The catalyst must be highly selective, with high recyclability, and high hydrogenating activity because it must catalyse multiple reactions, not only those of the cleaved reactive species, but also those to upgrade monolignols into monomers. In this sense, metal catalysts (Pd/C, Rr/C, Ni [30]) have demonstrated the best performance in RCF and are highly suitable because the reductive conditions can protect them from oxidation and subsequent deactivation.

If these three steps occur between 200 – 250 °C, a rich-in-monomers liquid, and a rich-in-sugars solid will be obtained. The solid part can undergo a subsequent upgrading to EG, for example, while the liquid can be immediately used after a product's separation. Depending on the catalyst, the produced monomers will change. However, guaiacol and its alkylated compounds, vanillin, phenols (toluene, benzene, phenol), and hydrocarbon fuels are among the most desirable products (Figure 5). Guaiacol, for example, has great value because it can be upgraded to hydrodeoxygenated compounds, similar to those of petroleum (cyclohexanol, cyclohexanone, cyclohexane [31]). Guaiacol alkylated compounds are precursors of epoxy resins [29], aromatizing agents in the food and perfume industry, antiseptics, and insecticides [32]. Vanillin is probably one of the highest value-added lignin products due to its low natural production from vanilla. It produces benzoic acids (4-hydroxybenzoic acid and salicylic acid) [33] and biobased polymers (polyacetals, polyaldimines, polyurethanes, polybenzoaxines) [29] through its oxidative dimer: divanillin.

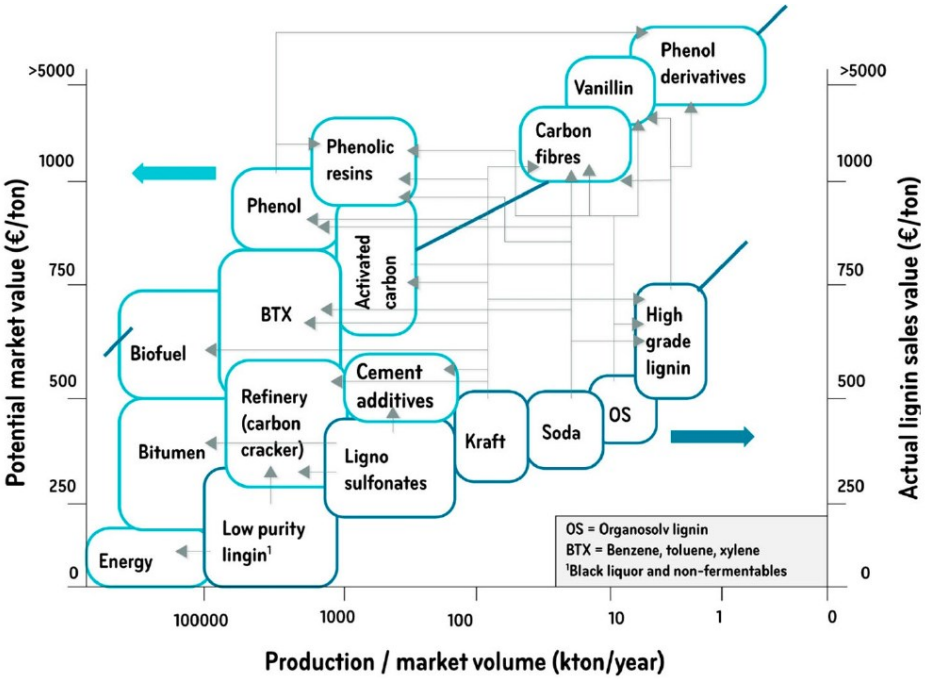

Figure 5. Lignin-derivatives market price and market volume [34].

As seen, lignin upgrading to monomeric compounds can successfully replace several petroleum-based products, supporting a sustainable and smooth transition in the chemical industry. This is why it is necessary to find effective ways for lignin upgrading, just as RCF.

1.10 Research question

Since RCF and biomass hydrogenolysis rely on similar key components: a high temperature, a solvent, a reductive environment (60 bar H_2), and a catalyst, it is possible that holocellulose and lignin conversion can occur simultaneously. This will lead to the production of more than one high-value-added product at once and a more efficient use of biomass, especially because the EG production is low. Considering this, we formulated the research question:

Can the optimal conditions for EG production also support lignin depolymerization with similar results to RCF?

To answer this question, we looked at the effect the catalyst, temperature, hydrogen, and pH had in the reaction. Also, as the process has been performed at a laboratory scale, the biomass feed is not sufficient to support its scaling up. Hence, we also increased the feed to prove that the process can move to the next step.

From the main research question and the analysed components, the following sub-questions appear:

- *What are the optimal conditions for EG production and the maximum yield?*
- *What are the lignin monomers produced by the catalyst for EG?*
- *What is the maximum extracted and converted lignin?*

2. Methodology

2.1 Materials

Ethylene glycol (anhydrous ≥99.8% Sigma Aldrich), propylene glycol (≥99.5% Sigma Aldrich), mannitol (BP reference standard, Sigma Aldrich), xylitol (analytical standard, Sigma Aldrich), D-(+)-glucose (BioXtra, ≥99.5% Sigma Aldrich), fructose (≥99% Sigma Aldrich), 1,4-butanediol (1,4-BDO, 99% Sigma Aldrich), acetic acid (99% Sigma Aldrich), guaiacol (≥99% Sigma Aldrich), 2-methoxy-4-methylphenol (4-methyl guaiacol, ≥98% Sigma Aldrich), 4-ethyl guaiacol (≥98% Sigma Aldrich), 2-methoxy-4-propylphenol (4-propyl guaiacol, ≥99% Sigma Aldrich), homovanillic acid (analytical standard, Sigma Aldrich), tetrahydrofuran (THF, ≥99.9% Sigma Aldrich), dichloromethane (DCM, ≥99.8% Sigma Aldrich), acetone (≥99.9% Sigma Aldrich), and sodium hydroxide (≥98%, pellets (anhydrous), Sigma Aldrich) were used for experiments and HPLC, GPC, GC-MS and UV-Vis analysis

Raney Nickel (W.R. Grace and Co. Raney 2800) and sodium polytungstate (WOx) (85% Sigma Aldrich), respectively hydrogenation and retro-aldol condensation catalysts, were used for hydrogenolysis reaction. Organic solvent was composed by a 50 wt.% of organic phase (48 wt. % of 1,4-BDO and 2 wt. % of acetic acid) and a 50 wt.% of distilled water. Pine biomass was used as the biomass feedstock for all the experiments presented here. It received a mild acid-leaching pre-treatment to remove inorganics and extractives ([35]), which is executed as follows: 1 wt.% of biomass is added to a 10 wt.% acetic acid solution, agitated for 24 hours, thoroughly washed until no change of colour in the water is visible and dried in the oven at 110°C for 24 hours. The dry acid-leached pine biomass (BM) was stored in a glass container until used.

2.2 Setup

Figure 6 a shows the setup of the 45 mL autoclave. It has two gas lines, one for hydrogen and one for nitrogen. They are operated manually and supply the gas to the autoclave; once this process finishes, they are disconnected from the autoclave. There are also two containers: a cold-water reservoir (right) and a fluidized sand bed (left). The fluidized bed uses hot air from a pre-heater and an oven to reach the desired temperature, while the cold-water reservoir only uses cold tap water. The autoclave is moved and immersed into these reservoirs aided by a pneumatic arm.

Inside the autoclave (Figure 6 b), there is a temperature couple at the bottom that aids in monitoring the temperature. At the top, a mechanical stirrer is connected to mix the solution throughout the reaction. It consumes 10 V to mix at approx. 1 300 rpm while a cold-water system cools it down. As the procedure works at high pressure, the setup is located inside a bunker to ensure safe conditions for the users.

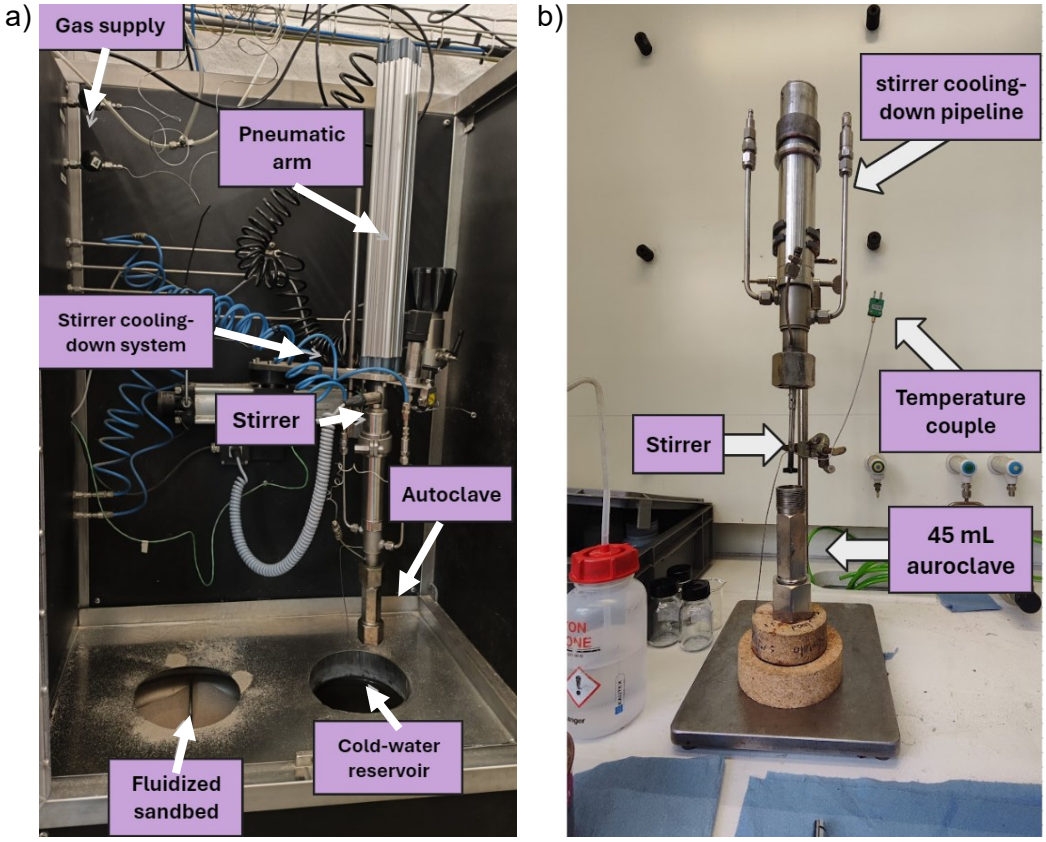

Figure 6. a) Setup and b) 45 mL autoclave.

2.3 Experimental procedure

The process started when the 45 mL autoclave was filled with biomass, catalysts, and solvent. Upon closing the reactor, we slightly shook the autoclave. Before starting any reaction, we ran a leakage test.

In it, we flushed the autoclave with 120 bar N_2 (room temperature). Then, with leak foam, we checked all the connections in the autoclave. If we did not detect any leakage, the pneumatic arm submerged the autoclave in the cold-water reservoir. If no bubbles were visible, we raised the autoclave, released N_2, and now filled it with 70 bar H_2 (room temperature). We re-checked leakages with H_2 in the same way we did for N_2. If none were detected, we released some H_2 to reach only the desired pressure (room temperature). After this, we turned on the stirrer and its cooling system. The autoclave was ready to perform the reaction.

The pneumatic arm introduced the autoclave into the fluidized bed to start heating it. Once the autoclave reached the desired temperature, we took the time. Pressure and temperature were monitored throughout the reaction. After two hours, the autoclave was moved to the cold-water reservoir to terminate the reaction. When the reactor reached 16°C – 18°C, we opened it, put the effluent in a glass container, weighed it, and left it in the fridge for one day before analysis.

2.3.1 Base experiment

The starting point of this research is based on the experiments and previous research of Di Sabatino [19]. In his work, the reactions had the feed composition shown in Table 2

and were performed at 245°C and 60 bar H_2 for two hours. Since these conditions showed good selectivity but low EG yields, they served as the base of this work and were improved. Every section of this work will describe the changes made to these conditions.

Table 2. Feed composition of the base experiment [19].

Biomass [g]	**0.75**
WOx [g]	0.021
Ni [g]	0.09
Solvent [g]	14.25

2.3.2 Catalyst loading

The impact of each catalyst on the EG yield was studied in this section. Three different amounts of Raney Ni (0.090 – 0.270 g) and five of WOx (0.021 – 0.105 g) were used. The exact quantities appear in Table 8, Appendix I. The increase of each catalyst was based on the amounts shown in Table 2, and the total feed was kept constant at around 15.25 g to maintain consistency. Finally, to study a possible poisoning of WOx on the hydrogenating catalyst, the WOx/Ni mass ratio was calculated.

All the reactions were performed at 245°C and 60 bar for two hours. There were no more changes in these experiments.

2.3.3 Biomass feed

The feed of the base experiment is composed of approx. 5 wt.% biomass, which translates into low mass EG production. To increase the production, the solid load (biomass feed) of the experiments of this section increased to 10 wt.% and 12 wt.% with a WOx/Ni ratio of 0.93 at 245°C and 60 bar H_2 for two hours. The feed composition of the experiments appears in Table 3.

Table 3. Feed composition of the solid load experiments. Reaction conditions: 245°C, 60 bar H2, 2 hours, and 0.93 WOx/Ni ratio.

Solid load [wt%]	**5**	**10**	**12**
Biomass [g]	0.750	1.525	1.830
WOx [g]	0.084	0.168	0.205
Raney Ni [g]	0.231	0.462	0.564
Solvent [g]	14.19	13.10	12.65

To determine if longer reaction times were necessary for high solid loads, we ran an experiment for 4 hours and 12 wt% biomass. No other modifications were applied in these experiments.

2.3.4 Temperature

To investigate the effect of temperature, seven temperatures were tested: 200°C, 215°C, 230°C, 245°C, 260°C, 280°C and 295°C. To determine its influence on lignin upgrading, five-hour experiments at 200°C and 260°C were performed. For all the experiments of this section, we chose a solid load of 10 wt.%. The feed was composed as shown in Table 4. These experiments used a WOx/Ni ratio of 0.93 and 60 bar H_2 for 2 hours. No other modifications were applied in these experiments.

Table 4. Feed composition of the experiments of temperature. Reaction conditions: 60 bar H2, 2 hours, and 0.93 WOx/Ni ratio.

Solid load [wt%]	10
Biomass [g]	1.5252
WOx [g]	0.168
Raney Ni [g]	0.462
Solvent [g]	13.10

2.3.5 Hydrogen and pressure

In this section, we studied the effects of pressure and hydrogen concentration. For this purpose, we lessen the initial hydrogen feed to 40 bar, 20 bar, and 0 bar H_2 (room temperature). We did not fill the autoclave with other gases, so this pressure also corresponds to the total pressure of the reaction. To complement the analysis, we conducted other experiments using 60 bar N_2 and 20 bar H_2 + 40 bar N_2 (room temperature) to understand whether the results were caused by the low hydrogen concentrations or low pressures.

Moreover, as the results at low hydrogen concentrations resulted in a low WOx catalyst detection, one more experiment for 4 hours was conducted to determine its remaining catalytic activity. In it, for the first two hours, the autoclave was filled with 60 bar N_2 (room temperature) and the same feed as that of Table 4. After completion, we released N_2 and loaded 60 bar H_2 (room temperature) for the last two hours. The reactor was not opened until the whole experiment was finished. This is the last experiment of this section. We ran all the experiments of this section at 260°C. No other changes were applied.

2.3.6 pH

We tested more acidic and alkaline solvents in this section. The original solvent has a pH of 3.13. As the sole purpose of these experiments is to study the pH effect, we maintained the original composition of the solvent (50 wt.% water + 48 wt.% 1,4-BDO + 2 wt.% HAc). Five pH were used: 2.3, 4.1, 5.1, 6.5, and 8.3. For a pH of 2.3, we added more HAc; for a pH of 4.0, 5.1, and 8.3, we poured more droplets of a 2 wt.% NaOH solution; and for a pH of 6.5, only water and 1,4-BDO were mixed (51% water / 49% 1,4-BDO). We performed these experiments at 260°C, 60 bar H_2 for two hours with the same feed shown in Table 4. No other modifications were applied in these experiments.

2.4 Analysis method

2.4.1 High Performance Liquid Chromatography (HPLC)

It is a kind of liquid chromatography used to separate, identify, and quantify compounds of a mixture. In this, the sample is injected in an inert liquid (mobile phase), pumped through a column that contains the stationary phase (usually silica or polymeric beads) that will separate the different compounds without reacting with them and will finally send them to a detector that will measure the intensity with which the molecule reflects or absorbs light. Every compound has a particular intensity, so to quantify them, we need calibration curves.

Here, the HPLC analysis was performed on an Agilent 1200 series in a Hi-Plex-H^+ column with 5 mM H_2SO_4 as a mobile phase at a temperature of 65°C. The results were measured through a Refractive Index (RID) and a Variable Wavelength Detector (VWD) at 285 nm. The identified and quantified products are EG, PG, glycerol, and sugar alcohols (sorbitol and xylitol). The samples are prepared by diluting 1 g of effluent in water in a 1:2 ratio and then diluting this solution again in water in a 1:1 ratio. The final solution is filtered (Whatman 0.2 um filter) before analysis. The calibration curves appear in Appendix IV. The weight yield calculations (wt.%) are based on the following formula, which uses holocellulose as its basis:

$$yield\ (wt\%) = \frac{m_{product}}{m_{feed}(1\ -\ f_{lignin}\ -\ f_{ash}\ -\ f_{acetyl\ groups})} \times\ 100$$

Where $m_{product}$ is the mass of the lignin derivative, m_{feed} is the biomass loaded in the autoclave, f_{lignin} is the content of lignin in pine biomass (0.274), f_{ash} the portion of unconverted biomass due to immediate combustion within the reactor (0.001), and $f_{acetyl\ groups}$ are the acetyl groups of holocellulose(0.016) [36].

