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Catalytic Fractionation of Larch Wood

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I Abstract

With the depletion of fossil based carbon sources it will be of increasing interest to find a suitable, sustainable and renewable replacement. One promising candidate for this is lignocellulosic biomass. Therefore, the effects of different conditions and catalysts on a simultaneous fractionation and depolymerization of lignin from larch wood via a so-called ECCL (**E**arly stage **C**atalytic **C**onversion of **L**ignin) process were investigated. The main aim of this thesis was to gain maximum yields of the so-called bio-oil with least possible pulp degradation. Additionally, the experimental conditions were optimized to achieve the highest possible aromatic monomer content in the oil, due to them being the most economically valuable compounds originating from lignin.[1] In order to achieve this, 16 experiments were conducted in a 500 ml batch reactor. Of each experiment the yields of oil, aromatic monomers, solid lignin, pulp and residual lignin in the pulp were determined. The effects of hydrogen, various temperatures, different types of metallic catalysts, their support material (kaolin), and sulfuric acid on the yields of the process were examined. Sawdust from larch wood was chosen as feedstock. The metallic catalysts (NiO on kaolin and Raney nickel) and the support material alone (kaolin) showed no sufficient effect on lignin depolymerization. However, molecular hydrogen, increasing temperatures and sulfuric acid increased the yields of oil. In addition, 0.11 vol% sulfuric acid lead to a better pulp quality. The yields of aromatic monomers were determined via GC-MS and GC-FID and the molecular size was determined via a size exclusion chromatography. The following experimental conditions – 35 g of larch sawdust (on a dry basis), 350 mL ethanol/H_2O 75/25 v/v, 179 °C, 1 h, 40 bar H_2, 0.11 vol% H_2SO_4 – achieved the best results with yields of 53.0 wt% oil, 6.7 g pulp, a delignification efficiency of 89.8 %, 35.6 wt% solid lignin and 4.30 wt% of aromatic monomers.

II Kurzfassung

Da die fossilen Kohlenstoffquellen nicht erneuerbar sind, ist es für die Zukunft wichtig Alternativen zu ihnen zu finden, wofür Lignozellulose ein vielversprechender Kandidat ist. Daher wurden die Auswirkungen von verschiedenen Prozessbedingungen und Katalysatoren auf die gleichzeitige Depolymerisierung und Separation von Lignin aus Lärchenholz mittels eines sogenannten ECCL (**E**arly stage **C**atalytic **C**onversion of **L**ignin) Prozesses untersucht. Ziel war es insbesondere eine größtmögliche Menge von sogenanntem Bio-Öl zu erhalten ohne den wertvollen Pulp abzubauen. Im Öl wiederum sollte der Gehalt der aromatischen Monomere maximiert werden, da sie den höchsten wirtschaftlichen Wert haben.[1] Dazu wurden 16 Versuche in einem 500 mL Batch Reaktor durchgeführt. Von jedem Versuch wurden die Ausbeuten an Öl, aromatischen Monomeren, festem Lignin, Pulp und Restlignin im Pulp festgehalten. Es wurden die Auswirkungen von Wasserstoff, variierenden Temperaturen, unterschiedlichen metallischen Katalysatoren bzw. deren Trägermaterial (Kaolin) und Schwefelsäure auf die Ausbeuten des Prozesses untersucht. Als Rohstoff wurden Lärchensägespäne verwendet. Die metallischen Katalysatoren (NiO und Raney Nickel) zeigten keine ausreichende Effektivität, allerdings hatten Wasserstoff, erhöhte Temperaturen und Schwefelsäure positive Effekte auf die Ölausbeuten. 0.11 vol% Schwefelsäure erhöhten zudem die Qualität der Zellulosefasern. Die Ausbeuten von aromatischen Monomeren wurden mittels GC-MS und GC-FID bestimmt. Durch Größenausschlusschromatographie wurde die Molekülgröße ermittelt. Unter den folgenden Bedingungen – 35 g Lärchensägespäne (wasserfrei), 350 mL $EtOH/H_20$ 75/25 v/v, 179 °C, 0.5 h, 40 bar H_2, 0.11 vol% H_2SO_4 – wurden die besten Ausbeuten mit 53,0 Gew.% Öl, 6,7 g Zellulosefaser, 88,3 % Delignifizierungseffizienz, 35,6 Gew.% festem Lignin und 4,30 Gew.% aromatischen Monomeren erzielt.

III Danksagung

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IV Table of contents

1. Introduction

Lignin is the most abundant aromatic polymeric biomolecule in the world. It typically occurs together with cellulose and hemicellulose in so-called lignocellulose, which is the main constituent of wood.[2] At the moment the main source of lignin is the pulp and paper industry where it occurs in a highly altered form as a by-product named black liquor. Due to its good heating values and its poor quality for further chemical processing it is mostly burned directly at the paper mills to produce energy. There is, however, the possibility to convert lignin into valuable chemicals due to its aromatic monomer constituents – see Figure 1 and Table 1. Recent literature lays a focus on approaches that treat lignin as a valuable side product – if not even as the main product ("lignin first approaches") – instead of treating it just as a low value fuel.[3,4] For an effective valorization, it would be desirable to completely convert lignin to a monomer with high market value, such as vanillin. However, it is extremely difficult to adjust the processing conditions to depolymerize the relatively stable lignin quantitatively without extensive degradation of the pulp. Due to this limitation, a suitable catalyst has to be found that facilitates the depolymerization of lignin under relatively mild conditions. This catalyst also has to be separable from the product streams to be reusable. Therefore, the active material of the catalyst should be impregnated on a pelletized carrier material for better handling.

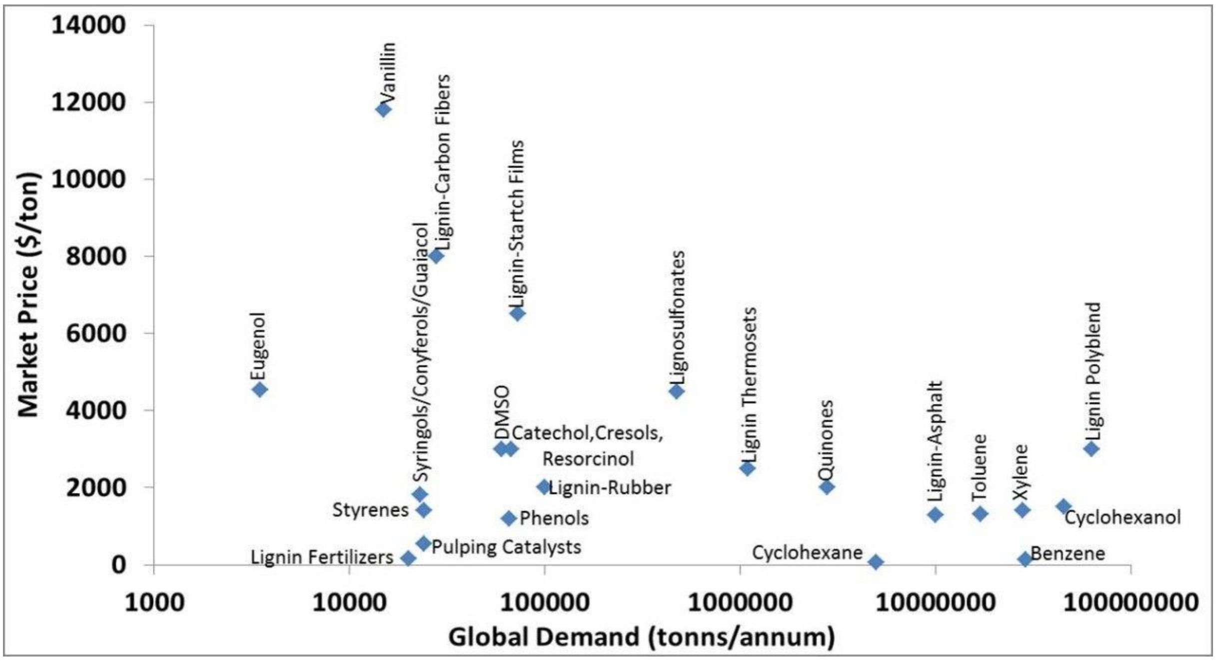

FIGURE 1: Market prices of lignin derived monomers[1]

TABLE 1: Market prices of wood products

Product	Wood	Humidity [wt%]	Price/ton [€]
firewood	beech	22	71-85[5,6]
building timber	larch	22	172-210[5,7,8]
pulp	-	10	700-750[9,10]
vanillin (synthetic)	-	-	8700-10400[1]
black liquor*	-	-	140-337

*calculated from its heating value (12-14 MJ/kg)**[5]** x the price of a kWh of combustion energy of heating oil (4-9 cents/kWh)

The aim of this thesis was to find a process for the effective fractionation of larch wood saw dust from European larch (*Larix decidua*) that enables maximum valorization of the lignin fraction. We decided that depolymerization of the polymeric lignin to its monomeric units would be preferable, as they have the highest economic potential.[1] Therefore, a literature screening for fractionation processes was performed and it was decided to study the recently developed **E**arly stage of **C**atalytic **C**onversion of **L**ignin (ECCL) approach. The basic idea behind ECCL is to generate a one pot process with simultaneous valorization of both, the lignin and the cellulose fractions.[3,4] Considerations for an effective valorization of lignin have also to take the quality of the pulp fraction into account because of its distinctly higher market value compared to lignin. Due to this, we tried to find a way to depolymerize lignin, whilst preserving the pulp. For this, we tried various catalysts and co-catalysts and we varied the reaction conditions i.e. the temperature, the atmosphere (H_2 or N_2), the reaction time and the pH.

2. Theoretical background

2.1 Lignocellulosic biomass

In order to become independent of decreasing fossil oil, it is necessary to find a suitable alternative. Biomass, as a renewable and naturally in high amounts occurring matter, is a promising candidate to be this substitute.[11] It delivers both, energy and raw materials for the chemical industry, and there are already many technologies in use for biomass valorization, most prominently the pulp and paper industry, and the combined heat and power production (CHP).[12] However, in order to completely replace fossil carbon sources with biomass, a lot more effort has to be put into the valorization of it. Wood consists mainly of lignocellulose, which is a mixture of cellulose, hemicellulose, and lignin. The amounts of the respective compounds change for different plants and different sorts of wood i.e. hard or soft wood.[2] Table 2 shows the relatively high degree of variation in between the compositions of the different species.[13]

TABLE 2: Distribution of the main constituents in different wood species

Feedstock	**Cellulose [wt%]**	**Hemicellulose [wt%]**	**Lignin [wt%]**	**Extractives[b] [wt%]**
Scots pine[14]	40.7 ± 0.7	26.9 ± 0.6	27.0 ± 0.0	5.0 ± 1.0
Norway Spruce[14]	42.0 ± 1.2	27.3 ± 1.6	27.4 ± 0.7	2.0 ± 0.6
Larch[15–17]	41[a]	30[a]	24–32	1.6–6.6
Silver Birch[14]	43.9 ± 2.7	28.9 ± 3.7	20.2 ± 0.8	3.8 ± 1.3
Sugarcane Bagasse[18,19]	42	25	20	NA

[a]These values are taken from *Larix sibirica* not *Larix decidua*. [b]These are non-structural organic and inorganic components like waxes, fatty acids, resin acids, terpenes, proteins, ash etc.[20,21]

The three polymeric macromolecules cellulose, hemicellulose, and lignin are the main components of the cell walls of plants and are responsible for their structural stability. Cellulose is made up of glucose units that are linked via β-1,4-glycosidic bonds. It is the most abundant bio component (several billion tons/year) and has a very important role in earth's carbon cycle.[22] Cellulose is insoluble in water, dilute acidic solutions and dilute alkaline solutions at room temperature. It's main components are carbon, hydrogen and oxygen with 44.44 wt%, 6.17 wt% and 49.39 wt% respectively.[23] The polymeric cellulose chains (degree of polymerization: 1000–10000) are grouped together and form micro fibrils by hydrogen- and van der Waals bonds.[22] These micro fibrils are bundled together to form cellulose fibers. Hemicellulose is the second most abundant carbohydrate based polymer of lignocellulose (20–50 wt% of lignocellulose biomass). It surrounds the cellulose fibers and is linked to lignin via chemical bonds.[23] It is not as homogeneous as cellulose and consists of various 5- and 6-carbon sugars such as arabinose, galactose, glucose, mannose and xylose, as well as glucuronic acid, acetic-, ferulic and p-coumaric acids.[23,24] In addition, it is highly branched and has shorter molecular chains (degree of polymerization: ≤ 200) compared to cellulose.[22,23] Lignin, as a large, hydrophobic biopolymer consisting of phenylpropanoids as monomeric units, acts as a glue between the cell walls, as a structure stabilizer, and as water channel.[12] However, there are more components that make up wood biomass like waxes, resins, terpenes, lipids, proteins and other smaller molecules such as vitamins, colorants and odorants. One difficulty of using wood as feedstock for raw materials is the strong interaction of its various components. It is not easy to separate the respective parts i.e. lignin and cellulose, in a non-destructive way. One big industrial process where cellulose and lignin are separated, is the so-called kraft process in the paper industry. Here, wood is treated with Na_2S and NaOH in order to dissolve the lignin.[25] However, this highly alters the chemical structure of lignin and at the moment there are very limited ways to chemically valorize it further, so that it is just used as a low value fuel. Nevertheless, due to its high amount of aromatic compounds, it is very tempting to develop a process for lignin valorization.[1]

2.1.1 European larch

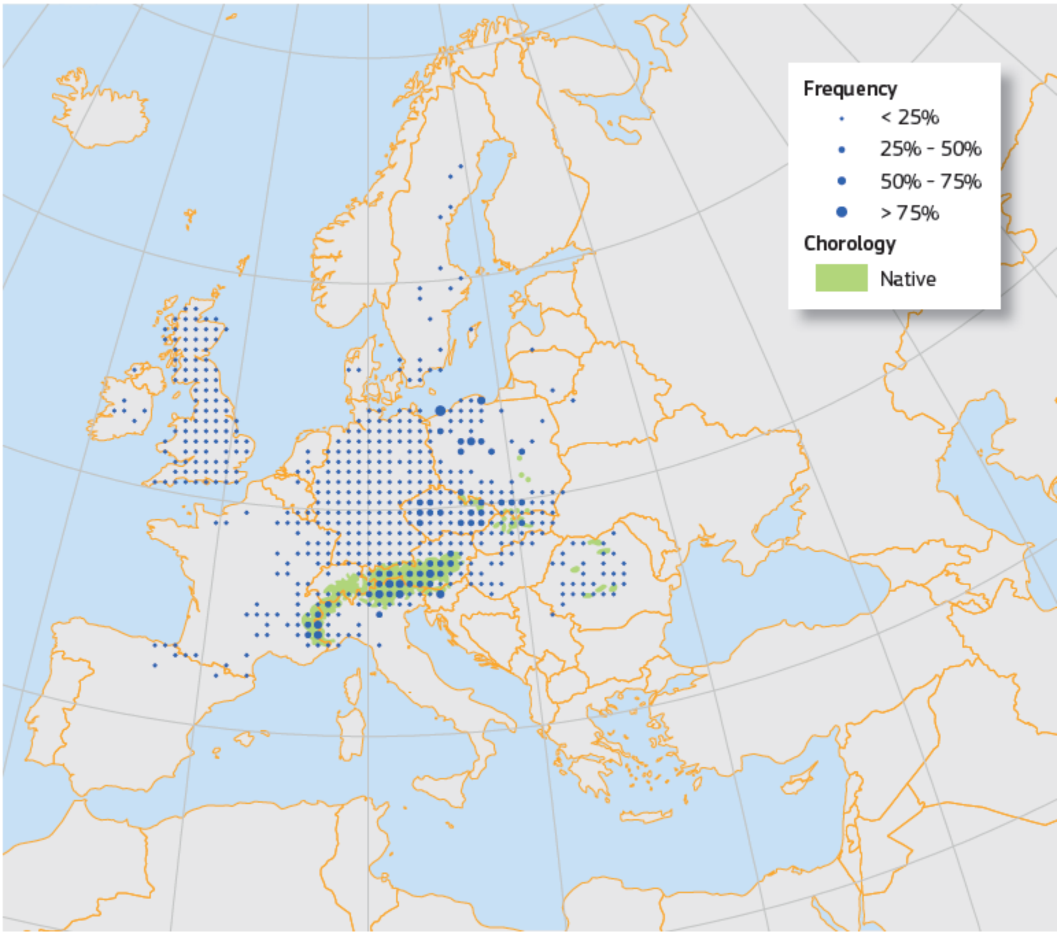

FIGURE 2: Distribution of European larch[26]

The European larch (*Larix decidua* Mill) is native mainly in the Alps and the Carpathians – see Figure 2. It is part of the bigger family of the Larix species, which is distributed from the Alps in central Europe to large areas in northern America, the Taiga in Siberia, as well as to China and Japan.[27] It grows up to 45 m, its diameter reaches up to 1.5–2.5 m and the wood has a high resistance to pests, high durability and good fiber properties.[26] European larch can life for a maximum of 800 years. They are pioneer plants which means that they grow fast (10 m^3 ha^{-1} y^{-1}) at a juvenile stage but their growth slows down when they get older.[27] 26 % of the Austrian total forest area are covered with larch. Its wood has a very high strength (the strongest amongst softwoods in common use) and in addition to the linear growth of its stem, has good properties to be used for furniture. However, due the coloring of its wood and the high amount of bark (16 – 24 %) it is not very desired for the pulping industry.[27] The Klason lignin (method of total lignin determination in wood or pulp – see chapter *3.3.4 Klason* *lignin determination*) content of European larch is in between 26.6 – 32.0 wt% with an average of 29.1 wt%.[16]

2.2 Lignin

Lignin is the second most abundant biopolymer after cellulose with a share of approx. 30 % of the organic carbon in the biosphere.[28] In addition, it is the largest source of aromatic compounds in nature, providing a huge potential for industrial applications.

