
Hydrodeoxygenation of lignin

Optimizing phenolic content for adhesive production



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Abstract

Environmental concerns and future shortage have increased the research on alternatives for fossil derived products. Lignocellulosic biomass is the world's most abundant renewable material and is considered as a promising alternative for the renewable production of fuels, chemicals, and energy. The lignin fraction in lignocellulosic biomass is often considered as waste. However, lignin is rich in phenolic fragments and these could serve as valuable precursors for a range of bulk chemicals. Phenol for example, is widely used in commercial applications, such as: wood adhesives and synthetic plastics.

Catalytic hydrodeoxygenation (HDO) is used in this research as a technique to obtain phenolics from lignin. This thesis focuses on the catalytic HDO in a semi-continuous reactor setup. The objective was to develop and construct a semi continuous reactor setup for the optimization of low molecular weight phenolic yields from lignin.

Experiments were conducted with ALCELL[®] Lignin and a Ruthenium on carbon (Ru/C) catalyst at a temperature of 400°C, hydrogen pressure in the range of 80-160 bars, and hydrogen flow in the range of 0-200 ml. min⁻¹. Highest light oil production was obtained with a hydrogen pressure of 130 bars and a hydrogen flow of 200 ml. min⁻¹. The light oil yield was 25 %-wt. However, the used catalyst, Ru/C, was too active at the proposed reaction condition. The chemical composition of the light oil consisted mainly of linear alkanes and aromatics.

The second objective of this thesis was to explore the possible use of HDO lignin oil as phenol replacement in phenol formaldehyde (PF) resins. Based on the composition of the HDO lignin oil, several model components were selected for the formulation of a PF resin. Those PF resins were tested according to the EN-314 standard. The results indicate that all prepared resins pass the standard test value. However, increasing the amount of phenol replacement with model compounds resulted in decreased tensile properties.

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1. An introduction towards the valorization of lignin

1. Introduction

Environmental concerns and future shortage have increased the research on alternatives for fossil derived products. Lignocellulosic biomass is considered as a promising alternative for the renewable production of fuels, chemicals, and energy. Several governments are actively promoting the replacement of fossil fuels by renewable resources. In the Netherlands, the Dutch ministry of Economic Affairs set goals to derive 30% of transportation fuels from biomass and to have 20-45% of fossil-based raw materials substituted by biomass by 2040 [1]. The platform Groene Grondstoffen improved this vision and aims to substitute 30% fossil fuels with natural resources in 2030 [2].

This thesis will give an introduction to bio-refining and suitable ways to obtain valuable chemicals from biomass. The focus of this thesis will be on the conversion of lignin toward low molecular weight phenolics and the use of those phenolics as a wood adhesive.

2. The use of lignocellulosic biomass

2.1 Lignocellulosic biomass

Lignocellulosic biomass is the world's most abundant renewable material and is mainly composed out of cellulose (38-50%), hemicellulose (23-33%) and lignin (15-25%) [3].

Both the polysaccharides cellulose and hemicellulose, provides strength to the cell walls while the lignin acts like a resin which holds the carbohydrate matrix together. A schematic representation of lignocellulosic biomass is presented in Figure 1.

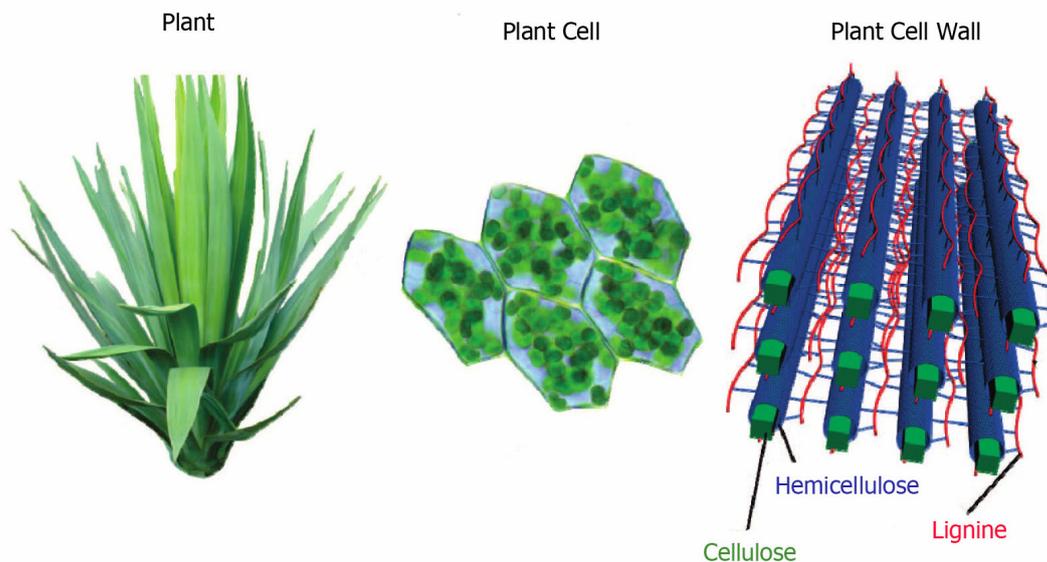


Figure 1. Schematic representation of lignocellulosic biomass [6]

Lignocellulosic biomass has played an important role as raw material for a wide range of application in the human history and continues to do so in many poor countries (for example in applications such as construction and fuel). New methods of retrieving energy and chemicals from liquefied cellulosic biomass were discovered in the past centuries. Until now, fossil fuels have been the most commonly used raw materials for transportation fuels, chemicals, and energy production.

The future shortage and environmental concerns of fossil fuels resulted into a new interest in using biomass as raw material for the production of transportation fuels, chemicals and energy. Two third of the renewable energy production in Europe is already obtained from biomass, which is higher than the total energy obtained from all other renewable resources: hydropower, wind power, geothermal energy, and solar power [4].

The main advantages of the use of biomass are that it is readily available with fast replenish times, at low costs, and the natural uptake of carbon dioxide in the growing process. Especially the uptake of carbon dioxide fits the vision of the Dutch ministry of Economic Affairs. A closed carbon dioxide cycle with a short cycle line would decrease the alarming concerns about the greenhouse effect. A schematic representation of the carbon dioxide cycle for fossil resources and biomass for transportation fuels is presented in Figure 2.

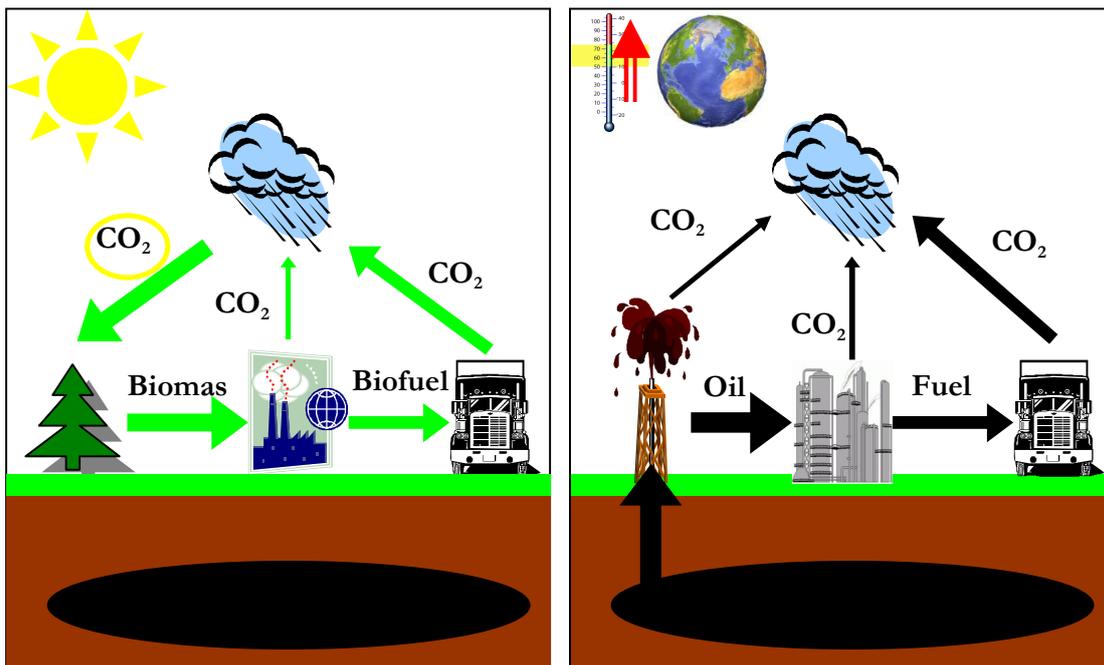


Figure 2. Carbon dioxide cycle for the use of biomass (L); and fossil resources (R)

The main disadvantages of the use of biomass are the solid form and the chemically stable structure. Therefore the conversion of biomass into liquid intermediates is the subject of intensive research. Pyrolysis is a typical process to convert biomass into a liquid intermediate. This process involves relative high temperatures (450°C) and a short gas residence time, typically 2 seconds, and the biomass is converted to a brown liquid product. However, the aim of the pyrolysis process is to optimize the liquid yield instead of the production of specific compounds [5].

The possibilities for the use of biomass are enormous. For instance European may produce 190 million tons of oil equivalents of biomass by 2010 with possible increases up to 300 million tons of oil equivalent of biomass by 2030 [6]. If it is possible to upgrade such oil, it could be a major resource for the refinery of chemicals.

In line with a petroleum refinery, a bio-refinery should be able to produce fuel, power and bulk chemicals. There are already processes discussed in literature to produce ethanol from cellulose and hemicellulose [7], and vanillin from wood lignin [8]. There are also several reviews discussing the possible use of lignin for the production of transportation fuels [9-12]. For that reason it would be more beneficial to fractionate lignocellulosic biomass into the main components and process the individual components towards more valuable products.

Phenol for example, is widely used in commercial applications, such as: wood adhesives and plastic. The phenolic structure is widely represented in the aromatic structure of lignin and it would be more attractive to degrade lignin towards such a valuable product. The next chapter will discuss the nature and possibly use of lignin.

2.2 Lignin structure and applications

Lignin is a large, cross-linked amorphous polymer consisting of three main fragments: coumaryl-, coniferyl-, and sinapyl alcohol (Figure 3). It is relatively hydrophobic and contains large amount of aromatics.

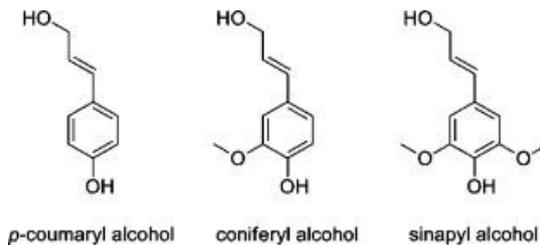


Figure 3. The three lignin monomers

The complex structure of lignin is a result of the randomly linked fragments, which differs by plant source. For example, the composition, molecular weight, and amount of lignin decrease in the order of: softwoods > hardwoods > grasses [6]. A schematic representation of the lignin structure of softwood is given in Figure 4.

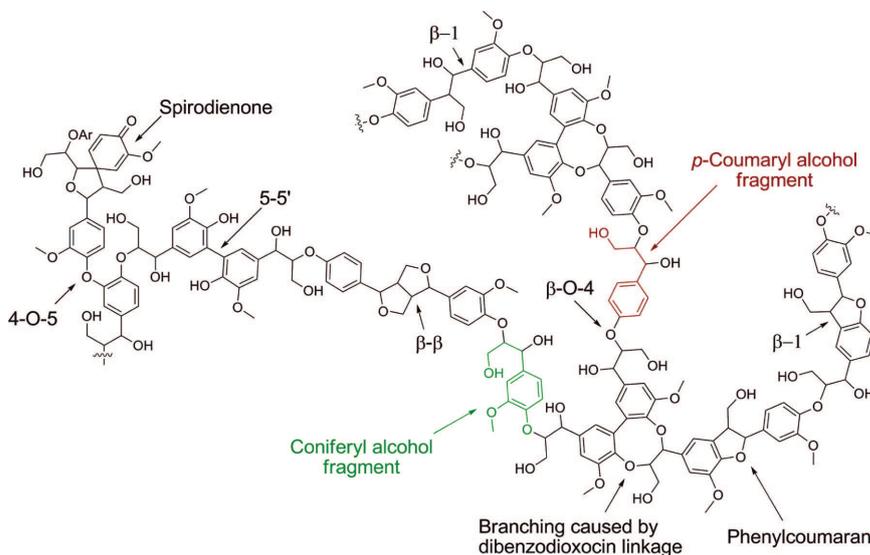


Figure 4. Schematic representation of softwood lignin structure [6]

Lignocellulosic biomass is widely used for several industrial applications. For example, polysaccharides are used in the pulp and paper industry. However, lignin is often considered as waste and mainly used for combustion. The pulp and paper industry produces 40-50 million of tons of lignin annually but only 2% is used for commercial applications, such as dispersing or binding agent. The main disadvantage of lignin is the stability and it is therefore difficult to depolymerize. The next chapter will discuss several techniques to fractionate lignin from biomass.

2.3 Lignin separation

Several techniques exist to separate lignin from the lignocellulosic biomass. In earlier work of Dale et al. [6] several pretreatment processes were discussed and divided into four categories: physical pretreatment, solvent fractionation, chemical pretreatment and biological treatment. The type of pretreatment has a great influence on the chemical structure and properties of the obtained lignin.

The pretreatment of lignin may lead to degradation into smaller components, and sometime causes other chemical modifications. A summary of different pretreatment methods and the influence on the chemical structure is presented in Table 1.

Table 1. Monomer molecular formulas and weights of lignin from various sources [6]

Type	Monomer Molecular Formula	Average molecular weight	Monomer molecular weight
Kraft lignin	$C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$	2000 – 3000	180
Technical kraft lignin	$C_9H_{7.98}O_{2.28}S_{0.08}(OCH_3)_{0.77}$		177
Unreacted kraft lignin	$C_9H_{8.97}O_{2.65}S_{0.08}(OCH_3)_{0.89}$		190
Lignosulfonate lignin (softwood)	$C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$	20000 – 50000	215-254
Lignosulfonate lignin (hardwood)	$C_9H_{7.5}O_{2.5}(OCH_3)_{0.39}(SO_3H)_{0.6}$		188
Organosolv lignin	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$	<1000	Unknown
Pyrolysis lignin	$C_8H_{6.3-7.3}O_{0.6-1.4}(OCH_3)_{0.3-0.8}(OH)_{1-1.2}$	unkown	Unknown

2.3.1 Kraft lignin process

The kraft lignin process is the dominating pulping technique for commercial applications. Kraft lignin is commercially produced from the black liquid waste stream in the paper industry. The black liquor is an aqueous solution of lignin residues, hemicellulose, and the chemicals used in the process. Lignin is degraded stepwise at high pHs (± 10) consuming considerable amounts of aqueous sodium hydroxide and sodium sulfide at temperatures in range of 150-180°C for about 2 hours. In addition, the kraft process is highly energy consuming, which makes it less likely to be the primary source for bio-refining chemicals.