2.4.2 Gel Permeation Chromatography (GPC)

It is a type of liquid chromatography that separates polymers of a solution depending on their size, avoiding chemical interaction with them. As lignin is an amorphous, large, and challenging-to-upgrade polymer, GPC is one of the most common analytical techniques to study its depolymerization rate.

Here, the analysis was performed in an Agilent 1200 series equipment with a variable wavelength detector (VWD). The samples were prepared by dissolving 100 µL of effluent in 3 mL THF, then filtered (Whatman 0.2 um filter) and placed in glass vials for their analysis. THF was taken with glass syringes to avoid the dissolution of plastic syringes in the sample.

To further study lignin depolymerization, the GPC spectrum was divided into the five weight ranges shown in Table 5. This, in combination with the results of the UV-Vis analysis, served as a meaningful tool to determine the advances in lignin depolymerization and extraction. All the resulting curves were normalized prior to calculations.

Table 5. Weight ranges for the division of the GPC spectrum according to Wang et. al. [37].

	Weight range (Da)	
Light	94-185	Monomers
	186-318	Dimers
	319-636	Trimers and tetramers
Heavy	637-1068	Pentamers, hexamers, and heptamers
	>1069	Octamers and heavier

2.4.3 Gas Chromatography Mass Spectrometry (GC-MS)

It is an analytical tool composed of two different techniques. The Gas Spectrometry (GC) separates volatile components of a liquid, gas, or solid sample by heating them until their vaporization. Then, an inert gas (mobile phase) like helium, hydrogen, or nitrogen, carries the sample through a column (stationary phase) that will separate the mixture into its different components based on its boiling points and polarity [38]. When the components of the sample are unknown, the Mass Spectrometry (MS) serves as an identification tool. By measuring the mass-to-charge ratio (m/z) of charged particles [39], the molecular weight of the components can be calculated and compared to those available in the different MS libraries. As GC-MS can work as a qualitative and quantitative tool, especially for complex mixtures like those coming from lignin upgrading, we decided to use it to identify and quantify the derived lignin monomers.

Here, the GC-MS analysis was performed in an Agilent GC 7890A MS 5975C equipment. The samples for this analysis required a Liquid-Liquid Extraction (LLE) prior analysis. Their preparation was as follows: 2 g of effluent was diluted in 10 g DCM and stirred for 24 hours at 400 rpm. Then, the water-soluble compounds (upper layer) were removed, and the remaining liquid was left for three days to allow evaporation of DCM at ambient conditions. The sample was weighted after the second day to compare its weight with the weight of the third day. If no or minor differences were registered, the sample was diluted into 1 mL acetone, filtered (Whatman 0.2 um filter), and put into a glass vial for analysis. After the identification, calibration curves were built to quantify the lignin derivatives (Appendix V).

2.4.4 Ultraviolet-Visible spectroscopy (UV-Vis)

It is a non-destructive analysis technique that quantifies compounds depending on the amount of ultraviolet or visible light they absorb. It is extensively used in the food and pollutant removal industry. However, it has been reported that it can also offer an easy, fast, and accurate way to quantify the solubilized lignin [40].

Here, a Hach DR 5000TM UV-Vis spectrophotometer was used for the analysis. The samples were prepared by dissolving 5 µL of effluent in 5 mL of a 0.035M NaOH solution. Similarly to HPLC, every compound absorbs light differently, so a calibration curve is needed. Dried softwood lignin (previously extracted by T.D.J. te Molder) was used for this purpose and its absorbance measured at 280 nm. The extracted lignin was calculated as follows:

$$\%\, extracted = \frac{c_{ex\ lig}}{c_{feed}(f_{lignin})} \times 100$$

Were $c_{ex\ lig}$ is the extracted lignin, c_{feed} is the initial concentration of biomass loaded in the autoclave, and f_{lignin} is the content of lignin in pine biomass (0.274).

3. Results

3.1 Catalyst loading

3.1.1 Main hydrogenolysis products

Previous studies about the hydrogenolysis of biomass succeeded in the production of EG from raw biomass with high selectivity (<25 wt.% yield) using catalyst ratios of 0.12 (Raney-Ni/Biomass) and 0.026 (WOx/Biomass) [19], [35]. The low quantities aimed to study the catalyst sensitivity to inorganic species of biomass (Ca^{2+}, Mg^{2+}) and their influence on the reaction [35], so it is possible that the EG yields are low because of the low catalyst content. Hence, in this section, we studied the impact higher catalyst ratios have on EG yields.

Figure 7 shows the effect of different catalysts ratios on the EG yield. The 0.1 Raney Ni/Biomass ratio (original ratio) registered the major changes, but it is thanks to the increase of WOx that the EG yield rise is possible. Hence, the more WOx is present, the more EG it produces. That is true up to 0.11 WOx/BM ratio when the experiment reached a yield of 33 wt.%, 10% more than using the original ratios and the maximum from these experiments. However, the increase of WOx has a limit that is evident when using a 0.14 WOx/BM ratio. There are two possible explanations.

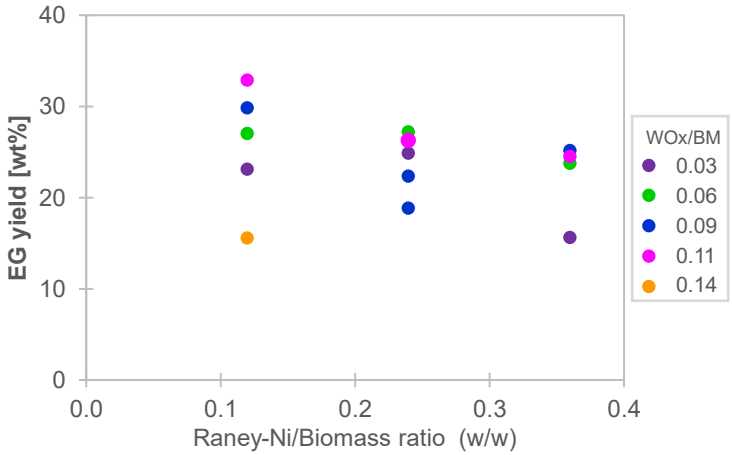

Figure 7. Influence of Raney nickel® and WOx in the EG yield.

The first one is related to the kinetics of the reaction. The hydrogenation of GA to EG is faster than the retro-aldol condensation of glucose [9]. This means that the retro-aldol condensation requires support to produce more GA, being WOx the responsible for that. However, when GA is over-produced, it can condensate and form recalcitrant C-C bonds, which will result in a lower products yield [9], so a balance between the production and conversion is necessary. Probably, at a 0.14 WOx/BM ratio, this balance is lost

The second explanation could be the adsorption of WOx species on the surface of Raney Ni. The idea comes from previous suggestions of te Molder et. al. [35], who noticed the consumption of some tungstate catalyst in the presence of Raney Ni. As the first may adhere to the surface of the second, there is a reduction of the active hydrogenating sites that worsens with the presence of passive WOx. It is important to stress that the slow production of glucose can enhance the passivation of excessive amounts of WOx as the catalyst transforms glucose faster [17]. Thus, the more WOx is present, the faster the

passivation of the catalyst is, and so the adsorption to Ni. This comprises well what may be happening in the first minutes of the reaction and explains why, with the highest amount of WOx, there is still some EG production. This conclusion is supported by Zhang et.al. [17], who also used a tungstate and a metal catalyst (AMT and Ru/C) and observed less hydrogenating activity. Therefore, one must be careful with the ratio between the catalysts to avoid their passivation or inactivation.

In this sense, we built a new plot using the previous results but calculating the WOx/Ni (active nickel) ratio this time. The resulting graph is depicted in Figure 8 and makes evident the influence WOx has on EG without affecting the production of PG, enhancing the overall glycols yield (>36 wt.%). On top of that, the maximum ratio between catalyst is clear now and must not be above 1 to maintain good EG yields. Moreover, we confirm that Raney Ni does not support the hydrolysis of cellulose as there are some points with the same WOx/Ni ratio and similar EG yields, showing that the original ratio of 0.12 Ra/BM is sufficient.

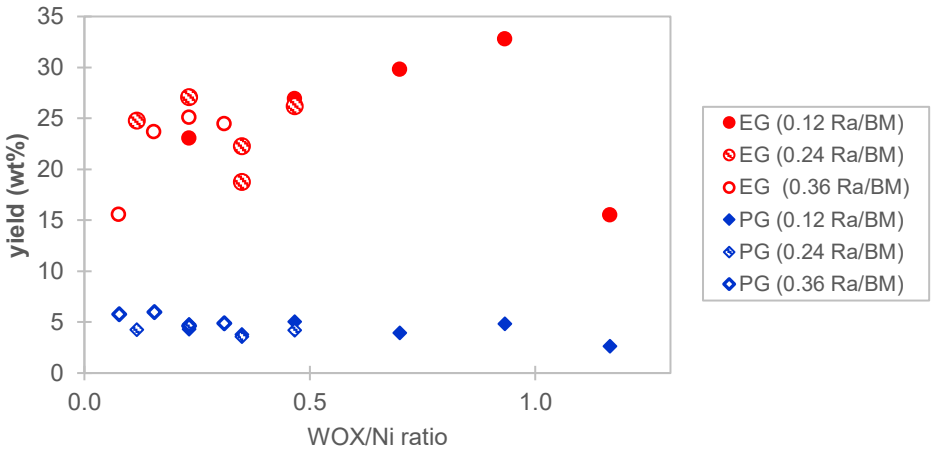

Figure 8. WOx/Ni ratio influence in the EG yield (wt.%).

Another possible answer to the low EG yield at high WOx/BM ratio is that glucose is going to the side reactions. However, Figure 9 shows that it is not and suggests that the hypothesis about WOx adsorption on Raney Ni is true as the side reaction yields are also the lowest, meaning that there is low hydrogenating activity. It demonstrates that a glucose deficit leads to the poisoning of the hydrogenating surface. Therefore, ratios above one must be avoided.

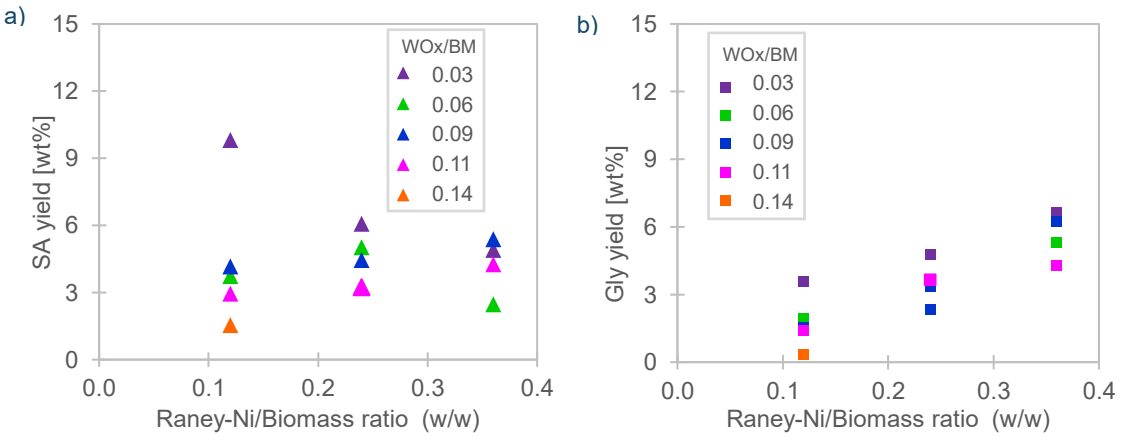

Figure 9. Effects of the catalyst load in a) sugar alcohols (SA) and b) glycerol (Gly) yield.

(Confidential)

3.1.2 Lignin

Regarding lignin, Figure 10 shows the impact the catalyst ratio has on the average molecular weight (MW) and the extraction of lignin in combination with the five categories in which the GPC spectrum was divided (Table 5). There are no substantial changes, except for the MW at a 1.16 WOx/Ni ratio. This may be a consequence of more availability of the catalyst to depolymerize lignin rather than to convert holocellulose. Although the depolymerization of lignin is a much slower process than the production of EG [9], [41], [42] and may not require high amounts of catalyst, the large chains of the polymer and many unstable products may be benefited by the excess of catalyst. That is why, the different amounts of catalyst affect the composition of the light products (monomers, dimers, and trimers (Figure 10c)) and increase when the production of EG is blocked, as at a WOx/Ni ratio of 1.16. The result suggests that in our system, EG and lignin are in a competition for the catalyst, implying that a total biomass upgrading may be challenging to achieve in a one-pot procedure.

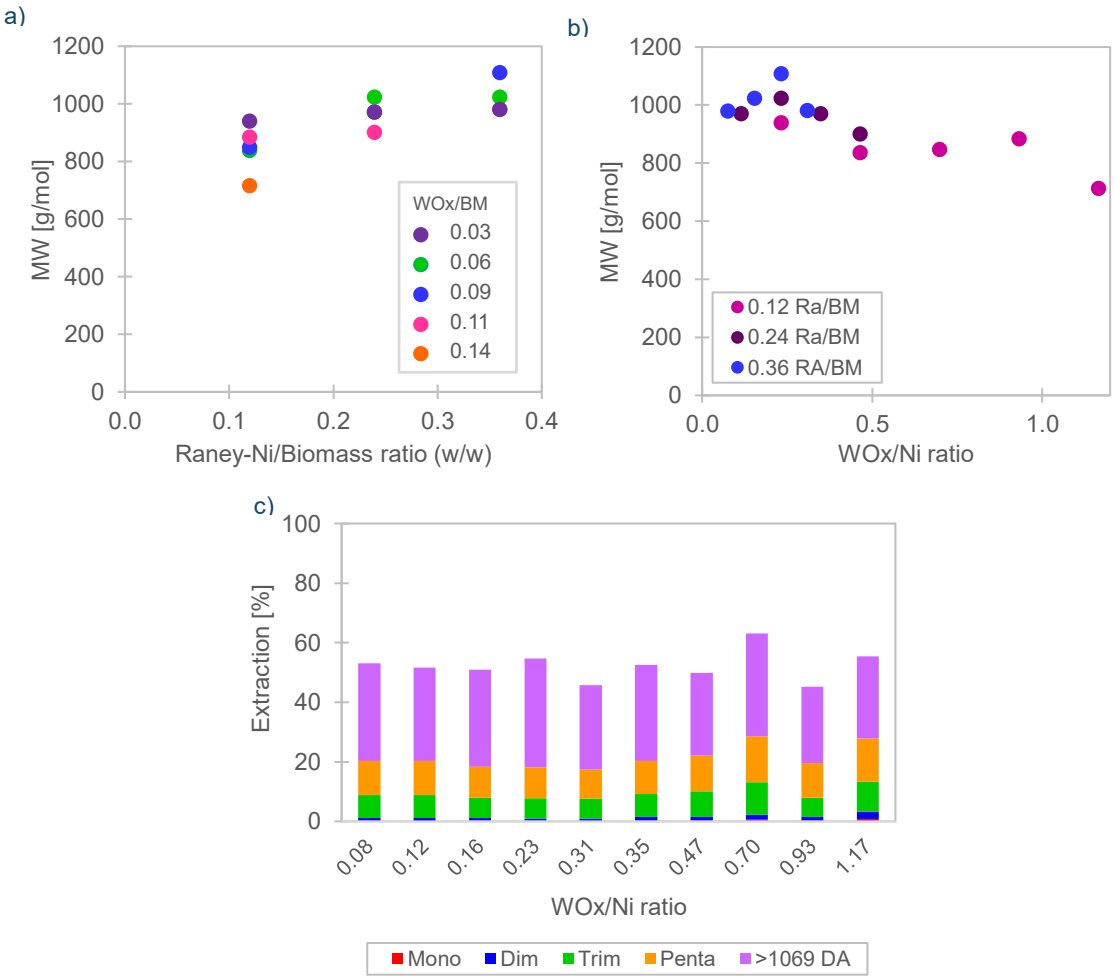

Figure 10. Effect of the Raney Ni/Bm ratio (a) and catalyst ratio in the mean weight (MW) (b), and composition of the extracted lignin (c).

On the other hand, although the production of monomers is still minimal, their presence helps us determine to what degree RCF is still achievable and what is the nature of pine lignin. As the experiments with 0.12 Raney Ni/BM showed the most important results for EG, we decided to analyse only those in this part. Five main compounds were identified: guaiacol, 4-methyl guaiacol (4-MethG), 4-ethyl guaiacol (4-EthG), 4-propyl guaiacol (4-

PropG), and homovanillic acid (HVAc). Their detection shows that guaiacyl units (G-units) are the main components of pine biomass, presenting another big challenge as they can be very branched, leading to random breaking [21]. The quantification through GC-MS (Figure 11) shows good selectivity towards guaiacol and 4-PropG. This result suggests the breakdown of the β-O-4 bond, the second strongest and most common C-O bond in lignin [20], as 4-PropG and HVAc come from multiple hydrogenations to this bond (Figure 12) [43]. Therefore, the presence of a hydrogenating catalyst such as Raney Ni enhances their production and is the one controlling its breakdown as a random cleavage of the G-units produces 4-MethG and 4-EthG [44], which are minimal here.