Lignin has several biological functions:

- It gives rigidity to cell walls and makes plant fibers stiff, so that it mechanically strengthens stems and branches.
- It acts as a glue and sticks the cells together.
- It makes the cell wall hydrophobic. Due to this, lignin is very important in the water transport within in the plant and acts as a water channel. Carbohydrates are hydrophilic and therefore attract water, which would cause them to swell, making them not suitable to act as water channels.
- Lignin is very resistant to bio degradation. Only a few specialized bacteria and fungi can degrade it.[29]

Lignin is a complex three-dimensional polymer mainly consisting of three phenol-containing monomers: Synapyl alcohol, coniferyl alcohol and paracoumaryl alcohol – see Figure 3.[30]

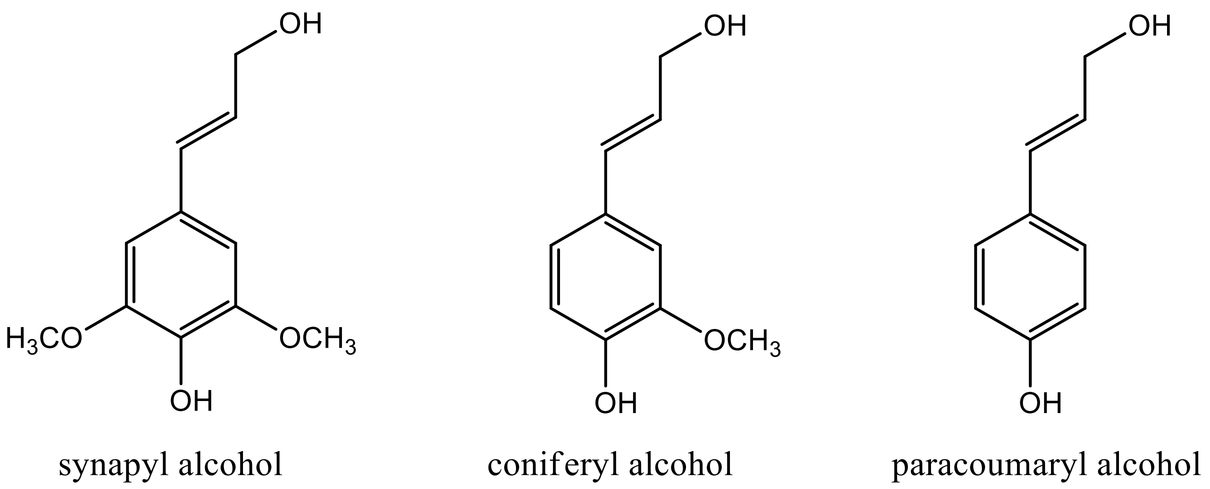

FIGURE 3: The three basic monomers of lignin. Calvo-Flores – 2015[12]

As shown in Table 3, the actual composition of lignin varies between different tree species. Hardwood lignin contains more sinapyl groups, whereas softwood lignin is mainly built up by conferyl groups. Grass lignin on the other hand consist mainly of p-coumaryl groups, which are very seldom found in the other mentioned species.

TABLE 3: Composition of some classes of lignin[22,24]

Scientific name	Common name	p-Coumaryl alcohol [%]	Coniferyl alcohol [%]	Sinapyl alcohol [%]
Coniferous	Softwoods	<5	>95	0
Eudicotyledonous	Hardwoods	0-8	25-50	45-75
Monocotyledonous	Grasses	5-35	35-80	20-55

Due to the different structures of the monomers – see Figure 3 – they also tend to prefer different bonding patterns. Sinapyl for instance, has no free C atom next to the OH group on the six membered ring. This leads to less CX-C5 bonds and to a preference of β-O-4 ether linkages, which in turn can be easier cleaved by different measures. As hard woods contain more Sinapyl alcohol, their lignin can be easier isolated and depolymerized, if the cleavage of the β-O-4 bond is the dominating mechanism to achieve depolymerization.[31] Because of the random polymerization of the monomeric units, there are a lot of different binding motifs. In fact, there are over 20 known bonding patterns for the linkage of the various monomeric units. The most important ones are: β-O-4 ether bonds (45-48 % in native lignin), β-5 phenylcoumaran bonds (> 12 %) and smaller percentages of β-β' pinoresionol, diphenyl ether 4-O-5' and β-1' diphenyl methane bonds.[28] The exact amounts of the respective bonding patterns vary from species to species. For purposes of lignin valorization, the most interesting binding motif is the β-O-4 because it can be cleaved relatively easy compared to the others. However, it is not possible to cleave all the bonds of the lignin macromolecule without heavy losses of the aromatic structure. Additionally, re-polymerization can occur during processing. It is suggested that the depolymerization works via a radical intermediate, which is very reactive so that it can attack another carbon atom to form a stable C-C bond, which cannot be cleaved anymore. Unfortunately, up to now lignin mainly occurs as an unwanted byproduct in processes that produce cellulose, e.g. the paper production. Most of the lignin produced is present as so-called black liquor, which is a waste stream in the Kraft process (most important process in the paper industry – see chapter 2.3.1 *Kraft lignin*) and is mainly burned directly at the production facilities. Lignin has a much lower oxygen content than carbohydrates and therefore has a higher heating value.[32] In fact 95 % of the worldwide industrially isolated lignin is used for heat and energy production.[33] So, why is lignin not used more extensively in chemical industry, despite being able to supply high value aromatic compounds that are otherwise only available from petrochemistry? The answer lies in its very complex and inhomogeneous structure. Lignin fractionation is hindered due to its linkages to cellulose and hemicellulose via chemical bonds and van der Waals interactions. Different species, like hard or soft wood trees, have different lignin structures and the structures in the species itself vary for instance with the seasons or the compartments e.g. the bark or the stem.[27]

2.2.1 Industrial lignin sources

Each year the United States alone consumes approximately 10 million tons of industrial organic chemicals and 325 million tons of liquid transportation fuels.[22] Currently, the United States converts approximately 15 million tons of agricultural products into liquid fuels (ethanol and biodiesel) and discards approximately 270 million tons of agriculturally derived residues in the form of harvestable crop residues, animal manure, forest residues, and the organic fraction of municipal solid wastes.[22] There are several technical processes for the valorization of lignocellulosic biomass available, including pyrolysis, gasification, thermochemical liquefaction (pyrolytic process including H_2, CO and CO_2 + catalysts), hydrolytic liquefaction (includes the use of acids or alkalis), fermentation and pulp/paperboard production.[22] Harsh treatment however, leads to severe changes of the structure in lignin. It is better for the efficiency of a process if the substrates are as uniform as possible and in order to get this uniformity it is advantageous to use a rather mild process that keeps the lignin close to its native condition. An example for that is the organosolv process.[34] In Figure 4, a scheme of lignocellulosic biorefinery is shown. The three main streams, cellulose, hemicellulose, and lignin yield different products respectively. Due to different further work up, they have to be separated in order to achieve maximum valorization. Lignin, if it is not burned, at the moment is mainly used in its polymeric form as an additive to natural binders in plastics. Hemicellulose is mainly broken down to its monomers. It is, however, also used in its polymeric form in adhesives or emulsifiers to some degree.

Cellulose can also either be valorized in its polymeric or monomeric form. Cellulose fibers are a high value product used in the textile production and in paper making. The monomer (glucose) can be fermented to ethanol, which is a bio-fuel, or converted to hydroxymethylfurfural which can be used as a platform chemical for the chemical industry.

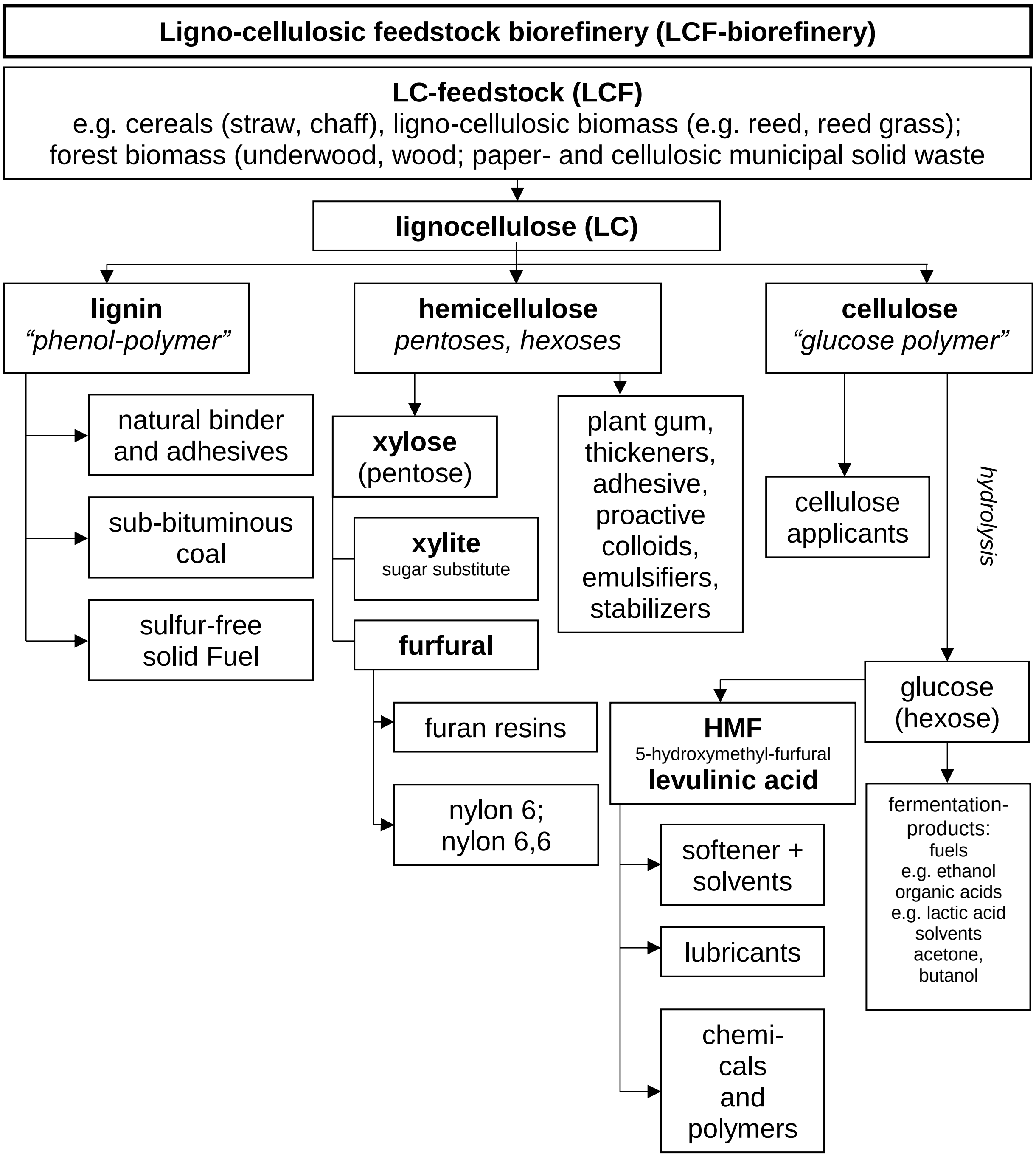

FIGURE 4: Pathway of biomass valorization. Redrawn from Kramm, Gruber et al. 2006[22]

As mentioned before, the common technical processes in which lignin occurs in larger quantities highly alter lignin and change its structural properties. Table 4 shows a comparison of properties of different technical lignins. Of particular interest are the sulfur content and the water solubility, which are linked to each other – a higher sulfur content in the lignin leads to better water solubility.[22] This is the main reason for the higher water solubility of lignosulfonate in comparison to kraft lignin or soda lignin. During pulping, a lot of polar, charged sulfonate groups get attached to lignosulfonate, making it more water soluble than kraft lignin where sulfur gets attached to the lignin in form of sulfides which forms either thiols or carbon-sulfur-carbon bonds. Although both of these bonds are polar, they lack charge, in contrast to the sulfonate groups. Soda lignin in comparison uses no sulfur containing reactant at all and thus has the lowest water solubility.

TABLE 4: Comparative properties of commercial lignins[22]

Property	Softwood Kraft lignin	Softwood lignosulfonate	Soda lignin from straw
carbon %	66	53	56
hydrogen %	5.9	5.4	7.5
methoxy, %	14	12.5	N/A
ash %	3	2.5	<2.5
sugars %	Low	Up to 50 %	2.5-3.5
sulfur %	1.6	6-7.9	N/A
water solubility	Low	Very high	Very low
T_g, °C	140	Not detected	150
mol. wt.	2000	400-150000	2300-2900

2.3.1 Kraft lignin

The kraft process was developed 1879 in the town of Danzig by Carl Dahl and is named after the German term for strength “Kraft”, due to the superior robustness of its pulp.[35] It is currently the most important process for the paper and pulping industry, using NaOH and Na_2S at elevated temperatures and pressures to pulp wood.[36–38] The main advantages are the high strength of kraft pulp, the efficiency of lignin removal, the ability of the process to handle different feedstocks, and the high recovery efficiency of chemicals, which is about 97 %.[38] Each year approximately 130 million tons of kraft pulp are produced, which accounts for around 80 % of the global pulp production.[35,39] The first steps of all pulping techniques (kraft, sulfite process, etc…) is the debarking of the wood. The bark can be further processed to products like poultry litter and bark mulch or just be burned to generate heat. Then, the debarked wood is brought to a uniform size via a mechanical chopping process to assure consistent chemical penetration during the reactions.[40] After this, the chips are brought into a reactor where they are cooked with a solution of Na_2S and NaOH (“white liquor”) at temperatures from 155–175 °C for several hours. Subsequently, the pulp is separated from the cooking liquor and both streams are treated separately. These harsh conditions are able to delignify the wood to a range of 90–95 %, whilst creating a lignin enriched liquid phase (“black liquor”) and the solid pulp. The lignin in the black liquor is depolymerized, highly altered and contains significant amounts of sulfur, which makes it almost completely unsuitable for any further valorizations. Therefore, black liquor is typically concentrated via several evaporators and concentrators to a solid content of 60-70 % (of which 30-34 % are lignin) until it can effectively be burned in a recovery boiler.[40] In order to isolate kraft lignin from the black liquor, it is acidified (pH 1–4) leading to the precipitation of the lignin.[12] The commercially available kraft lignin is gained via separation from the black liquor. This is usually done by ultrafiltration or via acidification, which makes the lignin insoluble, and subsequent filtration.[41,42] The optimal concentration of dry substances in the liquids for precipitation is shown to be 27 % for pine kraft liquor and between 30–35 % for birch liquor.[43] Therefore, the liquor for precipitation is withdrawn from the third evaporation stage in the recovery system. It is possible to separate different fractions of lignin from black liquor with different molecular sizes via the precipitation conditions i.e. the pH. Larger molecules will precipitate at higher pH values than smaller ones. Studies have shown that the sulfur content in the smaller molecules is higher than in the larger ones. The composition of kraft lignin obtained from diluted black liquor (~17–18 % dry matter) at different pH values is shown in Table 5.[44] During pulping, Na_2S (in the form of HS^-) reacts with lignin leading to the odors characteristics of kraft lignin via the formation of volatile, sulfur containing, molecules like methyl mercaptan and dimethyl sulfide.[40] The sulfur content of the precipitated technical lignin is increasing with harsher precipitation conditions. This phenomenon can be explained due to the sulfur containing groups being responsible for the increased water solubility.[44]

TABLE 5: Precipitation of technical lignin depending on the pH[44]

Sample	Carbohydrate	Klason lignin	Acid-soluble lignin	Precipitated material
	%	%	%	%
original pH 9	2.7 ± 0.2	93.7 ± 0.2	2.0 ± 0.1	3.3 ± 0.2
1 kDa perm., pH 9	0.2 ± 0.0	98.2 ± 2.2	3.7 ± 0.0	3.5 ± 1.0
1kDa perm., pH 7	0.1 ± 0.0	96.1 ± 1.0	3.7 ± 0.0	4.3 ± 0.4
1 kDa perm., pH4	0.1 ± 0.0	91.7 ± 0.6	6.2 ± 0.3	4.3 ± 0.4

Inorganic sodium and sulfur in the liquor are recovered via a smelt that mostly contains Na_2S and Na_2CO_3. This smelt then is transferred to another tank, where it is dissolved with water to form the so-called “green liquor”. This liquor is sent to the causticizing plant, where it reacts with CaO (lime) and the Na_2CO_3 is converted to NaOH again with an efficiency of around 80–83 %. The Na_2S is not affected by this step. After the caustization, the green liquor is called white liquor again and is reused for the pulp production. The $CaCO_3$ (lime mud) from the caustization reaction is washed and sent to a kiln, where it is recycled to CaO.[38] In Figure 5 a flow chart of the Kraft process is shown.

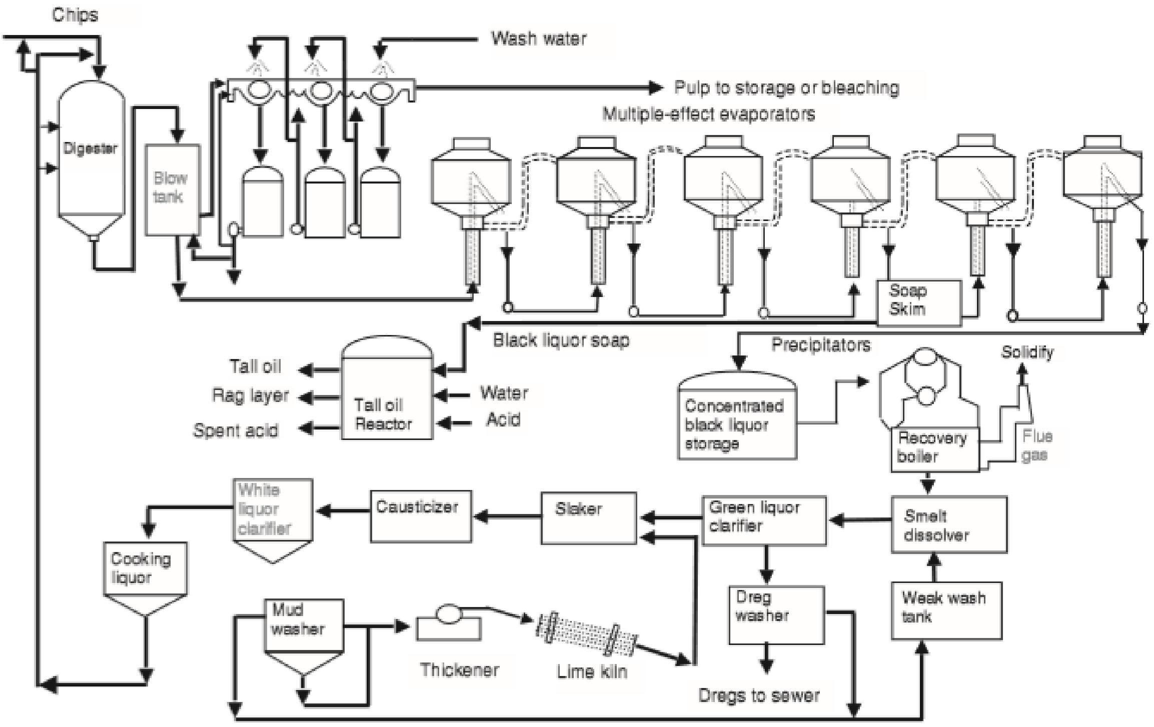

FIGURE 5: Flow chart of the Kraft process. Taken from Pratima Bajpai - 2010[45]

2.3.2 Sulfite process

The sulfite process was patented in 1867 by Benjamin Tilghman and improved by Fry and Ekman, so it is known for a longer time than the kraft process. The first commercial mill was founded in 1874 in Sweden.[46] Today, this acidic process is the economically second most important process in the pulp and paper industry. As in the kraft process, the wood has to be debarked and chipped to a uniform size. The pulp then is separated from the liquor, washed, screened, and bleached. A flow chart of the sulfite process is shown in Figure 6. The acid of choice is sulfurous acid, from which a part is converted to its salts (Ca^{2+}, Mg^{2+} or Na^{+} sulfites or bisulfites) to buffer the solution.[40] During the pulping (~pH 1.5) the lignin molecules are attacked by protons, which causes them to form carbocations. These carbocations react with the sulfites in the solution. After digestion, the so-called red liquor is separated from the pulp and concentrated via various evaporators. Diluted spent liquor from sulfite pulping usually is acidic with a pH of around 3–4. The average content of dry solids in this liquor is 16–17 wt%.[47] Then it is usually fed into a furnace where the organic residues are burned, leaving a magnesium sulfite ash. At the given, high temperatures the magnesium sulfite ash dissociates into MgO and SO_2. The solid MgO is removed from the furnace, brought into water to from a slurry and reacts later with SO_2 to regenerate $MgSO_3$. The SO_2 is scrubbed by water to reform sulfurous acid.[40] The recovery of chemicals is possible if Mg^{2+} or Na^{+} are used but it is difficult with Ca^{2+} due to the poor water solubility of $CaSO_3$ and $Ca(HSO_3)_2$. Most sulfite process pulping mills recover their chemicals, so the isolated lignosulfonates originate from mills that produce more liquor than they have the capacity to burn.[22] It is more challenging to separate lignin from black liquor from the sulfite pulping process than from the kraft process, due to its higher sulfur content compared to kraft lignin. The sulfur content makes it better soluble in water which leads to the necessity of membrane filtration to isolate it.[47]