2.3.2 Lignosulfonate process

The black liquid waste stream in the paper industry may also be treated using the lignosulfonate process. The process is conducted in a pH range between 2 and 12 using magnesium sulfate or calcium sulfate. The obtained lignosulfonates have a slightly increased molecular weight, which is a result of the addition of sulfonate groups. The additional sulfonate groups are not desirable for the future processing of lignin toward more valuable chemicals.

2.3.3 Organosolv process

Organosolv lignin is obtained by the treatment of wood or bagasse with various (mixtures of) organic solvents. Bagasse is the fibrous residue that remains after plant material is crushed to extract juice or sap. ALCELL[®] Technologies Inc., a subsidiary of REPAP Enterprise, developed a process to produce lignin from a hardwood mixture of 15% poplar (*Populus tremuloides*), 50% maple (*Acer rubrum*) and 35% birch (*Betula Papyrifera*). The product, a brown powder with one of the lowest molecular weight lignin ($M_w = 2100 \text{ g. mol}^{-1}$) reported in literature, was obtained by 18 wt-% yield on dry wood intake.

The advantage of the organosolv process is that it produces separate streams of cellulose, hemicellulose and lignin, and the process is considered environmentally friendly. A disadvantage is the high cost of solvent recovery.

2.3.4 Pyrolysis as a pretreatment step

Pyrolysis of biomass is widely reported in literature for the production of bio-oils. However, the harsh reaction condition used for the pyrolysis process leads to the degradation of biomass to lower molecular weight components. The pyrolysis process typically involves relatively high temperatures (450°C), and short gas residence times, typically 2 seconds [6]

The pyrolysis of lignin is also widely discussed in literature. It has been suggested that pyrolysis lignin has structural characteristics different from the other pretreatment processes. Pyrolytic lignin contains C₈- rather than C₉-derived lignin monomers, which opens a unique opportunity to make specific aromatic hydrocarbons not available by means of the other treatments [13,14].

3. Lignin degradation

Considerable effort has been placed to convert lignin into low molecular weight phenolics. One of the main problems is the high stability of the polymer structure of lignin, which requires harsh conditions to break. Phenol could be a typical degradation product from lignin. Phenol is commercially used in a large range of applications (synthetic polymers, phenol formaldehyde adhesives, etc). Figure 5 gives a schematic representation of possible degradation pathways of the lignin fragments towards phenolics.

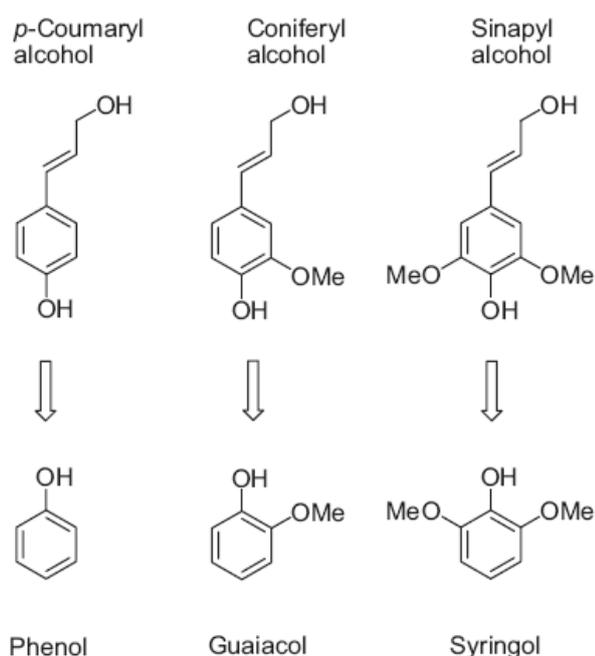


Figure 5. Proposed degradation pathways of the lignin monomers toward phenolics [5]

The van Krevelen plot is a useful tool to show the required change in elemental composition to obtain phenolics from lignin. The van Krevelen plot in Figure 6 represents the elemental composition of commonly used components in the petroleum industry.

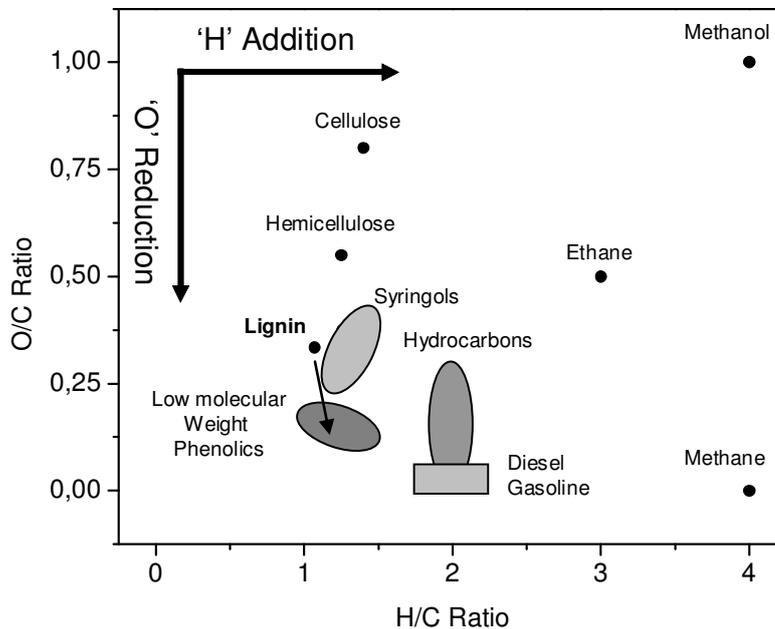


Figure 6. Van Krevelen plot for commonly used components in the bio- and petroleum industry

According to the van Krevelen plot, lignin needs to be deoxygenated and slightly hydrogenated to obtain phenolics. This can be accomplished by breaking down of the polymer structure to lignin monomers. The lignin fragments can then be selectively degraded towards phenolics. Catalytic hydrodeoxygenation (HDO) is a promising technique to lower the oxygen content and to break down the lignin polymer.

3.1 Catalytic hydrodeoxygenation

Catalytic hydrotreatment is used on large scale in the petroleum industry for the removal of sulfur (HDS) and nitrogen (HDN) compounds from fuels. In contrast with HDS and HDN, hydrodeoxygenation (HDO) has attracted considerable attention to upgrade pyrolysis oil towards transportation fuels. The major disadvantages of bio-oils are their high oxygen content, high viscosity and instability for storage. The HDO of pyrolysis oil was used to lower the oxygen content and further degrade components to obtain a fuel with high energy content. Typically harsh conditions are mentioned, like temperatures in a range of 200-400°C and hydrogen pressure in a range of 50-200 bars [9]. The HDO of bio-oil is considered as useful parallel to the HDO of lignin.

Catalyst selection for the HDO experiments is of utmost importance. HDO experiments for lignin, with the conventional CoMo and NiMo catalyst, have already been reported in the literature [6]. Some disadvantages are the addition of sulfides, rapid deactivation by coke formation, and possible poisoning by water. The selected catalyst needs to be resistant against water and highly selective towards oxygen removal. Promising results for ALCELL[®] Lignin were obtained by batch scale HDO experiments with a ruthenium on carbon catalyst.

3.1.1 Typical reaction pathways

The overall hydrogenation reaction of a typical ALCELL[®] lignin towards phenol may be generalized by:



The hydrotreatment of lignin involves a complex reaction mechanism. A summary of typical hydrogenation reactions are listed below:

- Hydrodeoxygenation reaction: the break up of C-O bonds with the formation of water
- Hydrogenation reaction: the saturation of C=C double bonds and the addition of hydrogen to carbonyl groups to form alcohols.
- Decarboxylation reaction: the removal of oxygen in the form of carbon dioxide
- Hydrocracking reaction: the break down of components toward lower molecular weight components.

Lignin needs to be deoxygenated and slightly hydrogenated according to Figure 6 to optimize the low molecular weight phenolic content.

3.2 History of hydrotreatment of lignin

The hydrogenation of lignin is a widely discussed topic in literature. Harris and co-workers reported the hydrogenation of lignin mediated by a copper chromium oxide catalyst in 1938. The harsh condition used resulted in a full degradation of the aromatic structure and products consisted mainly out of cyclohexanol and methanol (with liquid yield of 70 %-wt based on lignin intake) [6]. Pepper et al studied the hydrogenation of lignin with several types of catalyst, including: Raney Ni, Pd/C, Rh/C, Rh/Al₂O₃, Ru/C, Ru/Al₂O₃. Lignin was converted to yield monomeric products (with a liquid yield of 52 %-wt based on lignin intake): 4-propylguaiacol and dihydroconiferyl alcohol.

The Noguchi process, which was patented by Crown Zellerbach in the early 1960's, was probably the first process with commercial intention. The hydrogenation experiments were conducted at high temperature (250-450 °C) and pressures (152-456 bars). The lignin was solved in a mixture of lignin tars and phenols and the reaction was mediated by a Iron(II)sulfide catalyst. The Noguchi process claimed a lignin conversion into monomeric phenolics with a yield of 40 %-wt. The high yield of monomeric phenolics were caused by alkylation of the phenolic solvent during the process, but nevertheless a phenolic yield of 21 %-wt was obtained [6, 15].

A modification of the Noguchi process was claimed by Urban et al. in 1988. A substantially increase of monomeric phenolic yield was obtained with the addition of methanol. The catalyst consists of ferrous sulfide with smaller amounts of other metal sulfides as promoters. Cresols yields of 45% and monophenols yields of 65% were obtained from alkali lignin from the kraft process [6]

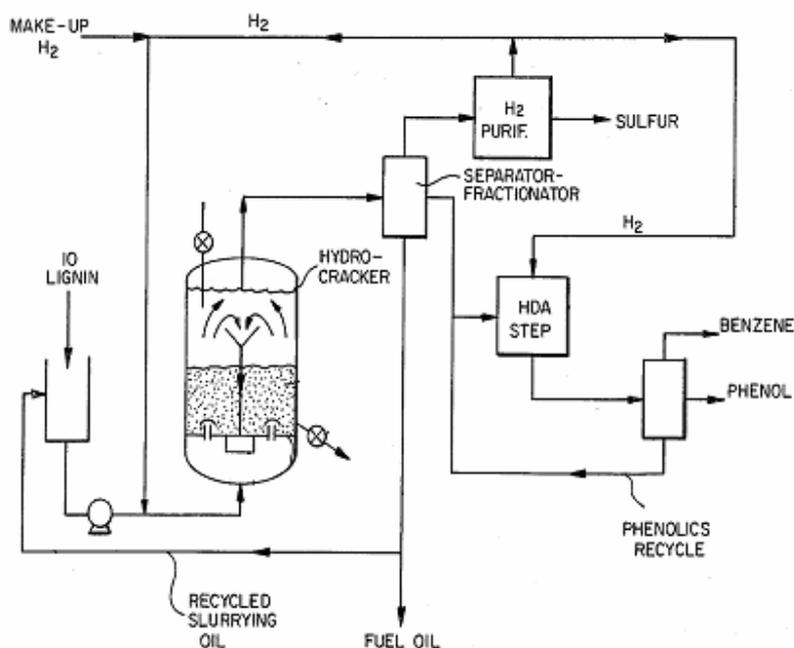


Figure 7. Schematic representation of the lignol process [16]

Probably the most discussed process in literature is the HRI® Lignol process (Figure 7), which was patented in 1983 [16, 17]. HRI successfully developed a process to degrade lignin to yield mono-phenolics. The process was based on a boiled catalytic bed consisting of lignin, recycled product and catalyst. The optimal conditions were a bed at 440°C in presence of an iron on alumina catalyst at a hydrogen pressure of 69 bar. The yield of mono-phenols was 37,5 wt-% based on the lignin intake, which was higher than obtained with the Noguchi process. However, the HRI results have not been confirmed in literature [5].

A summary of reported hydrogenation experiments is given in the work of Zakzeski et al. and is summarized in Table 2. For the full report of hydrogenation experiments on lignin the reader is directed towards the work of Zakzeski et al. [6].

Table 2. Hydrogenation experiments of lignin with heterogeneous catalyst [6]

Author/ Year	Catalyst	Support	Reaction conditions			Feed	Major products	Oil yield (%)
			T(°C)	P(bar)	t(min)			
Haris 1938	Cu-CrO	None	260	220	1080	Lignin	Methanol 4-n-propylcyclohexanol, 4-n-propylcyclohexanediol, glycol	70
Brewer 1948	Cu-CrO	None	250	200	300	Hydrol Lignin	3-cyclohexyl-1-propanol 4-n-propylcyclohexanol 3-(4-hydroxycyclohexyl)-1-propanol	12
Kashima 1964	FeS	None	250- 450	152-456	60-120	Lignin	Phenols, Bezenes	unk
Urban 1988	FeS	None	375- 425	50-150	60	Kraft Lignin	Monophenols C6-C9	Unk
Ratcliff 1988	Co-Mo	Al ₂ O ₃	400- 450	70	5-60	Organosolv Lignin	Insoluble residue	Unk
	Co-Mo	Al ₂ O ₃	340- 450	70	60	Organosolv Lignin	Insoluble residue, Phenols	unk
Shabtai 1999	Mo	Al ₂ O ₃	340- 450	34-170	Unk	Depolymerized lignin	Phenol, cresol, alkylphenols, Alkylbenzenes	Unk
	Co-Mo	Al ₂ O ₃	350- 375	100-150	Unk	Depolymerized lignin	Toluene, ethylbenzene, xylenes, Trimethylbenzenes, alkylbenzenes	Unk
Shabtai 1987	Mb-Mo	Al ₂ O ₃	200- 300	35-138	5-15	Depolymerized lignin	Phenols	Unk
Meier 1994	Ni-Mo	Al ₂ O ₃	375- 400	100-180	Unk	Organocell lignin	phenol, cresols, alkylphenols, xylenols, guaiacol	unk
		Zeolite A	375	100	Unk	Organocell lignin	Cresols, alkylphenols, xylenols, Guaiacol	Unk
Meier 1992	Pd	Activated charcoal	380	100	15	Organocell lignin	Oils	15
	Fe ₂ O ₃	None	380	100	15	Organocell lignin	Oils	17
	Raney Ni	None	380	100	15	Organocell lignin	Oils	53
	Ni-Mo	SiO ₂ - Al ₂ O ₃	380	100	15	Organocell lignin	Oils	53
	Ni-Mo	Zeolite	380	100	15	Organocell lignin	Oils	17
Oasmaa 1993	Ni-Mo	SiO ₂ - Al ₂ O ₃ Or Zeolite	400	100	40	Organocell lignin	Oils	49-71
Engel 1987	Ni-W	SiO ₂ -Al ₂ O ₃	300- 450	35-240	Unk	Lignin	Phenolics	Unk
		SiO ₂ -Al ₂ O ₃ -PO ₄						
Yan 2008	Pt	Carbon	500	40	240	Lignin	Monomers, dimmers	42
Oasmaa 1993	Mo	None	400	70-100	65	Lignin	Oils	Unk

4. Bio-based wood adhesives

Wood adhesives from renewable resources, also known as bio-based adhesives, gained a lot of interest in the past century. Nowadays, the general raw material for adhesion is obtained from the petroleum industry [19].