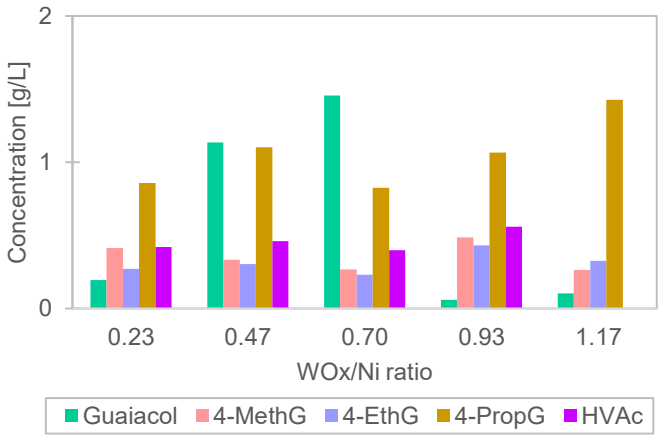

Figure 11. Main monomers from lignin (Max. possible concentration: 14.4 g/L).

On the other hand, WOx seems to be controlling the guaiacol production as its increase causes an increase in guaiacol, and suppresses an over-hydrogenation of the aromatic ring [45] (Figure 11). This is possible thanks to the Bronsted acid sites of WOx that provide oxygen vacancies [46], where the C-O bonds of lignin undergo a hydrogen transfer and rearrangement that can produce guaiacol. However, its generation can be limited by EG production. As WOx prioritizes the conversion of glucose to GA because of the faster production of glucose, the yield of guaiacol decreases, as shown in the optimal-for-EG WOx/Ni ratio (0.93) (Figure 11). This suggests that the selectivity will move towards 4-PropG every time higher EG yields are achieved. A higher production of 4-PropG is not a problem since the alkylated compound is a high-value added chemical. However, it emphasizes that the optimization of EG yields may potentially reduce the upgrading of lignin.

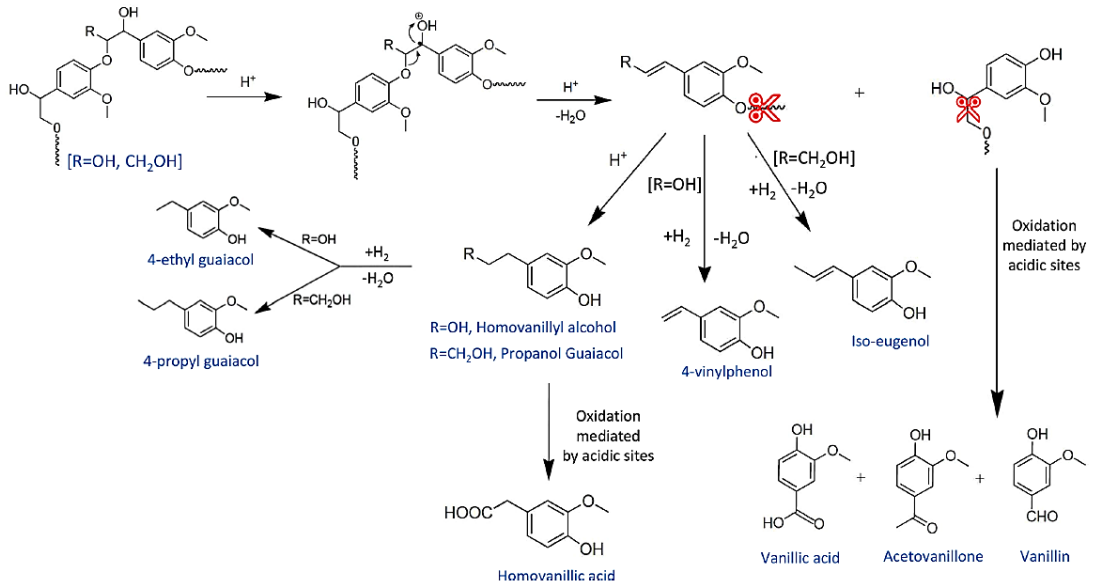

Figure 12. Lignin depolymerization pathway of guaiacyl units [43].

A final observation regarding the poisoning of Raney Ni comes from HVAc. It is hypothesized that the acidic sites of the hydrogenating catalyst controlled its oxidation [43], and as there may be a few or none at a WOx/Ni ratio of 1.17, its production is blocked. Therefore, the HVAc production could also indicate the activity of the Raney Ni surface. Nonetheless, the poisoning of Raney Ni requires more studies.

To conclude this subsection, we built a graph combining the results of EG yield and MW of lignin (Figure 13). It shows that there is some support from each other, but also a trade-off, especially at a WOx/Ni ratio of 1.16. Although it does not show the trade-off also affects the monomers yield, it is important to recall its implications as the upgrading of lignin is a complex process in which the MW does not offer the absolute answer. As we aim to extract and selectively depolymerize lignin, one must be careful with the analysis. Moreover, the main goal of this research is optimizing the production of EG, so it gives the final decision, which in this case leads to the use of a WOx/Ni ratio of 0.93. Although it does not significantly lower the MW of lignin and extracts it less, the ratio leads to good monomers selectivity, and more importantly, it avoids the poisoning of the metal catalyst. Then, the following experiments will use this ratio.

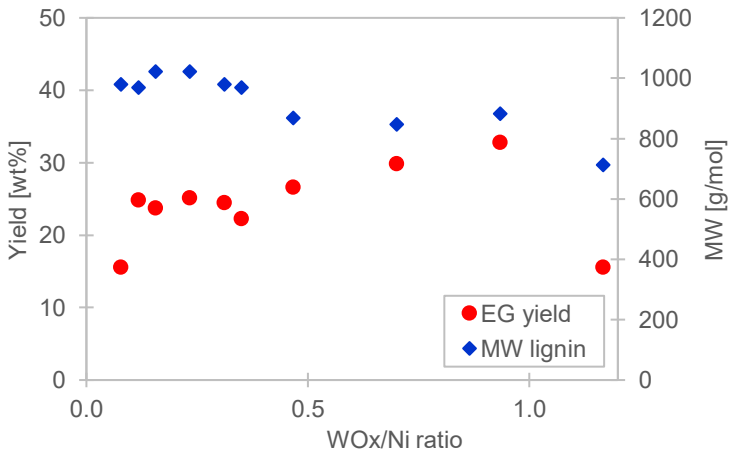

Figure 13. Summary of the impact of the catalyst in the EG yield and MW of lignin.

3.2 Biomass feed

3.2.1 Main hydrogenolysis products

The first step in finding the optimal conditions for high EG yields resulted in a significant increase. However, as the feed consists of only 5 wt.% of biomass, the EG mass production is still low (0.175 g, (Table 6)), and it is left beyond industrial feeds that can process up to 26 wt.% of biomass [47]. Therefore, it is necessary to increase the load to make it more industrial appealing and increase the EG production.

Figure 14 shows the results of this increase. In our attempt to treat a higher solid load (<15 wt.% [48]) the reaction encountered mass transfer limitations from 12 wt.% onwards. This was due to the quick absorption of the solvent in the dry biomass. Although the water present in the solution is forty times higher than that required for cellulose hydrolysis, even at a solid load of 12 wt.% (0.147 g vs 6.352 g) according to (Eq. 1, section 1.2), the liquid fulfils another task. Water is necessary for an homogeneous and low-density mixture [48] that allows interactions catalyst – reactant, removal of products and local inhibitors from the catalyst, and homogeneous mass and heat transfer [49], especially necessary in the first minutes of the reaction [50].

Therefore, in a mixture with limited water, it is unsurprising that the yield of the main products significantly decreases, as observed in Figure 14, where a 12 wt.% solid load only resulted in a 19 wt.% yield of EG in two hours. This is one of the primary challenges in utilizing biomass as a feedstock. Various strategies have been proposed to address this issue, with the most effective being a reduction in the solid load. Even when it means less products, a bigger water footprint and lower production, it has the advantage of low energy demands for mixing (less dense solutions) and more constant catalytic activities. Overall, advantageous. Therefore, the feed should contain a maximum of 10 wt.% of biomass to avoid mass transfer restrictions. Even though with 10 wt.% biomass, the yield is still lower than with 5 wt.%, the EG mass is almost twice (0.175 g vs 0.302 g) (Table 6), so the increase is substantiated for a two-hours reaction and can still improve.

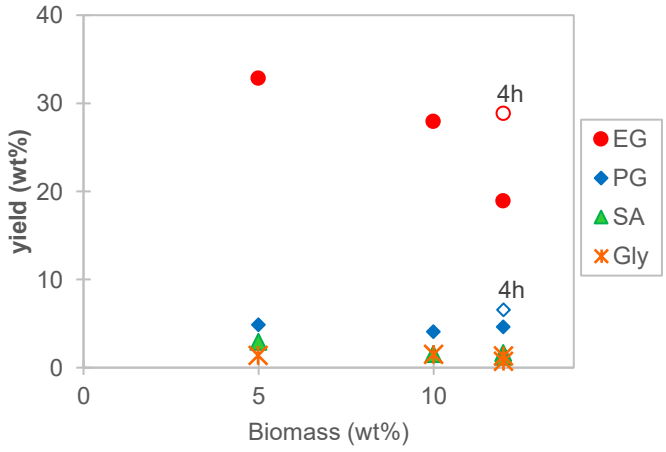

Figure 14. Effects in the EG yield due to high-solid loads.

Another solution to high-solid loads is an extension of the reaction time. In this case, twice the original time as we used approx. twice the initial feed (12 wt.%). The result of this experiment also appears in Figure 14. It shows that the extension increases the yield close to that of 10 wt.% in only two hours. The result is logical as the mass transfer

barriers are overcame with the production of liquid products from the solid biomass, resulting in a lower solid content. It represents a substantial improvement and stresses the importance of the liquid mixture. However, the extension to four hours is still unfavourable because two times the load of 10 wt.% of biomass will produce more than one time a load of 12 wt.%, in terms of mass (0.604 g vs 0.374 g). Hence, a load of 10 wt.% biomass is the optimal and maximum for our procedure.

Table 6. EG yield and mass production with higher solid loads.

Biomass feed [%]	EG mass [g]
5	0.175
10	0.302
12	0.245
12 (4h)	0.374

3.2.2 Lignin

Lignin, on the other hand, registered minimal differences in its MW and extraction with the biomass feed increase (Figure 15), but it is noteworthy that the 12 wt.% feed does have a decrease in its MW despite a lower extraction. This can be a consequence of the poor hydrogenating competitivity with GA, which favours the depolymerization of lignin rather than its extraction, being the last one supported by lengthy reactions. That is why the four-hours experiment extracted more than 50% of lignin, registering one of the highest values (until now) with still good depolymerization activity. The result is not surprising because RCF and other lignin-first strategies can last up to eighteen hours [29], showing that our procedure is fast. Also, this result stresses that lignin extraction becomes slower after the first hours and so the constrain of water in the first minutes can affect its performance, although slightly less than in holocellulose because of its slow kinetics [51].

We can conclude that, even when 12 wt.% is more favourable for lignin, 10 wt.% will be chosen for the following experiments as the main objective of this research is finding the optimal conditions for EG production. However, the effect on lignin is not negative at all and may improve through the other aspects we studied here.

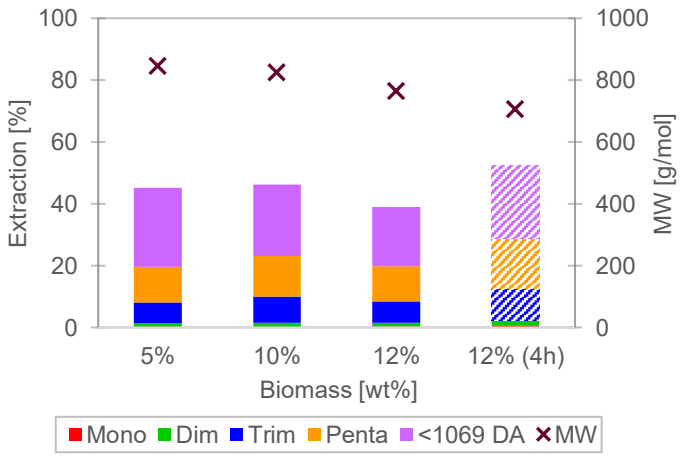

Figure 15. Effects in the MW of lignin and the composition of extracted lignin.

3.3 Temperature

3.3.1 Main hydrogenolysis products

A temperature of 245°C has demonstrated good selectivity towards EG. However, the overall glycol yield is still below the maximum obtained with pure cellulose (44 wt.% of EG + PG) [35], which has now decreased with the increase in the biomass feed (Figure 14). One way to improve its production is by increasing the temperature of the reaction. Generally, the hydrolysis of cellulose and hemicellulose starts at temperatures around 220°C and 100°C (respectively) when using a diluted acid (1 wt.% solutions) [7]. Furthermore, if we consider that biomass absorbed a substantial part of the solvent (more dense mixture), we end up with significant mass transfer limitations for their breakdown [49]. Thus, we can increase the temperature to lessen the density of the mixture and accelerate the cleavage of lignin and holocellulose.

Moreover, as seen in the experiments of the increase of catalyst, the poisoning of the hydrogenating catalyst is a leading problem that, according to Zhang et. al. [9], can be attenuated through high temperatures. In this sense, García et. al. [14] also point out that Raney Ni can suffer poisoning from organic products, which can be removed at temperatures above 250°, aided by the free liquid in the solution. From this, we decided to use temperatures above 245°C, as shown in Figure 16. To understand better the effect of temperature, we also used lower temperatures, but not below 200°C as they favour the production of SA [14], [18].

Figure 16 shows that there is a correlation between the temperature and the glycol yield between 200°C and 260°C, reaching with the last a value of 41.9 wt.% (EG+PG) (Figure 16), the highest one registered until now, with significant improvement to the experiment at 245°C (32 wt.%). Although these experiments do not assure that the hydrogenating catalyst poisoning was minimized, we can confirm that the hydrolysis of holocellulose improved as there was an increase in PG, which was not registered before. Even when its production comes from the glucose isomer (fructose) that can also lead to SA and glycerol, we see that the side product yield is still low (and even minimized).

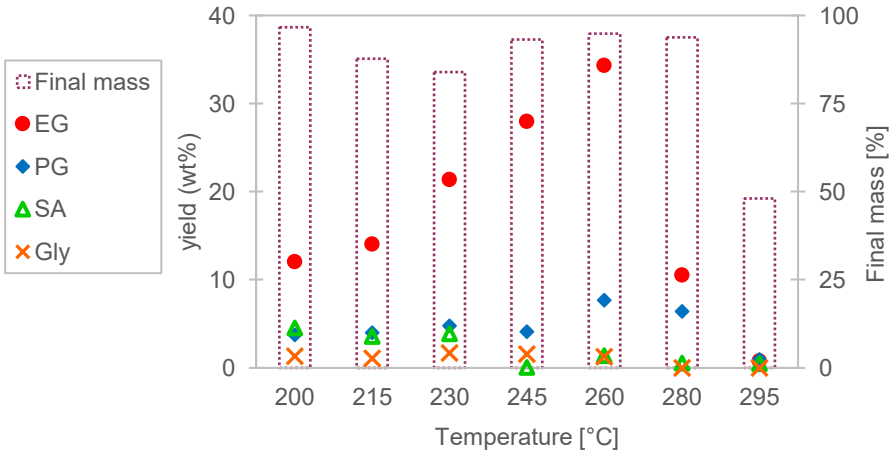

Figure 16. The effect of temperature in the main products yield and the mass balance.

However, one must be careful with the increase in temperature as it can lead to the opposite effect. Figure 16 shows that at a temperature of 280°C, there is a drastic reduction of the EG yield (only 10.5 wt.%). It can be the result of the hydrolysis of

cellulose at high temperatures as it has been reported that they can lead to the production of furfural (FF) and hydroxymethyl furfural (HMF) [7], which are precursors of humins [12].

Even though its presence was not deeply investigated, we believed that the reaction moved to this route as the yield of PG, which comes from fructose, was also high at this temperature. According to the study of van Zandvoort et. al. [52], fructose can form slightly higher amounts of humins than glucose. Thus, the isomerization of glucose to produce PG and humins could be the reason behind the decrease in EG. To this point, biomass gasification is not the root problem because the rough mass balance (Figure 16) shows that most of the mass remains in the effluent. However, as hemicellulose is less stable than cellulose [8], it undergoes random degradation pathways and starts a gasification process [51] as shown in Figure 36 (Appendix III). There, we can see that after an hour and a half, the pressure started increasing again. Fortunately, the probable produced gases (tars [53], alcohols, ketones, etc. [11]) recondensed after cooling down. That is why we still see a complete liquid mass balance (Figure 16). Although this is good, such high temperature should be avoided because all these humins, tar, and condensable products are of low value.

At 295°C, biomass gasification is unavoidable. Its pressure profile demonstrates that after approx. 45 minutes, there a significant increase of pressure that reaches 140 bar. This is the highest pressured registered and contrary to 280°C, this gas products do not condense after cooling down, and around 50% of the initial mass is lost (Figure 16). As holocellulose is easier to break down than lignin, it gasifies easily, so the production of EG is very limited. Although the high pressure maintains biomass in the liquid for a longer time, the mass transfer limitations of the first minutes can enhance biomass gasification. In addition, the two-hour reaction may allow the early-produced condensable volatiles to undergo a second crack-down [8], which leads to a mass lost if not recovered, as in our case. Therefore, the maximum and best temperature for glycol production is 260°C since it still avoids gasification reactions and produces a high amount of EG. However, more studies are still needed to confirm humins production at this temperature.