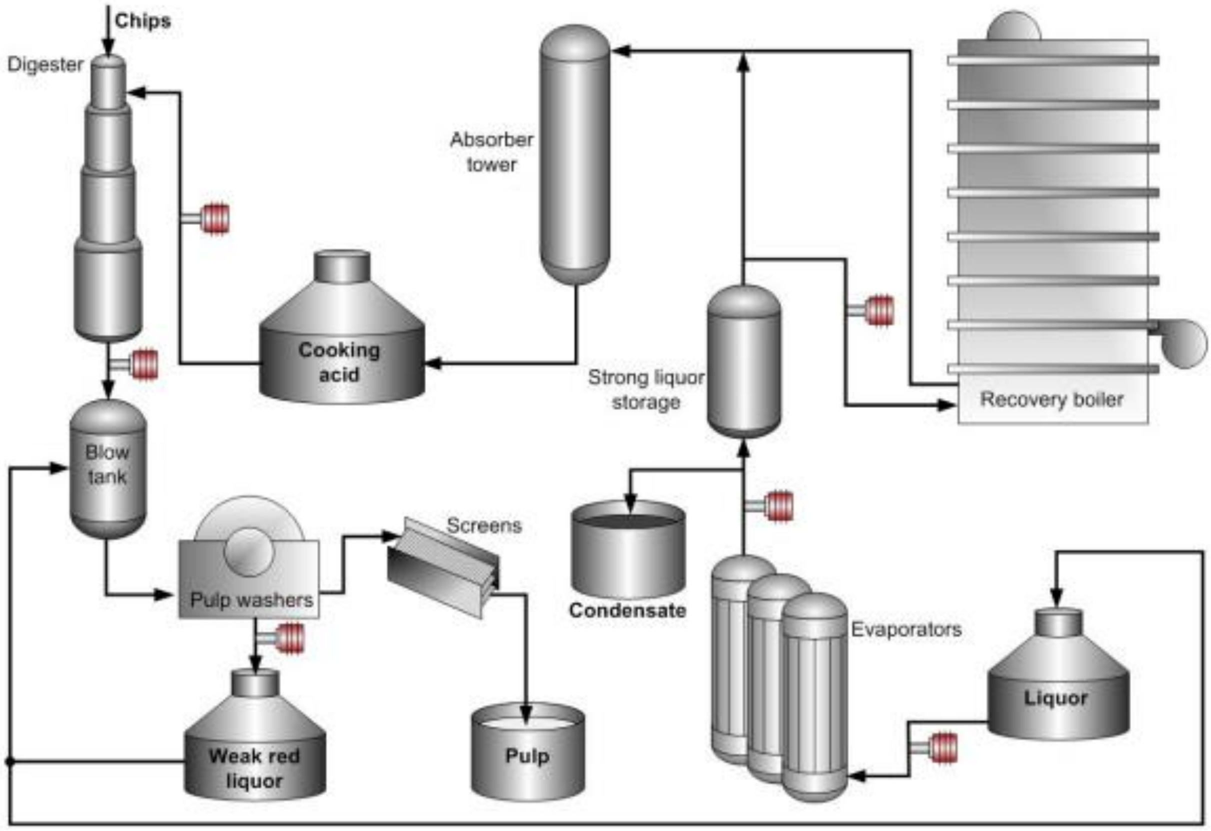

FIGURE 6: Flow chart of the sulfite process[48,49]

The water soluble lignosulfonates already have some applications besides being used as fuel.[41] In Table 6 some examples are given for applications of crude spent liquor of the sulfite process and the lignosulfonate itself. Table 6 also shows that today lignosulfonates are used either without considerably chemical reprocessing directly as filler materials or in a refined state.[22] Amongst the several already used applications is the production of vanillin from sodium lignosulfonates. Natural vanillin is obtained by extraction from the bean or pod of the vanilla orchids. However, the price for natural vanillin is very high, so that most of the global demand for vanillin is fulfilled via petrochemical conversion of guaiacol to vanillin (~85 % of world supply) or oxidation of lignosulfonate or kraft lignin (~15 %).[50,51]

TABLE 6: Major applications of lignosulfonate products[22,50]

Applications of crude spent liquor lignosulfonates	**Applications of refined lignosulfonates**
feed and pellet binders	oil well drilling fluids
feed molasses extenders	dye and pigment dispersants
dust suppression and road stabilization	protein precipitants
granulation and agglomeration	tanning agent
plant micronutrients and horticulture	gypsum board manufacture
agricultural dispersants and emulsifiers	cement manufactures
grinding aids	concrete admixtures
metal ore processing	refractory clays and ceramics
	carbon black
	phenolic resins
	lead acid storage battery plates
	vanillin production

2.3.3 Organosolv lignin

The organosolv process is an efficient process to separate lignin from the carbohydrate streams with organic solvents at elevated temperatures, that is preserving the lignin and the pulp.[52] It was developed in 1931 by Kleinert and Tayanthal.[46] The high quality of this so-called organosolv lignin compared to kraft lignin or lignosulfonate gives the potential for a further valorization.[34] Organic solvents are mixed with water to give final concentrations from 35–75 % and added to the lignocellulosic feedstock, with a solid to liquid ratio from 1:4–1:10 w/w. Acidic, basic, and neutral catalysts can also be used. The operating temperatures range from 120–200 °C, the duration of the reaction time is between 30 and 90 minutes and the pH of the medium ranges from 2 to 12, depending on the used catalyst.[34] The first stages of the organosolv process are the chipping and subsequent pulping of the lignocellulosic feedstock. Pulping with organic solvents under either acidic or basic conditions leads to the ether cleavages of the lignin- and lignin-carbohydrate bonds. According to Figure 7, this creates a solid phase that mainly consists of cellulose and hemicellulose and a liquid phase containing dissolved lignin. This two-phase system then is filtrated in order to separate the streams. The solid is washed with warm pulping liquor to prevent lignin precipitation and then is further washed with an excess of warm water to get rid of residual organic solvent. Subsequently the filtrate (solvent) is recovered via distillation. During this distillation, the concentration of the organic solvents decreases which causes the lignin to precipitate. The concentrated liquor is filtrated, isolating the solid lignin phase, the solvent, and dissolved hemicellulose degradation products, like furfurals and acetic acid.[34] The solvent is again purified via distillation. It should be mentioned that organosolv can also be used as a pretreatment step. In future also other applications for lignocellulosic biomass valorization than pulp and paper making may become of increased importance, so a non-disruptive way of separation might become more important.

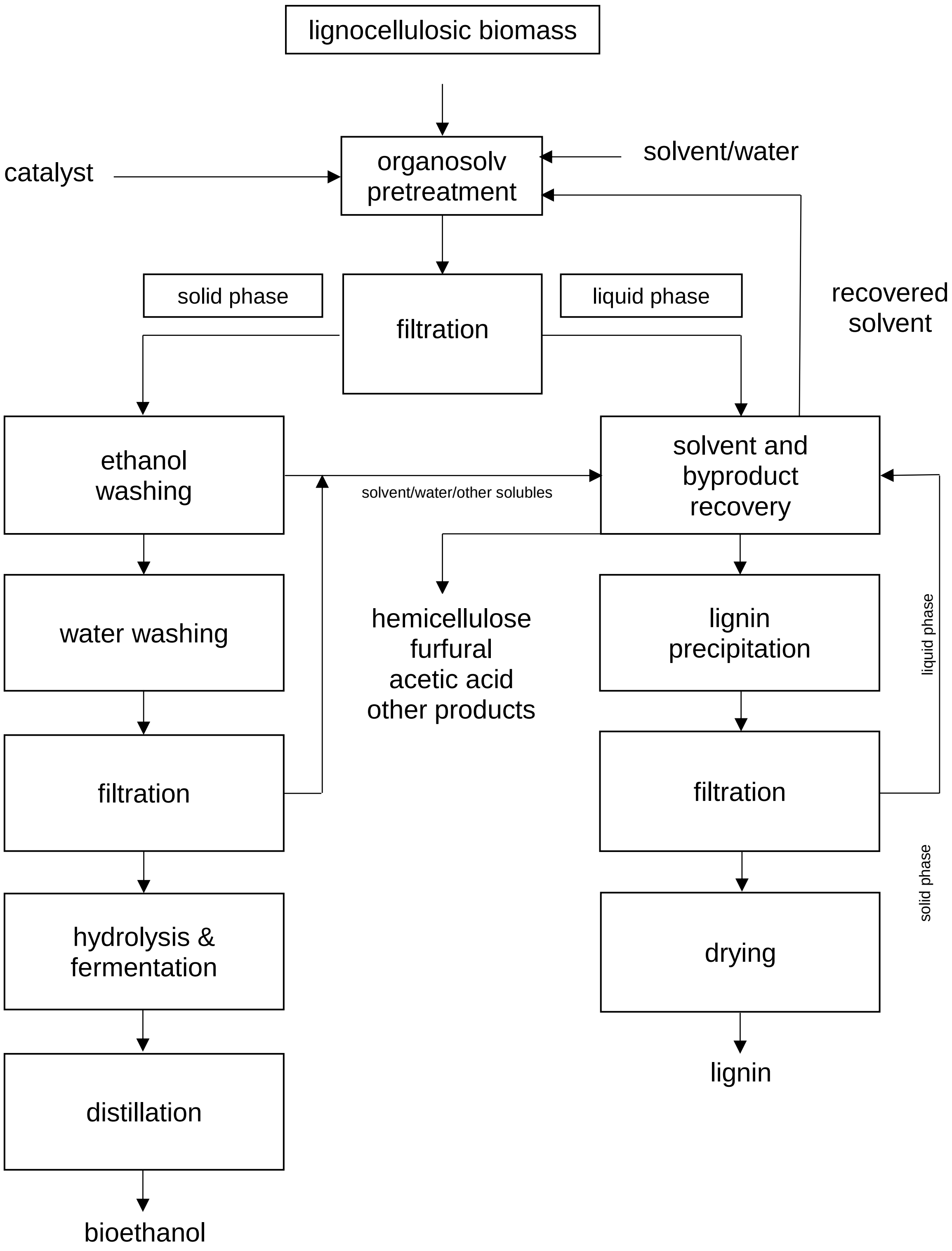

FIGURE 7: Biorefinery concept inclucing organosolv pretreatment, redrawn from Borand, Karaosmanoğlu – 2018[27]

The main advantages of the organosolv process are[34]

- The clean, in comparison to kraft and sulfite pulping, less-disruptive separation of the three streams i.e. cellulose (solid), hemicelloluse (dissolved in water) and lignin (first dissolved then precipitated).
- Due to the mild conditions, each of the three streams can be further converted to value added products.
- In contrast to sulfite- and kraft pulping, organosolv pulping uses no sulfur compounds. This has a positive impact on the environment and benefits for downstream valorization, as sulfur is a catalyst poison.
- The solvents can be recovered.
- Both, woody and nonwoody biomass, can be used as feedstock.
- Renewable solvents with low boiling points can be easier recovered than NaS/NaOH or $MgSO_3H$.
- There have been already pilot plants operating, yielding outputs of over 5000 tons of pulp per year. However, no plant is still operating at the moment.[53]

The main disadvantages include[34,54]

- The high solvent consumption.
- Extra caution has to be applied due to the volatile and explosive solvents being used.
- The solvent recovery is energy intensive.
- High initial investment costs

Currently, the organosolv process plays an underpart in the global pulping industry, which is dominated by kraft and sulfite pulping. There are several reasons for this:

- Kraft and sulfite pulping are very old processes, so a lot of optimization has already been done e.g. in terms of chemicals recovery.
- Even though kraft and sulfite pulping give lignin in very poor quality as a byproduct, its heating value alone generates value and these plants are self-sufficient in regards to energy.
- Organosolv plants do not generate energy, they need energy for the solvent recovery.

The quality of organosolv lignin is very high due to its mild process conditions. However, there still is no significant market potential for lignin because the valorization of it is currently not developed far enough.

2.3.4 Pulp bleaching

After digesting, the pulp has to be further processed i.e. oxidized to remove lignin and bark residuals and make the paper brighter and white. Unfortunately, especially kraft pulp has a strong brown color.[45] The brightness of the pulp is measured by the ability of sheets of paper made of the pulp to reflect light of a wavelength of 457 nm. Quality paper should have a brightness of around 90 %. This means 90 % of the incoming light with a wavelength of 457 nm is reflected. The quality and brightness of paper determines its printability. The better the quality of the paper, the better is its printability.[48] Historically, hypochlorite was used to bleach paper, which then was displaced by elemental chlorine. A typical sequence of pulp bleaching was **c**hlorination – **e**xtraction – **h**ypochlorite bleaching (CEH). The chlorination oxidizes the lignin up to mostly carboxylic acids and quinones. However, those compounds are not very soluble in acidic environments, so a basic extraction step had to be performed. Therefore, NaOH was added to the slurry, which converted the carboxylic acids into their respective salts. As a last step, a hypochlorite bleaching was carried out which lead to a final brightness of 85 %. The next development step was the use of ClO_2 instead of elemental Cl_2, which lead to a brightness of 90 %. An additional advantage was that ClO_2 reacts very specifically with lignin and barely touches the carbohydrates. Over the time, more and more stages were added and after the displacement of hypochlorite the common sequence was CEDED (**c**hloriniation – **e**xtraction – **c**hlordioxide – **e**xtraction – **c**hlordioxide). In the 1960s the environmental issues, such as the coloring of the eluents, lead to the use of hydrogen peroxide in the extraction step. The company Sappi in South Africa also started to use oxygen due to a lack of water supply. Both measurements decreased the load of the effluents. In later years it was attempted to get rid of the highly corrosive chlorine which also forms toxic, halogenated compounds. This was achieved by substitution of elemental chlorine with chlorine dioxide and led to the now common ECF (Elemental Chlorine Free) method. It was also attempted to get completely rid of chlorine containing substances (TCF – **t**otal **c**hlorine **f**ree). However, they did not prevail due to economic and technical restrictions.

Meanwhile, typical softwood sequences are highly complex. Oxygen is used under alkaline conditions at 90–100 °C followed by a treatment of the pulp with ClO_2. Subsequently, an alkaline extraction is done during which O_2 and H_2O_2 are added to the slurry. After this, the pulp is again treated with ClO_2 followed by an additional extraction with added H_2O_2 and finally a last treatment with ClO_2 is done.[48] For hardwood, a less tedious procedure can be applied, omitting several steps and thus making it easier to bleach.[48] Apparently, the duration of the different steps has a very high impact on the quality and yield of the pulp. At the beginning, mainly the hemicelluloses and lignans go into solution followed by the lignin itself. After a certain period the degradation of lignin considerably slows down and the degradation of cellulose dominates. In order to find the correct time to stop a particular step, it was necessary to develop a quick method to determine the amount of residual lignin in the pulp. Therefore, the kappa number analysis was developed, which is very fast in contrast to the time consuming Klason lignin method. The basic idea behind is to take a pulp sample and completely oxidize all of its double bonds with potassium permanganate ($KMnO_4$). After ten minutes the reaction is stopped with potassium iodide and the amount of iodine set free is titrated with thiosulfate. The lower the kappa number, the less lignin (or better – less double bonds) is in the pulp.[48] The kappa number does not detect lignin specifically – it detects the amount of double bonds – a fact that always should be considered. During paper pulping, also reactions of non-lignin compounds occur that form compounds with double bonds. One example is the reaction of the xylene (hemicellulose) side group 4-O-methylglucuronic acid, which gets converted (under the release of MeOH) to 4-deoxy-hex-4-enuronic acid. These hexenuronic acids are formed due to the reaction conditions whilst pulping and distort the results of the kappa number measurement. Hardwoods contain more xylenes and therefor their respective reaction step has to be stopped at lower kappa numbers compared to soft wood pulps.[48]

2.4 Non-industrial lignin sources

Besides the big industrial players i.e. kraft-, and sulfite process, and the organosolv process, several other sources for lignin are available, albeit on a much smaller scale.