A lot of different types of thermosetting and thermoplastic resins are used for wood adhesives. Two types are dominating the field of wood adhesives: Amino-plastic and phenol-formaldehyde (PF) adhesives. The PF resin is preferred for exterior use, due to water, weather, and high temperature resistance.

The condensation reaction of phenol with formaldehyde was indicated by Beakeland in the early 19th century. This condensation reaction led to the first commercial produced synthetic polymer ever developed (Bakelite) and eventual led to the PF resins used for wood adhesion.

Condensation resins based on formaldehyde are the largest volume within the wood adhesive field nowadays. They are prepared by the reaction of formaldehyde with various chemicals like urea, melamine, phenol or resorcinol [18].

The chemistry of the condensation reaction of phenol with formaldehyde is well described in literature; however the real chemistry is still not fully understood. This is a result of the complex reaction mechanism, were formaldehyde can react with phenol on the para and ortho position. The several types of PF adhesives currently produced for commercial purpose are therefore completely depended on the formulator [18].

4.1 Phenol formaldehyde chemistry

The raw materials for the current commercially used PF resins are based on fossil derived components. Phenol is derived from petroleum based benzene and propylene and formaldehyde is the principle end market of methanol [19]. Different manufacturing routes lead to two types of PF resins: Resol and Novolak. The initial reaction of phenol with formaldehyde is similar for both types of PF resin. Formaldehyde reacts with phenol to form either o-methylolphenol or p-methylolphenol. A schematic representation of condensation reaction is given in Figure 8.

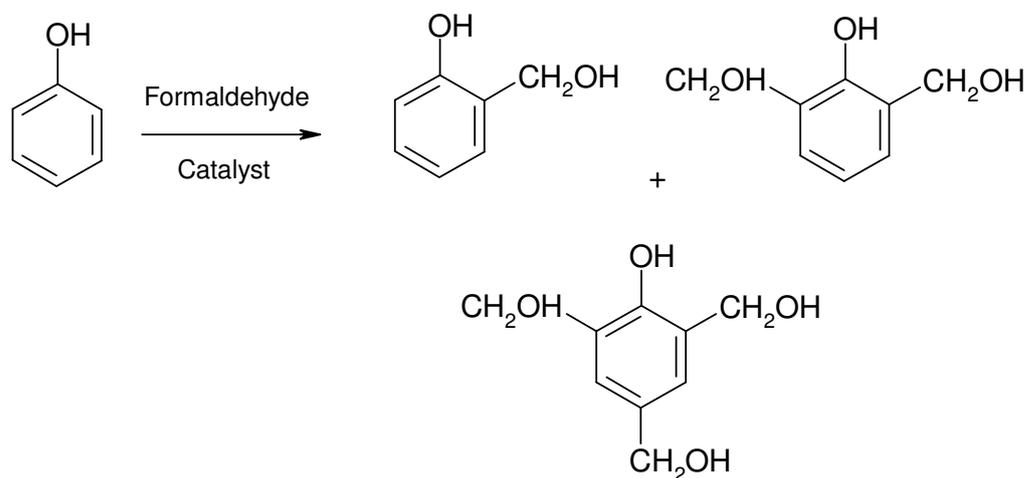


Figure 8. Initial reaction of phenol with formaldehyde

The ratio of either o- or p- methylolphenol is depended on pH, catalyst and the polarity of the solvent [19].

4.1.1 Resols

Resols are obtained in the presence of an alkaline catalyst and an excess of formaldehyde. The formed resin does not require a cross-linking agent to cure (one stage resins). Typical resols are formed with one mole of phenol to 1.3-2.3 moles of formaldehyde and sodium hydroxide as catalyst at a temperature between 70-100°C. The schematic condensation reaction is represented in Figure 9.

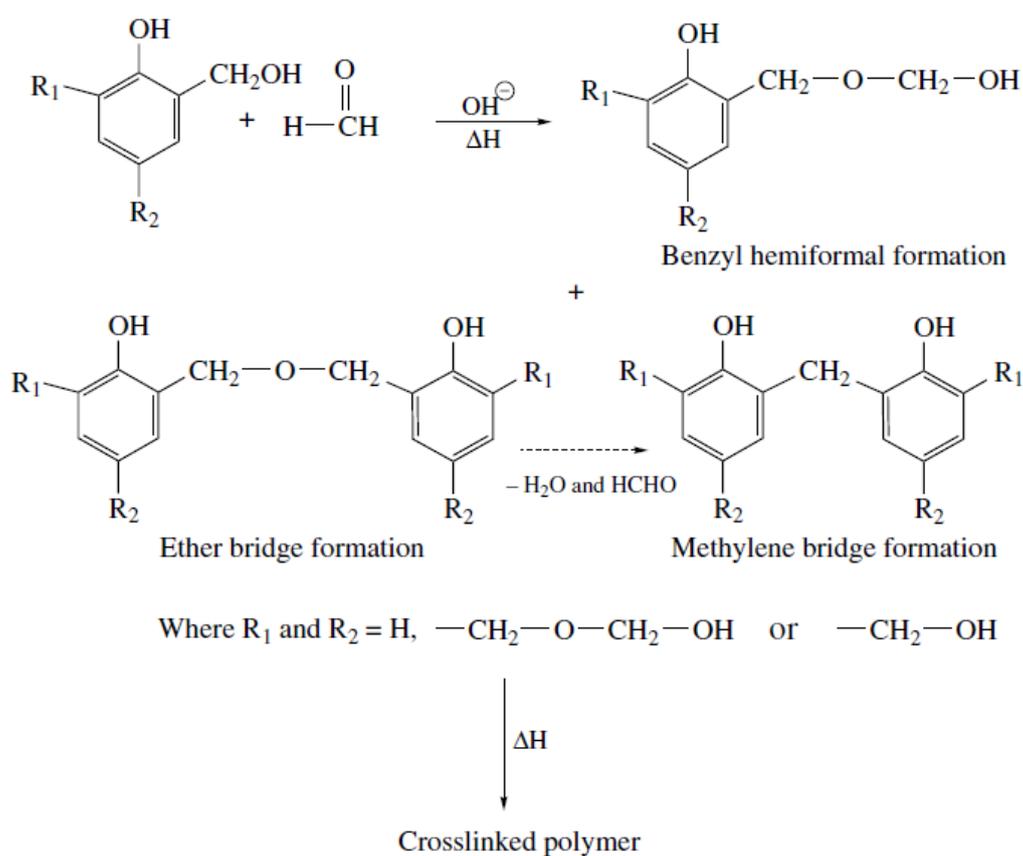


Figure 9. Reaction mechanism of the formation of resols

The curing mechanism is based on the ether bonds in the resin. The ether bonds will react further toward methylene linkages and cause a rapid gelation of the resin. Cooling helps to prevent this reaction. The final result is a liquid resin of mono- and polymethylolphenols.

The resin is cured by heating, which activates the further reaction of the ether groups. The cured resin becomes infusible and insoluble in water.

4.1.2 Novolak

Novolaks are obtained with an acid catalyst and an excess of phenol. The formed resin requires a crosslinking agent to cure (two stage resins). Typical novolak resins are formed in acidic conditions at 100°C with one mole of phenol to 0.7-0.85 mole of formaldehyde. The methylolphenols condense rapidly to linear methylene-linked polymers. A schematic representation is given in Figure 10

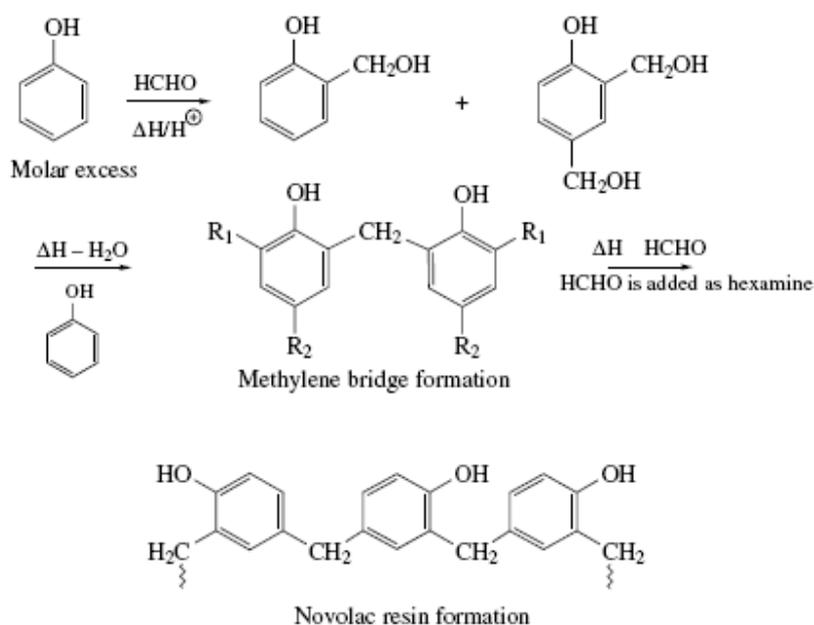


Figure 10. Reaction mechanism of the formation of novolak

The novolak resin is dehydrated at the end of the reaction and the result is a powder which still can be melted for further processing. The major difference with a resol resin is the absence of the methylene ether linkages, which is essential to cure the resol resin.

To achieve a cured resin, further formaldehyde needs to be added. Suitable components are hexamethylene tetramine and paraformaldehyde, which both break down to formaldehyde up on heating. The formed formaldehyde cross-links and cures the resin.

4.2 The use of lignin in bio-based wood adhesives

The use of lignin in wood adhesive is intensively reported in literature. The phenolic structure of lignin looks as a perfect material for wood adhesion. However, the reactivity towards formaldehyde, or other aldehydes, is much lower compared to phenol.

The low reactivity of lignin towards formaldehyde causes that any percentage of lignin added in a PF resin results in a longer press time. The cost advantage of using lignin is lost in the longer press time. One of the only industrial applications based on lignin resin is based on the pre-reaction of lignin with formaldehyde in a reactor. The methylolated lignin is then reacted with phenol at a percentage of 20-30%-wt [20].

A lot of other possible methods to use lignin are reported in literature. A lot of those reports are based on the simple substitution of lignin in a PF resin. However, this method is an old technology which never resulted in industrial use. These reports do not seem to be aware of the slow press rate, which results from the addition of lignin into a PF resin. This can be summarized with a quote from Antonio Pizzi: *“they lead new researchers in the field to believe they are doing something worthwhile with parameters that do not satisfy the requirements of press rate of the panels in manufacturing”* [20].

The degradation of lignin towards lower molecular weight components would be another way to use lignin in bio-based wood adhesive. This thesis will mainly focus to optimize a phenolic oil yield from hydrogenated lignin for the production of a PF resin.

5. Objectives and goals

Earlier exploratory batch scale hydrogenation experiments by A. Kloekhorst showed promising results for the conversion of lignin towards low molecular weight phenolics. The formed phenolics could be used for wood adhesives. To explore the field of wood adhesive a large amount of product is required. A continuous reactor setup would increase the production of lignin oil. The goal of this thesis will be the design, construction and optimization of a (semi-) continuous reactor setup for the HDO of lignin.

The second goal is an exploratory research on the possible substitution of phenol obtained from the HDO of lignin in commercially used phenol formaldehyde resins. This involves the formulation of model resins substituted with typical components formed in the HDO of lignin process.

6. Approach

This thesis was divided in a number of specific tasks:

Semi continuous hydrodeoxygenation of lignin

- Design of a (semi-) continuous reactor setup based on literature
- Constructing the semi continuous reactor setup
- Testing the continuous setup
- Optimizing the continuous setup to obtain low molecular weight phenolics

Bio-based wood adhesive

- Literature research for possible application of HDO lignin oils in bio-based wood adhesives
- Screening typical products obtained from HDO experiments with lignin
- Formulation and testing of model resins
- Formulation of resins based on HDO lignin oil

2. Semi-continuous hydrogenation of lignin

1. Introduction

Catalytic HDO seems to be a promising technique to convert lignin into more valuable products, like low molecular weight phenolics. This chapter will propose and optimize a semi-continuous reactor setup for the hydrotreatment of lignin.

2. Materials and methods

2.1 Materials

ALCELL[®] Lignin was obtained from the Lignovalue consortium and the typical properties are listed in Table 3. The same batch of lignin was used for all hydrogenation experiments. The noble metal catalyst, ruthenium on carbon (Ru/C), was obtained as powder from Sigma Aldrich and contained 5 %-wt of active metal. The dispersion of the catalyst is 11 % and the specific area is 886 m². g⁻¹. [21]

Hydrogen of analytic grade (>98% purity) was from Hoek Loos (Schiedam).

Tetrahydrofuran (THF) and di-n-butyl ether (DBE) were obtained from Sigma Aldrich. Di-chloromethane and toluene were obtained from Acros. All chemicals used were of analytical grade (98-99.99% purity)

Table 3. Typical properties of ALCELL[®] Lignin[22]

Median particle size	20-40	µm
Softening, ring and bal	145	°C
Glass transition temp.	90-100	°C
Sugars:	0.3	%
Ash	0.0	%
Moisture	> 3	%
M _w ^a	2100	g. mol ⁻¹
M _n	900	g. mol ⁻¹
Elemental composition ^b		
C	65.3	%
H	5.8	%
O	28.9	%
N	>0.1	%

a. Molecular weight was determined with GPC analyses.

b. Elemental composition was determined with an Euro Vector 3400 CHN-S analyzer

2.2 Experimental setup

Hydrogenation experiments were carried out in a semi-continuous setup. The setup was described already in earlier work of Meier et al. [23, 24]. A schematic representation of the reactor setup is given in Figure 11.

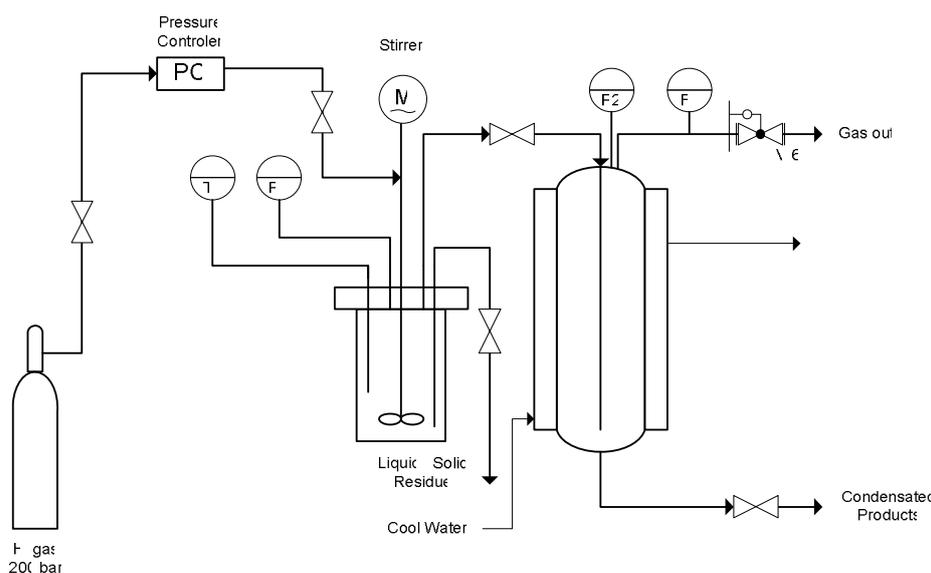


Figure 11. Schematic representation of the semi-continuous reaction setup

The reactor is a standard 100 ml autoclave reactor connected to a 400 ml water cooled high pressure condenser. The gas outlet from the reactor to the condenser was traced (temperature range: 0-350°C) to prevent earlier condensing of evaporated products. Temperature, pressure and hydrogen flow were measured and monitored with a PC. The reactor content was stirred at 1200 rpm with a magnetically driven gas-inducing impeller. The impeller was of the Rushton type with four blades (diameter: 24 mm, height: 12 mm, and thickness: 5.5 mm).