3.3.2 Lignin

In the case of lignin, we know that an increase in temperature successfully breaks it down (e.g. pyrolysis) [23]. Hence, the results of Figure 17 a) are not surprising: the higher the temperature, the lightest the extracted lignin. Logically, in translates in a significant increase in monomers at 280°C and 295 °C (6.4% and 10%, respectively) (Figure 17 b), meaning that the latest is optimal for lignin depolymerization.

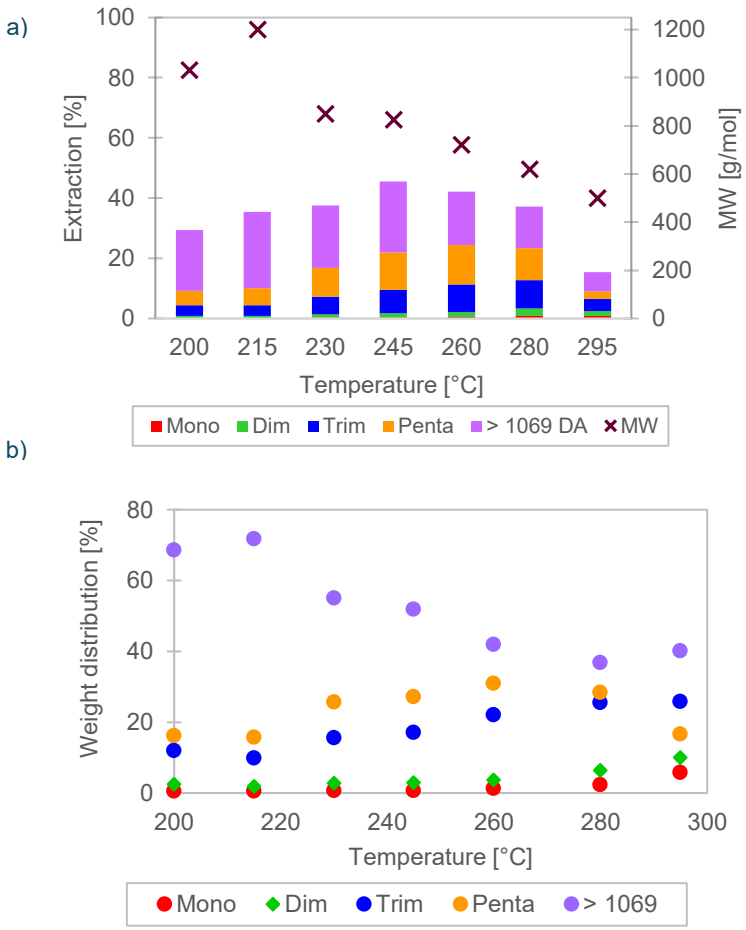

Figure 17. Effect of temperature in (a) the MW and (b) weight distribution of extracted lignin.

At 295°C notwithstanding, there was a loss of mass of 50% (Figure 16) that also affected the amount of extracted lignin, as seen in Figure 17a). When we compare the extractions, we see that the monomer production is overshadowed by the little mass remaining in the effluent, which reduces the advances in the depolymerization of lignin. Moreover, this breakdown seems random as the five-tracked monomers experienced a significant decrease, starting at 280°C. Therefore, despite the high pressure, the reaction temperatures must not be above 280°C.

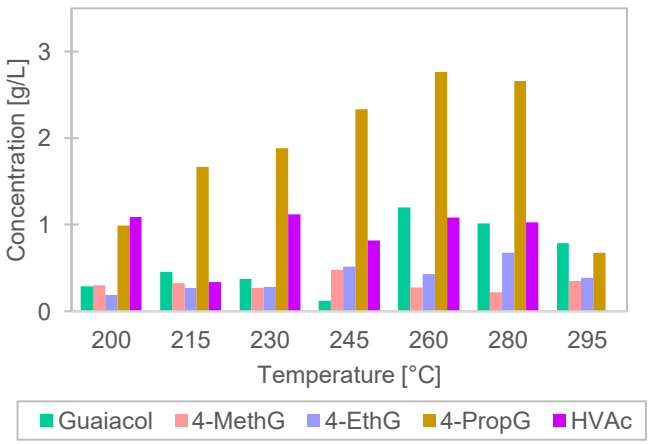

Figure 18. Influence of temperature in the monomer selectivity (Max. possible concentration: 31.9 g/L).

(Confidential)

However, the usual temperatures at which RCF works (below 250°C [29]) also do not show significant differences at this point because they gradually extract and upgrade lignin, which is why they take a few more hours to complete. Still, in our case, the extraction increases with temperature and reaches a maximum at 245°C (Figure 17a), and in combination with the MW and weight distribution of Figure 17, they show that this temperature is suitable for lignin. Nonetheless, 260°C (optimal for EG) can also be a good candidate for lignin. It may not reach the same extraction values as 245°C, but the divergence is low. Additionally, at 260°C, there is a substantial reduction of heavy molecules compared to 245°C (42% vs 51.8% (Figure 17)), which is more severe than that from 260°C to 280°C as the last depolymerizes and volatilizes more products, which leads to pyrolytic results. Thus, such high temperatures must be avoided in our process considering the good selectivity we have until 260°C, where 4-PropG and guaiacol are still the most favoured. Noteworthy that with temperature, 4-PropG has a higher production. It may be due to the low availability of WOx to produce guaiacol as there is a higher conversion of glucose. However, guaiacol is still necessary in the liquid because it can avoid the formation of precursors of solid residues [54] (FF or HMF [12], [54]), which may be the reason why at 260°C there is still a good degree of depolymerization and EG yield.

3.3.3 Five-hour reaction

Temperature showed the most significant changes for lignin and EG until now, and since the latter has faster kinetics, it may hinder lignin depolymerization. Considering this, an experiment of five hours was performed to determine if holocellulose kinetics are the main barrier in lignin upgrading. Two temperatures were chosen: 200°C and 260°C. On the one hand, the first has a low EG production, demonstrating the low holocellulose conversion and, consequently, a probable higher lignin conversion. On the other hand, the second temperature has the highest degree of depolymerization before gasification. Given the difficulty of breaking the G-units of lignin [21], a prolonged exposition of lignin to such a severe condition can support its conversion even more.

The results of a five-hour reaction compared to those after two hours appear in Figure 19 a. They revealed that temperature is more influential on lignin depolymerization than time, being 260°C the most optimal temperature for lignin upgrading. At this temperature, despite the extended reaction, lignin extraction and MW surprisingly remained constant, demonstrating that the maximum upgrading was achieved in only two hours. Although the result is surprising regarding the reaction time, it is reasonable because softwood lignin is the most challenging to upgrade [21]. Moreover, the result suggests that softwood lignin only changes in highly energetic conditions (solvolityc depolymerization) and quickly. That is why, at 200°C we hardly reached the same lignin extraction value of 260°C but with a heavy-product composition.

A two-hour reaction is supported by the tracked monomers (Figure 19 b) since they registered a decrease in their yields with extended reactions at both temperatures. Although at 200°C the tracked monomers yield is much lower than at 260°C, there is a 50% decrease after five hours, which could be the result of sparse gasification after the fourth hour, where slight bounces are visible in the pressure profile (Appendix VII). At 260°C, biomass gasification is enhanced after 3 hours (Appendix VII), where monomers

are more likely to degrade to CO and CO2 and lead to some mass loss, as seen in Appendix VIII, Figure 50. Therefore, there are no benefits in extending the reaction, and we confirm that 260°C is the best temperature for lignin upgrading.

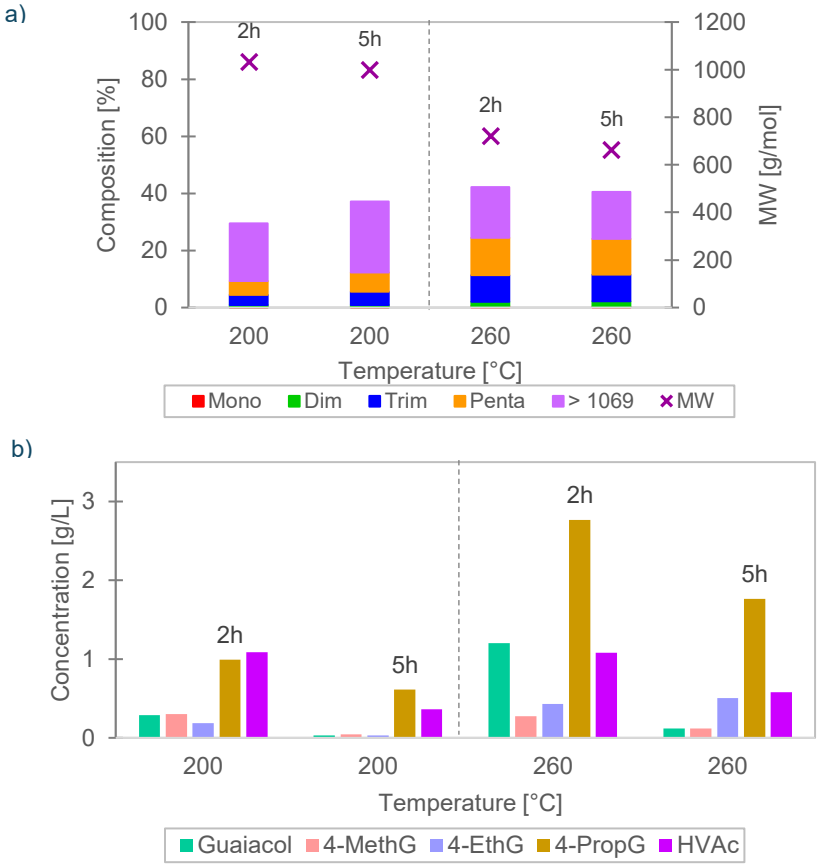

Figure 19. Influence of temperature in a) lignin extraction and MW, and b) monomer selectivity (Max. possible concentration: 31.9 g/L) of a 2- and 5-hour reaction.

To sum up, it seems that regarding temperature, there is good agreement between EG and lignin (Figure 20). 260°C depolymerizes lignin more, has higher selectivity towards 4-PropG, and is also the best for EG. Moreover, it was confirmed that two hours are sufficient and the best for lignin and EG, so 260°C and two-hour reactions are chosen for the following experiments.

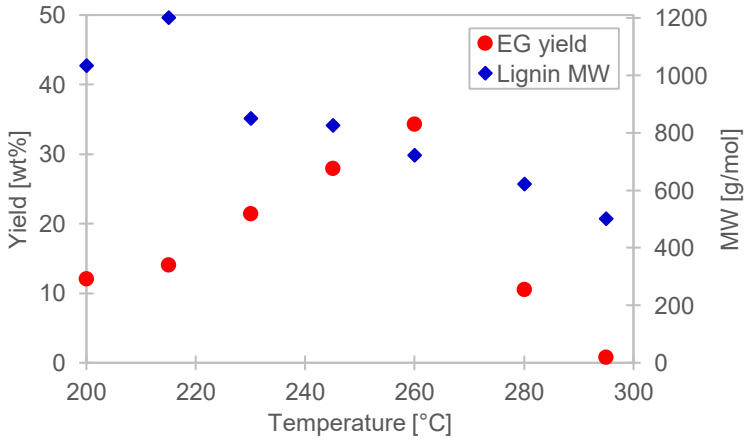

Figure 20. Summary of the effect of temperature in the EG yield and MW of lignin.

3.4 Hydrogen and pressure

3.4.1 Main hydrogenolysis products

Hydrogen, in combination with the presence of Raney Ni, is key to producing EG. However, it is expensive [55] and can considerably increase the price of the whole process. From the previous experiments, we noticed that the reaction consumes 20 bar hydrogen (approx.). Although we have not analysed the final gas composition, we estimate that over 90% of it remains as pure hydrogen, allowing for multiple recycling. However, the initial amount of hydrogen could be reduced as it is not totally consumed. If we can do it while maintaining the yield and selectivity, the process can be more cost-effective. Therefore, in this section, we studied the effect hydrogen and pressure have on EG and lignin.

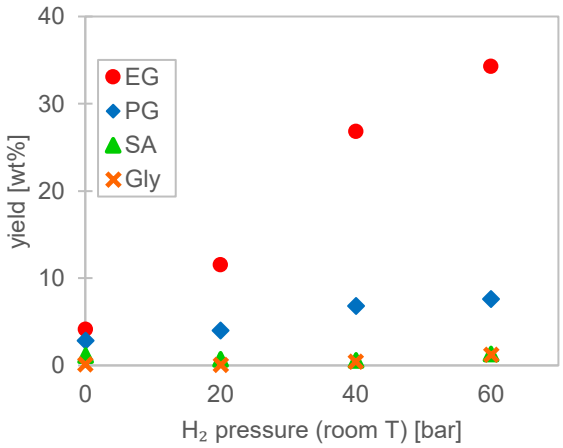

Figure 21. Influence of hydrogen pressure in the EG yield.

Figure 21 depicts the effect of hydrogen pressure on the EG and side reaction yields. As can be seen, the EG yield has a direct relationship with hydrogen: the more hydrogen is present, the higher the EG yield. This result could suggest a first-order reaction, but since the production of EG from glucose follows (at least) two intermediate reactions, the reaction order cannot be directly stablished [9]. Moreover, as the initial pressure decreased, the maximum pressure the reaction reached was lower, enabling easier biomass gasification, especially seen at 0 and 20 bar H_2 (Figure 22). It demonstrates that high pressure is also necessary in the reaction environment. Hence, to better understand its effect, we ran an experiment with only 60 bar N_2. As 1,4-BDO is an excellent hydrogen donor (in combination with Raney Ni) [18], the experiment also served to demonstrate the capability of the diol to provide H_2.

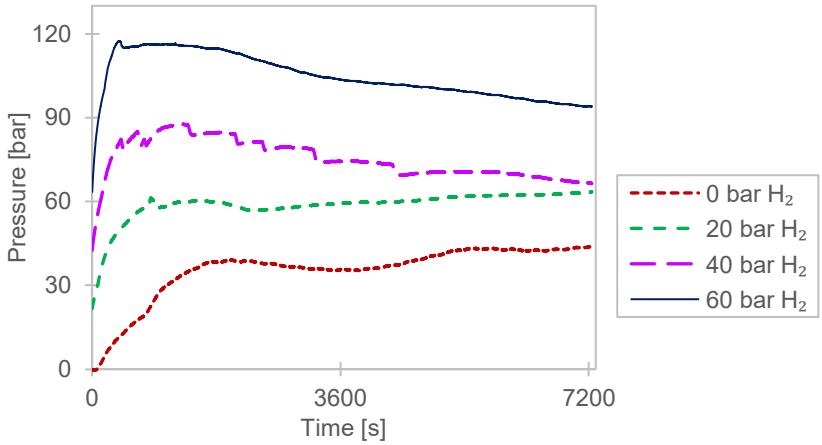

Figure 22. Pressure inside the autoclave when changing the initial H2 pressure.

The results of this experiment compared to those of 60 and 0 bar H_2 are shown in Figure 23 a. It is clear that hydrogen gas is more necessary than pressure and that the diol cannot provide all the hydrogen or not as fast as it is needed, especially to stabilize reactive molecules (such as GA [17]) from which undesired products can be easily produced [9]. Also, we must remember that hydrogen is needed for lignin depolymerization and possibly some hydrolysis of holocellulose because the H^+ acts as a catalyser [7]. Hence, an excess of hydrogen is fundamental to achieving good results.

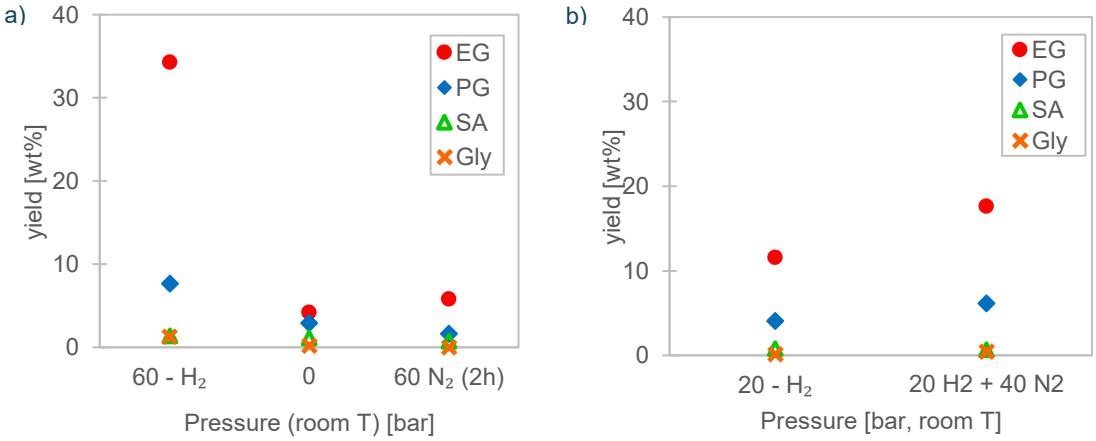

Figure 23. Effect of a) pressure in the main products yield and b) of 20 bar hydrogen as total and partial pressure.