2.4.1 Milled wood lignin

The so called milled wood lignin (MWL) is obtained by vibratory ball milling extractive-free woodmeal under a nitrogen atmosphere with a non-swelling solvent, like toluene, for 48 h. The temperature should be below 35 °C, which is accomplished by regulation of the air temperature. The toluene is removed after grinding via centrifugation and the residue is extracted with a dioxane-water mixture (96/4, v/v, 5–10 ml/g of milled wood) for 24 h. After removal of the extract via centrifugation, a fresh dioxane-water mixture is added. This step is repeated, the extracts are combined and the solvents are removed. Subsequently, the lignin (sample size ~ 1 g of extract) is purified by, for example, first dissolving the sample in 28 mL of a mixture of pyridine-acetic acid-water-chloroform with a following extraction with 36 mL of chloroform. This slurry is centrifuged until the organic phase is completely clear. The organic phase is removed via a syringe and the aforementioned steps are repeated. After solvent removal the residue is dissolved in 10–20 mL of 1,2-dichloroethane-ethanol (2:1, v/v) and the solution is added dropwise to ether (250 ml). The precipitated lignin is centrifuged, washed twice with ether and dried.[55] MWL is structurally very close to native lignin, which makes it very interesting for the investigation of natural lignin. However, due to the complex work up procedure and the low yields of lignin, MWL is only interesting for scientific applications.[56,57]

2.4.2 Steam explosion lignin

This is a method where woody biomass is heated under hot steam at temperatures from 180–230 °C for 1–20 min at pressures ranging from 14 to 30 bar. After this, the pressure suddenly is released, causing a partial degradation of hemicellulose and the cleavage of lignin. This procedure yields water insoluble lignin that is partially degraded because some of the inter-lignin bonds get cleaved off. The basic principle of this method is that steam diffuses into the micropores of the biomass at high pressure. When the pressure is released, a big gradient between the pressure inside the small pores and the environment occurs. The pressure gradient causes a force in the pores, leading to the explosion of the fibers. This method is often combined with enzymatic hydrolysis to produce carbohydrate rich streams for fermentation. Also attempts to pretreat biomass with SO_2 and H_2SO_4 to increase the efficiency of the separation have been carried out. The absence of dangerous and corrosive chemicals (when not using H_2SO_4) and the good yield of hemicelluloses are furthermore beneficial.[12]

2.4.3 Pyrolysis lignin

Pyrolysis is used for a long period by mankind and historically the conversion of biomass to charcoal is one of the oldest applications of this method. Pyrolysis principally describes the degradation of matter at high temperatures (350 – 700 °C) under a limited amount, respectively the exclusion, of oxygen.[58–60] Several pyrolysis-based technologies can be used in the future to produce valuable products from biomass e.g. slow-, intermediate- and fast pyrolysis of wood. Pyrolysis of biomass produces a dark brown to black liquid that contains a high amount of carbohydrate degradation products and lignin-derived useful aromatic chemicals. In addition, gaseous products, which can be used as fuel, and a carbon rich solid, called char are produced.[61] The effects of reaction temperature and time on the distribution of the products are shown in Table 7. The overall trend leads to more coal, with lower temperatures and longer vapor residence times.[61]

TABLE 7: Product distribution of lignin from different pyrolysis modes

Mode	Temperature [°C]	Duration	Liquid [%]	Solid [%]	Gas [%]
fast	500	1 s	75	12	13
intermediate	500	10-30 s	50	25	25
slow	400	hours -> days	30	35	35
gasification	750-900	NA	5	10	85

Taken and modified from Bridgewater – 2012[61]

However, pyrolysis has the big disadvantage that it is very unselective. Attempts have been made to convert biomass to syngas (a mixture of CO and H_2) via a Fischer-Tropsch route but the formation of char and tar cause serious problems due to catalyst clogging. Additionally, the Fischer-Tropsch process is very unspecific and gives a wide range of products.[59]

2.4.4 Enzymatic hydrolysis lignin

Enzymatic hydrolysis lignin (EHL) is usually extracted from the solid waste of bioethanol production from biomass, which usually includes steps like pretreatment of the biomass (e.g. steam explosion- or hydrothermal – e.g. 190 °C for 10 min with a solid to liquid ratio of 1:10 – pretreatment[62]), enzymatic degradation and further fermentation of the carbohydrates to ethanol or sugar derived acids.[63] The enzymes used are mainly hemicellulases (e.g. xylanases, mannanases, esterases and α-glucuronidases) and cellulases i.e. mostly glycosyl hydrolases (e.g. endoglucanases and exoglucanases) that are capable of cleaving the 1,4-β-glycosidic bonds occurring in the cellulose macromolecule, as well as oxidative enzymes, like polysaccharide mono-oxyganases.[63] Biodegradation of lignocellulose is a very slow process without any pretreatment due to poor accessibility of the substrate for the enzymes. Therefore, various methods are applied, such as steam explosion. Due to the relative mild process conditions, EHL has good quality and is not as highly altered as kraft lignin or lignosulfonate. However, it usually still contains rather high amounts of non-hydrolyzed cellulose and high contents of ash. The distribution in EHL of the various lignocellulosic compounds derived from processed sugarcane bagasse is approximately 47 % lignin, 40 % cellulose, 4.5 % hemicellulose and 8.4 % ash.[62] The lignin content is therefore doubled compared to its initial amount in sugarcane bagasse. EHL occurs as a brown water insoluble powder.[12,64]

2.4.5 Early stage catalytic conversion of lignin (ECCL)

Early stage Catalytic Conversion of Lignin (ECCL) is the term for a new approach regarding lignin valorization. It describes the concurrent extraction and catalytic conversion of lignin from plant biomass. Technical lignins (e.g. kraft lignin) are usually highly recondensed, which means they have a lot of stable C-C bonds that can only be broken under harsh conditions. This is avoided with the ECCL approach. Here the separation and depolymerization is typically facilitated via a heterogeneous catalyst (e.g. Raney nickel) in one step. Therefore, the lignin fraction is more reactive and less condensed compared to kraft lignins. Even though organosolv already delivers high quality lignin, ECCL still offers the advantages of having fewer process steps and a concurrent lignin and cellulose valorization. ECCL yields a mixture of depolymerized lignin fractions – the so-called oil, solid lignin, and a solid residue consisting mainly of cellulose – the pulp. However, also hemicellulose (solid or as degradation product in solution) and residual lignin in the pulp occur.[35] In literature, different strategies have already been reported. One experiment that showed the typical characteristics of ECCL, including the direct use of lignocellulosic feedstock and a heterogeneous catalyst, is the reductive hydrogenolysis performed by van den Bosch.[65] They used 2 g of extracted birch sawdust as feedstock, 40 ml methanol as solvent, 0.2 g Ru/C respectively 0.2 g Pd/C as catalyst in a 100 ml batch reactor under a pressure of 30 bar H_2 and a temperature of 250 °C. With Ru/C they achieved a delignification efficiency of 85 % (48 % phenolic monomers) and with Pd/C 90 % (49 % phenolic monomers) respectively. The focus of this work was particularly on the amount of -OH groups detectable in the oil-like product they achieved, consisting mainly of phenolic mono- and oligomers. Rinaldi and Ferrini achieved a delignification efficiency of 87 %, of which 26 % were isolated as oil using poplar wood as feedstock, 2-PrOH/H_2O 7:3 v/v as solvent, and Raney nickel as catalyst.[3] Amongst the differences between van den Bosch and Rinaldi was the high amount of reduced aliphatic compounds derived from the originally aromatic monomers of lignin, reported in the latter publication. Parsell et al also reported a route of lignocellulosic conversion into a lignin derived oil and a solid cellulose derived fraction.[66] They used natural and genetically modified poplar wood, MeOH as solvent under a H_2 atmosphere of ~34 bar (500 psi) at 250 °C and a bimetallic catalyst consisting of ZnPd(1:0.1)/C. Interestingly, both metals in conjunction showed a remarkable synergistic effect and underperformed severely when used in solitaire. They were able to achieve lignin-derived phenolic monomer yields of up to 54 %. This is a good value compared to other working groups but the highlight of their results is the very high selectivity of up to 100 % (19 % yield) in regards to dihydroeugenol. Although one has to object that this result was achieved by using a genetically modified tree (WT-lodgepole pine) as feedstock. Considering that one of the main weaknesses in ECCL is the lack of selectivity of the depolymerization, also selectivities of 50 % are still very impressive. They reached a selectivity of 45 % for dihydroeugenol and 55 % for 2,6-dimethoxy-4-propylphenol (total yield of phenolic monomers 54 %) respectively with poplar WT-LORRE as feedstock. However, their research effort is more directed towards converting the leftover solid carbohydrate fraction into ethanol via enzymatic hydrolysis instead of using the pulp for paper production, which would be severely hindered due to the high residual lignin content. The price of ethanol (~650-700 €/ton – at 95 % purity[67]) is very much comparable to the price of pulp (~700-750 €/ton[9]), so this could be an economically interesting approach. Although it should be stated that pulp is a raw product that is further valorized to paper (< 1.100 – < 10.000 €/ton depending on the paper quality[68]), whilst ethanol is an end product. According to Parsell et al, they achieved a conversion of the carbohydrate fraction to glucose giving 95 % of the theoretical yield.

2.4.6 Metallic catalysts

A catalyst principally is a substance that enhances chemical reactions via lowering its activation energy without being consumed. Catalysts do not change the chemical equilibrium but they enable reactions to take place at lower temperatures.[69] The facilitating of reactions at lower temperatures also enables reactions that would not be feasible due to limited substrate stability. The first step in each heterogeneous catalysis is physisorption. The close alignment of catalyst and substrate lead to a stabilization of the substrate via van der Waals interactions. The power of this interactions is around 25 kJ/mol, which is a lot weaker than classical chemical bonds (~432 kJ/mol for H-H, ~410 kJ/mol for C-H and ~346 for kJ/mol for C-C bonds respectively[70]). Van der Waals interactions however, can show catalytic effects by itself and they can facilitate the chemisorption of the substrate on the catalyst surface. This can highly alter the electronic state and therefore the reactivity of the substrate. Mostly, the transition from physi- to chemisorption is energetically hindered but in some cases the hindrance is very small, so that no elevated temperatures are needed. Hydrogen for instance can chemisorb on nickel metal at room temperatures. The chemisorption of oxygen is slightly hindered, whilst the chemisorption of nitrogen is highly energetically hindered.[71] After chemisorption and reaction of the substrate with the reactant, the final product has to desorb and the catalytic cycle can start again.[72]

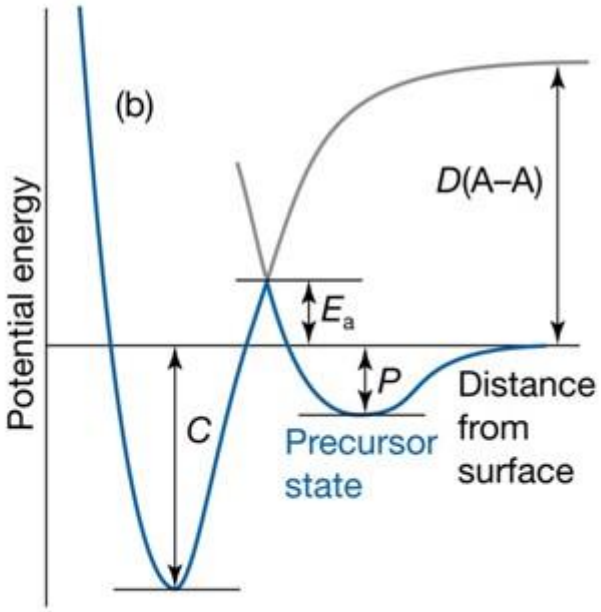

FIGURE 8: Lennard-Jones potential of the interaction of a catalyst surface with a substrate[71]

The catalytic properties of transition metals depend on the distribution of their valence electrons (VE) in the valence and conduction band (VB and CB respectively). In nickel, for instance, the distribution of its 10 VE is circa 0.6 electrons in the (4s) conduction band and 9.4 electrons in the (3d) valence band.[71] The appearance of electrons in the CB generates a lack of electrons in the VB, thus causing a state of electron depletion. Therefore, Ni^0 is an electron acceptor. The degree of its willingness to accept electrons can be controlled via the introduction of different atoms. Elements left in the periodic table of elements (e.g. Mo) will lower the Fermi level of nickel, which leads to an increased acceptance of electrons, while elements right in the periodic system of the elements (e.g. Cu), raise the Fermi level of nickel leading to a stronger nucleophilic behavior. In contrast, a non-metallic compound like hydrogen, has its electrons in very discrete energy levels. H_2 has a fully occupied molecular orbital with two σ-electrons and it can only form new chemical bonds, if it gets rid of electrons in advance. This is exactly what hydrogen is doing when it binds to nickel: It transfers electrons until the intramolecular H-H bond breaks. This causes a positive polarization of the H-atoms, thus making it more susceptible for a chemical reaction. Ammonia, hydrochloric acid, oxygen, and olefins show a similar behavior.[71] Besides electronic properties, in catalysis also micro- and macroscopic morphological properties have an effect on the performance. Due to the necessity of adsorption, the surface area of a catalyst should be as high as possible. Another morphological effect is the occurrence of surface defects. Despite them being called defects, they are actually beneficial for catalysis because they facilitate desorption of the products. Additionally, it is beneficial for the reaction, if the substrate is not chemically bonded too strongly to the catalyst.[71] Amongst the vast fields of application for heterogeneous catalysts are the ammonia synthesis ($Fe_{1-x}O$ powder mixed with small amounts of alumina, CaO and potassium[73]), the synthesis of sulfuric acid (V_2O_5[74]), and the catalytic cracking and reforming in the petrochemistry (e.g. zeolites, amorphous alumosilicates,Ni, Pd, Pt).[75]

2.4.6.1 Nickel

Nickel is a lustrious, silvery-white transition metal of the first period in the periodic table with the electron configuration of $[Ar]3d^8 4s^2$.[71] It crystallizes in a face centered cubic crystal lattice, has a lattice parameter of 3.5238 Å and an atomic radius of 1.24 Å.[71] It is ferromagnetic and its Curie temperature is at 253 °C, which means that it loses its magnetic properties above this temperature. It has a density of 8.78–8.88 g/cm^3 at 25 °C, a melting point of 1453 °C and a boiling point of 2730 °C. The earth crust contains about 0.02 % of Ni, which is comparable to copper. Nickel naturally mainly occurs as sulfide, silicate, oxide, and arsenide.[71] About 69 % of the global nickel production is used to manufacture stainless steels. 15 % are used for the manufacturing of other steels and non-ferrous alloys, which are often used for highly specialized industrial, aerospace, and military applications.[76] Nickel alloys are also often used for coins.[71] 11 % are used for plating, foundries and castings, another 3 % are used for batteries, and only about 2 % go into uses such as chemicals, dyes and catalysts.[76] The first industrial use of nickel was as a galvanic plating in 1843, however, the quality was rather poor. That changed when electrolytic refinement was discovered in 1870. Today, nickel is purified via the carbonyl process, where Ni reacts with CO at 50 °C and 1 atm pressure, which forms the volatile $Ni(CO)_4$ that decomposes at 180 °C to pure Ni and CO. Riley was the first to report the beneficial properties of nickel for metal alloys, which improves the strength, the toughness, the wear resistance, the corrosion resistance, and the heat and cold resistance.[71] Nickel is extensively used for hydrogenation reactions in the industry, for instance for fat hardening.[77–79] The famous chemist J.P. Sabatier discovered the application of a nickel catalyst for the hydrogenation of ethylene, for which he was rewarded the 1912 Nobel Price in Chemistry.[80] Nickel is also extensively used in petrochemistry, for instance, it catalyzes the methanization of syngas ($CO_2 + H_2 \rightarrow CH_4 + H_2O$) and the steam reforming of methane (Ni on support, typically

Al_2O_3).[72,81] Ni is also used for the Fischer Tropsch process with the advantage of being relatively selective for smaller molecules e.g. methane.[72] In addition, there are a lot of applications for homogenous nickel catalysts investigated, for instance Ni compounds as catalysts for C-C coupling.[82] It is also used as a bimetallic catalyst together with Mo or Co for hydrodeoxygenation reactions. It has the advantage of a relatively low price compared to other, more noble metal catalysts.

TABLE 8: Price comparison of different catalyst precursors[77]

Compound	**$NiCl_2$**	**$PdCl_2$**	**$PtCl_2$**	**$AuCl_3$**	**$RhCl_3$**
Price in USD (per 1mmol)	0.1	5.8	32.2	35.6	51.8

2.4.6.2 Nickel oxide

NiO occurs as a green or black (after calcination – partly converted to Ni_2O_3) powder, has a density of 6.67 g/cm^3 and a melting point of 1955 °C.[83,84]
It is used in the following applications:

- Production of electrical ceramics e.g. thermistors and varistors.
- Pigments for ceramics and glasses.
- As transparent electrode material in optoelectronic devices.[85]
- As cathodes for solid oxide fuel cells.[84]
- For the reduction to metallic nickel.[71]

2.4.6.3 Raney nickel

Murray Raney invented the so-called Raney nickel in 1926 and got a patent for it in 1927. The common industrial catalyst for hydrogenation at that time was a nickel catalyst that was prepared via the hydrogen reduction of supported nickel oxide. In order to enhance the effectivity of nickel catalysts, he began to research and developed a high surface nickel catalyst by leaching a 50 wt% Ni-Al alloy in aqueous sodium hydroxide.[86] During this procedure aluminum is converted into $[Al(OH)_4]^-$, which is water soluble and can be washed out. The remaining skeletal sponge metal has a very high surface area and thus shows great catalytic activity.[71] However, caution is appropriate when working with Raney nickel; due to its high surface area it is pyrophoric and burns when exposed to air. Raney nickel is still a widely used catalyst for a range of applications including desulfurization, deamination, deoxygenation, and hydrogenation.[87]

2.5 Fractionation products of lignocellulose

2.5.1 Pulp

The principal production of pulp has been already described in chapter 2.3.1 *Kraft lignin*. Pulp consists mainly of cellulose fibers and is the feedstock for papermaking. It is gained mainly from wood via different pulping mechanisms i.e. the separation of cellulose fibers from the other constituents. 50 % of the paper in the EU in 2008 were won by the repulping of recycling paper.[88] Different feedstocks (e.g. hard wood, soft wood etc.) have different cellulose fiber properties and not all products (e.g. newspaper or cardboard) have the same quality requirements to the fibers/pulp. Amongst the characteristics of pulps are; the moisture content, the fiber length and fines content, the pulp viscosity (gives information about the degree of polymerization of the cellulose), the brightness, and the freeness (CSF – Canadian Standard Freeness), which gives information about the degree of the fiber to fiber linkages.[89] All these characteristics effect or are effected by the fiber morphology, which in turn effects the properties of the pulp. To increase or tune the properties of the pulp, it is refined. The main goal of refining is to increase the fiber – fiber interaction. This is done via different measures but the basic principle is to roughen up the surface of the fibers to increase friction in between them. Refining can include the “pumping” of water into the cell wall to make it more flexible. The additional water in the morphology of the cellulose polymer breaks hydrogen bonds and causes swelling. Another way is fibrillation which is an exposure of fibers, thereby increasing the surface area of them. For example, the surface area of Kraft softwood pulp at a CSF of 700 is around 1 m^2/g and at CSF 350 it is around 5 m^2/g. The third way is via a delamination of the first and second cell wall, which causes the second cell wall to pierce through the first one, leading to an increased surface area and roughness. All three measures increase the strength of the pulp, although they can reduce the length of the individual fibers.[89] Figure 9 shows pulp samples in different stages of refinement.