The reactor was filled with 20 gram ALCELL[®] lignin and 2 gram Ru/C catalyst. The setup was flushed three times with hydrogen to remove remaining oxygen and pressurized with 20 bar of hydrogen pressure at room temperature. The reactor was heated to pre-defined temperature with a heating rate of 16°C. min⁻¹ and kept at this temperature for the pre-defined reaction time. The hydrogen pressure was set at the predetermined value and kept constant with a pressure controller. A constant hydrogen flow was adjusted after reaching the ramp temperature and measured with a flow controller. At the end of the reaction, the hydrogen feed was closed and the reactor was cooled with water overnight.

The products obtained after every hydrogenation experiment were defined as: light oil: evaporated low molecular weight oil was trapped in the condenser; water: evaporated water which was trapped in the condenser; heavy oil: the remaining oil in the reactor; and char: the acetone insoluble solids remaining in the reactor corrected for the catalyst intake.

The oil fraction in the condenser was released from the condenser and the whole fraction was dissolved in dichloromethane (DCM) to separate water from the light-oil. The water phase was extracted 3 times with DCM to remove remaining water soluble components and measured by weight. The DCM was evaporated and the remaining light-oil was measured by weight. The remaining oil and solids in the reactor were dissolved in acetone. The solids were filtered out of the acetone solution and were extracted with acetone in a soxhlet apparatus overnight. The remaining solids were considered as char and measured by weight and corrected by catalyst intake. The remaining acetone fraction was evaporated and heavy-oil was measured by weight.

Gas samples were taken from the outlet of the hydrogen gas flow. Four samples with intervals of 15 minutes were taken in the first hour and three samples were taken in the remaining 3 hours. Each sample presents the gas composition at the give time interval and the last sample presents the gas composition at the end of the reaction.

2.3 Analyses of the reaction products

2.3.1 GC-MS, 2D-GC and GPC

Product oils were diluted with THF to 10 %-wt. DBE was used as internal standard.

GC-MS analysis were performed on a Quadrupole Hewlett Packard 5972 MSD attached to a Hewlett Packard 5890 GC equipped with a 30 m x 0.25 mm i.d. and 0.25 μm film sol-gel capillary column. The injector temperature was set at 250°C. The oven temperature was kept at 40°C for 5 minutes then heated up to 250°C at a rate of 3°C. min⁻¹ and then held at 250°C for 10 minutes.

2D-GC analyses were performed on a trace 2D-GC from Interscience equipped with a cryogenic trap system and two columns, a 30 m x 0.25 m i.d. and 0.25 μm film of sol-gel capillary column connected to a 148 cm x 0.1 mm i.d. and 0.1 μm film Restek 1701 column. An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the coldtrap is 60°C. Helium was used as the carrier gas (flow 0.6 ml. min⁻¹). The injector temperature and FID temperature were set at 250°C. The oven temperature was kept at 60°C for 5 minutes then heated up to 250°C at a rate of 3°C. min⁻¹. The pressure was set at 0.7 bars. The modulation time was 6 seconds.

GPC analyses were performed on a HP1100 from Hewlett Packard equipped with three 300 x 7.5 mm PLgel 3 mm MIXED-E columns in series. Detection was made with a GBC LC 1240 RI detector. Calculations of the average molecular weight were made with the software PSS WinGPC Unity from Polymer Standards Service. The following operating conditions were maintained: eluent: THF (used as delivered); flow rate: 1 ml. min⁻¹; pressure: 140 bars; temperature columns: 42 °C; injection volume: 20 ml; sample concentration: 10 mg. ml⁻¹

2.3.2 Elemental composition, water content and NMR analyses

The elemental compositions of the product oils (C, H and N) were determined using a Euro Vector 3400 CHN-S analyzer. The oxygen content was determined by difference.

The water content was determined with a Karl Fischer titration, using a Metrohm Titrino 758 titration device. A small amount of product (20-200 mg) was added to an isolated glass chamber containing Hydranal (Karl Fischer solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant Composit 5K (Riedel de Haen). All measurements were performed in duplicate.

^1H -NMR spectra were recorded on a 400 MHz NMR (Varian). The samples were dissolved in dimethyl sulfoxide- d_6 (DMSO- d_6) and measured at a temperature of 60°C.

2.3.3 Gas phase analyses

The gas samples were taken from the constant flow released out of the reactor. The samples were stored in gasbags (SKC Tedlar 3 Liter Sample Bag (9.5" x 10")) and analyzed with a GC-TCD analyses on a Hewlett Packard 5890 Series II GC equipped with a Porablot Q $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column and a Molecular Sieve (5A) column. The injector temperature was set at 150°C, the detector temperature at 90°C. The oven temperature was kept at 40°C for 2 minutes then heated up to 90°C at 20°C. min^{-1} and kept at this temperature for 2 minutes. A reference gas containing H_2 , CH_4 , CO , CO_2 , ethylene, ethane, propylene and propane with known composition was used for peak identification and quantification.

3. Results and discussion

The hydrogenation experiments described in this thesis were carried out in a semi-continuous setup as described in chapter 2.2. All the experiments were carried out with the same batch of ALCELL[®] Lignin and mediated with a Ru/C catalyst. A summary of all the HDO experiments with the corresponding process parameters is listed in Table 4.

Table 4 Reaction parameters and mass balances for the hydrogenation experiments.

Exp Code: CLRxxx	Lignin Mass (g)	Catalyst ^a Mass (g)	Reaction conditions					Product Composition						
			T(°C)	P(bar)	Φ_v, H_2 (ml. min ⁻¹)	t(h)	Tr (°C)	HO ^b (%-wt)	LO ^b (%-wt)	H ₂ O ^b (%-wt)	Char (%-wt)	Gas (%-wt)		
001-004	20	2	350	100	10	4	0					0		Unk
005-008	20	2	400	100	100	4	0					0		Unk
009	20	2	400	120	100	4	0					0.5		Unk
010	20	2	400	160	100	4	250	37.2	1.1	6.5	0.2			Unk
011	20	2	400	130	100	4	250	43.8	2.1	12.6	1.1			Unk
012	20	2	400	100	100	4	250	44.5	2.9	9.4	2.6			Unk
013	20	2	400	130	200	4	250	44.7	9.5	8.5	4.6			Unk
015	20	2	400	80	200	4	350	26.4	12.8	14.8	9.6			Unk
017	20	2	400	80	200	4	250	26.4	13.5	11.3	8.1			Unk
019	20	2	400	130	200	4	350	22.8	23.8	18.3	1.3			Unk
020	20	2	400	100	200	4	350	33.9	11.7	12.2	2.9			Unk
021	20	2	400	80	200	4	350	22.5	12.0	12.8	11.7			Unk
023	20	2	400	160	200	4	350	34.6	8.4	13.1	3.4			Unk
024	20	2	400	130	200	4	350	23.3	24.9	21.2	2.9			29.8
025 ^L	20	2	400	130	200	4	350	32.2	9.5	12.1	4.1			24.2
026	20	2	400	130	200	4	350	20.8	25.1	21.5	3.3			29.5
028 ^L	20	2	400	130	200	4	350	34.0	6.4	5.0	3.3			55.0
032 ^X	10	2	400	130	200	4	350	48.9	3.5	0	Unk			37.4
033 ^X	10	2	400	130	200	4	350	28.8	4.4	5.5	unk			43.7

a: All experiment were carried out with a Ru/C catalyst.

b: HO = Heavy oil fraction; LO = Light oil fraction; H₂O = water fraction

L: Leakages

X: Additional experiments with Heptadecane as solvent (15 gram)

Unk: Not measured

Note: Missing experiments were failed by an defect or leakages

3.1 Optimization of the oil yield

The most time consuming part of this research was the optimization and development of the semi-continuous setup. Initial experiments did not result in the production of light-oil. The problem was early condensation of the products in the gas tubing connecting the reactor with the condenser. This problem was solved by applying a heated tracing tube (heating range 0-350°C).

Three hydrogenation experiments were carried out with the heated tracing. The process parameters were selected based on earlier experiments and reported work of Meier et al. [23, 24] and listed in Table 4 (CLR010-012). The mass balances in this paragraph were only based on the liquid and solid products, due to a defect in the gas analyses.

The result was a low yield of evaporated light-oil and water trapped in the condenser. A large amount of oil remained in the reactor. The mass balances are presented in Figure 12 and compared with the result of earlier work of Meier et al. (Figure 13) [24]. The mass balance of Meier considered light-oil as the total amount of evaporated liquid, including water.

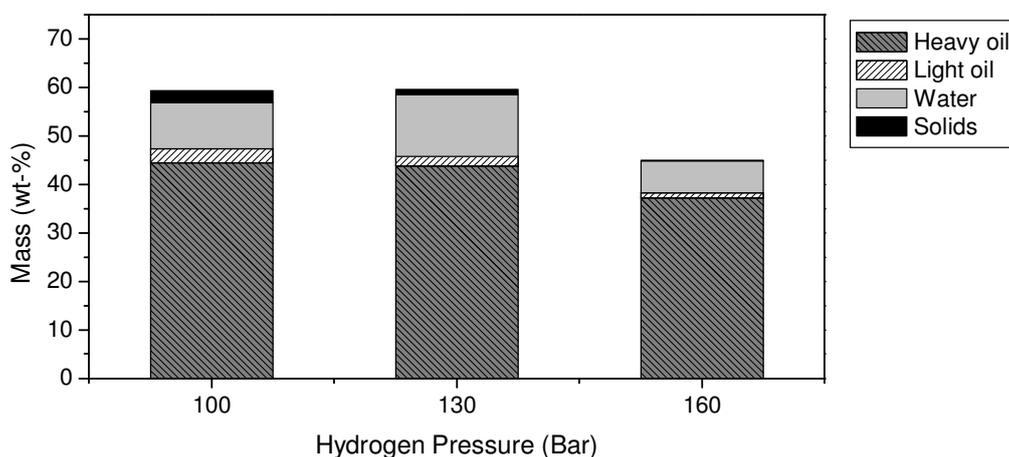


Figure 12. Mass balances for the HDO of ALCELL[®] lignin at different pressures (CLR010-012)(400 °C, 80-160 bar, 100 ml.min⁻¹, 4 h, T_{tracer}: 250 °C)

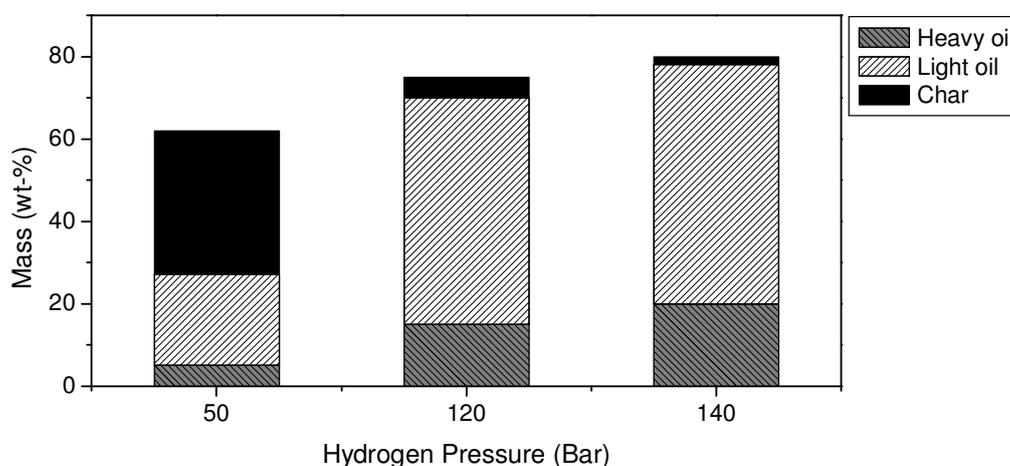


Figure 13. Mass balances for the HDO of mild wood lignin (MWL) at different pressures based on the work of Meier et al. (400°C, 500 ml. min⁻¹, 4h) [24]

The light oil fraction suggested in Meier et. al. is the total evaporated oil yield including the water fraction. A lower light oil yield and relative higher yield of heavy oil was observed compared to the results of Meier et. al. Furthermore the solid content decreases with an increase in the hydrogen pressure. The lower light oil yield is the result of a limit transfer of evaporated light oil through the gas tubing connected to the condenser.

To optimize the transfer of evaporated light oil through the gas tubing several experiments with variable tracer temperature and hydrogen flow were carried out. A summary of those experiments can be found in Appendix A. The results showed that an increased hydrogen flow and tracer temperature gave an increased amount of light oil. Based on the optimal reaction condition observed in these experiments, 4 hydrogenation experiments were carried out with pressure varied between 80-160 bars. The process parameters are listed in Table 4 (CLR019-021, 023) and the mass balances are represented in Figure 14.