One last experiment attempted to reduce H_2 pressure was performed. As previously mentioned, the reaction consumes approx. 20 bar H_2, so we decided to combine it with 40 bar N2 to investigate if this could be adequate to produce EG. The result of this experiment and its comparison with that of only 20 bar H_2 is shown in Figure 23 b. There, we can see that although the EG yield is 6 wt.% higher than with only 20 bar H_2, the difference is insufficient to allow a combination of the two gases. Indeed, the result shows again that pressure avoids some biomass gasification. However, pure hydrogen gas is preferred to a mix with nitrogen. Thus, the use of 60 bar H_2 is imperative for high EG production.

3.4.2 WOx stability

An element not previously discussed is the detection of WOx species (through HPLC) because it was relatively constant throughout the past experiments. However, at low or no hydrogen gas, WOx was not detected, as seen in Figure 24. The answer to this low detection may lie in the generation of (or retrieval from) other WOx catalytic species.

Wang et. al. [15] suggest that the tungsten bronze species (H_xWO_3) are the catalyst of the retro-aldol condensation. In his work, he states that independently of the nature of the tungstate species, under reductive conditions, WOx is transformed into this homogeneous compound that can penetrate the crystalline cellulose structures easily than heterogeneous species. The production of tungsten bronze species is only possible in-situ due to its low stability at low temperatures and in contact with air [15], meaning that their production requires H_2. As hydrogen is necessary in multiple upgrading reactions within the system, the deficit could enhance leaching and precipitation of the catalyst, which leads to limited productions of GA and so EG (Figure 21).

Another explanation is due to chemical changes in the catalyst. Tungsten has multiple oxidation states that grant him the catalytic activity. For EG production, W^{5+} species (Bronsted acid) are thought to be responsible of the retro-aldol condensation, mainly, because they provide oxygen vacancies that allow hydrogen transfer and rearrangement of glucose [46]. To maintain a strong Bronsted acid, H_2 is necessary to retrieve W^{6+} to W^{5+} [56]. Therefore, in hydrogen deficient environments, oxidation of tungstate is enhanced, which makes it lose its catalytic activity and blocks GA production. Additionally, since hydrogen is not aiding retrieve W^{5+} species, the catalyst could be suffering complexation with glucose or other side products [57], which could be limiting its detection even more.

Determining whether WOx underwent chemical changes, leaching and precipitation, or complexation is not possible through HPLC, more studies are necessary. However, it demonstrates that hydrogen is necessary for more than merely the conversion of biomass.

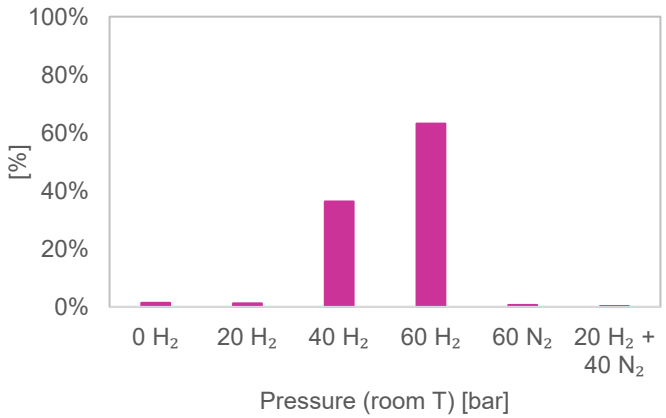

Figure 24. Effect of hydrogen and pressure in the detected WOx by HPLC.

To quickly investigate to what degree WOx is damage, we ran an experiment of 4 hours. In the first two hours, the reaction performed at 60 bar N_2, and in the next two (with the same catalysts) at 60 bar H_2. The results appear in Figure 25. There is an increase of 20% in the detection of WOx after its interaction with H_2, while the EG yield only

increased by 4 wt.% at the end of the experiment. On the one hand, the low EG yield is reasonable because no more biomass was added before filling the autoclave with H_2, and due to the high temperature and extended reaction, holocellulose must have degraded to small and unknown products. On the other hand, the result demonstrates that WOx cannot be directly reused after a hydrogen deficient reaction, it requires a reactivating treatment.

Although this experiment does not offer an absolute answer to what is happening to WOx, it makes clear that hydrogen plays a crucial role beyond the conversion process; it protects the catalyst. Hence, the 60 bar H_2 cannot be reduced, they assure catalyst recycling, and the gas must be sufficiently supply when scaling up the process.

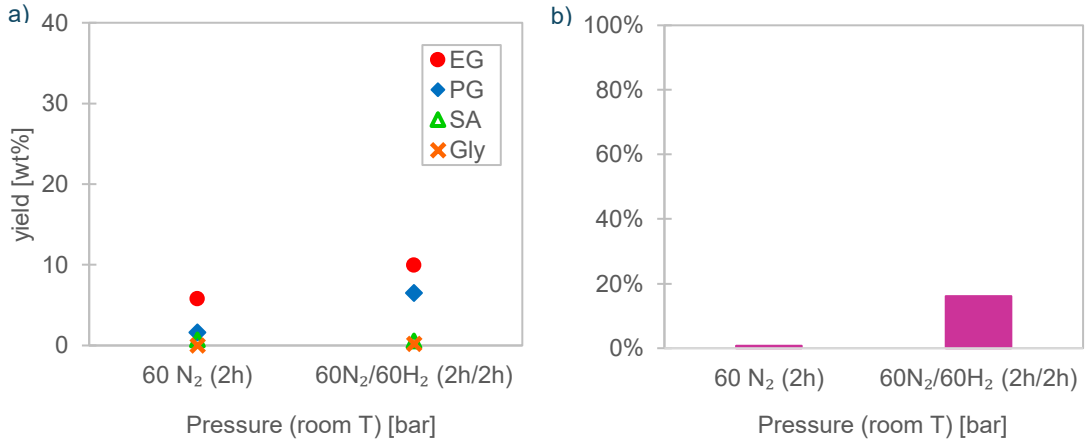

Figure 25. Comparison on a) the activity and b) detection of WOx after a reaction without hydrogen.

3.4.3 Lignin

In the case of lignin, for the first time, we had a change of colour of the effluent that became more distinct after a liquid-liquid extraction (with DCM) (Figure 26). The solution became darker with the decrease of hydrogen. The change can be associated with the presence of lignin in the solution. The darker the solution, the more lignin is present, which seems true according to the results of the UV/Vis (Figure 27).

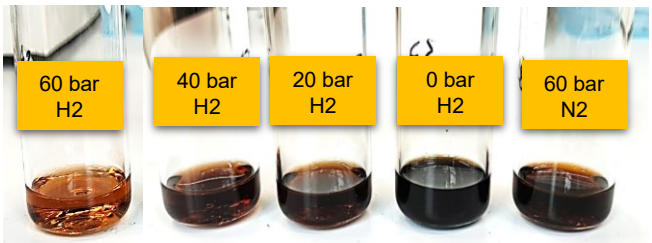

Figure 26. Visible changes due to the difference in colour of the organic phase (after DCM separation).

Contrary to EG, a high hydrogen pressure negatively affects the extraction of lignin, being the absence of hydrogen the best to extract and depolymerize it as the column of monomers is more appreciated in the composition of the extracted lignin (Figure 27). However, when the reaction happened at high pressure without hydrogen (60 bar N2), almost 80% of lignin was extracted, where only 20% corresponded to heavy products, a surprising result. Logically, this decrease is also reflected in the MW of the solution, as seen in Figure 27, where 60 bar N2 is the lightest solution.

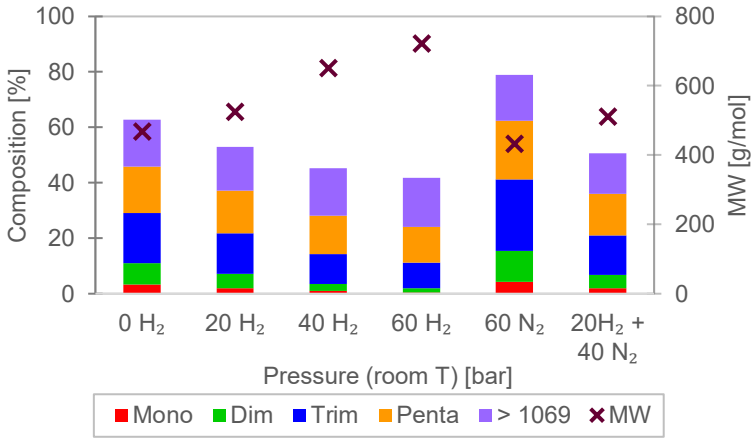

Figure 27. Effects of hydrogen and pressure in the composition and MW of extracted lignin.

The result suggests that lignin is favoured by contrary conditions to EG, mainly because the kinetics of the second are faster than those of lignin [9], [41], [42]. Hence, when the EG production is blocked, lignin takes all the available resources at the highly energetic condition. It stresses once more the existent competition within the system, now for hydrogen from the gas and the diol. Even though the last provides less (or gradual) amounts of the element, its availability is very limited. Remember that the diol is fundamental for lignin extraction, but its good-hydrogen-donor nature supports the hydrogenation of GA first because of its fast kinetics, limiting the amount of diol ready for the extraction.

The situation changes when there is a deficiency of hydrogen because the holocellulose upgrading is limited, resulting in more availability of the diol (and the element) to extract lignin that later depolymerizes. Even though there is limited hydrogen, the slow kinetics of lignin are an advantage in this case because the reaction gives time to the system to provide it, being holocellulose and its derivatives the main source [5]. That is why a hydrogen deficiency favours lignin extraction and is much better when there is high pressure because biomass and hydrogen remain in the liquid more time [51]. However, a severe hydrogen deficit affects the selectivity of the depolymerization.

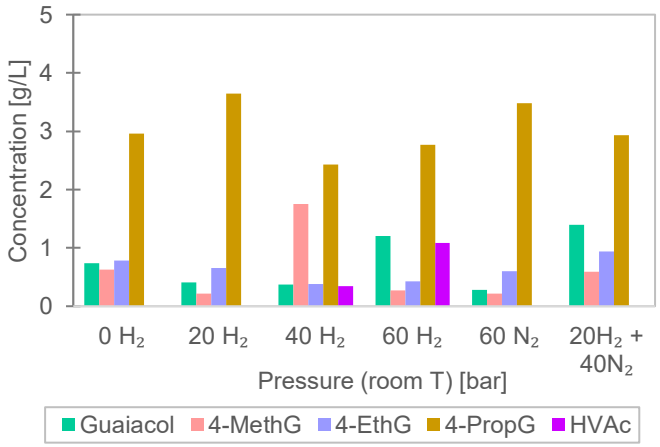

Figure 28. Monomer selectivity of extracted lignin and the total yield of the tracked monomers (Max. possible concentration: 31.9 g/L).

Figure 28 shows that the selectivity of the five tracked compounds remains constant and that 4-PropG is still the most favoured one. However, according to the UV/Vis and GPC results, there should be a more significant monomer production at low and no hydrogen pressures. It is not happening because lignin is breaking down in an ample and random variety of light molecules, as observed in the GC-MS analysis (Appendix IX). It is a severe problem because this lignin upgrading is at the expense of low selectivity, leading to pyrolytic mixtures with many unstable and re-polymerizable products. The reason of this low selectivity lies in the catalysts.

On the one hand, it was demonstrated that WOx presence is low (Figure 24); therefore, its catalytic performance is low. On the other hand, Raney Ni does not properly work at H_2 pressures bellow 40 bar (room temperature), so its catalytic activity is low as well. As they both demonstrated high control over the β-O-4 bond cleavage (subsection 3.1), it is clear that, in combination with the lack of hydrogen and highly energetic conditions, lignin does not follow a controlled cleavage, which results in low selectivity, as shown in the GC-MS analysis (Appendix IX). Overall, no benefit in limiting the H_2 feed is found, and these reaction conditions should be avoided.

To sum up, even though the best conditions for EG and lignin seem like the opposite (considering the lignin MW) (Figure 29), the selectivity of the last is seriously affected and leads to random mixtures challenging to upgrade later (as in pyrolysis). Hence, despite the low but highly selective lignin upgrading of this two-hour reaction, 60 bar H_2 is the optimal condition, not only because of the high EG yields but also to protect the catalyst within the reaction environment.

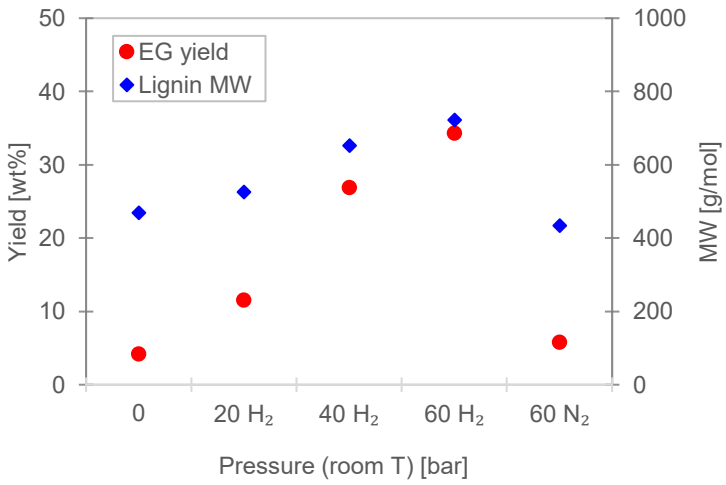

Figure 29. Hydrogen and pressure effect in lignin and the EG yield.

3.5 pH

3.5.1 Lignin

The previous results have demonstrated that the trade-off between high extraction with selective depolymerization cannot be overcome, so at least one should be maximized. The solution may be in the pH because alkaline conditions improve lignin removal (or extraction), while acidic conditions support its breakdown [29]. Hence, in this section, we studied its effect on lignin and EG by modifying the solvent pH between 2.3 and 8.3.

The results appear in Figure 30 and show that while the lignin extraction is constant and independent of the pH, its breakdown is not. Acidic conditions seem to highly control and selectively break down lignin to 4-PropG, while alkaline mediums experience a significant decrease in the tracked monomers. According to Renders et. al [21], this can be the result of the re-polymerization of intermediates of G-units, which impact goes beyond lignin as it can cause a loss of cellulose, and so EG.

As there are no benefits in using more alkaline mediums for lignin, acidic conditions are preferred. Although the stronger the acid medium is, the higher the selectivity is, we must consider that extreme conditions become dangerous for the equipment and the waste would require a special treatment. Then, the original pH is the best option for the process. Also, because the difference in 4-PropG between 2.34 and 3.13 is not as sharp as that between 4 and 3.13, the risk is not justified.

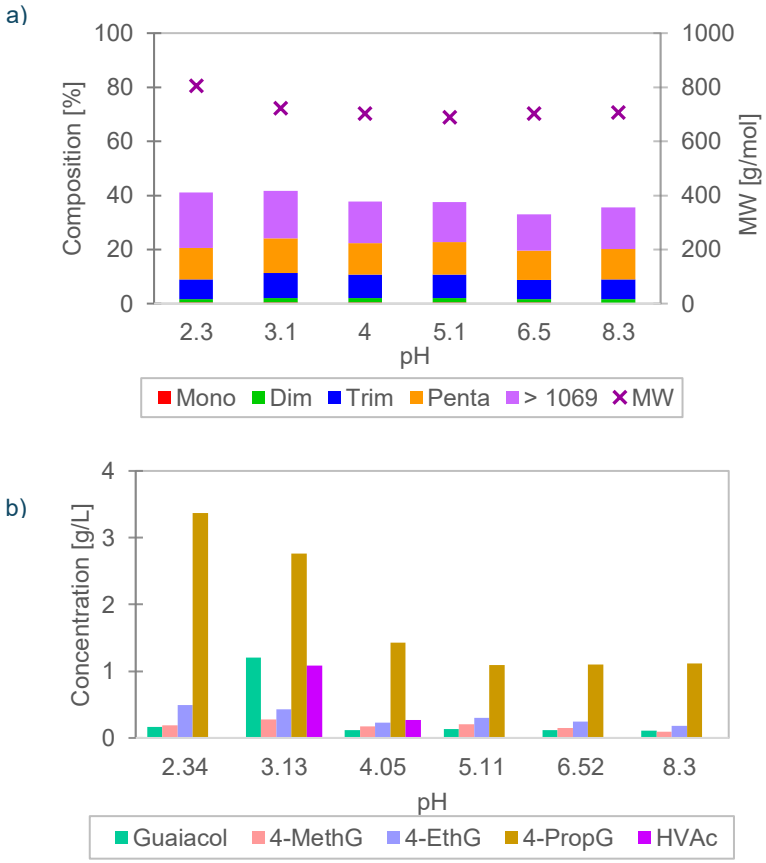

Figure 30. Composition of extracted lignin, its MW (a) and its produced monomers (max. concentration: 31.9 g/L) (b).

Also, the lignin MW (Figure 30 a) shows that a low pH depolymerizes slowly. The results were expected as we stressed before that a high extraction and depolymerization are not covered at once in a two-hour reaction. Nonetheless, alkaline and neutral conditions do not show an important change either. Although in this figure it is not clear whether there was re-polymerization of G-units under alkaline conditions, it is true that at least there was some depolymerization as there is a decrease in the MW. Hence, it is probable that the re-polymerization led to smaller molecules than the original ones, but no monomers. However, more studies are needed to determine these changes.

3.5.2 Main hydrogenolysis products

Figure 31 shows that similarly to 4-PropG, acidic conditions support overall glycol production. It is because the H^+ ions facilitate the hydrolysis of cellulose [7] and, to a certain degree, the acidic condition can maintain cellulose and lignin processes separated [21], significantly avoiding the intervention of lignin re-polymerization pathways in EG production and vice versa. This acidification is enhanced by the hydrolysis of cellulose, which cleavage produces acetic acid [7]. Hence, the influence of in-situ generated HAc demonstrates that EG production is supported in strong acidic mediums.