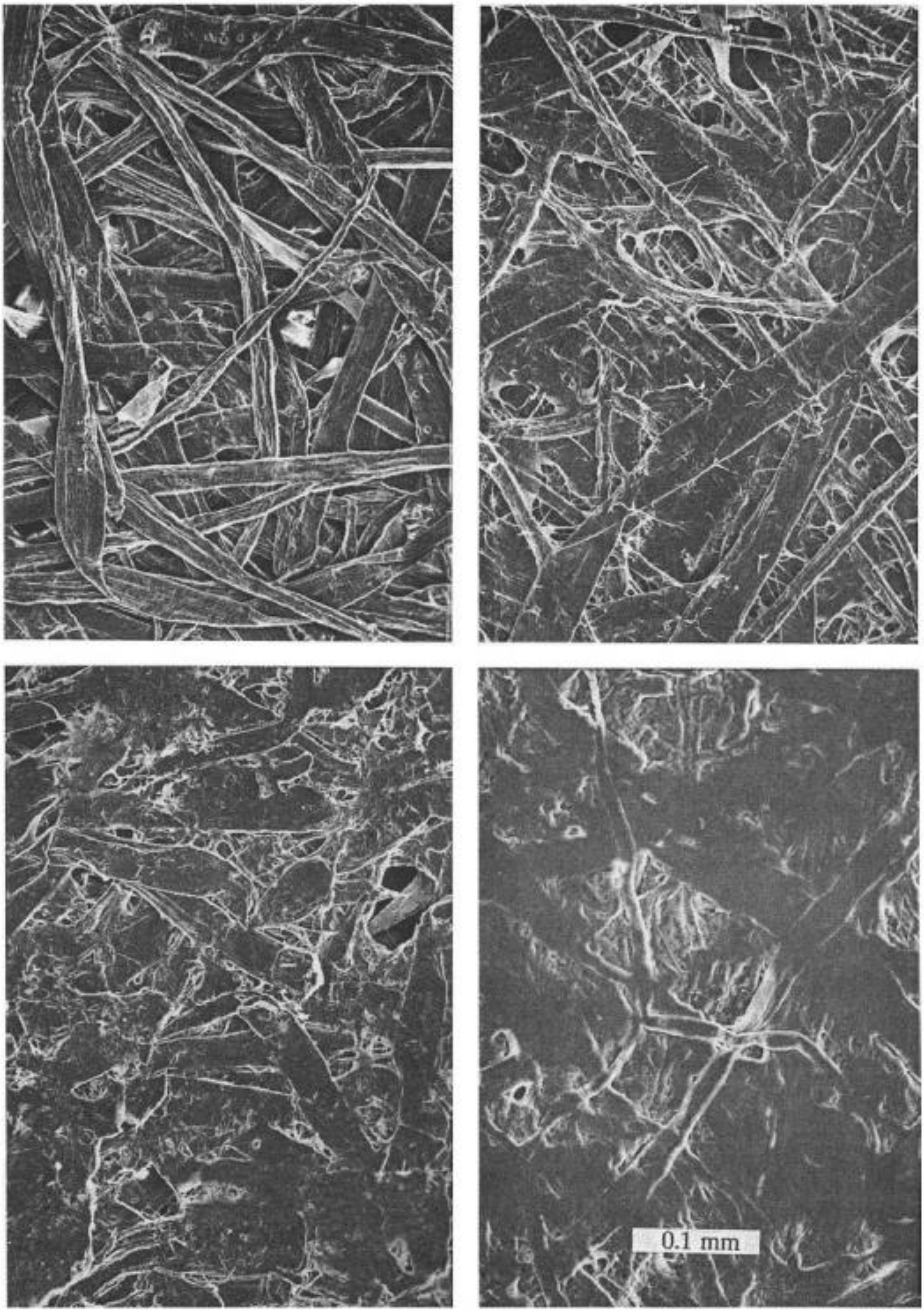

FIGURE 9: Pulp samples in different stages of refinement (increasing from left top to right bottom) C. J. Biermann – 1996[89]

2.5.2 Liquid oil fraction

Oil in this context is a generic term for the degraded, depolymerized stream of lignin obtained from biomass fractionation.[3] Usually, also carbohydrate degradation products like hydroxymethylfurfural, formic acid and levulinic acid are found in the oil.[66] The term "oil" is not very well specified and it is up to the regarding scientist what is defined as oil. Most papers specify it as the stream that is soluble in a specific solvent after pulping. Qui, Hayashi et al., for instance, defined oil as the part of lignin, that could be extracted with dichloromethane after fractionation – a definition that is also used by many other working groups.[65,66,90] The oil composition is usually very diverse and by GC-MS analysis a vast amount of different substances can be found already amongst the volatile constituents. The desired products are aromatic monomers; however, in ECCL also oligomers and carbohydrate-derived compounds can occur.[3] All in all, it is a challenging task to tune the ECCL process to a higher selectivity for aromatic monomers but there are progresses in this direction – see chapter 2.4.5 *ECCL*.[65,66] However, also potential uses for the oligomeric products are known, which could be used e.g. as antioxidants.[91] In the end, for a real application, the process has to become more selective because it is economically not feasible to separate too many different compounds in a reasonable way.

2.5.3 Aromatic monomers in oil

The aromatic monomers are the most valuable products achievable with ECCL so it is desired to increase their yields as much as possible.[1] The aromatic monomers are derived from the lignin monomeric units. Several possibilities are available to valorize them. One possible way is to concentrate on the BTX (**B**enzene, **T**oluene, **X**ylene) fraction[92], another one is to go for the high value vanillin. Although, it should be mentioned that the vanillin route is rather important for lignosulfonates.[51] In ECCL, yields of monomers in regards to total lignin of up to 44 % or even 54 % were achieved.[65,66]

2.5.4 Solid lignin

Solid lignin, in literature also referred to as char, usually is defined as the fraction of lignin that is not soluble in a certain solvent – mostly dichloromethane.[65,90] It consists of incompletely depolymerized or repolymerized lignin fragments. It is desired to convert as much of solid lignin into monomers as possible. The occurrence of solid, poorly depolymerized lignin is attributed to the presence of very stable C-C bonds in the lignin. These are existent in lignin naturally but they are also formed during processing. This is due to repolymerization that can occur due to the process conditions. In order to prevent the formation of solid lignin, capping agents like molecular hydrogen or hydrogen donors like protonic solvents (EtOH or 2-propanol) are used.[93]

2.5.5 Hemicellulose and its degradation products in solution

Hemicelluloses contain sugars that have acetyl- and methyl side-groups, like in methyl glucuronic acid that are easily cleaved off – see Figure 10. Therefore, it tends to degrade more easily than cellulose while processing.[94,95] In Figure 11 a proposed mechanism of carbohydrate degradation is shown.

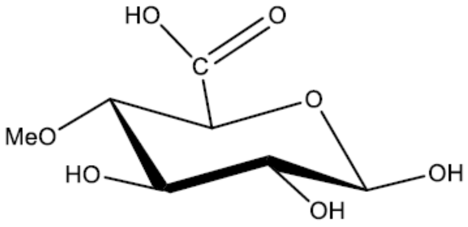

FIGURE 10: 4-O-Methyl-D-glucuronic acid

Other reasons for the fact that hemicelluloses are more easily degraded than cellulose during any kind of pulping are the higher amount of reducing ends (shorter chain length) and the lower degree of crystallinity compared to cellulose (this protects the cellulose from chemical attacks).[96] Amongst the common degradation products of hemicellulose are acetic acid, formic acid, various furfurals and levulinic acid.[97]

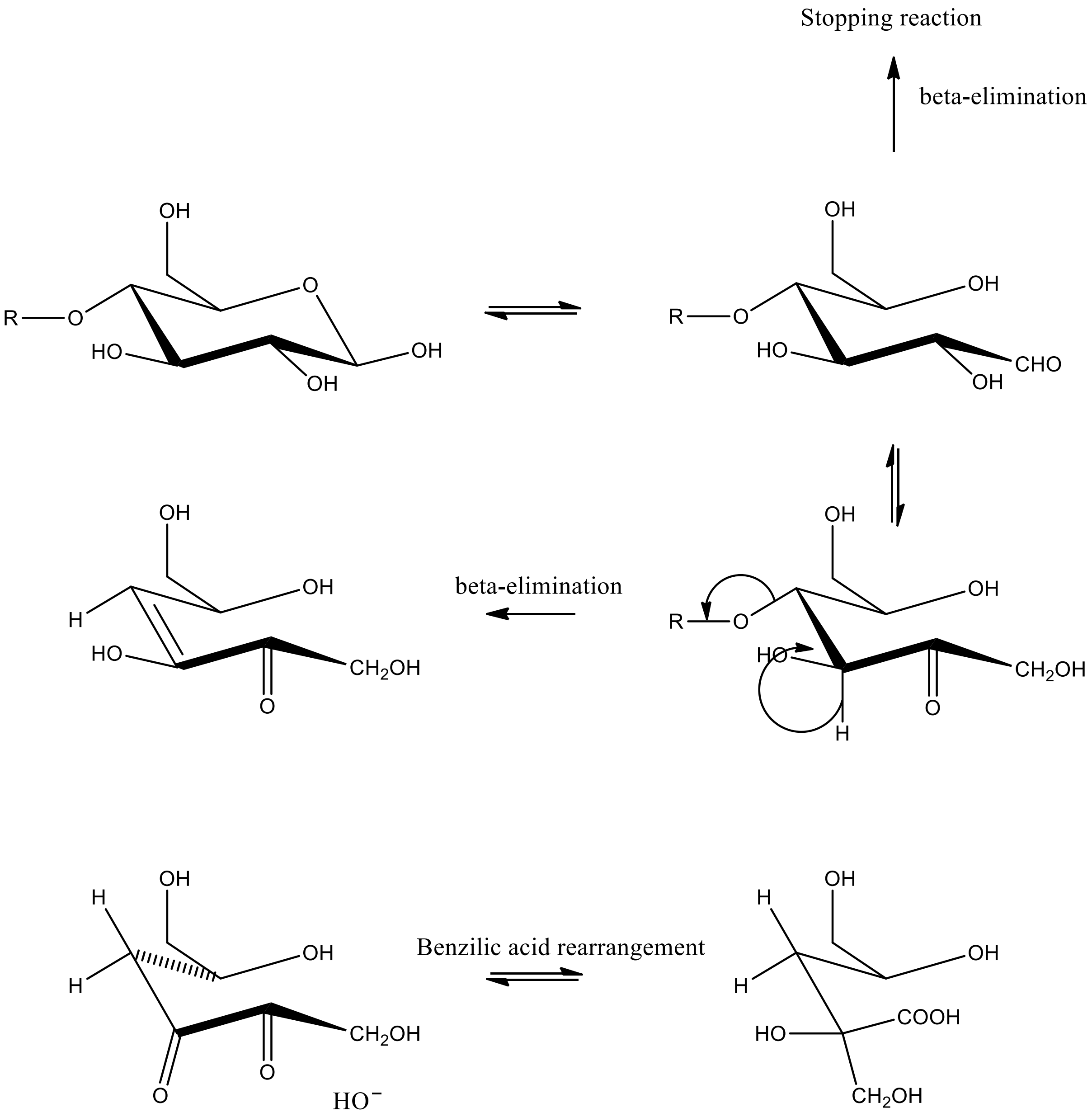

FIGURE 11: Proposed reaction mechanism of the peeling reaction on a cellulose or glucomannan chain. Redrawn from Gellerstedt – 2008[96]

3. Experimental

3.1 Materials

3.1.1 Feedstock

The used feedstock was European larch sawdust that was provided by the sawmill *Alfred Seebacher GmbH & Co KG* located in Gnesau (Carinthia, Austria). The approximate age of the trees when harvested was 100 years. They were harvested between November 2016 and March 2017 in the Nockberge region in Carinthia at an altitude of at least 1000 m above sea level. The logs were sawn in October 2017 without debarking. The sawdust was sieved to a particle size distribution between 0.5 x 0.5 mm and 2.0 x 2.0 mm and then stored in glass bottles in the fridge at 4 °C. A part of the sawdust was grinded with a MF 10 basic microfine grinder equipped with a MF 10.1 cutting-grinding head. The fraction smaller than 0.5 mm was used for chemical analysis of the sawdust. The analysis of the composition of larch wood sawdust was performed and provided by Dipl.-Ing. Markus Hochegger according to Hochegger – 2019.[98]

TABLE 9: Composition of larch wood sawdust

Component	Content on dry wood [wt%]
Ash	0.17 ± 0.02
Extractives (water + acetone)	12.02 ± 0.12
Klason lignin	26.90 ± 0.10
Acid soluble lignin	0.30 ± 0.02
Carbohydrates (as monomers)	Content on dry wood [wt%]
Glucose	51.15 ± 0.33
Arabinose	0.99 ± 0.02
Galactose	4.97 ± 0.25
Mannose	7.39 ± 0.07
Xylose	3.12 ± 0.14

3.1.2 Instruments

GC-MS: HP 6890 series GC system equipped with a HP-5 column (30 m x 0.32 mm x 0.25 µm), an Agilent 7683 series autosampler, a HP 7689 series injector and a HP 5973 MSD.

GC-FID: HP 6890 GC system equipped with a HP-5 column (30 m x 0.32 mm x 0.25 µm) and a HP 7683 injector.

Photometer: Cary 60 UV-Vis, Agilent Technologies

Freeze-drier: Alpha 1-4, Christ L-1, equipped with a Pfeiffer, D-35614 Asslar pump.

Reactor: Parr Instruments Company 4575A high pressure/high temperature batch reactor (max.: 350 bar, 500 °C), 500 ml, material: Hastelloy C-276; with a 4848B reactor controller; Software: Specview Version 2.5.

Reactor for solvent pretesting: 100 ml HEL stainless steel autoclave (max. 100 °C, 350 bar). The autoclave temperature was controlled externally with a metal heating jacket by Heidolph Hei-Standard (MR Hei-End) whereas the internal temperature was measured by a temperature sensor connected to the Heidolph Hei-Standard stirring and heating plate. The stirring was done via a Teflon®-coated 10 mm stirring bar.

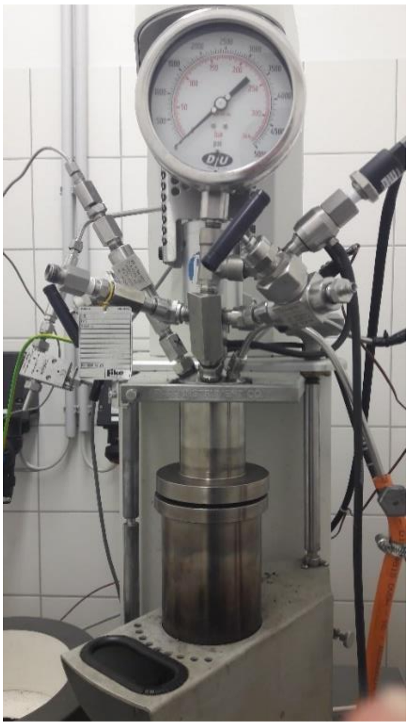

FIGURE 12: Batch reactor, Parr Instruments

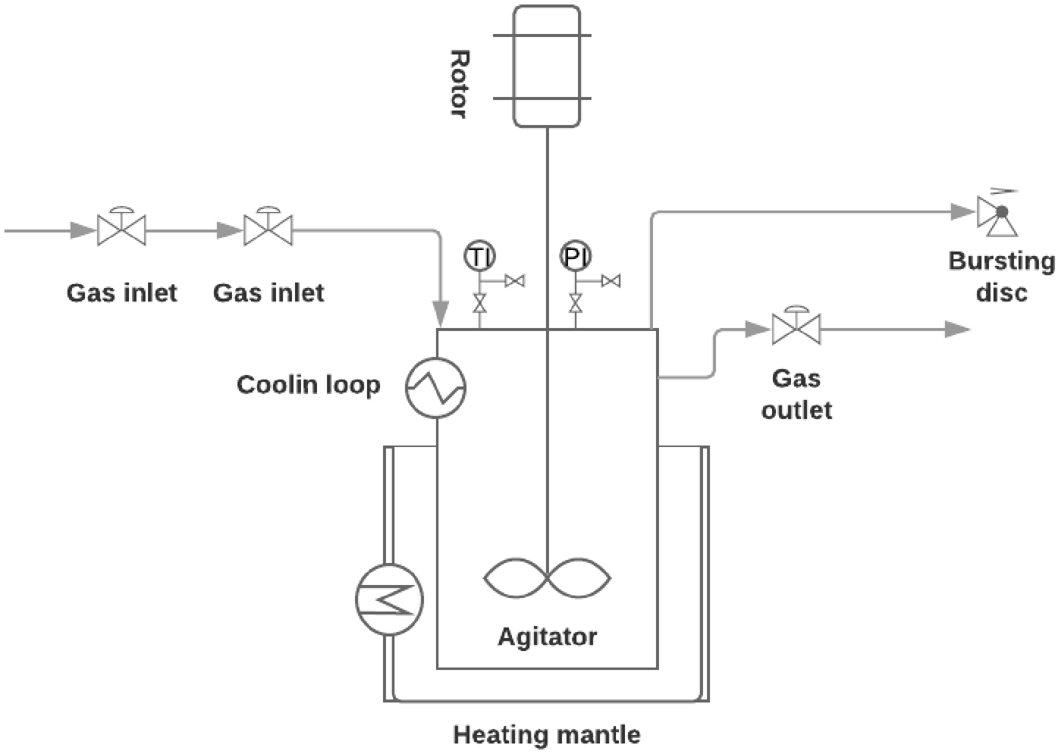

FIGURE 13: Flow Chart of the Parr Instruments Batch reactor

Analytical balances: VWR 254i, max. 250 g, d = 0.1 mg, Sartorius BP 210 S, max. 210 g, d = 0.1 mg, Sartorius AZ214, max. 210 g, d = 0.1 mg

pH meter: Metrohm 691

Muffle furnace: Heraeus thermicon T

Ultrasonic bath: Elma Transsonic T460/H

Rotary Evaporator: VWR IKA RV 10 digital & VWR IKA HB10 digital heating bath,

Vacuum pump: Vacuubrand slide vane vacuum pump

Autovortex: Stuart Scientific SA6

Size Exclusion Chromatography: HPLC: Agilent 1100 Series, Degasser: G1322A, QuatPump:G1311A, Colums: PL gel 5 µm 100 Å and PL gel 5 µm 1000 Å. Both columns had a length of 300 mm. A UV detector was used that scanned at 270 nm, the injection volume was 50 µm, the flow was 1 ml/min and the run time was 27 min. The dissolved samples were diluted to a final concentration of 0.2 mg/ml with THF as solvent.

ALS: G1313A, RI Detector: KNAUER K-2301

Magnetic stirrer hot plate: IKA Labortechnik, RCT basic

MA23 infrared moisture analyser (Satorius AG, Germany)

3.2 Chemicals

3.2.1 Solvents

Ethanol: euro denaturated 99 %, denaturated with 1 % Isopropanol, 1 % methyl ethyl ketone and 12 ppm denatonium benzoate – VWR Chemicals

Tetrahydrofuran: HPLC grade - Merck

Dichloromethane: stabilized with about 0.002 % of 2-methyl-2-butene – VWR Chemicals

Acetone: HPLC grade, Fisher Chemical, Lot: 1733781, Bishop Meadow Road, Loughborough, U.K.

3.2.2 Catalysts

Carrier material: Kaolin PoleStar 450 HP, Imerys, France + 0.9 wt% polyvinylacetat as binding agent that was formed to a pellet and calcinated. The binding agent disappeared during the sintering process. Pore volume of the calcinated pellets: 0.38 ml/g

Active material: Nickel(II) nitrate hexahydate, purum p.a. crystallyzed, ≥ 97.0 % (KT), Sigma-Aldrich, Riedstraße 2, 89555 Steinheim, Deutschland, LOT:BCBF2717V

Raney Nickel: Aluminium-nickel alloy, purum, 50 %, Al basis, 50 % Ni basis, Fluka Analytical, sodium borohydride, granular, 10-40 mesh, 98 %, Aldrich Chemistry, NaOH, 99 %, VWR

Sulfuric acid: Rotipuran, 98.53 %, Charge – 367262782, Carl Roth GmbH + Co. KG-Schoemperlenstr. 3-5, D76185 Karlsruhe, Germany

3.2.3 Others

Sodium sulfate: 99 %, anhydrous for analysis, Merck KgaA, 64271 Darmstadt, Germany

3.3 Methods

3.3.1 Determination of wood composition

Klason lignin and acid insoluble lignin contents of the feedstock were determined by the standards published by the Technical Association of the Pulp and Paper Industry (TAPPI).[99] The purity of the lignin (organosolv lignin) was determined by dissolving 1.5 g in 10 ml of HPLC grade acetone with subsequent filtering through a 0.45 µm nylon filter. Then, the solvent was removed in the rotary evaporator. In the end, the lignin was dried in a vacuum desiccator over $CaCl_2$ and weighed again. This analysis was performed by Dipl.-Ing. Markus Hochegger according to Hochegger – 2019.[98]

3.3.2 Catalyst preparation

3.3.2.1 NiO loaded kaolin pellets

Precalcinated pellets that contained 0.9 % of polyvinylacetate as binder were supplied by IMERYS. The pore volume was determined by weighing 100 g of the calcinated pellets, then adding an amount of water until it does not get adsorbed anymore and then weighing again. The difference of mass gives the pore volume. The determination of the pore volume (0.38 ml/g) was performed by MSc. Maximilian Meissner. 20 g of pellets were impregnated with a solution of 11.89 g $Ni(NO_3)_2 \times 6\, H_2O$ in 13.41 ml water and 2 x 7.68 mL were sprayed on the pellets. Between the two spraying procedures the pellets were dried at 120 °C with 40 rpm at the rotation evaporator for 60 min of which in the last 10 min a vacuum of 40 mbar was applied. After the second spraying, the pellets were dried at 120 °C for 3 h and then a vacuum of 30 mbar was applied. Finally, all of the pellets were calcinated with the following temperature program:

$$25\,°C \xrightarrow{60\,min} 255\,°C \xrightarrow{60\,min} 255\,°C \xrightarrow{120\,min} 450\,°C \xrightarrow{60\,min} 500\,°C \xrightarrow{30\,min} 500\,°C \xrightarrow{over\ night} 25\,°C$$

The pellets were sent for further analysis to Prof. Gössler at the institute of analytical chemistry of the Graz University. He took 100 mg and digested it with 4 ml HNO_3 and 1 ml HF in a MNS Ultraclave. The temperature was ramped to 250 °C and held for 30 min. The samples were diluted and analyzed by an ICPMS (Agilent 7700ce).