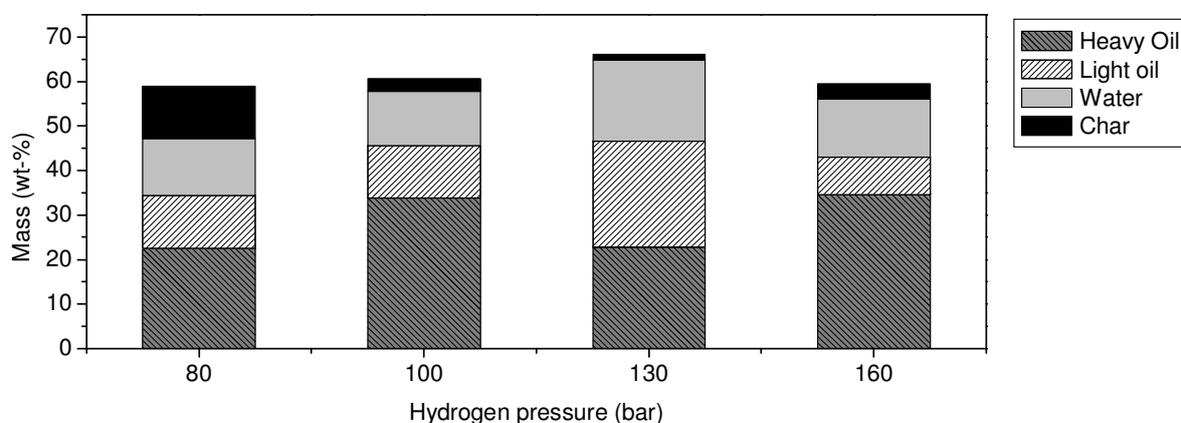


Figure 14. Optimized mass balances for the HDO of lignin at different pressures (CLR019-021, 023) (400 °C, 80-160 bar, 200 ml.min⁻¹, 4 h, T_{tracer}: 350 °C)

The result shows an increased amount of light oil and water compared to the results presented in Figure 12. The light oil and water yields are comparable to earlier work of Meier et al. Increased hydrogen pressure resulted in an increased light oil yield and decreased amount of char formation. An optimal light oil yield of 25 %-wt was obtained with a pressure of 130 bars. Higher pressures limit the evaporation of low molecular weight phenolics. The optical observation of the viscosity of the heavy oil results in a lower viscosity with increased hydrogen pressure. The molecular weight of these oils should be lower. The results of the oil composition are given in chapter 3.3 and a proposed reaction mechanism is discussed in chapter 3.4.

3.2 Mass balance closure

Two hydrogenation experiments were carried out to obtain information regarding the mass balance and the reproducibility of the reaction. The reactions were conducted at 400°C, 130 bar of hydrogen pressure, 200 ml. min⁻¹ hydrogen flow and a reaction time of 4 hours.

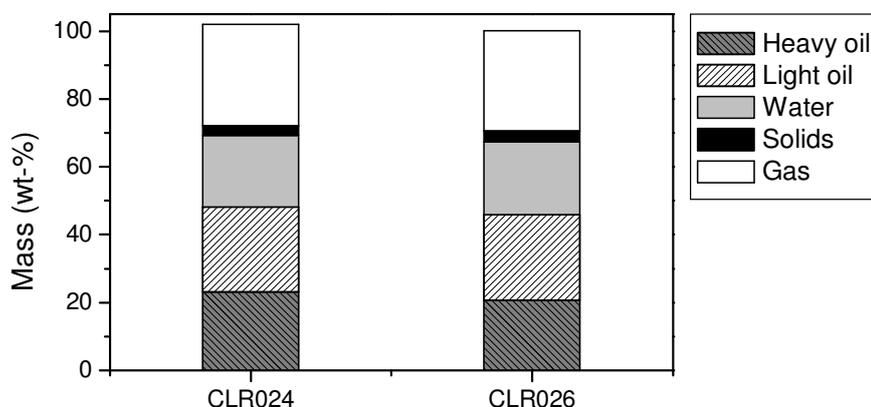


Figure 15. Mass Balance for the hydrogenation of lignin using a Ru/C catalyst (400°C, 130 bar of hydrogen, 200 ml. min⁻¹, 4 h)

The products in the condenser resulted in two liquid phases, a yellowish water phase and a transparent brownish light-oil phase with a density lower than the water phase. The remaining heavy oil in the reactor was a dark brown liquid with a relative higher viscosity compared to the light-oil fraction. The mass of each fraction was measured by weight and the results are presented in Figure 15.

Mass balance closure was up to 100 %-wt ($\pm 5\%$) for both experiments and the composition are almost identical. A light oil yield of 25 %-wt and low char content of 3 %-wt was obtained.

The collected gas samples were analyzed on a gas GC. The moles of gas were calculated with the ideal gas law with the assumption of ideal gas behavior. A detailed explanation of the calculation can be found in Appendix B. The gas composition as function of time is presented in Figure 16 and the overall gas composition is presented in Figure 17.

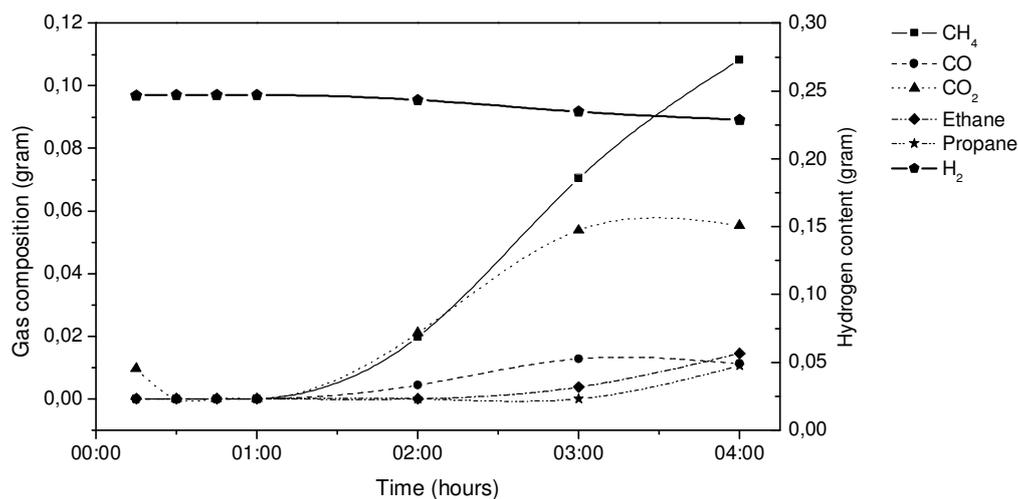


Figure 16. Gas phase composition at different reaction times (CLR026) (400 °C, 130 bar, 200 ml.min⁻¹, 4 h)

The gas composition indicates un-reacted hydrogen over the whole reaction time, which indicates that hydrogen was not limiting the reaction. The main products formed were methane and carbon dioxide (CO₂). The formation of propane and ethane at the end of the reaction indicates cracking.

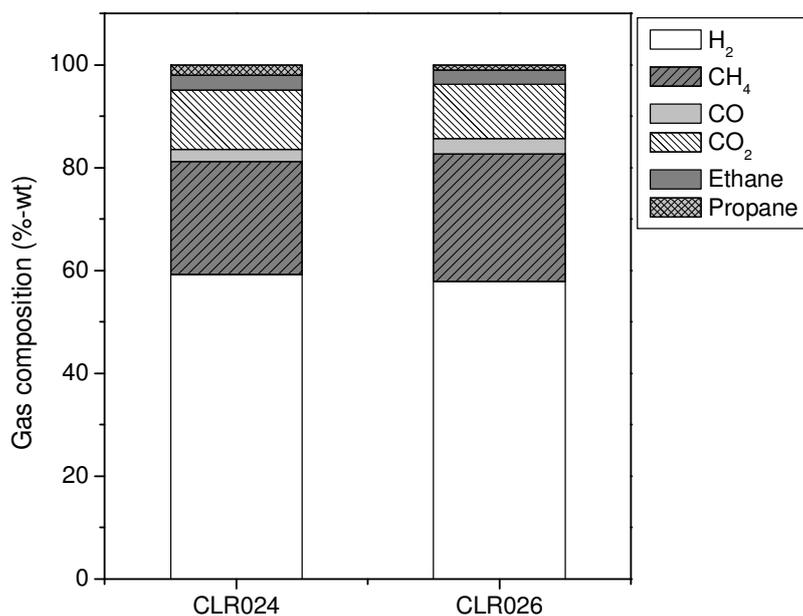


Figure 17. Total gas composition for the hydrotreatment of Lignin (400 °C, 130 bar, 200 ml.min⁻¹, 4 h)

The total gas composition was identical for both experiments. Based on these results, reproducible experimental data could be obtained from hydrogenation experiments with a mass balance closure up to 100 %-wt ($\pm 5\%$).

3.3 Product Composition

The van Krevelen plot [25] is a useful tool for the representation of the elemental composition. Figure 18a presents the elemental composition of commonly used components in the bio- and petroleum industry. Figure 18b presents the elemental composition of the light and heavy oil obtained from hydrogenation experiments presented in Figure 14 (CLR019-021, 023) compared to phenolics and lignin.

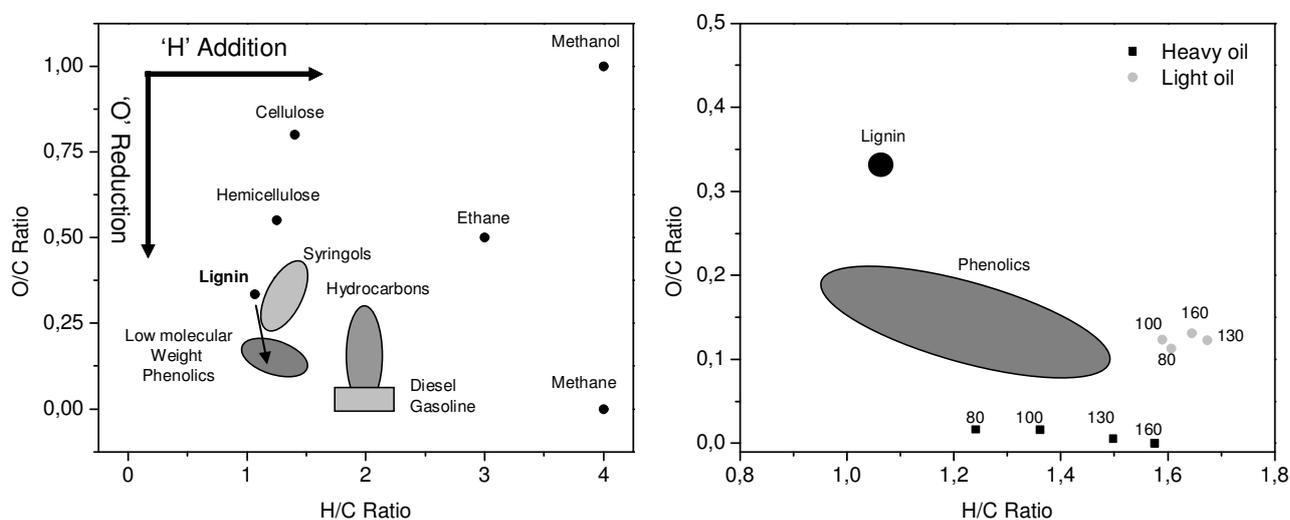


Figure 18. Van Krevelen plot of (A) common used components in the bio- and petroleum industry HDO of lignin (B) The light- and heavy-oil produced between 80-160 bar of hydrogen pressure (CLR019-021, 023)

The van Krevelen plot indicates that the heavy oil fractions are almost fully deoxygenated at all pressures. The increased H/C ratio indicates increased hydrogenation activity at higher pressures. The elemental compositions of the light oil are not depended on hydrogen pressure. The O/C ratio of the light oils are in the same order as phenolics, however the H/C ratio is too high, which could be a result of the hydrogenation of double bonds or ring opening reactions.

$^1\text{H-NMR}$ was used to gain insight in the different molecular composition of the oils. The functional groups analysis used by Ingram et al. [26] was applied for quantification.

The $^1\text{H-NMR}$ spectra was divided into certain regions. Each region was classified to a certain functional group. The relative amount was calculated by dividing the peak area of the group by the total area of the $^1\text{H-NMR}$ spectra. A typical $^1\text{H-NMR}$ spectra of lignin, light oil and heavy oil is presented in Figure 19.

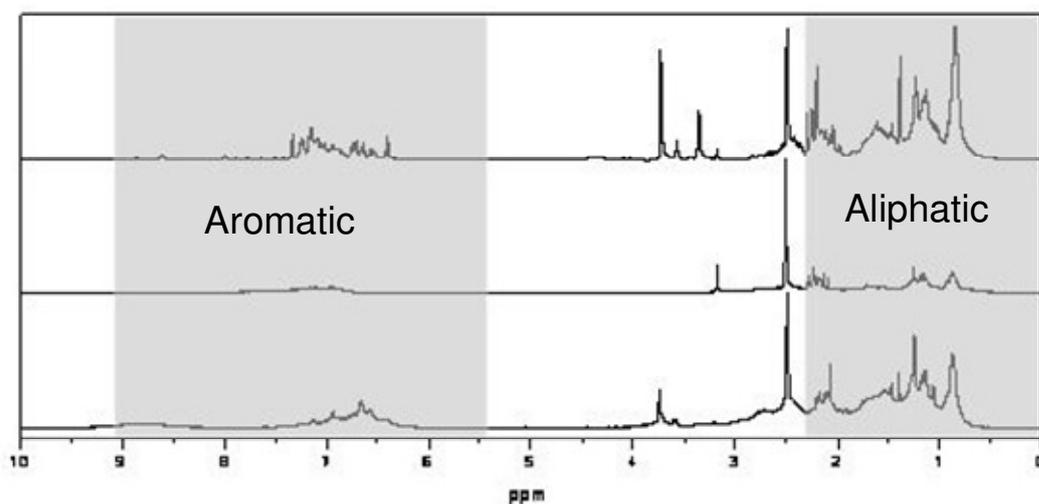


Figure 19. $^1\text{H-NMR}$ spectra of ALCELL[®] lignin (bottom), produced heavy oil (middle) and produced light oil (top)

The main difference between the heavy oil compared to ALCELL[®] lignin is a decreased amount of peaks in the aromatic section (8-6.4 ppm), which in the case of heavy oil completely disappeared. The main difference between the light oil compared to ALCELL[®] lignin is an increased amount of aliphatic (2.2-0 ppm) and an increased amount of methoxy / hydroxyl groups (4.2-3.0).

Table 5 present the functional group analyses of the light oil compared to the ALCELL[®] lignin.

Table 5. Functional group analyses of the light oil fractions obtained from HDO experiment between 80-160 bar of hydrogen pressure compared to ALCELL® lignin

Chemical shift region (ppm)	Type of protons	Hydrogen content (% area of total)				
		Lignin	80	100	130	160
10 - 8.0	-CHO, -COOH, downfield ArH	10.5	0.0	0.0	0.1	0.0
8.0 - 6.8	ArH, HC=C, (conjugated)	12.9	8.6	6.9	8.7	4.2
6.8 - 6.4	HC=C, (nonconjugated)	5.7	8.6	6.0	4.2	5.9
6.4 - 4.2	CH _n -O-, ArOH, HC=C (nonconjugated)	13.2	0.8	0.6	0.5	1.5
4.2 - 3.0	CH ₃ O-, -CH ₂ O-, -CHO-	41.8	20.5	21.6	7.4	20.4
3.0 - 2.2	CH ₃ C(=O)-, CH ₃ -, Ar-, -CH ₂ Ar	6.9	15.6	13.0	12.2	9.9
2.2 - 1.6	-CH ₂ -, aliphatic OH	3.4	15.2	14.0	16.0	14.2
1.6 - 0.0	-CH ₃ -, -CH ₂ -	5.4	30.8	38.1	50.9	44.0
Aliphatic/ Aromatic ^a		0.5	2.8	4.0	5.2	5.8
Atomic H/C ^b		1.1	1.6	1.6	1.7	1.6

a. Ratio of the area % at 2.2 – 0 ppm and 8 – 6.4 ppm

b. Ratio according to the elemental composition

Table 5 indicates that the aliphatics content depends on the pressure. Increased pressure results in more aliphatics, with an optimum at 130 bars. The hydroxyl and methoxy group (4.2-3.0) is at a minimum at 130 bars, which indicates increased hydrodeoxygenation activity and the possible break down of phenol towards cycloalkanes (and even linear alkanes). The aliphatic/aromatic ratio increases with hydrogen pressure, which indicates increased ring opening activity at higher pressures.