Although the results of pH 6.5 and 8.3 seem to contradict the last statement and could promote the use of neutral and alkaline conditions (Figure 31), it is necessary to recall that NaOH is traditionally used for retro-aldol condensation reactions [15], [16]. Thus, its over-addition supports glucose breakdown that, accompanied by the on-site production of acetic acid, increase the EG yield. However, the content of NaOH must be moderate because it is not always selective towards C_2-C_3 compounds [16], which can harm the selectivity of the system. Hence, the addition of the acid is necessary to maintain a selective production of EG. In addition, acidic conditions demonstrated being the best for lignin depolymerization and since lignin does not interfere with the EG production, acidic mediums can be chosen. However, we cannot use the most acidic condition due to the risk to the equipment, especially when there is a moderate difference in the EG yields between 2.34 and 3.23 (36.8 wt.% vs 34.3 wt.%).

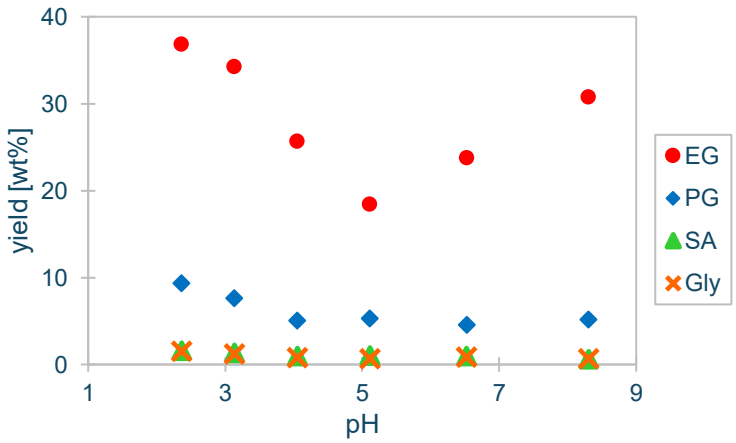

Figure 31. pH influence in the main products yield.

To summarize, a variation of pH has a stronger effect than expected in lignin and EG, being strongly acidic conditions undoubtedly preferred by both (Figure 32). While lignin saw a high selectivity towards 4-PropG with slow depolymerization, EG faced an increase in the yield of both glycols. However, by choosing the most acidic condition, we compromise the equipment lifespan and waste disposal, so the original pH remains as the optimal condition for EG production.

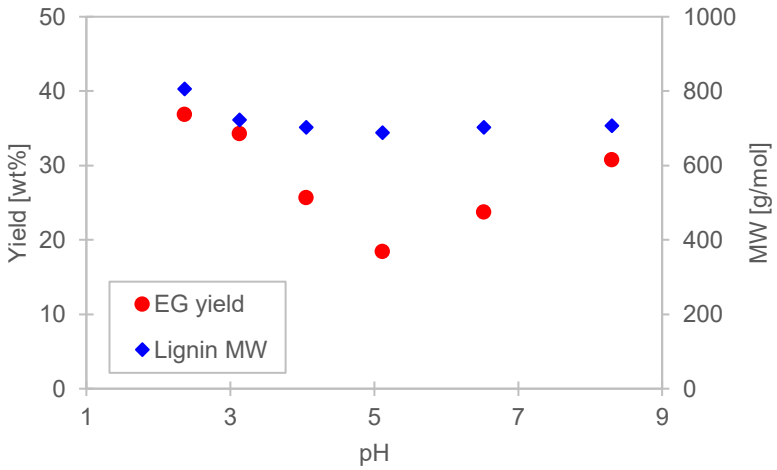

Figure 32. Summary of the effect of pH in the EG yield and lignin MW.

3.6 Sustainability beyond a yield improvement

The improvement of the EG yield is a successful result for the technical side of the process because now we produce more EG (from 0.12 to 0.37 g) with a slight increase in resources (temperature and catalyst). Nonetheless, this improvement impacts other areas out of the scope of this work, such as greenhouse gas emissions (GHG), primary fossil energy depletion, acidification, etc. Their analysis would need another complete work; however, other studies have estimated that an increase of 10% in biomass product yields (especially above 40 wt.%), can reduce approx. 10% of the total GHG emissions of the EG production process [55]. Definitely, a meaningful decrease.

However, although biomass-based processes always claim to be sustainable because they use a renewable source, "from cradle-to-grave" or life cycle analysis (LCA) demonstrate that this can be questionable several times. When considering energy consumption, feedstock harvesting, hydrogen use, and catalyst and solvent production, for example, biomass conversion processes can sometimes fail to be more environmentally friendly than their fossil counterparts. This does not only make their benefit doubtful to society but also less attractive to the market in which they must compete with cheap and more consolidated fossil products and processes (Figure 33).

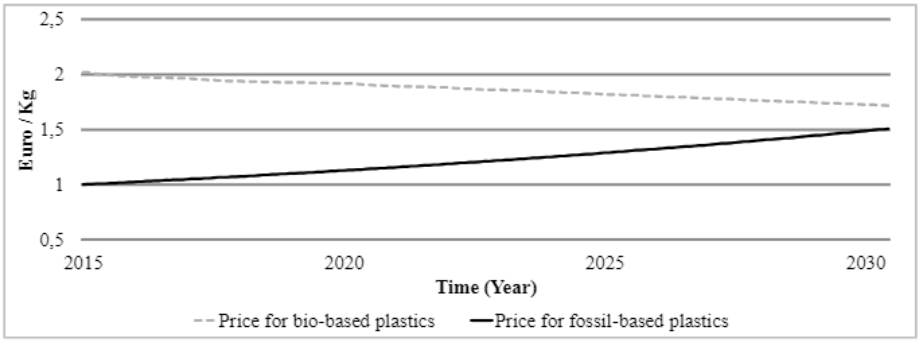

Figure 33. An example of price competitiveness for bio-based plastics versus fossil-based plastics [58].

Therefore, a higher EG yield, a higher biomass processing and simultaneous holocellulose and lignin upgrading are indeed meaningful efforts from the technical side to produce more bio-chemicals but to support its scaling up, in-depth studies are required to ensure their environmental friendliness. For example, the separation processes and selectivity must be considered because azeotropes can promote energy-intensive separation processes that will result in more indirect GHG emissions than their fossil counterparts. Selectivity is not a severe problem in the current results, but separation must be carefully analysed later to avoid this problem. That is why, a lignin upgrading (like RCF) and its removal, followed by a hydrogenolysis of the sugars for EG production must be analysed and compared to the simultaneous process. Especially because, independently of how more than one product is obtained, the whole environmental impact must be lower than that of petrochemicals.

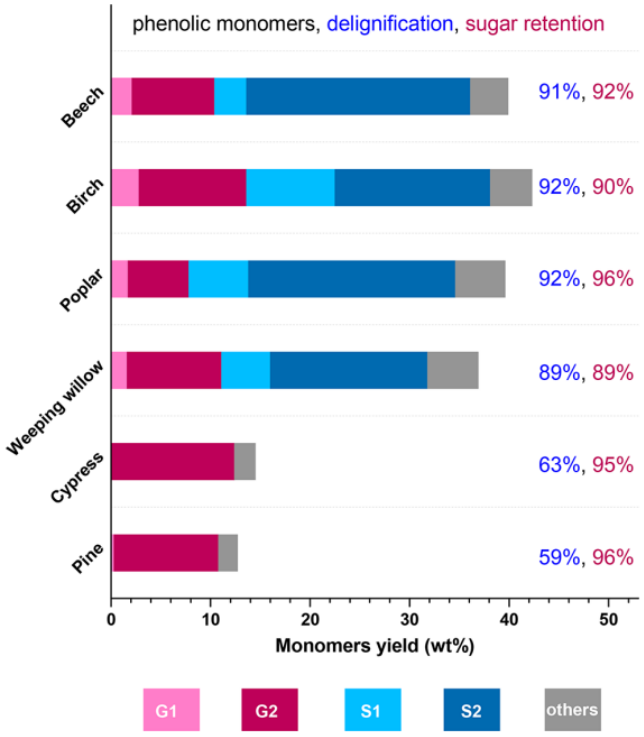

Figure 34. RCF of some wood lignocelluloses and their derivatives: coniferyl alcohol (G1), coniferyl methyl ether (G2), sinapyl alcohol (S1) and synapyl methyl ether (S2)

That is why LCA must be performed before decision-making. In this sense, we also suggest a comparison with other kinds of biomass [59] since pinewood biomass has a medium content of cellulose (Table 1) and a high content of recalcitrant guaiacyl units, which could be limiting the EG yield and lignin upgrading. Undeniably, using woody biomass is advantageous against growing dedicated crops. Nonetheless, by aligning conversion processes with biomass composition (Figure 34), more sustainable and efficient practices can be developed, regardless of scale.

Biomass suitability also needs to be considered depending on the location and availability of the feedstock since transportation can substantially increase the GHG emissions [60]. Therefore, it is advisable to use regional forestry feedstocks, which means the bio-chemical industry will have to change its traditional centralized production models to regional decentralized models that make them truly sustainable. Although this is a radical change, it would bring significant benefits to the regions, where not only technological and intellectual development will be supported but also employment and sustainable forestry practices. A LCA by Rannisto [61] in Central Finland estimated that refining mill lignin instead of its combustion would slightly increase the environmental effects. Meanwhile, employment and (municipal and national) taxes would increase 11.2 and 6.9 times those of combustion, respectively (Table 7).

Table 7. Environmental and economic impacts in Central Finland when changing from lignin combustion to refining [61].

Environmental and economic impacts	Lignin combustion	Lignin refinement
Total production impact	1	9.7
Employment impact	1	11.2
Taxes	1	6.9
Global warming potential	1	1.25
Acidification potential	1	2.2

In fact, this cannot be compared to the impact that bio-chemicals from RCF and biomass hydrogenolysis have, but still demonstrates that lignin conversion into high-value-added products impacts beyond environmental aspects and can have meaningful benefits when the biorefinery is regional. Therefore, it is important to perform LCA in biorefinery before implementation and plan its construction at a regional scale because even when biomass is a constant sustainable feedstock, it still has high and low seasoning production. Hence, to avoid deforestation and other social and environmental problems, more considerations beyond the technical aspects must be considered.

4. Conclusion

In this work, we improved the EG yield from biomass hydrogenolysis and studied its effects on lignin to determine if a total biomass upgrading was possible. The obtained results let us answer the main research question which is as follows:

- ***Can the optimal conditions for EG production also support lignin depolymerization with similar results to RCF?***

By studying the effects that the catalyst loading, biomass feed, temperature, H_2 pressure, and pH have in the system, it was demonstrated that the lignin upgrading is limited during biomass hydrogenolysis. While the EG production significantly improved, lignin conversion and extraction were relatively constant. The result is a consequence of competence with EG for H+ species and the catalysts during the reaction, where the faster kinetics of cellulose hinder lignin upgrading. Nonetheless, the structure of pinewood lignin also blocks its upgrading itself as the experiment of five hours at 260°C demonstrated that there were no improvements despite the highly energetic conditions of the system.

It was previously stated that RCF can extract up to 99.9% of lignin and convert it with a selectivity up to 75%, but softwood lignin is the most challenging kind of lignin to upgrade. Hence, it is likely that the maximum possible upgrading for this kind of lignin is reached under the optimal conditions for EG, which could even be the same for RCF of pinewood.

Having answered the main research question, the results also allowed us to answer the research sub-questions, which are:

- *What are the optimal conditions for EG production and the maximum yield?*

The most optimal conditions to produce EG are a WOx/Ni ratio of 0.93 (w/w), a Raney Ni/Biomass ratio of 0.12 (w/w), and a feed of 10 wt.% at 260°C and 60 bar H2 in a solvent with a pH of 3.13, which resulted in an EG yield of 34.3 wt.% and a PG yield of 7.6 wt.%. It is a significant improvement to the original yields (23.1 wt.% EG and 4.6 wt.% PG), and in mass terms because the original conditions only converted 5wt.% of biomass. Hence, the most optimal conditions tripled the mass of the first experiment (from 0.12 to 0.37 g) with a small energy and resources increase (from 245°C to 260°C and from a catalyst ratio of 0.3 to 0.93).

- *What are the main lignin monomers produced by the catalyst for EG?*

Five main monomers are produced during biomass hydrogenolysis: guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol, 4-propyl guaiacol, and homovanillic acid, where only the first could be a result of WOx. Among them, 4-propyl guaiacol is the most favoured one in all the tested conditions.

- *What is the maximum extracted and converted lignin under the most optimal conditions for EG?*

Under those conditions, only 41% of lignin was extracted and converted to 4-PropG and guaiacol (9.4 wt.% and 5.9 wt.%, respectively). It is a much lower conversion than that

of RCF (99.9% extraction with 75% conversion), but the result is a consequence of the softwood lignin structure, which is one of the most challenging to upgrade.

In conclusion, more than the fact that lignin and holocellulose require opposite conditions to upgrade, the results demonstrate a competition for some resources (where the fast kinetics of the last favour it) and that the nature of lignin limits itself from upgrading. Therefore, the one-pot conversion of pinewood lignin during EG production in two hours is very significant and supported because its derivatives (guaiacol, for example) aid in avoiding re-polymerization of holocellulose (to humins) and lignin (to tars and char), which grants higher product yields. Hence, the one-pot procedure can be the best option for this kind of biomass and to increase its potential, more focus on the oligomers production is suggested.

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6. Appendix

I. Catalyst loading experiments

Table 8. Feed composition of the catalyst load experiments. Reaction conditions: 245°C, 60 bar H2, and 2 hours.

			Raney Ni/Biomass ratio (w/w)		
			0.12	0.24	0.36
WOx/Biomass ratio (w/w)	0.03	Biomass [g]	0.750	0.750	0.750
		WOx [g]	0.021	0.021	0.021
		Ni [g]	0.090	0.180	0.270
		Solvent [g]	14.25	14.02	13.79
		WOx/Ni ratio (w/w)	0.230	0.120	0.080
	0.06	Biomass [g]	0.728	0.750	0.750
		WOx [g]	0.042	0.042	0.042
		Ni [g]	0.090	0.180	0.270
		Solvent [g]	13.803	14.00	13.77
		WOx/Ni ratio (w/w)	0.470	0.230	0.160
	0.09	Biomass [g]	0.711	0.750	0.750
		WOx [g]	0.063	0.063	0.063
		Ni [g]	0.090	0.180	0.270
		Solvent [g]	13.43	13.98	13.75
		WOx/Ni ratio (w/w)	0.700	0.350	0.230
	0.11	Biomass [g]	0.750	0.750	0.750
		WOx [g]	0.084	0.084	0.084
		Ni [g]	0.090	0.180	0.270
		Solvent [g]	14.19	13.96	13.73
		WOx/Ni ratio (w/w)	0.930	0.470	0.310
	0.14	Biomass [g]	0.750		
		WOx [g]	0.105		
		Ni [g]	0.090		
		Solvent [g]	14.17		
		WOx/Ni ratio (w/w)	1.170		

(Confidential)

II. UV-Vis of lignin and guaiacol at 225 nm and 280 nm

According to Lee et. al. [40], 225 nm and 280 nm are the most representative wavelengths of lignin. To choose the most accurate, we built a calibration curve with guaiacol. Since guaiacol is the smallest phenolic molecule of guaiacyl units and these are the main component of softwood lignin [21], it serves as a suitable model for comparison. Figure 35 shows that at 280 nm, lignin and guaiacol have similar linear equations, closer than 225 nm. Hence, 280 nm was the chosen wavelength to quantify the extracted lignin in our experiments.

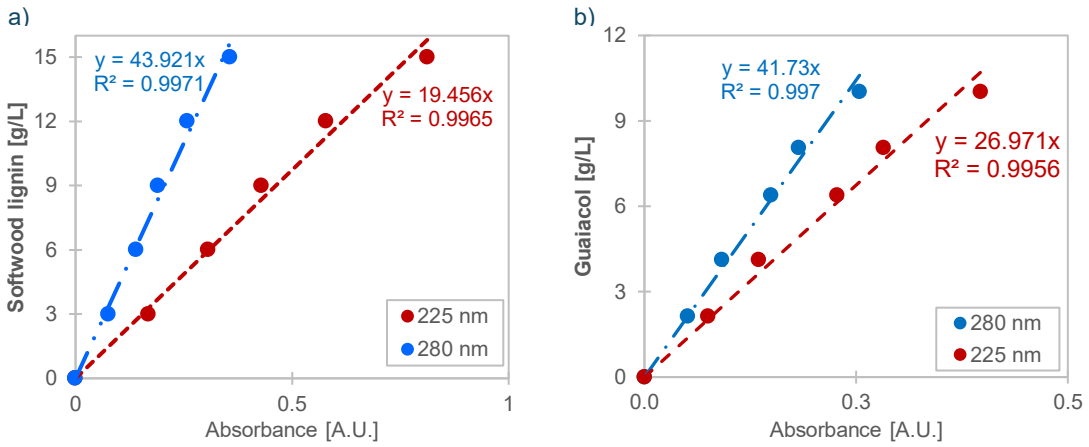


Figure 35. Calibration curves of (a) softwood lignin and (b) guaiacol.