3.2.2.2 Raney Nickel

700 mg of the NiAl alloy were taken and put into 150 ml of hydrogen saturated water (hydrogen was purged through the water to remove oxygen). Then, 5 ml of 20 % NaOH were added. The reaction was performed under 80 °C for 45 min. After this, the suspension was washed with 150 ml of hydrogen saturated water until the washing water was pH neutral. The washing water was removed via a syphon (device to remove excess solvent from above). 350 mg Raney nickel suspended in 10 ml water were used for the reaction. This was achieved by transferring the suspension into a graduated flask and filling the volume up to 10 ml with water.

3.2.2.3 Sulfuric acid 1.1 vol%

354 ml of an EtOH/H_2O mixture 75/25 v/v were prepared to which 4 ml of concentrated sulfuric acid (98.5 %) were added. 350 ml of this mixture are taken for the reaction.
pH of the mixture: 0.73

3.2.2.4 Sulfuric acid 0.11 vol%

40 ml of a 1.11 vol% mixture (see above) of sulfuric acid and 360 ml of an EtOH/H_2O mixture 75/25 v/v were prepared. They are combined to 400 ml of a 0.11 vol% mixture and 350 ml of it are taken for the reaction.
pH of the mixture: 1.90

3.3.3 Moisture determination

The water content of the sawdust was determined with a MA23 infrared moisture analyser (Satorius AG, Germany). For this, the sawdust is heated by an IR-heating spiral on a balance. After no more mass changes occur the measurement is completed. The humidity is automatically calculated by the loss of mass.

3.3.4 Klason lignin determination

In order to determine the residual lignin content in the pulp after processing, it was treated with 12 molar sulfuric acid, that was prepared via dilution of concentrated sulfuric acid according to TAPPI method T 222 om-02.[99] Therefore, 65 mL of 98.5 % H_2SO_4 were diluted with water to a finale volume of 100 ml. The concentration of the acid was determined via titration with 0.1 N KOH, whilst phenolphthalein was used as indicator. Then, 1 g of pulp was weighed in a small beaker. 15 ml of the 12 N sulfuric acid were added to the beaker under cautious stirring. During this procedure, the beaker is kept in an ice bath. Then, a vacuum was applied via a desiccator to get rid of air bubbles and ensure uniform wetting of the substrate with sulfuric acid. This slurry was digested for 2 h at room temperature. Then the material was transferred to an Erlenmeyer flask and diluted with water to a volume of 575 ml. After this, the suspension was boiled without a reflux condenser for 4 h. During this time, water is constantly added to keep the volume constant at 575 ml. Subsequently, the solution was filtrated in a pre-weighed filter crucible (porosity 3) and the solid residue was determined, yielding the amount of acid insoluble lignin in the pulp. The filtrate then was measured threefold at 205 nm with a photometer to determine the amount of acid soluble lignin in the pulp via the extinction coefficient, which was 110 l/mol*cm.

3.3.5 ECCL reaction conditions

Table 10 shows the reaction conditions for the 16 performed experiments. The feedstock (sieved larch sawdust ≤ 0.5 mm ≤ 2.0 mm), the feed stock loading (35 g on a dry basis) and the solvent (350 ml of an EtOH/H_2O 75/25 v/v mixture) were kept constant, whilst over the course of this thesis, the catalysts, the temperatures, the reaction time, and the pH were varied. In order to perform the experiments, the solvent mixture was prepared by mixing 750 ml of EtOH with 250 ml H_2O. The catalyst and the sawdust were weighed and put into the reactor vessel. Then, 350 ml of the solvent mixture were added. A graphite seal was used to ensure the tightness of the reactor. In order to prolong the durability of the graphite seal, silicon oil was applied to the contact site of the reactor vessel. The reactor was sealed with a torque wrench and the reaction was started. The stirring speed was always 500 rpm. The temperature and the duration depended on the respective experiment. After the reaction was completed, the heating mantle was removed and the reaction was quenched with a bucket of cold water, when the temperature of the reactor reached 130 °C. Then, the reactor was opened with the torque wrench and the reactor head was cleaned with 20 ml of the solvent mixture at 55 °C, which were collected into the reactor vessel. After this, the reactor vessel was transferred to a second laboratory and a work up procedure according to 3.3.6 *Work up procedure* was applied.

TABLE 10: Overview of process conditions

Ex	Catalyst	Temp [°C]	Pressure	Time [h]
1	-	210	1 atm N_2	3
2	-	210	40 bar H_2	3
3	3.5 g support	210	1 atm N_2	3
4	3.5 g support	210	40 bar H_2	3
5	3.5 g NiO loaded[a] support	210	1 atm N_2	3
6	3.5 g NiO loaded support	210	40 bar H_2	3
7	3.5 g NiO loaded support	182	40 bar H_2	3
8	3.5 g NiO loaded support	190	40 bar H_2	3
9	3.5 g NiO loaded support	220	40 bar H_2	3
10	0.35 g Raney nickel	210	40 bar H_2	3
11	0.35 g Raney nickel	210	40 bar H_2	3
12	H_2SO_4 1.1 % + 3.5 g NiO loaded support	179	40 bar H_2	3
13	H_2SO_4 1.1 % + 3.5 g NiO loaded support	179	40 bar H_2	1
14	H_2SO_4 0.11 % + 3.5 g NiO loaded support	179	40 bar H_2	1
15	H_2SO_4 0.11 % v/v to solvent	179	40 bar H_2	1
16	H_2SO_4 0.11 % v/v to solvent	179	40 bar H_2	0.5

The substrate loading was 35 g of sawdust on dry wood basis, solvent: 350 mL of an EtOH/H_2O mixture 75/25 v/v. [b]The loading of the support with active material was 8.2 wt%.

3.3.6 Work up procedure

After the reaction was completed, the reactor vessel was removed and the reactor head was cleaned with 20 ml of the EtOH/H_2O mixture 75/25 v/v solvent at 55 °C, which were collected into the reactor vessel. Then, the products were filtrated via a Büchner frit and a filter paper (qualitative, 90 mm diameter, Whatman^{TM}) that had to be weighed before the procedure, in order to separate the solid pulp from the dissolved fractions. 260 ml of the solvent mixture at 55 °C were poured into the empty reactor vessel to clean it. Then the same, in total 260 ml, were used to wash the pulp. After this, the Büchner frit was transferred to another suction flask and the pulp was washed with 150 ml of water at 55 °C. The pulp then was transferred to a 500 ml round bottom flask, freeze dried overnight and weighed. The filter paper was dried under a fume hood and weighed again. The filtrate was transferred to a 500 ml round bottom flask and the solvent was removed with a rotary evaporator at 40 °C and 80–90 mbar vacuum. The process was stopped after enough of the solvent (approximately 450–500 ml) was removed to precipitate the lignin pellet quantitatively. Then, the aqueous phase was transferred to a separatory funnel. The solid lignin pellet was extracted 3 times with 50 ml of dichloromethane. The lignin enriched dichloromethane (50 ml) was poured into the separatory funnel containing the water. Then, the liquid/liquid extraction of the water and dichloromethane was carried out. These steps were repeated 3 times. After this, the dichloromethane phase was purified by an additional extraction step with 150 ml of water. Subsequently, the dichloromethane phase was dried with Na_2SO_4 and filtrated. CH_2CL_2 was removed via a rotary evaporator and the product was weighed. The solid residue that remained in the round bottom flask during the solid/liquid extraction with dichloromethane, was dried in the drying oven at 105 °C overnight and weighed.

3.3.7 Analysis of oil via GC-MS/FID

The entire oils of each experiment were dissolved in exactly 50 ml THF, except for Ex 12 (70 ml), for storage. Then, they were diluted each to a concentration of 0.01 g/ml previous to analysis. The GC parameters are summarized in Table 11.

TABLE 11: Gas chromatography method

GC-FID parameters	
injector type	(split/splitless)
injector temperature	260 °C
split ratio	20:1
carrier gas	helium
initial flow	1 ml/min
column	HP-5
length/diameter/film thickness	30 m/320 µm/0.25 µm
temperature program	50 °C (1 min) –150 °C (5 °C/min) – 300 °C (10 °C/min; 10 min)
GC-FID detector parameters	
temperature:	310 °C
hydrogen flow	40 ml/min
air flow	400 ml/min
nitrogen flow	40 ml/min
GC-MS parameters	
injector type	(split/splitless)
injector temperature	260 °C
split ratio	20:1
carrier gas	helium
initial flow	1 ml/min
column	DB-5ms ui
length/diameter/film thickness	30 m/320 µm/0.25 µm
temperature program	50 °C (1 min) –150 °C(5 °C/min) – 300 °C (10 °C/min; 10 min)

GC-MS detector parameters	
low mass	30 m/z
high mass	700 m/z
MS source	230 °C (maximum 250 °C)
MS quad	150 °C (maximum 200 °C)

The quantification of each compound was performed via comparison of the data from GC-MS (qualification) with the data from GC-FID (quantification). For the quantification, several standard chemicals were measured to determine the relation between concentration and signal of the detector.

TABLE 12: RF values of the measured standard compounds for quantification

Standards	**Ret Time [min]**	**Area**	**Concentration [mg/ml]**	**c/Area (RF)**
vanillin	21.28	446859	0.38	8.59E-07
guaiacol	13.05	536305	0.39	7.27E-07
eugenol	20.25	645467	0.40	6.17E-07
cis-isoeugenol	21.49	64403	0.05	8.24E-07
trans-isoeugenol	22.40	407807	0.34	8.24E-07
dihydroeugenol	20.50	757914	0.43	5.63E-07
acetovanillone	23.14	602751	0.42	7.02E-07
p-ethylguaiacol	18.22	658253	0.40	6.12E-07
averaged rf	-	-	0.40	6.94E-07

Relative response factors (RRFs) were used for quantification due to the lack of appropriate reference materials. In order to calculate the RRFs, a method published by Saint Laumer was used.[100] The response factor is the ratio of the signal to the actual concentration of a compound. Relative response factors for a certain compound are measured by analyzing the respective compound, a standard of equal concentration and comparing their response factors. A faster way to determine the relative response factor is to calculate them. The calculation is based on the theoretical combustion energy of the respective compound and therefore linked to the molecular structure.[100]

TABLE 13: List of found aromatic monomers with their respective retention times on the MS and the FID columns

MS **[min]**	**List of found aromatics** **compound**	**FID** **[min]**	**RRfs**	**Reference**
10.57	*cresol*	12.60	1.09	**guaiacol**
10.96	*guaiacol*	13.07	1.00	**guaiacol**
13.94	*p-cresol, 2-methoxy-*	15.94	1.26	**guaiacol**
16.18	*3',5'-dihydroxyacetophenone*	18.13	1.14	**acetovanillone**
16.32	*p-ethylguaiacol*	18.24	1.00	**p-ethylguaicol**
16.88	*monomeric aromatic compound*	18.64	1.00	**averaged**
17.32	*4-vinyl-2-methoxy-phenol*	19.15	0.94	**isoeugenol**
18.11	*chauvicol (pheno, 4-(2-propenyl)-*	19.80	0.81	**isoeugneol**
18.44	*eugenol*	20.27	1.00	**eugenol**
18.71	*dihydroeugenol*	20.52	1.00	**dihydroeugenol**
18.88	*monomeric aromatic compound*	21.12	1.00	**averaged**
18.99	*benzene, 1-methoxy-4-methyl-*	20.69	1.07	**guaiacol**
19.37	*phenol, 4-propyl-*	21.10	0.78	**dihydroeugenol**
19.54	*vanillin*	21.29	1.00	**vanillin**
19.78	*isoeugenol cis*	21.52	1.00	**cis-isoeugenol**
20.22	*2-methylresorcinol, acetate*	22.09	1.08	**acetovanillone**
20.91	*isoeugenol trans*	22.42	1.00	**trans-isoeugenol**
21.01	*monomeric aromatic compound*	22.61	1.00	**dihydroeugenol**
21.15	*ethyl vanillylether*	22.70	1.00	**dihydroeugenol**

MS [min]	List of found aromatics compound	FID [min]	RRfs	Reference
21.35	*benzene, 4-ethenyl-1,2-dimethoxy*	22.84	0.91	**isoeugenol**
21.69	*acetovanillone*	23.15	1.00	**acetovanillone**
21.94	*isovanilline*	23.35	1.00	**vanillin**
22.12	*1,2-dimethoxy-4-n-propylbenzene*	23.57	0.86	**dihydroeugenol**
22.25	*monomeric aromatic compound*	23.72	1.00	**averaged**
22.57	*1-(3-hydroxy-4-methoxyphenyl)propan-2-one*	23.97	1.03	**acetovanillone**
22.62	*monomeric aromatic compound*	24.16	1.00	**averaged**
23.13	*(z)-4-(2-ethoxyethenyl)anisole*	24.42	0.89	**isoeugenol**
23.45	*monomeric aromatic compound*	24.70	1.00	**averaged**
23.55	*propiovanillone*	24.82	1.03	**acetovanillone**
23.68	*ethyl vanillate*	24.88	1.17	**acetovanillone**
24.03	*monomeric aromatic compound*	25.67	1.00	**averaged**
24.28	*4-ethoxy-3-methoxyphenethyl alcohol*	25.86	1.00	**dihydroeugenol**
24.48	*aromatic monomer*	26.04	1.00	**averaged**
24.55	*ethyl homovanillate*	26.18	1.11	**acetovanillone**
24.65	*homovanillic acid*	26.61	1.24	**acetovanillone**
24.96	*monomeric aromatic compound*	26.44	1.00	**averaged**
25.21	*monomeric aromatic compound*	26.47	1.00	**averaged**
25.75	*2-propanone,1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-*	26.65	1.17	**acetovanillone**

MS	**List of found aromatics**	**FID**		
[min]	**compound**	**[min]**	**RRfs**	**Reference**
25.91	*coniferaldehyde*	26.93	1.07	**isoeugenol**
26.38	*2-isopropyl-3,4-dimethoxybenzaldehyde*	27.34	1.05	**vanillin**
28.17	*monomeric aromatic compound*	28.20	1.00	**averaged**

4. Results and Discussion

The aim of this thesis was to find appropriate process conditions for the subsequent fragmentation of larch sawdust and the depolymerization of lignin, with the target to achieve as high yields of bio-oil (the oil itself should contain a maximum of aromatic monomers) as possible. For this, a so called ECCL (Early stage Catalytic Conversion of Lignin) process was chosen. ECCL is a lignin first approach to biomass conversion and characterized by the use of heterogeneous catalysts to enable a fragmentation of biomass with simultaneous depolymerization of lignin, without damaging the carbohydrate fibers (pulp). This usually is achieved via a hydrogenolysis of the intramolecular lignin bonds with molecular hydrogen or hydrogen donating solvents. 16 experiments were conducted, in which the feedstock (sieved larch sawdust ≤ 0.5 mm ≤ 2.0 mm), the feed stock loading (35 g on a dry basis) and the solvent (350 ml of an EtOH/H_2O 75/25 v/v mixture) were kept constant. The influence of the atmosphere (N_2 or H_2), the support (3.5 g kaolin pellets) and the active material (8.2 wt% NiO on 3.5 g kaolin pellets) was investigated in the first six experiments. Therefore, the atmosphere of 1 atm N_2 was compared to 40 bar of H_2 at 210 °C. Then, the effects of the support were investigated under N_2 and H_2 atmosphere at 210 °C. After it was proven that the support showed no considerable effect, the active material (NiO on support) was investigated in N_2 and H_2 atmosphere at 210 °C. Again, no effects occurred. Following this, NiO was compared to Raney nickel, which was investigated under N_2 and H_2 atmosphere at 210 °C. Raney nickel also showed no impact on the depolymerization. Afterwards, the influence of the temperature on the oil yield, while using the NiO catalyst, was investigated at 182 °C, 190 °C, 210 °C and 220 °C. Thereafter, a lower pH was applied via the addition of 1.1 vol% H_2SO_4 to the reaction mixture containing the NiO catalyst under H_2 atmosphere at 179°C for 3 h and 1 h. Following this, the sulfuric acid concentration was reduced to 0.11 vol% and the effects were investigated with NiO and without NiO at 179 °C under a H_2 atmosphere for 1 h. One last experiment was performed with 0.11 vol% H_2SO_4 at 179 °C under H_2 atmosphere and a reduced reaction time of 0.5 h. An Overview of the various process conditions is given in Table 14. In order to separate and purify the lignin and carbohydrate (pulp) streams, the following work up procedure was applied: After the reaction was completed, the reactor was opened and the reactor head was cleaned with 20 ml of the solvent mixture, which were collected in the reactor vessel. The content of the reactor vessel then was filtrated and the lignin containing liquid liquor was separated from the solid pulp. Subsequently, the ethanol part of the solvent mixture was removed via a rotary evaporator and after most of the ethanol was evaporated, a solid lignin pellet precipitated. This lignin pellet was extracted three times with dichloromethane. The part of the pellet that went in solution was the so-called oil and the part that remained insoluble was called solid lignin. The oil was then purified with a water extraction and dried over Na_2SO_4, which was then removed via filtration. The oil was weighed to determine the yield. The solid lignin was dried over night at 105 °C and weighed to determine the yield. The pulp was dried over night at the freeze drier and weighed to determine the yield. In order to draw conclusions about the compositions of the obtained oils, a qualitative and quantitative analysis was performed via GC/MS and GC/FID.

TABLE 14: Overview of process conditions

Ex	Catalyst	Temp [°C]	Pressure	Time [h]
1	-	210	1 atm N_2	3
2	-	210	40 bar H_2	3
3	3.5 g support	210	1 atm N_2	3
4	3.5 g support	210	40 bar H_2	3
5	3.5 g NiO loaded[a] support	210	1 atm N_2	3
6	3.5 g NiO loaded support	210	40 bar H_2	3
7	3.5 g NiO loaded support	182	40 bar H_2	3
8	3.5 g NiO loaded support	190	40 bar H_2	3
9	3.5 g NiO loaded support	220	40 bar H_2	3
10	0.35 g Raney Nickel	210	40 bar H_2	3
11	0.35 g Raney Nickel	210	40 bar H_2	3
12	H_2SO_4 1.1 % + 3.5 g NiO loaded support	179	40 bar H_2	3
13	H_2SO_4 1.1 % + 3.5 g NiO loaded support	179	40 bar H_2	1
14	H_2SO_4 0.11 % + 3.5 g NiO loaded support	179	40 bar H_2	1
15	H_2SO_4 0.11 % v/v to solvent	179	40 bar H_2	1
16	H_2SO_4 0.11 % v/v to solvent	179	40 bar H_2	0.5

The substrate loading was 35 g of sawdust on dry wood basis, solvent: 350 mL of an EtOH/H_2O mixture 75/25 v/v. [b]The loading of the support with active material was 8.2 wt%

4.1 Influence of hydrogen, kaolin support and the NiO catalyst

4.1.1 NiO catalyst preparation

It was desired to generate NiO loaded kaolin pellets with a catalyst loading of 10 wt% after impregnation and calcination. The analysis of the pellets showed that a loading of 8.2 ± 0.5 wt% was achieved. It was decided that this loading was still sufficient and the pellets were used for the further experiments. Deviations of the targeted 10 wt% NiO loading may result from pore clogging respectively adhesion of the $NiNO_3$ solution on the glass wall of the round bottom flask during spray coating.