Table 6 present the functional group analyses of the heavy oil compared to the ALCELL® lignin.

Table 6. Functional group analyses of the heavy oil fractions obtained from HDO experiment between 80-160 bars of hydrogen pressure compared to ALCELL® lignin

Chemical shift region (ppm)	Type of protons	Hydrogen content (% area of total)				
		Lignin	80	100	130	160
10 - 8.0	-CHO, -COOH, downfield ArH	10.5	2.1	1.6	0.1	0.1
8.0 - 6.8	ArH, HC=C, (conjugated)	12.9	20.2	17.6	11.6	7.9
6.8 - 6.4	HC=C, (nonconjugated)	5.7	2.0	1.7	1.6	0.2
6.4 - 4.2	CH _n -O-, ArOH, HC=C (nonconjugated)	13.2	0.1	0.1	0.2	1.7
4.2 - 3.0	CH ₃ O-, -CH ₂ O-, -CHO-	41.8	4.2	6.5	6.2	27.4
3.0 - 2.2	CH ₃ C(=O)-, CH ₃ -, Ar, -CH ₂ Ar	6.9	18.6	18.8	17.5	10.5
2.2 - 1.6	-CH ₂ -, aliphatic OH	3.4	16.3	17.0	17.5	12.1
1.6 - 0.0	-CH ₃ , -CH ₂ -	5.4	36.5	36.7	45.3	40.0
Aliphatic/ Aromatic ^a		0.5	2.4	2.8	4.8	6.4
Atomic H/C ^b		1.1	1.2	1.4	1.5	1.6

a. Ratio of the area % at 2.2 – 0 ppm and 8 – 6.4 ppm

b. Ratio according to the elemental composition

The aliphatic content in the heavy oil indicates the same behavior as discussed with the light oil. A graphical representation of the aromatic and aliphatic content in the heavy oil compared to the average molecular weight (M_w) is given in Figure 20. The aromatic content decreases with increased pressure which results in a decreased molecular weight, which proves the proposed theory of cracking discussed earlier.

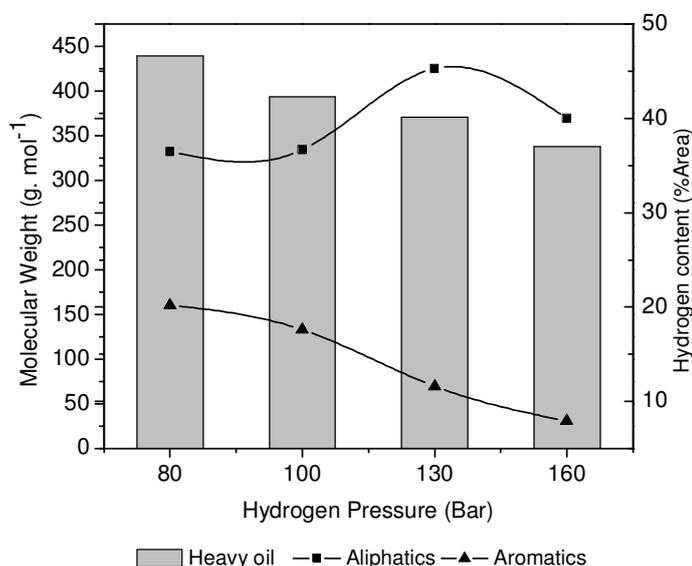


Figure 20. Average molecular weight, aromatic and aliphatic content of the heavy oil based on GPC and NMR data.

2D-GC and GC-MS measurements were used to get insight in the molecular composition of the oils. The GC-MS was used for classification and 2D-GC for quantification of the components.

The classification was based on earlier work on the HDO of pyrolysis oil [27, 28] and adjusted with some typical components formed in the HDO of lignin. A graphical presentation of the classified groups is presented in Figure 21. It should be noted that the 2D-GC analyses is not capable to detect high molecular weight components. The maximum molecular weight detectable on the 2D-GC is in the order of 300 g. mol⁻¹. The amount of undetectable oil was measured with GPC analyses. A typically composition of light and heavy oil is presented in Figure 21.

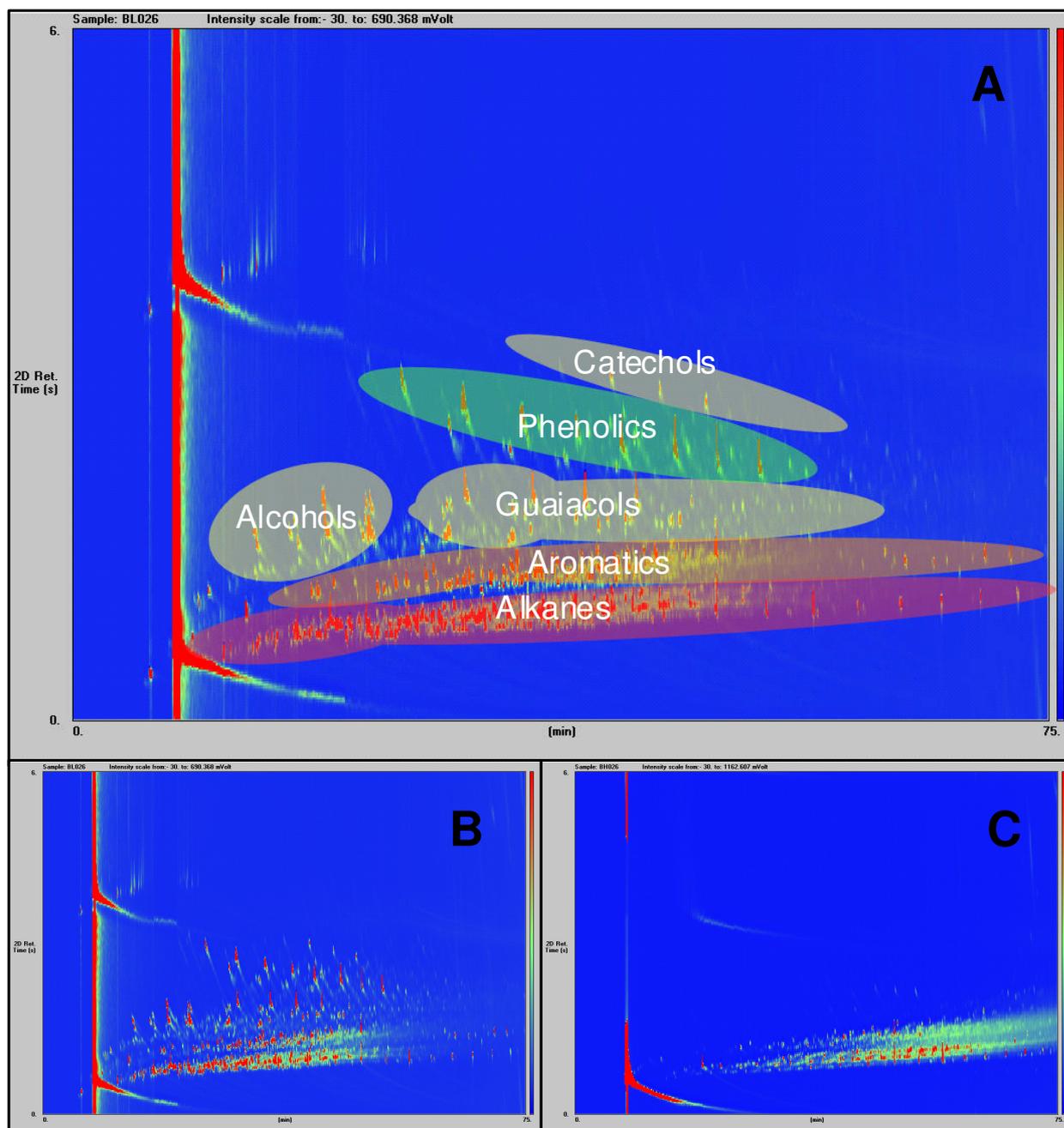


Figure 21. 2D-GC of (A) a typical light oil with a presentation of the classified function groups, (B) light oil and (C) heavy oil.

The principle of the semi continuous reactor setup was to evaporate lower molecular weight products. The light oil presented in Figure 21 indicates lower molecular products, products detected with lower retention time, compared to the heavy oil fraction. The light oil consists of a varied range of low molecular weight components; and the heavy oil mainly consists of higher molecular weight alkanes and aromatics. A GPC measurement of both oils is given in Figure 22, which will indicate the amount of undetectable components.

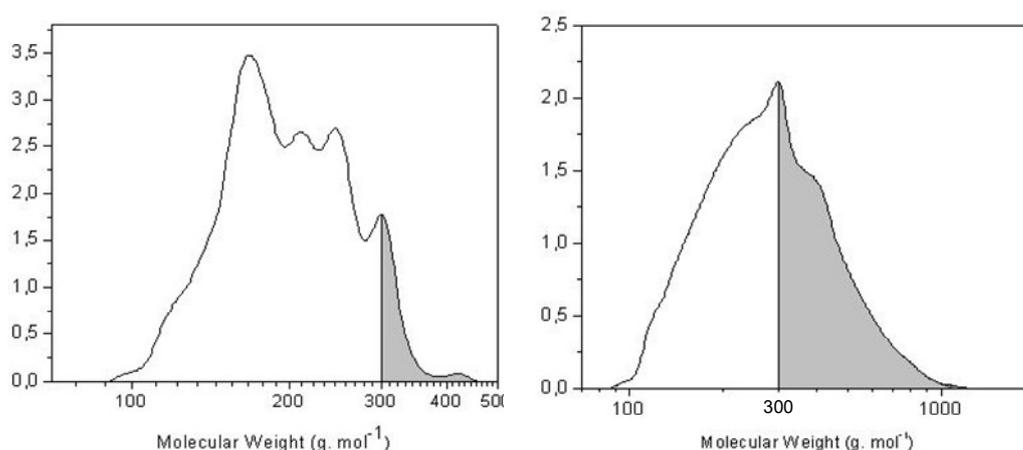


Figure 22. GPC measurement of the light oil (L) and heavy oil (R) which represent the detectable fraction of oil on the 2D-GC

As shown in the GPC result almost the whole light oil is detectable on the 2D-GC (93 %-wt). The average molecular weight of the light oil is 200 g.mol⁻¹. For the light oil almost 58 %-wt is detectable on the 2D-GC and the average molecular weight is 300 g.mol⁻¹.

A quantitative calculation based on 2D-GC analyses was made using relative response factors for the proposed classified groups. The results based on the produced light oils are presented in Figure 23.

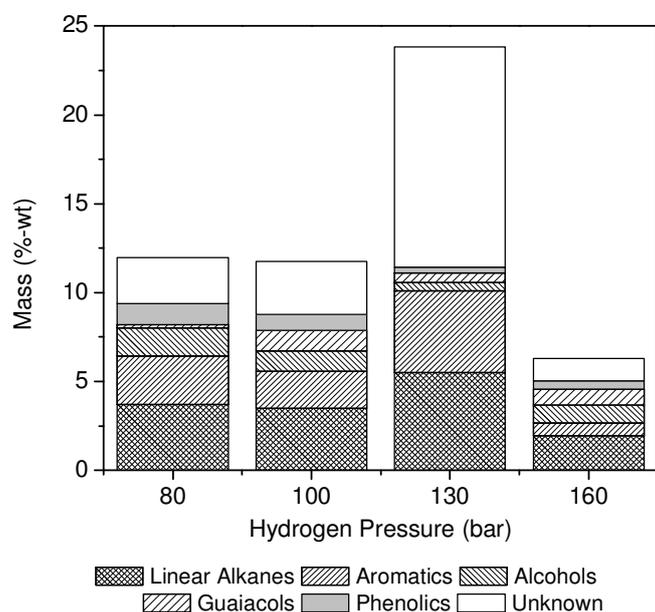


Figure 23. Quantitative calculation of produced light oil based on lignin intake

The chemical composition shows that the main products formed are linear alkanes and aromatics. Those product yields increase with increased pressure and have an optimum at 130 bars, which supports the observation made from the NMR data.

The phenolics yield decreases with increased pressure, which is the result of increased hydrogenation and cracking activity at higher pressures. The highest yield of phenolics is obtained with a pressure of 80 bars, which is the result of milder hydrodeoxygenation. However, the total light oil yield is lower and the char content is significantly higher at lower pressures.

3.4 Reaction pathways

The HDO of lignin involves various reaction pathways. A schematic representation for a possible reaction pathway is given in Figure 24. The scheme is based on batch scale HDO experiments in earlier work of Kloekhorst and the continuous HDO experiments in this thesis.

The lignin is melted in the initial heating phase of the reaction. The melted lignin thermally degrades towards lignin fragments and may react due to repolymerization towards char. Low amounts of char and increasing oil yields are obtained in the presence of hydrogen pressure and catalyst. The lignin monomers are further converted by HDO towards phenolics or cycloalkanes. The reaction towards phenolics is desired for the production of adhesives and is the result of mild HDO. The phenolics and even the lignin monomers may react further towards cycloalkanes and even linear alkanes, which depends on the type of catalyst, temperature and hydrogen pressure (Deep HDO).