III. Pressure profile at different temperatures

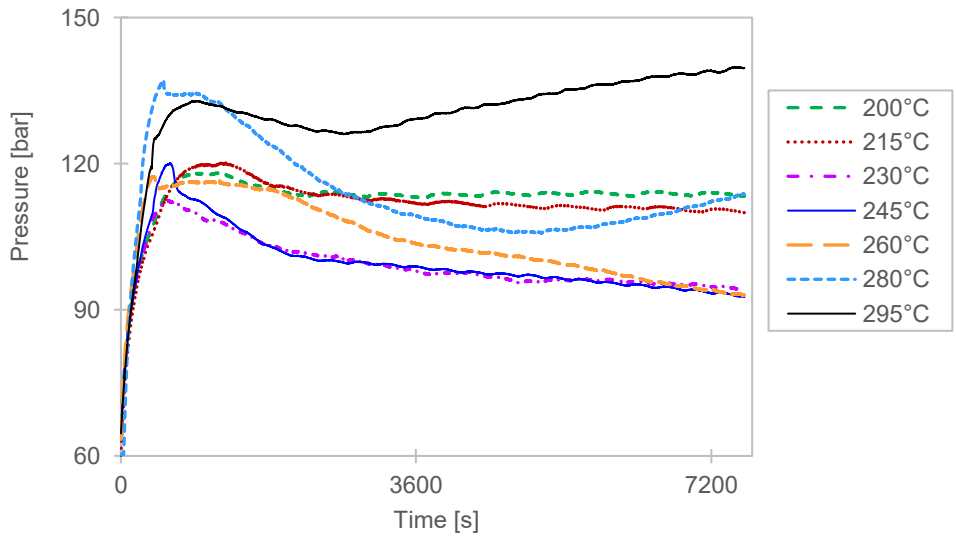


Figure 36. Pressure in the autoclave at different temperatures.

(Confidential)

IV. HPLC calibration curves

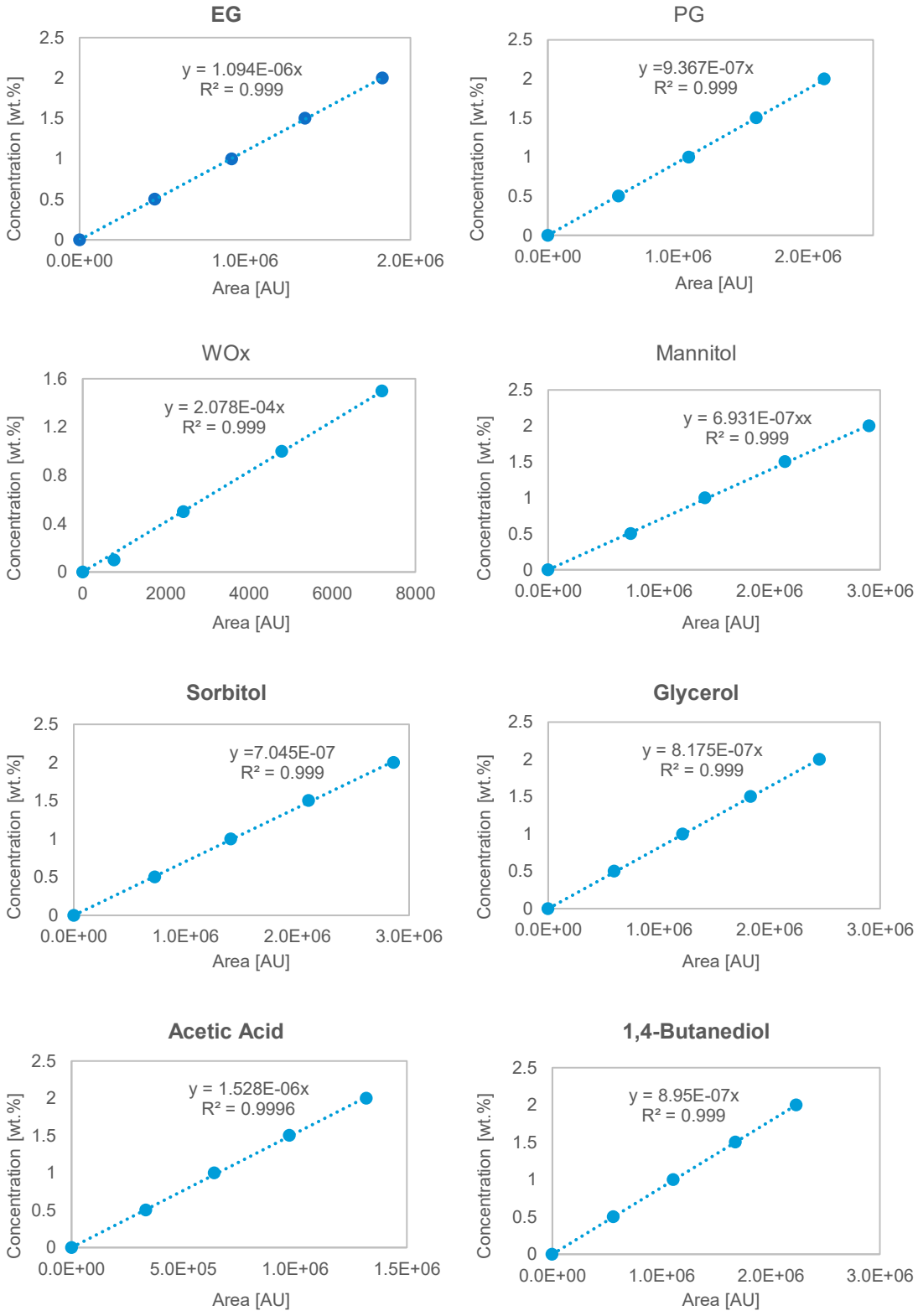


Figure 37. Calibration curves of the quantified compounds through HPLC. These compounds were quantified using the RID, expect WOx, which used the VWD.

(Confidential)

V. GC-MS calibration curves

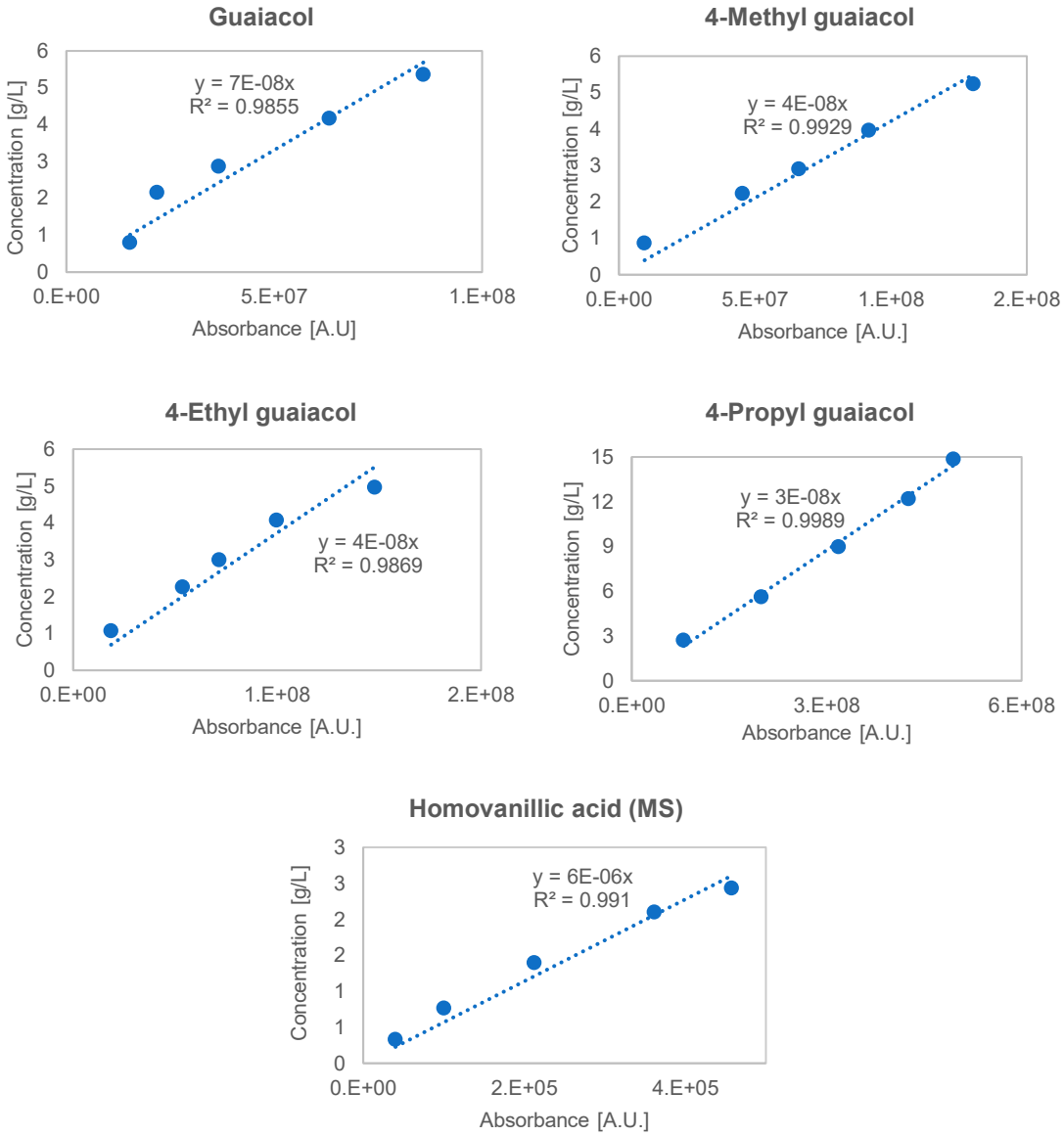


Figure 38. Calibration curves of the followed monomers in the GC-MS. Its absorbance was measured in the GC spectrum, except for homovanillic acid, which was measured in the MS spectrum due to the low visibility in the GC spectrum.

(Confidential)

VI. GPC spectrum

a) Catalyst loading

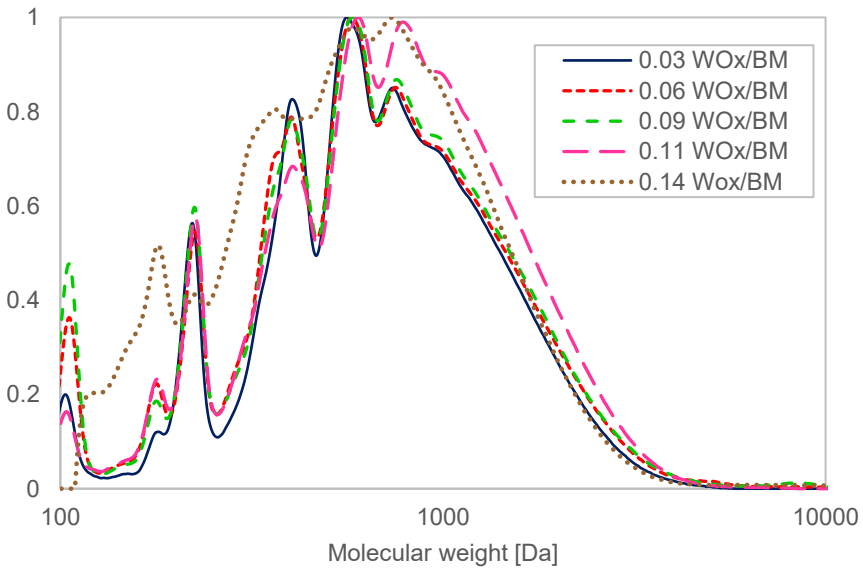


Figure 39. Normalized GPC VWD spectrum of lignin at 0.12 Raney Ni/BM ratio.

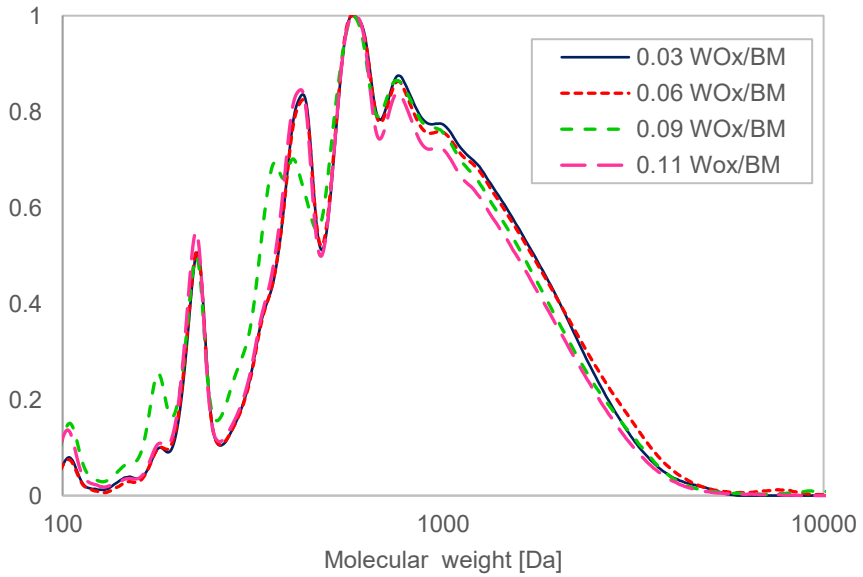


Figure 40. Normalized GPC VWD spectrum of lignin at 0.24 Raney Ni/BM ratio.

(Confidential)

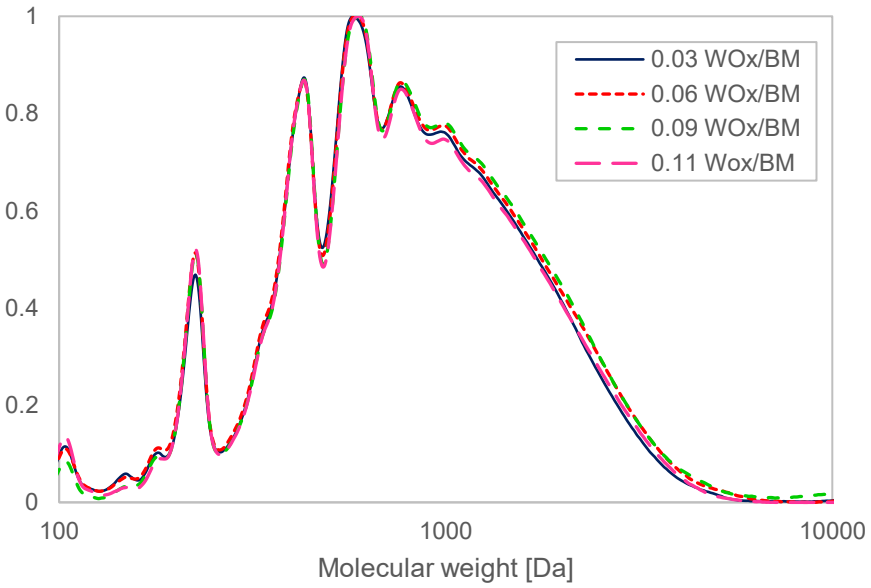


Figure 41. Normalized GPC VWD spectrum of lignin at 0.36 Raney Ni/BM ratio.

b) Biomass feed

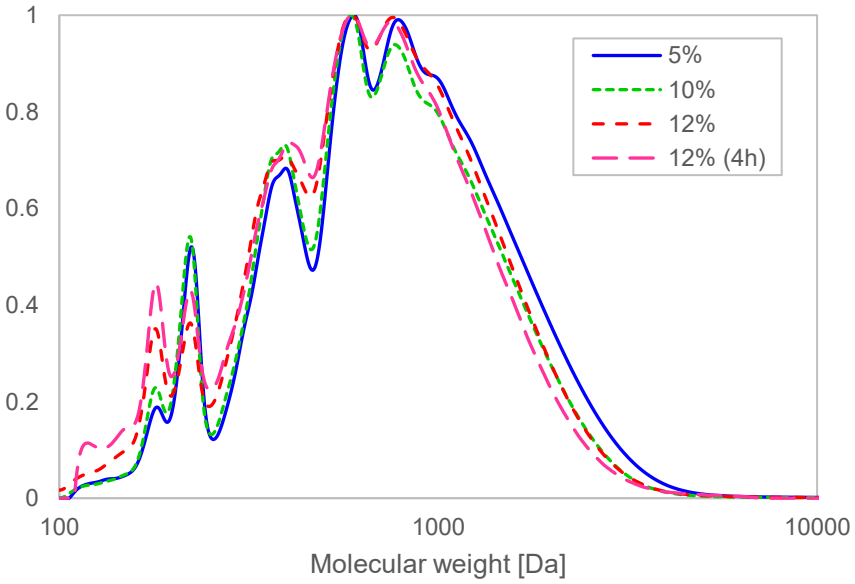


Figure 42. Normalized GPC VWD spectrum of lignin at different biomass feeds.