4.1.2 Influence of hydrogen, the support and NiO

The first series of experiments were conducted to determine the effect of the supported NiO catalyst. In order to achieve this, it was also necessary to investigate the influence of the conditions, the reactant (H_2) and the support alone. In Table 15 the yields of oil, pulp, and solid lignin are represented:

TABLE 15: Yields of the first test series

Ex	Catalyst	Pressure[a]	Pulp [g]	Oil [g]	Solid lignin [g]
1	-	1 atm N_2	19.84	3.34	6.38
2	-	40 bar H_2[b]	18.31	5.52	2.06
3	3.5 g support[c]	1 atm	19.16	4.00	7.01
4	3.5 g support	40 bar H_2	20.13	4.86	3.73
5	3.5g NiO loaded support[d]	1 atm N_2	19.24	2.69	5.36
6	3.5 g NiO loaded support	40 bar H_2	16.90	5.30	2.79

[a]The reactor was always purged three times with 10 bar N_2, [b]40 bar H_2, [c]3.5 g kaolin pellets, [d]Ni loading of the pellets was 8.2 wt%, The reaction conditions for all experiments were 210 °C for 3 h. Substrate: 35 g larch sawdust on a dry basis, 350 mL $EtOH/H_2O$ 75/25 v/v as solvent.

Table 15 shows that the pulp yields are rather high for all of the first 6 experiments. The oil yields, however, show a significant correlation with the use of hydrogen, as there is always more oil obtained when using it. The support alone shows no significant effect. The results also show no clear evidence about the effectivity of the NiO catalyst. Actually, the best result, regarding oil yields (5.52 g, Ex 2), was achieved with no catalyst or support at all and 40 bar H_2 as reactant. This suggests that the depolymerization occurs due to the conditions and is promoted by hydrogen. One possible explanation for the poor performance of NiO is that it is not present in an activated form (i.e. metallic Ni) at the given conditions. Other possible reasons for the bad performance of the NiO catalyst include poor impregnation, and clogging of the pores of the support, which would drastically reduce the surface area. However, for investigations about the morphology, an electron microscopy would have been necessary, which was not available at the working group. Even if the impregnation worked properly, it still could be possible, that pellets are not a suitable form to catalyze a depolymerization reaction, due to poor accessibility of the polymeric substrates. An easy solution for this would have been to use a homogeneous catalyst (which was applied later – H_2SO_4) or a powder (which also was applied in the form of Raney nickel). The latter one has the problem of a difficult separation from the solid byproduct – the pulp – and would require a catalyst cage. Later on in this thesis, attempts were made to increase the effectivity of the NiO catalysts via a change of reaction conditions i.e. an activation of the catalyst.

4.2 Comparison of NiO to Raney nickel

To gain further insight in the effectiveness of the in-house produced NiO on kaolin catalyst pellets, they were compared to Raney nickel (Table 16).

TABLE 16: Comparison of Raney nickel to no catalyst and NiO

Ex	Pressure	Pulp [g]	Oil [g]	Solid lignin [g]	Catalyst
10	1 atm N_2	19.54	4.00	3.73	Raney nickel[a]
11	40 bar H_2	19.43	4.52	3.44	Raney nickel
2	40 bar H_2	18.31	5.52	2.06	-
6	40 bar H_2	16.90	5.30	2.79	NiO on support[b]

[a] loading of Raney nickel: 350 mg, [b] loading of NiO: 3.5 g kaolin support with 8.2 wt% NiO

The yields of oil were quite low and actually, Ex 11 (with H_2 as reactant and Raney nickel) had one gram less oil than Ex 2 (only H_2 – no catalyst), which used no catalyst at all. Ex 11 also achieved worse results than Ex 6 (NiO on support – H_2 as reactant). This leads to the conclusion that Raney nickel is not a suitable catalyst for this specific process. However, the catalyst loading was very low (350 mg for 35 g of dry saw dust) and it is quite common in the field of lignin valorization to use Raney nickel. Rinaldi, one of the pioneers of ECCL, worked with Raney nickel and a catalyst loading above 50 wt% in regards to the substrate.[3] So possibly the reaction would have worked better with higher catalyst loadings. As in NiO, another explanation for the poor performance of Raney nickel could be the hindered accessibility of lignocellulose.

4.3 Influence of temperature

The influence of different temperatures was investigated. In order to achieve this, the reaction conditions (40 bar H_2 for 3 h), the amount of feedstock (35 g), the catalyst (3.5 g kaolin pellets loaded with 8.2 wt% NiO) and the solvent (EtOH/H_2O 75/25 v/v – 350 ml) were kept constant whilst the temperatures were varied. The chosen temperatures were 182 °C, 190 °C, 210 °C and 220 °C. The results, especially the oil yields, were compared and are shown in Table 17.

TABLE 17: Influence of temperature on the yields of the various streams

Ex	Temp [°C]	Pressure	Pulp [g]	Oil [g]	Solid lignin [g]
7	182	40 bar H_2	22.42	1.15	4.21
8	190	40 bar H_2	20.77	1.58	5.17
6	210	40 bar H_2	16.9	5.30	2.79
9	220	40 bar H_2	14.92	7.24	2.27

Substrate: 35 g larch sawdust on a dry basis, 350 ml EtOH/H_2O 75/25 v/v as solvent. Conditions: 40 bar H_2, 3 h, varying temperatures. Catalyst: 3.5 g kaolin pellets loaded with 8.2 wt% NiO.

The results clearly show, that the yields of oil are drastically affected by the chosen temperatures. Low temperatures give very low oil and very high pulp yields because less of the pulp is degraded. The effect is reciprocal regarding the yields of solid lignin, which are higher at lower temperatures because less lignin is cleaved into smaller fragments. Since it is the aim to achieve maximum oil yields, higher temperatures are preferential. In addition, it seems that at higher temperatures the solid lignin is converted to oil, which leads to the conclusion that higher temperatures facilitate the breakage of more intramolecular bonds of the oligomeric and polymeric lignin molecules, which is highly desired. Of course, care has to be taken not to promote repolymerization and obtain unreactive char but at 220 °C, under the given conditions, this does not seem to be the case. Due to sensorial optical assessment, it must be stated that the quality of the pulp is poor for all given temperatures at this conditions – see Figure 144. It is even possible, to still visually see the sawdust particles, so the conditions clearly are too mild. However, this conclusion is only based on visual determination of the quality, so there is no quantification behind it except for a Klason lignin determination of the pulp – see chapter 4.5.

FIGURE 14: Picture of a typical pulp obtained under 210 °C for 3 h under 40 bar H_2 (Ex 6)

4.4 Influence of pH

Based on the high yields of pulp and its optical appearance (crude and still sawdust like) it was attempted to enhance the fractionation. Due to in-house experience with the so-called organosolv process (a process where biomass is cooked in an organic solvent-water mixture and H_2SO_4), it was decided to combine the ECCL and the organosolv process. The use of H_2SO_4 seemed to be promising for an enhanced fractionation of wood due to its ability to degrade carbohydrates.

TABLE 18: Yields when using sulfuric acid as catalyst

Ex	Catalyst	Pressure	Pulp [g]	Oil [g]	Solid lignin [g]	Time [h]	Aromatic monomers [%][a]
Ex 12	NiO + 1.1 vol% H_2SO_4	40 bar H_2	7.63	10.64	0.73	3	3.69
Ex 13	NiO + 1.1 vol% H_2SO_4	40 bar H_2	6.61	9.94	1.31	1	3.00
Ex 14	NiO + 0.11 vol% H_2SO_4	40 bar H_2	8.48	5.75	6.24	1	3.61
Ex 15	0.11 vol% H_2SO_4	40 bar H_2	6.70	7.46	5.04	1	4.30
Ex 16	0.11 vol% H_2SO_4	40 bar H_2	8.63	5.78	5.10	0.5	4.04

[a] Percentages are given in regards to the total lignin found. Total lignin = oil + solid lignin + residual lignin in pulp – see chapter 4.5

The first experiment with the new approach was performed under the following conditions: 179 °C, 3 h, 35 g substrate (on dry basis), 350 ml solvent (again EtOH/H_2O 75/25 v/v), 3.5 g NiO loaded support, 40 bar H_2 and 1.1 vol% H_2SO_4.This was too severe and therefore the pulp was highly degraded and altered (the pulp is more valuable than the lignin!) after the reaction, even though the oil yields were quite high. However, the analysis of the oil in chapter 4.6 will show that a lot of the oil from Ex 12 and Ex 13 are carbohydrate derived. A second experiment with 1.1 vol% H_2SO_4 and a reaction time of only 1 h was performed but still the conditions were too severe and the pulp again was completely destroyed – see Figure 15.

FIGURE 15: Pulp obtained when using 1.1 vol% sulfuric acid as catalyst

After this, the acid concentration was reduced to 0.11 vol% for Ex 14–16. This worked out very nicely especially in regards to the pulp quality – see Figure 16. Again, no real analytic quantification and qualification of the pulp quality could be performed, but it was sensorial detectable that these experiments gave good results regarding pulp quality.

FIGURE 16: Pulp when using 0.11 vol% sulfuric acid as catalyst

This was the first time that the pulp had a cardboard-like appearance. Due to the success of Ex 14 with 0.11 vol% sulfuric acid and the NiO catalyst it was decided to repeat this experiment, except for omitting the NiO catalyst. Surprisingly the results were even better, if no NiO was used and the oil yields increased from 5.75 g (Ex 14) to 7.46 g (Ex 15). Another experiment was conducted without the NiO catalyst but this time the reaction time of the process was reduced to 30 minutes (Ex 16). The results were satisfying, even though the oil yields decreased to a small amount. In return, the yield of the pulp increased. As stated before, at this institute no real quantification technique of the quality of the pulp is available, except for a Klason lignin determination. Based on information about the pulp, one could choose, which conditions are more suitable. Ideally, an acid concentration could be found that degrades most of the hemicellulose, therefore making the lignin accessible for reactants, respectively a catalyst, without destroying the high value cellulose fibers (pulp).

4.5 Determination of residual lignin in the pulp via the Klason lignin method

In order to determine the delignification efficiency, the amount of residual lignin in the pulp was investigated – see Table 19. Therefore, 1 g of pulp was digested in 12 N sulfuric acid for 1 h, then diluted to an acid concentration of 3 wt% and cooked for 4 h. After this, the mixture was filtrated and the solid residue was dried and weighed, giving the amount of acid insoluble lignin. The yield of acid soluble lignin was determined via measuring the adsorption of light of a wavelength of 205 nm in the filtrate. The measurements of the acid insoluble and the acid soluble lignin were performed according to the so-called Klason lignin method.[99] This allowed to make conclusions about the relative conversion of lignin into oil and solid lignin because it gave information about the total lignin content in the used sawdust samples (oil + solid lignin + Klason lignin in the pulp). As shown in Table 19, the amount of residual lignin in the pulp is heavily influenced by the temperature and the pH. Interestingly, the first 6 experiments showed no decisive variation in the amounts of pulp, so neither the presence of hydrogen, the support nor the active species (NiO) had a remarkable influence. The experiments 7,8 and 9 showed, that with increasing temperatures less lignin was found in the pulp. Regarding residual lignin values, the application of light acid concentrations (0.11 vol% - Ex 14, Ex 15 and Ex 16) also showed a positive effect, except for Ex 15.

TABLE 19: Yields of Klason lignin

Ex	Pulp[a] [g]	AIL[b] [g]	AIL [%]	ASL[c] [mg]	ASL [%]	Pulp[d] [g]	AIL_{total} [g]	ASL_{total} [g]	$Lignin_{total}$ in pulp [g]	Lignin[e] in pulp [%]
1	1.00	0.21	20.79	1.8	0.18	19.84	4.12	0.04	4.16	20.97
2	1.00	0.22	21.76	2.0	0.20	18.31	3.98	0.04	4.02	21.96
3	1.00	0.20	19.57	1.8	0.18	19.16	3.75	0.03	3.78	19.75
4	1.00	0.22	19.56	2.0	0.21	20.13	3.94	0.04	3.98	19.77
5	1.00	0.20	20.44	1.9	0.19	19.24	3.93	0.04	3.97	20.63
6	1.00	0.20	20.27	1.8	0.18	16.90	3.43	0.03	3.46	20.45
7	1.00	0.27	27.23	1.9	0.19	22.42	6.10	0.04	6.15	27.42
8	1.00	0.24	24.08	2.0	0.20	20.77	5.00	0.04	5.04	24.28
9	1.00	0.23	23.15	2.0	0.20	14.92	3.45	0.03	3.48	23.35
10	1.00	0.23	23.03	2.5	0.25	19.54	4.50	0.05	4.55	23.28
11	1.00	0.21	21.37	2.1	0.21	19.43	4.15	0.04	4.19	21.58
12	1.00	0.99*	98.22*	1.4	0.14	7.63	7.49*	0.01	7.50	98.36*
13	1.00	0.96*	96.08*	1.2	0.12	6.61	6.35*	0.01	6.35	96.20*
14	1.00	0.190	18.52	1.3	0.13	8.48	1.57	0.01	1.58	18.65
15	1.00	0.25	24.55	1.6	0.16	6.70	1.65	0.01	1.66	24.71
16	1.00	0.14	14.03	1.7	0.17	8.63	1.21	0.01	1.23	14.20

[a]Amount of pulp used for the analysis, [b]acid insoluble lignin found in 1 g of pulp, [c]acid soluble lignin found in 1 g of pulp, [d]total pulp, AIL_{total}: Acid insoluble lignin calculated for the total pulp, ASL_{total}: Acid soluble lignin calculated for the total pulp, $Lignin_{total}$: AIL_{total} and ASL_{total} combined. [e]Combined percentual amount of AIL and ASL in the pulp.*These experiments were so severe that they transformed the pulp into insoluble material.

Table 19 shows that the variation in percentage is much lower than in absolute (mass) terms. This is related to the different yields of pulp achieved. Even though it is principally better to achieve high yields of pulp, also the quality should be taken in account. As mentioned earlier, the pulp qualities have been rather poor for all experiments that did not use 0.11 vol% sulfuric acid as catalyst. Therefore, it was decided to use the available data, determine the total lignin content, and calculate the delignification efficiency based on the comparison of total lignin to the amount of residual lignin in the pulp. The values of the total lignin found for each experiment are shown in Table 20. Apparently, the yield of total lignin always succeeds the theoretical yield (calculated from the input (35 g) and the amount of Klason lignin (29 %) in the used larch wood sawdust). As it will become apparent in later chapters, this results partly from the occurrence of carbohydrate derived compounds in the oil.

TABLE 20: Amount of total lignin found in the respective experiments

Ex	Total lignin [g]	Theoretical yield[a] [g]	Recovery rate lignin [%]
1	13.88	10.85	128
2	11.60	10.85	107
3	14.79	10.85	136
4	12.57	10.85	116
5	12.02	10.85	111
6	11.55	10.85	106
7	11.52	10.85	106
8	11.80	10.85	109
9	13.00	10.85	120
10	12.28	10.85	113
11	12.16	10.85	112
12	18.88	10.85	174
13	17.61	10.85	162
14	13.58	10.85	125
15	14.16	10.85	131
16	12.02	10.85	111

[a] Calculated from the input (35 g) and the amount of Klason lignin (29 %) in the used larch wood sawdust. The theoretical yield in reality is higher because during the depolymerization of lignin hydrogen and water get added to the molecules, thus adding more mass to the lignin fragments.

Table 21 shows the yields of pulp, oil, solid lignin, and the delignification efficiency of each experiment. Apparently, the delignification efficiency increases substantially at lower pH values during pulping. This is explained by a better accessibility of the lignin for hydrogenolysis due to the breakage of glycosidic bonds. Table 21 also shows the huge variation in regards to the yields of oil and solid lignin. Both are positively influenced by higher temperatures and the presence of hydrogen i.e. the oil yields increase and the solid lignin yields decrease.

FIGURE 17: Solid lignin (Ex 11)

One weak point of pulping under acidic conditions is the low conversion of solid lignin into oil. Even if the separation is satisfying, the conversion is still improvable. Solid lignin can either consist of monomers, whose bonds to its neighbors cannot be broken easily (no β-O-4 or other cleavable bond), or recondensed/repolymerized units of bonds that could not be broken for other reasons. Comparing Ex 1 to Ex 2, Ex 3 to Ex 4, and Ex 5 to Ex 6, it becomes apparent that hydrogen has a very positive effect on the depolymerization of lignin. From the comparison of Ex 9 (220 °C), Ex 7 (182 °C), Ex 8 (190 °C) and Ex 6 (210 °C) one can conclude that the amount of solid lignin decreases with increased severity i.e. there is much less solid lignin at 220 °C (2.27 g) than at 182 °C (4.22 g). Why there is more solid lignin at 190 °C cannot be answered and it is suggested that this is a statistical deviation rather than a mechanistic effect. The same pattern is true for the pH: the higher the severity (i.e. the lower the pH value [Ex 12 with 1.1 vol% H_2SO_4 – 0.73 g solid lignin]) the lower is the yield of solid lignin. This data therefore suggests, that the solid lignin mainly doesn't consist of repolymerized monomers but rather of lignin that has yet to be broken. Therefore, it should be possible to increase the severity without coming into the range of enhanced repolymerization. However, increased severity also increases the degradation of the valuable pulp, so a compromise between oil yield and pulp degradation has to be found. It also should be possible to convert more of the solid lignin into oil with a suitable catalyst, which yet has to be found.

TABLE 21: Amounts of lignin in the various streams

Ex	Oil[a] [%]	Residual lignin in pulp [%]	Solid lignin[%]	Delignification efficiency[b] [%]
1	24	29.96	45.98	70.04
2	48	34.68	17.74	65.32
3	27	25.57	47.41	74.43
4	39	31.67	29.69	68.33
5	22	33.01	44.61	66.99
6	46	29.93	24.18	70.07
7	10	53.38	36.60	46.62
8	13	42.75	43.84	57.25
9	56	26.81	17.45	73.19
10	33	37.05	30.40	62.95
11	37	34.50	28.30	65.50
12	56	39.74	3.89	60.26
13	56	36.09	7.46	63.91
14	42	11.65	45.96	88.35
15	53	11.70	35.59	88.30
16	48	10.20	41.93	89.80

[a] Percentual values are always in regards to the amount of total lignin. The total lignin is the sum of all found lignin i.e. the lignin in the oil, the solid lignin and the residual lignin in the pulp. However, these values always exceed the theoretical lignin due to various reasons, which will be explained in the next chapters. [b] This is the percentage of the summed lignin in the oil and the solid lignin compared to the residual lignin in the pulp.