The low molecular weight products (light oil fraction) may evaporate towards the condenser. The evaporation rate depends on the hydrogen flow and hydrogen pressure. Increased hydrogen flow will stimulate the gaseous products to flow towards the condenser. Increased hydrogen pressure could lead to a lower evaporation rate of the lower molecular weight products, due to the partial pressure of those components. However, a high hydrogen pressure is required for the HDO of lignin. From experimental research an optimal condensation pressure has been found at 130 bars, which is comparable to the result of Meier et al. [24]

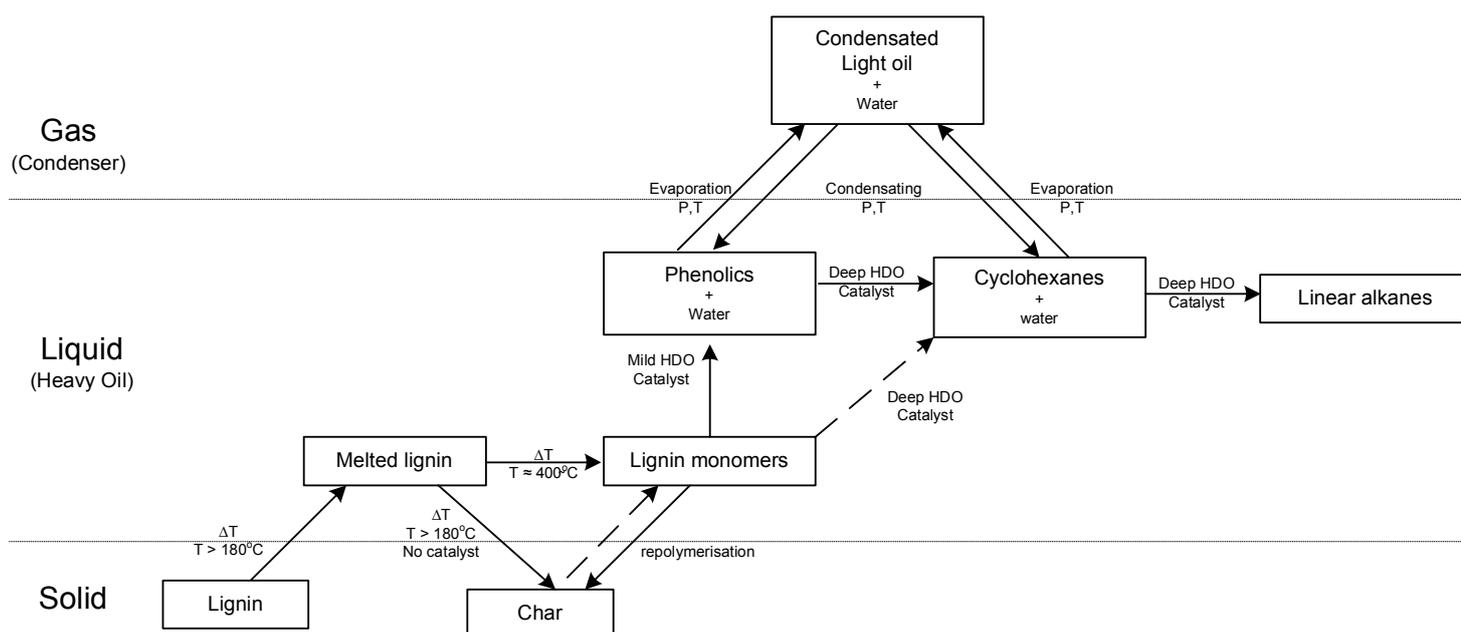


Figure 24. Proposed reaction pathway for the HDO of lignin

Mild HDO is the desired route for optimal lower molecular weight phenolics production. However, experiments in this thesis indicate mainly deep HDO of lignin. The mass balance presented in Figure 14 indicates that higher pressure are required for optimal light oil yields and the chemical composition presented in Figure 23 indicates a higher phenolic yield at lower pressure.

A main disadvantages with the low pressure experiments is the relative high char content (12 %-wt) and low light oil yield (12 %-wt) compared to higher pressures (25 %-wt). The deep HDO is the result of a too active catalyst at the process parameters used in this thesis. Lower amounts of catalyst or a less active catalyst could improve the phenolics yield.

The influence of the initial melting step could be reduced by adding a high pressure resistant solvent to solve the lignin. The reduced formation of char up on heating and a relative easier hydrogen donation would speed up the reaction [23].

4. Conclusions & Recommendation

Initial experiments showed that an increased amount of light oil was obtained with increased tracer temperature and hydrogen flow. Based on those optimal process conditions several experiments were carried out with various hydrogen pressures. The result indicated that an increased hydrogen pressure resulted in increased light oil yield and a minimal amount of char. An optimum of 25 %-wt light oil was obtained at 130 bars of hydrogen pressure.

Based on the chemical composition, the catalyst (ruthenium on carbon) used for the HDO experiments in this thesis was too active with the process parameters proposed in this thesis.

NMR and GPC data indicates higher hydrogenation activity at higher pressure, but the higher pressures are required to obtain a high yield of light oil and a minimum of char. A milder HDO catalyst or a lower amount of catalyst could lead to better results.

The influence of the initial melt step proposed in Figure 24 could be minimized by using a solvent. A liquid solvent would lead to increased interaction with catalyst and hydrogen upon heating, which could lead to improved light oil yields. The selected solvent needs to be chemical inert against the harsh condition in the HDO process. Meier et al. tested several solvents and showed increased amounts of light oil yield with low amount of char [23]. A preferred solvent would be a recycled product such as (or partly) the heavy oil remained in the reactor.

Future experiments should be concentrated on the intake amount of catalyst, the reaction time, the lignin source and testing the influence of solvents.

3. The use of hydrogenated lignin oil for wood adhesive

1. Introduction

Wood adhesives from renewable resources (bio-based adhesives) have gained interest in the past decades. This interest was already present in 1940, and grew as a result of the world's first oil crisis in 1970 [18]. The current interest is a result of the environmental concerns and future shortage of fossil fuels. Bio-based adhesives are defined as adhesives obtained from natural, non-mineral, origin which can be used, or after small modifications, to obtain adhesives with the same behaviour and performance as synthetic resins. Possible raw materials for such bio-based adhesives are: tannins, lignin, carbohydrates, unsaturated oils, liquefied wood and wood welding by self adhesion [20].

A lot of research reported on bio-based wood adhesive is based on the replacement of phenol with lignin or tannins [20]. The mechanical properties of such a resin are in the same order of conventional used resins. However, the press time to achieve the same tensile properties must be increased. This increased press time is a major disadvantage for the commercial industry. This chapter will research the possibilities use of HDO of lignin in PF resins.

2. Experimental

2.1 Materials

Phenol, catechol, 2-methoxyphenol, 4-ethylphenol, 2,3-dimethylphenol and formaldehyde were obtained from Sigma Aldrich. p-cresol and 4-propylphenol were obtained from TCI. Sodium hydroxide was obtained from Merck. All chemicals were of analytical grade (98-99,9% purity).

2.2 Resin Formulation

The phenolic resins were prepared according to the method described in patent: CA692702 [29]. A 100 ml three-neck-round bottom flask with a water cooled condenser was charged with 1 mol of phenol, 2 moles of formalin (37 %-wt formaldehyde dissolved in water), 5 moles of water and 0,15 mol of sodium hydroxide (50 wt-% aqueous solution). The mixture is stirred and gradually heated to reflux temperature. After maintaining reflux temperature for 30 min the reaction mixture is cooled down to 80-85 °C and an additional amount of 0,3 mol of sodium hydroxide is charged into the mixture. After 1 hour a third addition of 0,3 mol of sodium hydroxide is added and the mixture is rapidly cooled down to room temperature immediately after. The obtained mixture is used for wood adhesive testing.

In case of the preparation of model compound-based resins, 25-50% mol based phenol is replaced by a model compound. The procedure remained the same.

2.3 Analyses

The viscosity was measured on a AR 1000 rheometer (TA Instruments, USA), using an aluminum cone-and-plate fixture of 2° and 40 mm in diameter. The viscosity of all the samples were measured with a constant shear rate (5 s^{-1}) and temperature (21°C)

$^1\text{H-NMR}$ spectra were recorded on a 400 MHz NMR (Varian). The samples were dissolved in dimethyl sulfoxide- d_6 (DMSO- d_6) and measured at a temperature of 60°C.

2.4 Wood adhesive testing

All the wood specimens for adhesive testing (dimensions: 50 x 25 x 4 mm) were dried in a vacuum oven at 105 °C for 14 hours. The experiments were carried out according to the European standard (EN-314). One side of the wood specimen was applied with 150 g/m² resin and another specimen was placed on top of it (Figure 25). The contact interface was 25x25 mm. The lapped specimens were hot pressed at 200°C with a pressure of 30 bars for 5 minutes.

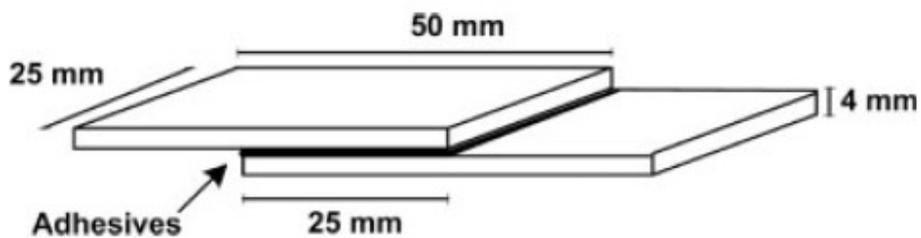


Figure 25: Lapped wood specimens for tensile testing

The prepared samples were immersed in boiling water for 72 hours. The tensile properties of specimens were tested on an Instron 4301 machine using 5kN power sensor with a crossing head speed of 2 mm. min⁻¹. Twelve replicates were performed for each experiment. The shear strength was measured from the tensile test and was defined as the load required for breaking divided by the area of the adhesive bond.

3. Results and discussion

The addition of lignin to a PF resin results in a longer press-time, which makes those resins not suitable for commercial use. Lignin can be degraded towards lower molecular weight phenolics to overcome the disadvantages of longer press times. This thesis uses the HDO process to degrade lignin which is described in chapter 2. However, the phenolics obtained from the HDO process have additional functional groups. In the study described in this chapter we investigate the influence of several functional groups on the properties of the adhesive. The selected model components, based on HDO experiments, are presented in Figure 26 and used for the formulation and testing of PF resins.

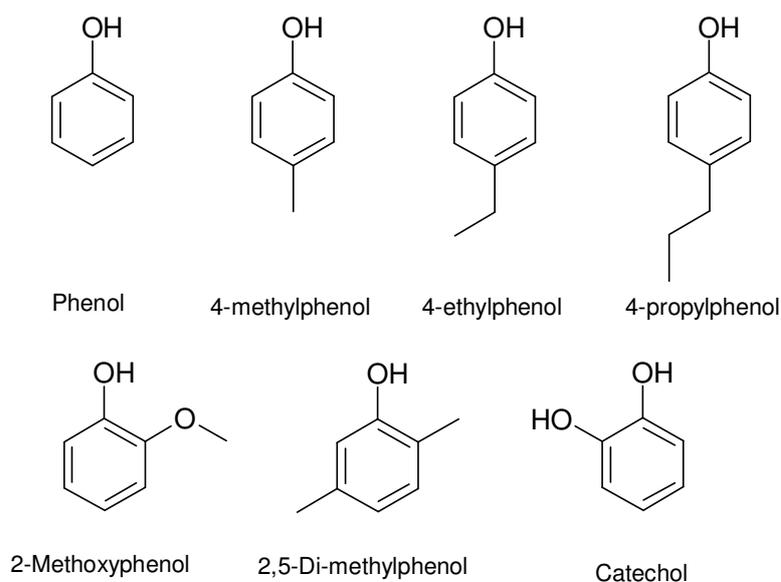


Figure 26: Model compounds used for phenolic resins

3.1 Phenol formaldehyde standard resin

The formulation of a resin has great influence on the properties of the adhesive. For instance, commercially used resins are specifically formulated for there type of application. For that reason two standard PF resins were prepared and used as reference. These resins were tested according to the European Standard for wood adhesive testing (EN-314). The results are presented in Table 7.

Table 7: Tensile properties of PF resins

	PF resin #1	PF resin #2
Stress at max Load (MPa)	3.083	2.866
Strain at max Load (%)	10.207	10.215
Stress at break (MPa)	2.387	2.955
Strain at break (%)	10.343	10.327
Modules (MPa)	113.9	145.1
Viscosity (Pa.s)		0.065

The tested wood specimens must fail by wood failure and contain fibers from the opposite wood specimen, indicating that the wood adhesion is stronger than the wood specimen. Typical tested specimens are shown in Figure 27. The shear strength should be higher then 1 MPa, which is the standard value of EN-314.



Figure 27. Tested wood specimens based on excellent, good and failed rupture.

3.2 Model compounds

Typical phenolic compounds formed during the HDO of lignin are alkyl phenolics. For this reason, four types of alkyl phenolics, methyl-, di-methyl-, ethyl-, and propyl phenol, were used for the preparation of a PF resin. The expectation would be that the formed resins have more reactivity toward the ortho side, due to the blocking of the para side with alkyl groups. This limitation would result in a less 3D-cross-linked structure, which could make the resin more vulnerable for water. In order to obtain chain building, the compound used should have at least two functional groups available [30]. For example, components such as alkyl guaiacols (4-alkyl, 2-methoxyphenol) have only 1 reactive position and function as chain breaker. The addition of such a component would result in decreased tensile properties. Other phenolics formed carry an additional hydroxide or ether group. Two common found components were selected: Guaiacol and Catechol. Resins were prepared with equal molecular ratios of model compound to phenol and tested as described in chapter 2. The results of the prepared resins with a replacement of 25 mol-% of phenol with model components are presented in Figure 28.

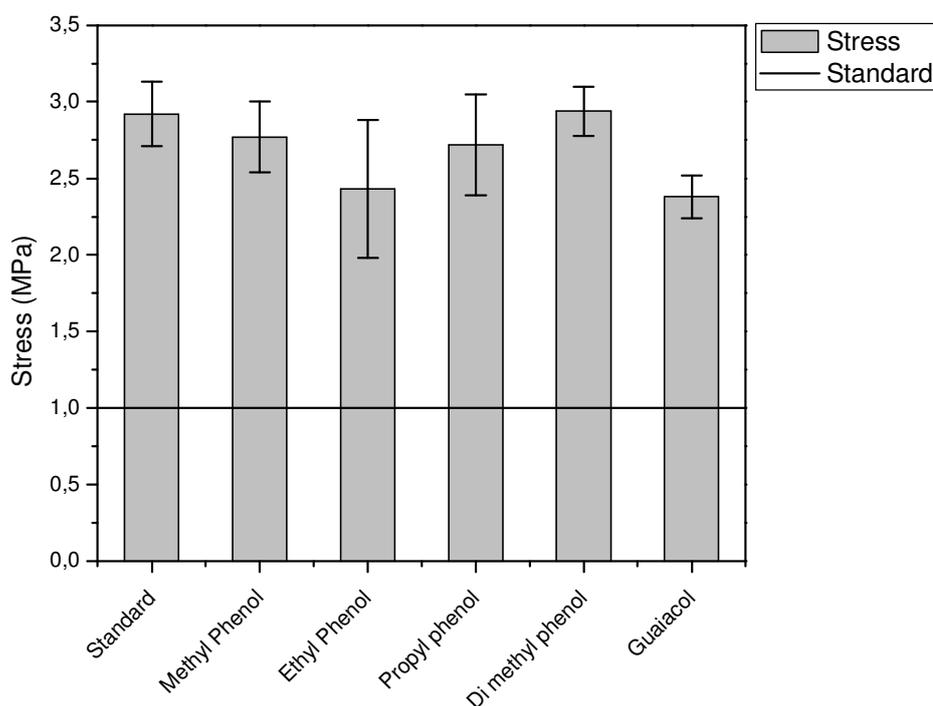


Figure 28. The effect 25 mol-% replaced phenol with model compounds on the shear strength of wood adhesives

The formulation of resins with catechol resulted in the rapid gelation of a solid brittle clod in the first 30 minutes of the reaction. The rapid gelation is the result of the additional hydroxyl group, which makes the resins more reactive towards the initial reaction with formaldehyde.