(Confidential)

c) Temperature

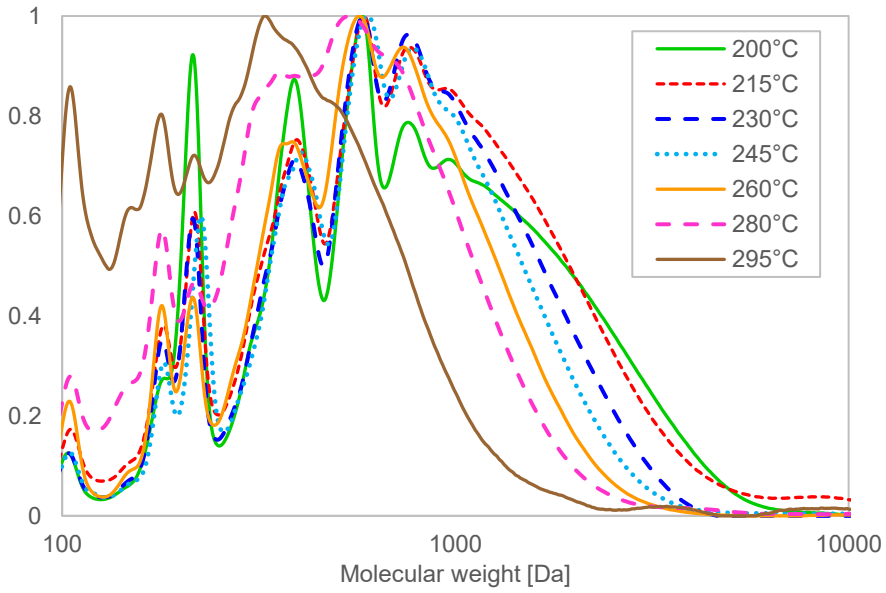


Figure 43. Normalized GPC VWD spectrum of lignin at different temperatures.

- Five-hour reaction

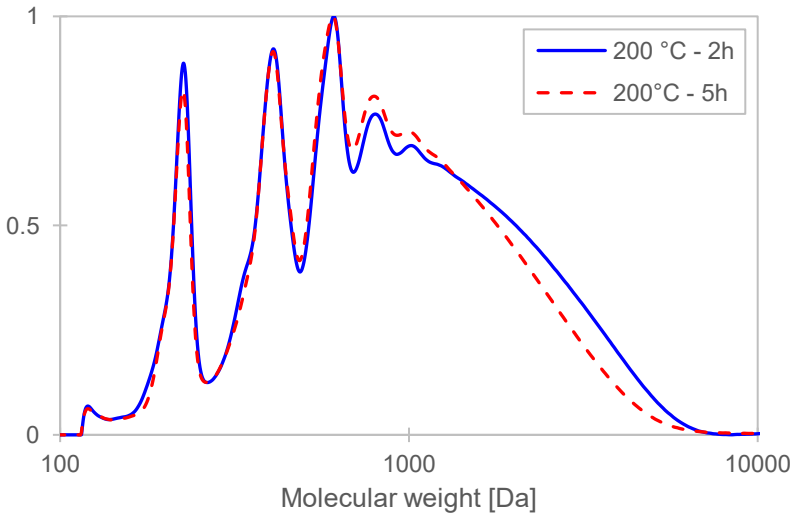


Figure 44. Normalized GPC VWD spectrum of lignin at different reaction times at 200°C.

(Confidential)

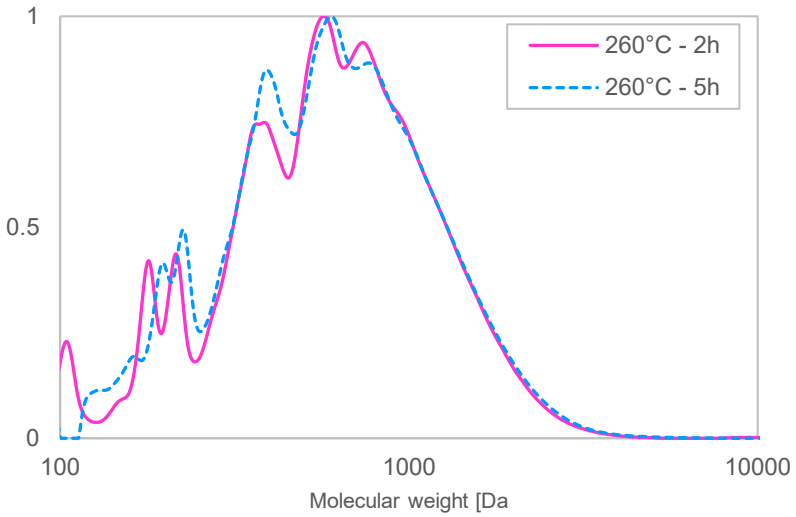


Figure 45. Normalized GPC VWD spectrum of lignin at different reaction times at 260°C.

d) Hydrogen and pressure

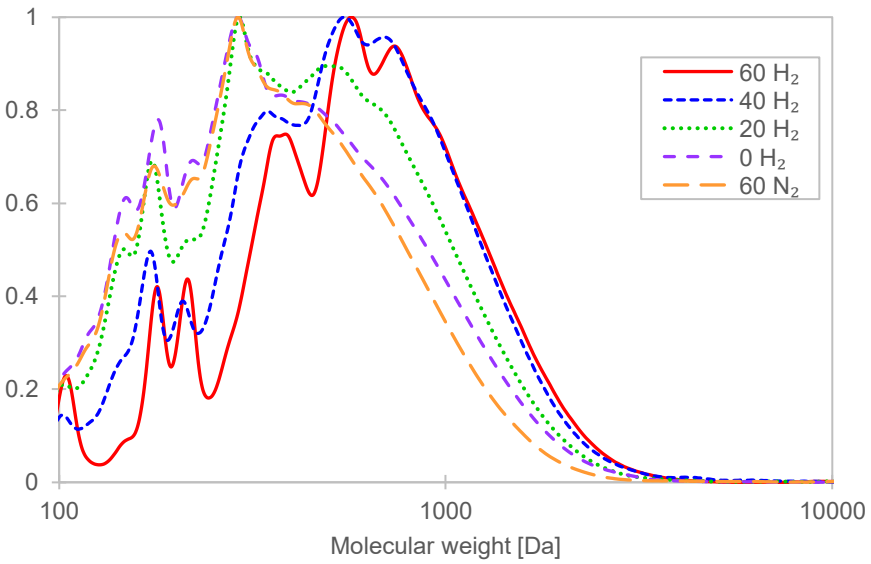


Figure 46. Normalized GPC VWD spectrum of lignin at different pressures.

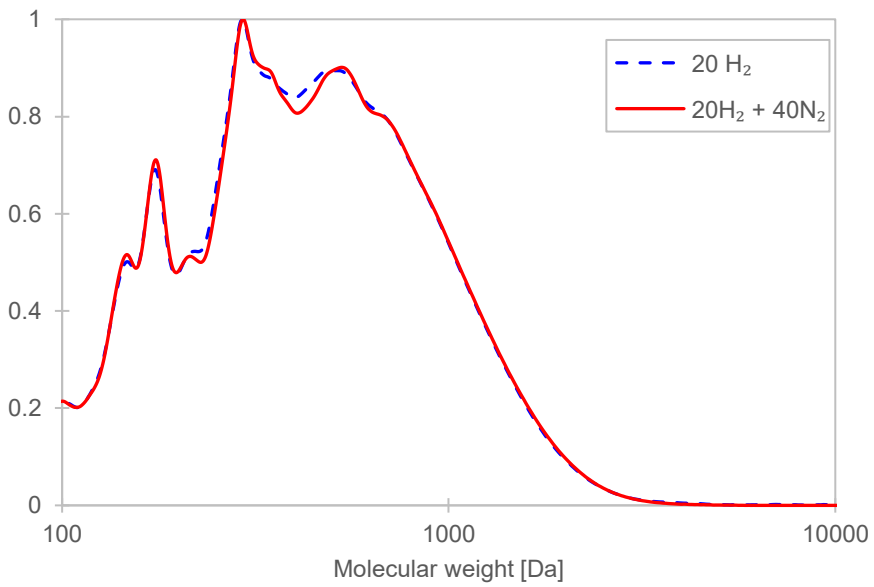


Figure 47. Normalized GPC VWD spectrum of lignin at 20 bar hydrogen (partial and total pressure).

e) pH

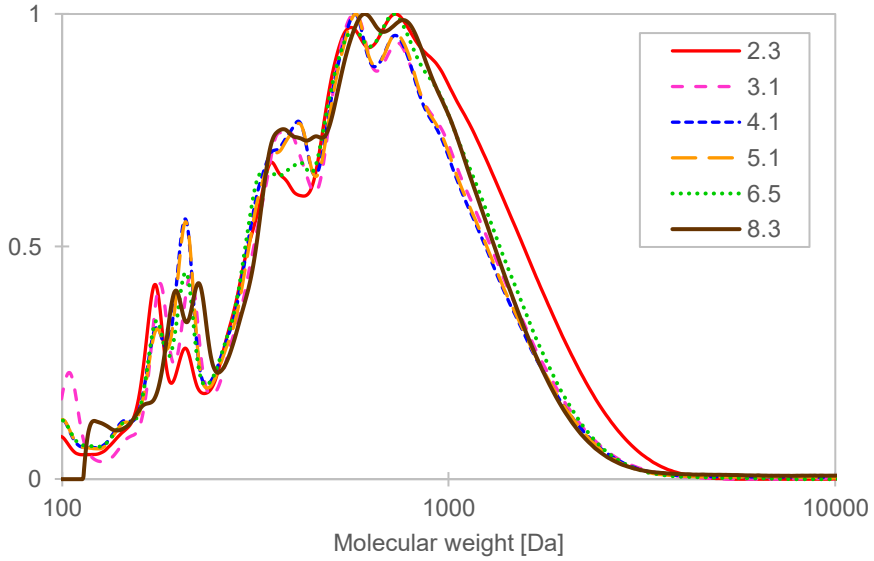


Figure 48. Normalized GPC VWD spectrum of lignin at different pH.

VII. Pressure profile of the five-hour reaction

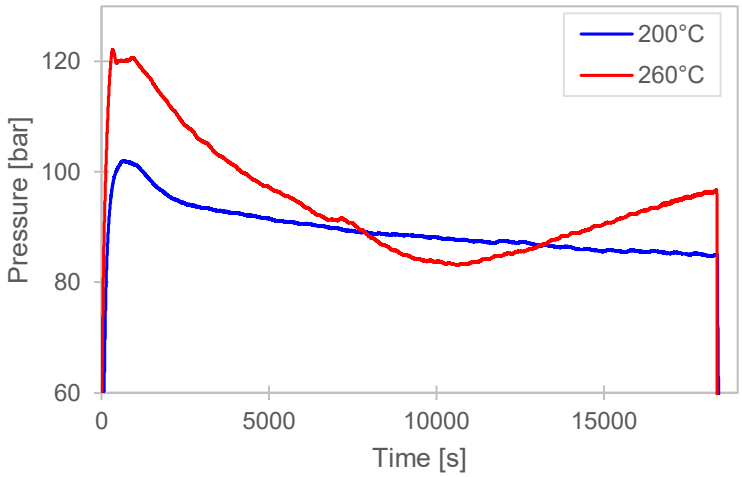


Figure 49. Pressure profile of five-hour reactions at 200°C and 260°C.

VIII. Main hydrogenolysis products of the five-hour reaction

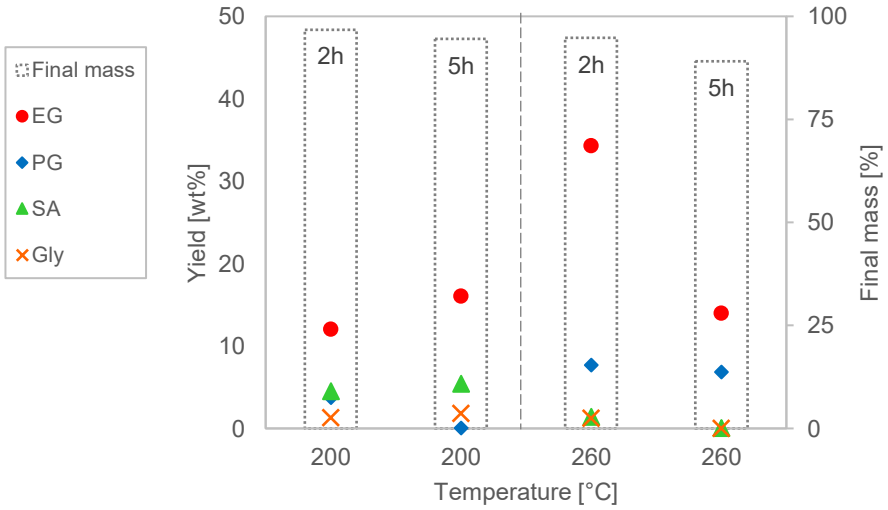


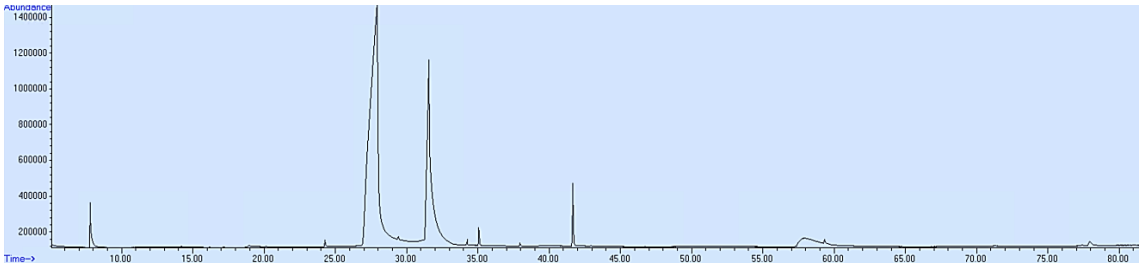
Figure 50. Influence of temperature in the main hydrogenolysis products in a 2- and 5-hour reaction.

(Confidential)

IX. GC-MS spectrum

a) 5 hours reaction

- 200°C



- 260°C

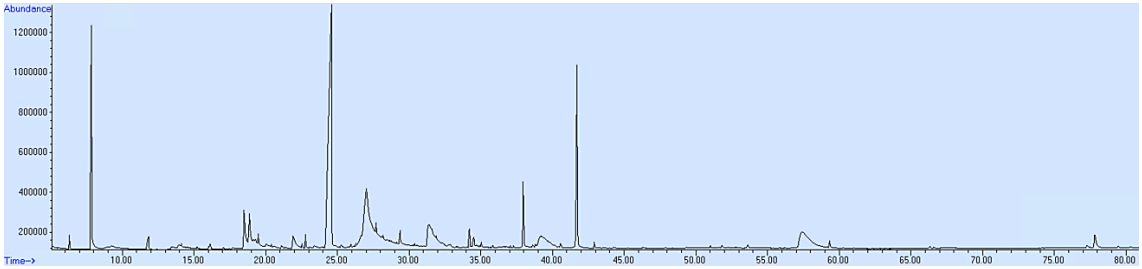
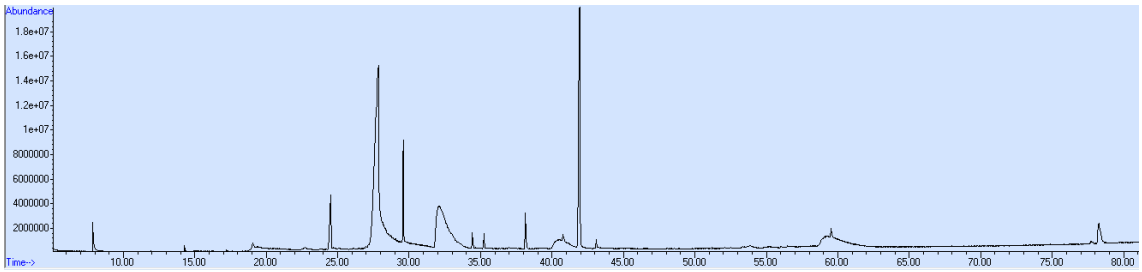


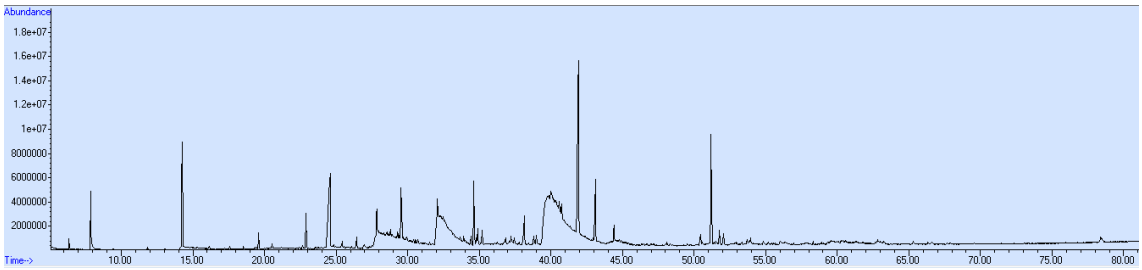
Figure 51. GC-MS spectrum at 200°C and 260°C.

b) Hydrogen pressure influence

- 60 bar H_2



- 0 bar H_2



60 bar N_2

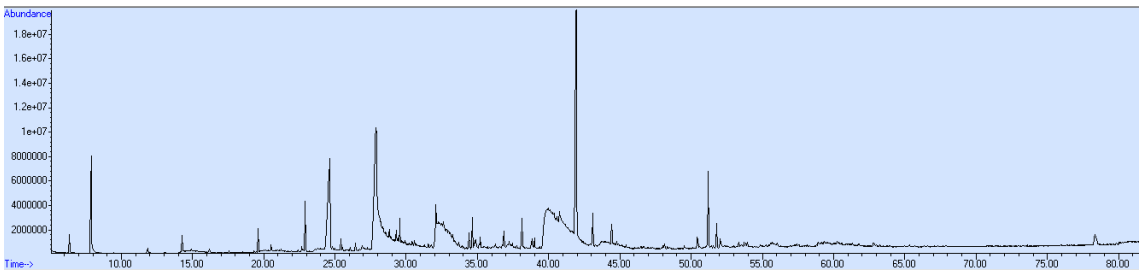


Figure 52. GC-MS spectrum at 60 and 0 bar H_2, and 60 bar N_2.