The result represented in Figure 28 indicates that all samples replaced with 25 mol-% model compound passes the EN-314 standard. The shear strength is in all cases significantly higher than the standard (almost 3 times the standard). The variation in the standard deviation of the samples is high, so there can only be spoken of speculative trends. All formed resins indicate results comparable with the standard; only the resin containing guaiacol shows decreased shear strength. The formed resin with guaiacol was, compared to the other resins, the only resin which was not transparent. This could lead to a higher amount of solids which would decrease the tensile properties.

Based on the good result obtained with 25 mol-% replacement, additional resins were prepared with 50 mol-% phenol replaced with model compound. The results are presented in figure Figure 29

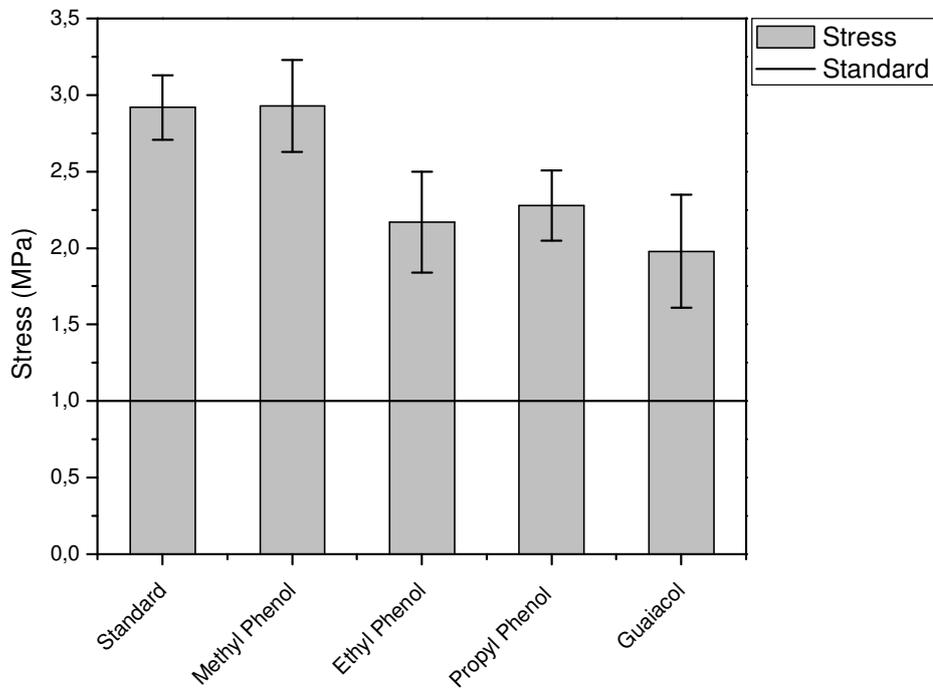


Figure 29. The effect 50 mol-% replaced phenol with model compounds on the shear strength of wood adhesives

The results represented in Figure 29 indicate that all samples replaced with 50 mol-% model compound passed the EN-314 standard. The shear strength is in all cases significant higher than the standard. The addition of higher molecular weight alkyl phenolics results in decreased shear strength, as methyl phenol gives comparable result with the standard and ethyl and propyl indicates decreased shear strength. This could be a result of the limited 3D-cross-linking due to the longer alkyl chain, which makes the resin more vulnerable for water [30]. The prepared resins with guaiacol gives decreased shear strength compared to the standard. All resins measured indicate decreased shear strength compared to the result obtained with 25 %-mol replacement, except for the methyl phenol, which gives comparable result with 25 %-mol replacement.

3.3 Mixtures

To simulate the influence of HDO oil on the adhesive properties, two mixtures were prepared based on the selected model compounds. The composition of the mixture is given in Table 8 and the results are presented in Figure 30.

Table 8. Chemical composition of prepared resin with a mixture of model compounds

Compound	Mixture 25% <i>(gram)</i>	Mixture 50% <i>(gram)</i>
Phenol	8.7	5.8
Cresol	0.75	1.5
Ethyl Phenol	0.75	1.5
Propyl Phenol	0.75	1.5
Guaiacol	0.75	1.5
Catechol	0.75	1.5
Formalin	20	20
Water	11.1	11.1
Natrium Hydroxide	1.5	1.5
1 st addition	3	3
2 nd addition	3	3

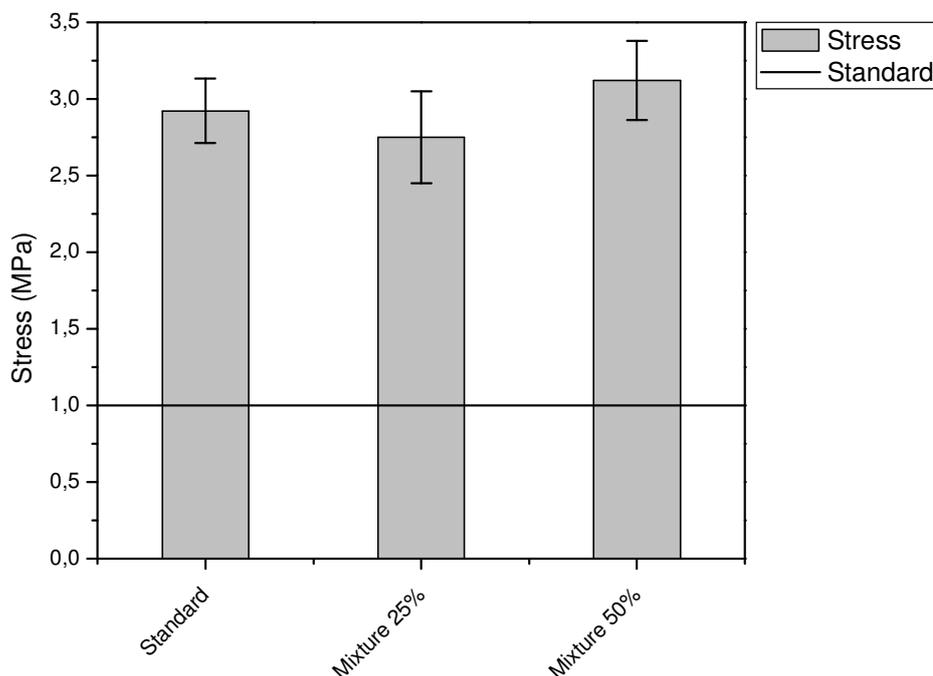


Figure 30. The effect 25 and 50 mol-% replaced of phenol with a mixture of model compounds on the shear strength of wood adhesives

The result represented in Figure 30 indicates that both mixtures pass the EN-314 standard and give results comparable with the standard. However, the shear strength of both mixture and especially of the 50 %-mol mixture indicates increased shear strength, which is conflicting with the observation made with the model compounds. The model compounds indicate decreased properties with increased amount of replacement. This could be a result of the addition of a small amount of catechol, which was not testable as model compound due to rapid gelation on formulation. The overall result of the mixture seems to be promising for further work. A replacement of 50 mol-% of phenol could produce a resin with the properties of a pure phenol based resin.

4. Conclusion & recommendations

All prepared model resins were far above the EN-314 standard of 1 MPa. Prepared resins with 25 %-mol phenol replaced with model compound gave results comparable to the standard. Only Guaiacol gave slightly decreased shear strength. The resins prepared with 50 %-mol phenol replaced with model compound gave decreased properties compared to the standard. Only methyl phenol gave similar results compared to the standard. Resins prepared with catechol resulted in a rapid gelation of the resins.

The model resins became more vulnerable for water with an increased replacement of model compound, which is the result of limited 3D-cross linking [30].

The prepared mixtures gave properties comparable to the standard. In the case of 50 %-mol replacement increased shear strength was observed, which is in conflict with the result from the model compounds. This could be the result of the small amount of catechol, which could positively increase the tensile properties of the resin.

Further exploration of the possible 75-100 %-mol replacement of phenol with model components is required. The prepared resins will give an indication of the maximum phenol replacement in a bio-based adhesive. After the model component study, real HDO oil needs to be tested. The HDO oils consist out of a complex mixture of components, which could lead to other properties compared to the model study.

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5. Appendices

A. Optimization experiments

This paragraph will give a short overview of the influence of several parameters in the setup on the oil yields. The parameters were selected based on the low light oil yield obtained from earlier experiment presented in Figure 12. The mass balances in this paragraph were based on liquid and solid yields.

Tracing the gas stream:

The first experiments in the continuous reactor resulted in no oil trapped in the condenser and a multiphase oil remaining in the reactor. To get rid of the possibility that evaporated light oil was trapped in the gas tube leading to the condenser, the gas tube was traced with a heating cord, with a temperature range between 0-350 °C. Two experiments with varied tracer temperature were carried out (Experiments: CLR015 and 017). The mass balances are presented in Figure 31

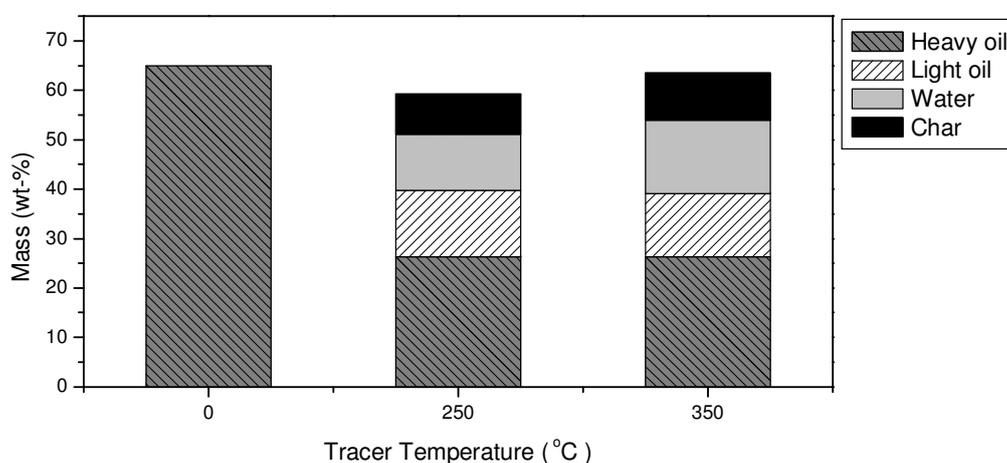


Figure 31. Mass balances for the HDO of ALCELL[®] lignin at different tracer temperatures (CLR015, 017)(400 °C, 80 bar, 200 ml.min⁻¹, 4 h)

The first observation with traced experiments was the production of light oil and water trapped in the condenser. The second observation was a slightly increased light oil yield with increased tracer temperature, but the difference is almost negligible. For remaining experiments a tracing temperature of 350°C was chosen.

Hydrogen flow:

Another interesting parameter in the reactor setup was the hydrogen flow. The hydrogen flow was measured in the beginning of the reactor with a flow meter and at the end of the reactor with a bubble soap flow meter. The flow was adjusted with a back pressure valve.

To gain insight in the influence of the hydrogen flow on the HDO of lignin two identical experiments (CLR011, 013) were carried out with different hydrogen flows. The mass balances are presented in Figure 32.

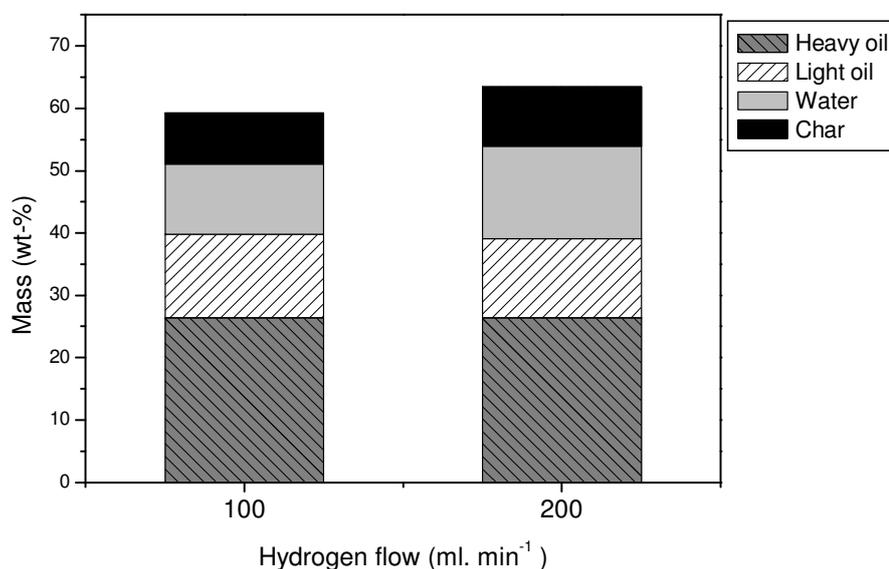


Figure 32. Mass balances for the HDO of ALCELL[®] lignin at different hydrogen flows (CLR011, 013)(400 °C, 130 bar, T_{tracer}: 250°C, 4 h)

The results in Figure 32 showed a small amount of light oil with a low hydrogen flow and a significant increased amount of light oil with a hydrogen flow of 200 ml. min⁻¹. Based on these result the future HDO experiment were carried out with a hydrogen flow of 200 ml.min⁻¹.

B. Gas analyses calculation

The gas composition was analyzed during the reaction. In the first hours 4 gasbags were collected with intervals of 15 minutes. After the first hour every hour one gas bag was collected. After the experiments the gasbags were measured on a gas GC.

With the assumption of ideal gas behavior, the moles of gas in the gas bags can be calculated for the pressure temperature and volume with the ideal gas law. The equation will be as followed:

$$n_{gas} = \frac{p \cdot V_{gas}}{R \cdot T} = \frac{p \cdot (t \cdot \Phi_{V,H_2})}{R \cdot T}$$

where:

n_{gas}	= number of moles in the gas phase inside the gasbag	[mol]
p	= Pressure inside the gasbag (assumed atmospheric)	[Pa]
V_{gas}	= volume occupied by gas in the reactor (gascap and bubbles)	[m ³]
T	= Temperature in the gasbag (assumed room temperature)	[K]
R	= gas constant	[J. mol ⁻¹ . K ⁻¹]

The gasbag measured at the end of the experiment was used for the total composition of the remaining gas in the setup. With again the ideal gas law and the concentrations measured above a total gas balance was taken over the system. The gas law for the last sample was slightly adjusted and the equation will be as followed:

$$n_{gas} = \frac{p \cdot V}{R \cdot T} = \frac{p_{reactor} \cdot V_{reactor}}{R \cdot T_{reactor}} + \frac{p_{condensor} \cdot V_{condensor}}{R \cdot T_{condensor}} + \frac{p_{nockbackvalve} \cdot V_{nockbackvalve}}{R \cdot T_{nockbackvalve}}$$

where:

n_{gas}	= number of moles in the gas phase in the whole system	[mol]
p	= Pressure the reactor, condenser or nock-back-valve	[Pa]
V	= Gas volume in the reactor, condenser or nock-back-valve	[m ³]
T	= Temperature in the reactor, condenser or knock-back-valve	[K]
R	= gas constant	[J. mol ⁻¹ . K ⁻¹]