4.6 Determination of oil composition via GC-MS/FID

The total lignin (equals to the sum of oil + solid lignin + residual lignin in the pulp) found in the experiments of this thesis always exceeded the theoretical value, so it became apparent that some of the obtained lignin streams also contained other non-lignin derived compounds. Due to this and the fact that the economic value of the oil is determined by its composition, it was decided to perform a qualitative and quantitative analysis of the oil (GC-MS/FID). Due to pretesting (not quantified GC-MS spectra), it was already known that the oil also contained compounds, like furfurals or ethyl levulinate that originated from carbohydrates.

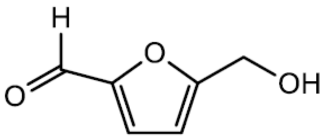

FIGURE 18: Hydroxymethylfurural

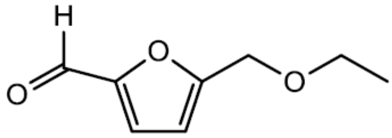

FIGURE 19: 5-Ethoxymethylfurfural

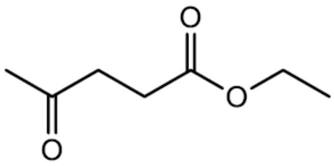

FIGURE 20: Ethyl levulinate

Acids tend to hydrolyze glycosidic bonds, yielding sugar monomers like glucose. However, under the given conditions and with diluted sulfuric acid, those monomers tend to further react to furfurals (mainly hydroxmethylfurfural for hexoses and furfural for pentoses), which then can further react to levulinic acid – see Figure 22.[101,22] This is exactly what happened during this process and high amounts of both components were found. However, HMF was actually mainly found in the form of 5-ethoxymethylfurfural and levulinic acid in the form of ethyl levulinate, especially when acid was used as catalyst. Due to the given (acidic) conditions and the ethanol in the solvent, it is suggested that levulinic acid reacted with ethanol to ethyl levulinate (esterification) and HMF reacted with ethanol to 5-ethoxymethylfurural (acid catalyzed etherification with ethanol).[102]

FIGURE 21: Oil (Ex 2) in 50 mL THF

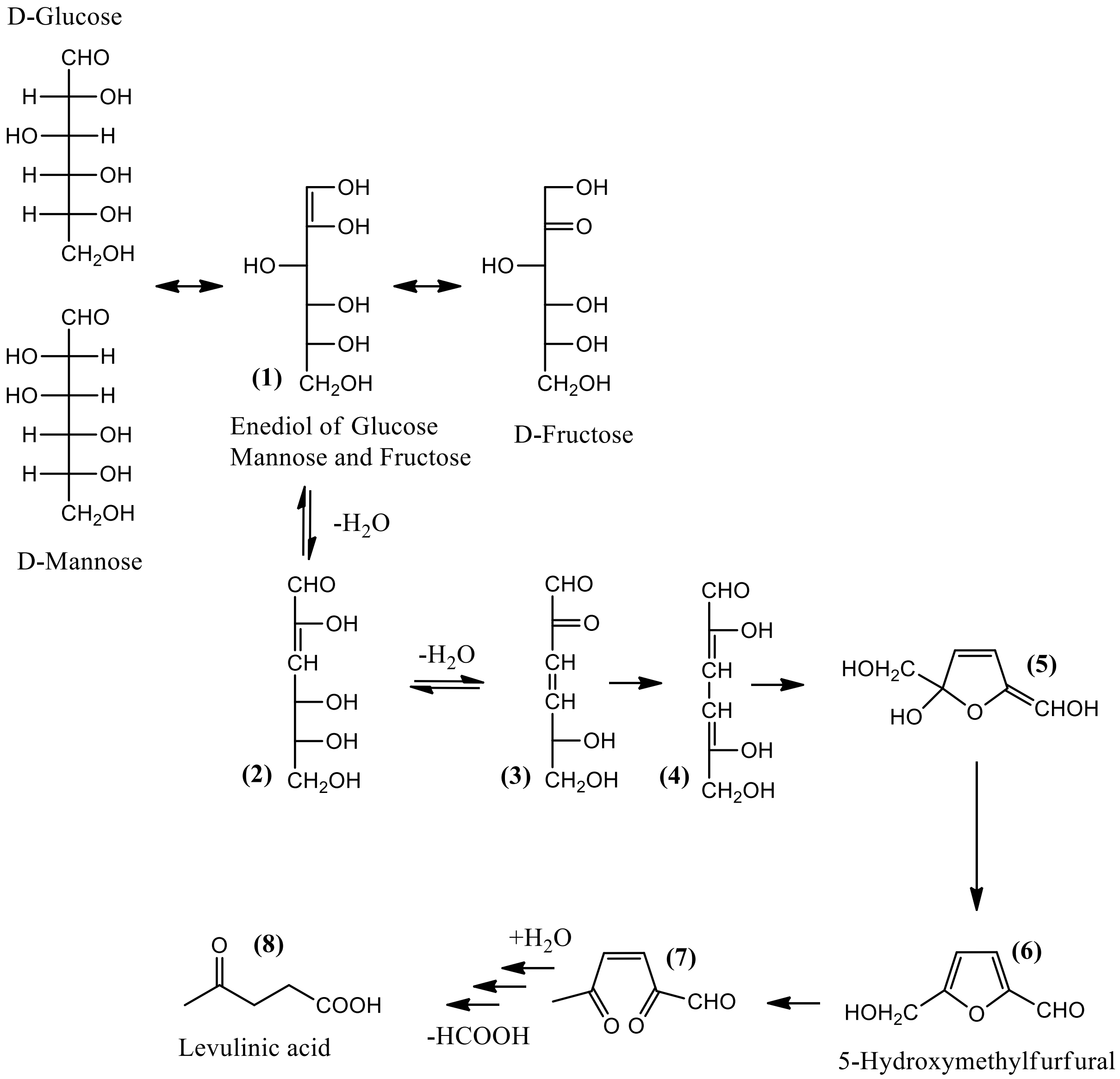

FIGURE 22: Conversion of carbohydrates to levulinic acid via 5-hydroxymethylfurfural[96,101,103]

The occurrence of these two compounds is quite interesting due to their high economic value.[104] Both, HMF and levulinic acid could become platform chemicals in the industry. Their market prices are around 2500 €/ton for HMF and around 5500 €/ton for levulinic acid, respectively. However, a price that high is rather a burden than an advantage due to the competition of crude oil derived products, where the market price for platform chemicals is in the range of 1 $ per kg.[105]

4.6.1 Yields and types of aromatic monomers in oil

The amounts and types of the aromatic monomers (the most valuable lignin breakdown products) are of most importance. Therefore, a qualification via GC-MS, coupled with a quantification via GC-FID was performed. The spectra were quite complicated because of the appearance of up to 91 different compounds in the volatile fraction of the oil. As a rule of thumb, one can say that (with the chosen method – see experimental part) the carbohydrate degradation compounds eluate in the first 18 minutes and the aromatic monomers eluate approximately from minute 12 to 28 in the GC-MS column – see Figure 23–25. Due to the fact, that the aromatic monomers are the most valuable compounds obtainable from lignin, it is desirable to maximize their yields. All 16 oil samples were analyzed with GC-MS and GC-FID. Six chosen standards (vanillin, guaiacol, eugenol, dihydroeugenol, isoeugenol, para-ethylguaiacol) with known concentration were measured with GC-FID for a quantification. Suitable standards were not available for all compounds present in the oil, so a method was chosen to calculate the relative response factors (rrf).[100] With the available standards and by the rrfs it was able to quantify the aromatic monomers.

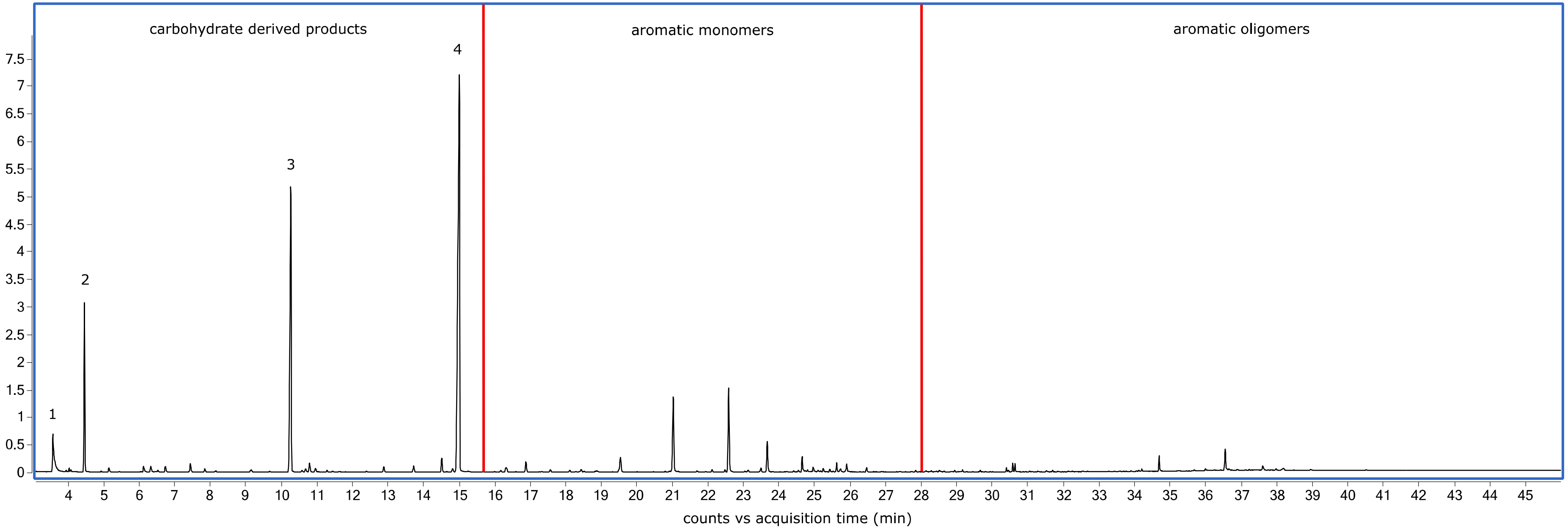

FIGURE 23: Chromatogram of experiment 15 with segmentation in areas in regards to carbohydrate derived products, aromatic monomers, and aromatic oligomers

TABLE 22: Retention time, % of total area and name of the main compounds found in the section of carbohydrate derived products

Peak	Retention time [min]	% of total area	Compound
1	3.576	3.82	2-hydroxytetrahydrofuran (from THF used as solvent)
2	4.464	8.32	furfural
3	10.270	22.19	ethyl levulinate
4	15.008	43.11	5-ethoxymethylfurfural

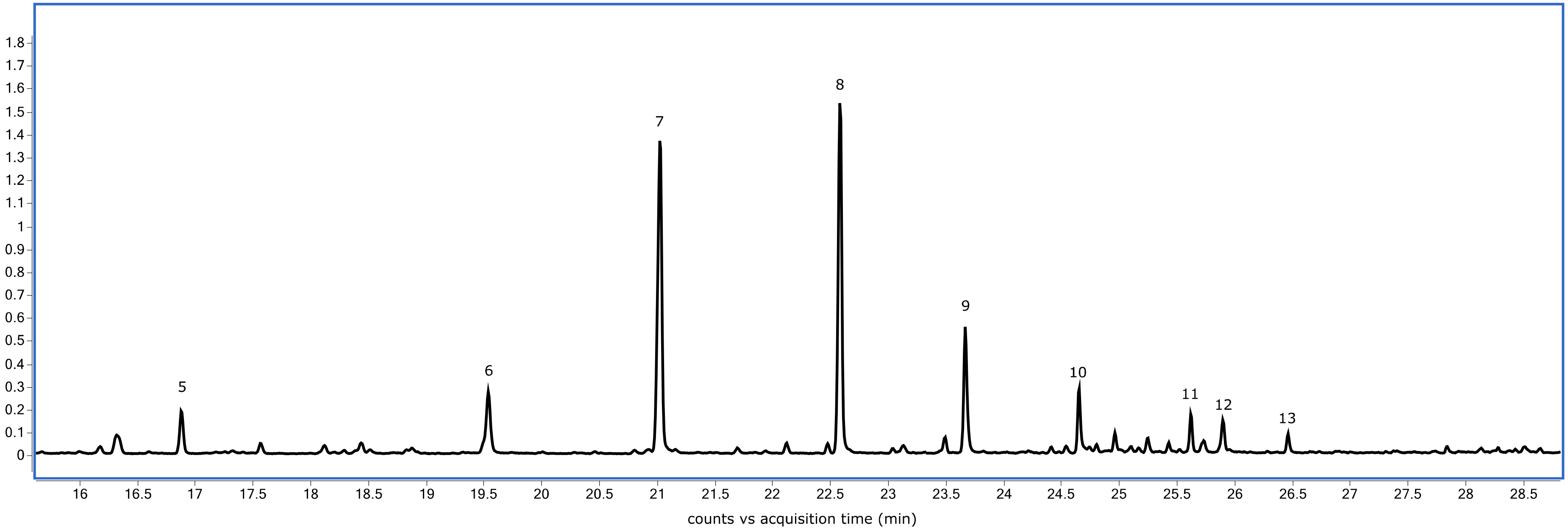

FIGURE 24: Chromatogram of experiment 15 with detail on the section of aromatic monomers

TABLE 23: Retention time, % of total area and name of the main compounds found in the section of aromatic monomers

Peak	Elution time [min]	% of total area	Compound
5	16.879	0.68	4-hydroxymandelic acid
6	19.537	1.24	Vanillin
7	21.023	5.89	2,4-dihydroxypropiophenone
8	22.583	5.43	p-ethylguaiacol
9	23.666	1.85	ethyl vanillate
10	24.650	0.90	homovanillic acid
11	25.619	0.50	undeterminable
12	25.897	0.52	conifer aldehyde
13	26.460	0.22	homovanillyl alcohol

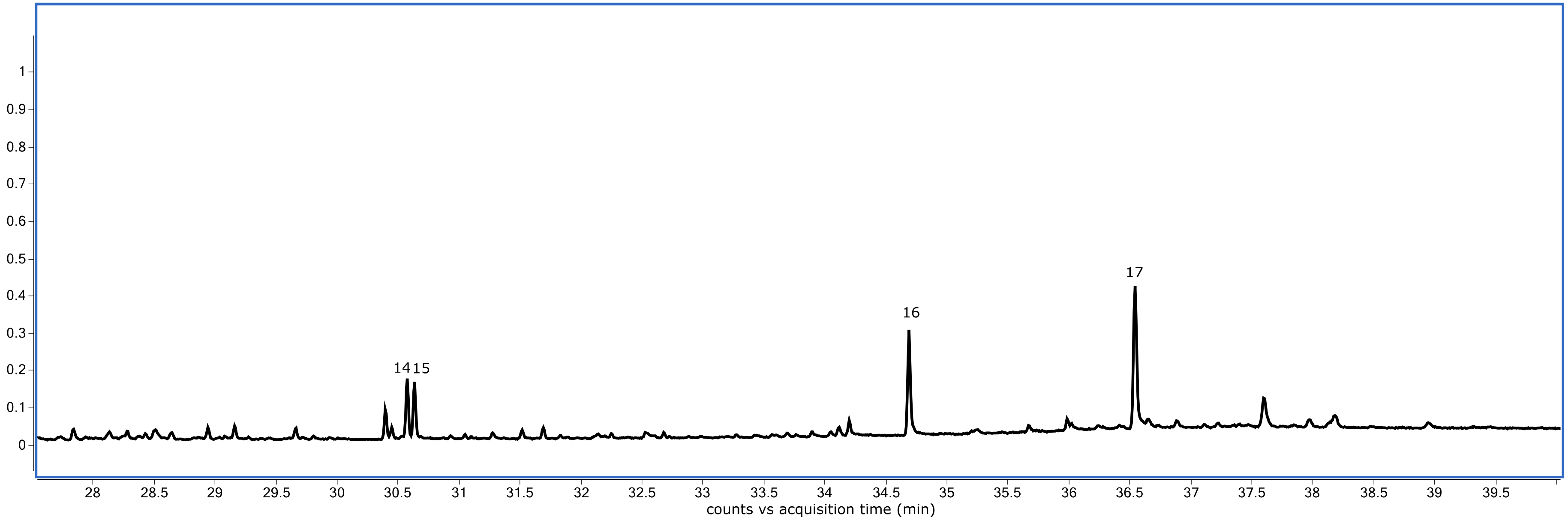

FIGURE 25: Chromatogram of experiment 15 with detail on the section of extractives and aromatic oligomers

TABLE 24: Retention time, % of total area and name of the main compounds found in the section of aromatic oligomers and extractives

Peak	Retention time [min]	% of total area	Compound
14	30.577	0.41	linoleic acid ethyl ester
15	30.638	0.38	ethyl oleate
16	34.693	0.77	4-Methoxy-4',5'-methylenedioxybiphenyl-2-carboxylic acid
17	36.547	1.16	anhydro-secoisolariciresinol

TABLE 25: Yields of the aromatic monomers in comparison to the total lignin and the oil

Ex	Yield oil [g]	Yield monomers in oil [g]	% monomers of total lignin	% monomers of oil
1	3.34	0.23	2.12	6.88
2	5.52	0.41	3.80	7.47
3	4.00	0.20	1.86	5.04
4	4.86	0.35	3.21	7.18
5	2.69	0.18	1.68	6.76
6	5.30	0.38	3.52	7.21
7	1.15	0.17	1.57	14.78
8	1.58	0.21	1.92	13.19
9	7.24	0.43	4.01	6.00
10	4.00	0.44	4.07	11.04
11	4.52	0.40	3.73	8.96
12	10.64	0.40	3.69	3.76
13	9.94	0.33	3.00	3.28
14	5.75	0.39	3.61	6.81
15	7.46	0.47	4.30	6.25
16	5.76	0.44	4.04	7.62

The yields of aromatic monomers ranged from 1.5 – 4.3 % regarding the total amount of lignin. These are rather low values compared to yields of up to 50 % (van den Bosch[106]) and 54 % (Parsell[66]); however, they either used very complicated and expensive catalysts or did not take the pulp quality into concern. For a detailed comparison of the achieved results see – chapter *4.8 Overview of product yields and comparison to literature.* It is clearly recognizable that the total amount of aromatic monomers increases with higher temperatures. The use of sulfuric acid (Ex 12–Ex 16) as catalyst showed an interesting effect. Already 0.11 vol% Sulfuric acid had very positive effects on the yields of oil and aromatic monomers (Ex 14–16). With higher acid concentrations (1.1 vol% = Ex 12 and Ex 13) the yield of monomers was lower than with milder conditions (acid concentration 0.11 vol% = Ex 14–16). In addition, Ex 14 has lower yields than Ex 15 and Ex 16, despite the fact that only in Ex 14 the NiO catalyst was present. This suggests that the catalyst had a negative effect on the depolymerization. This could be statistical fluctuations but the difference of the yields of aromatic monomers between Ex 14 and Ex 15 is quite impressive. The presence of hydrogen nearly doubled the yield of monomers even if no catalyst was used. This leads to the speculation that none of the used catalysts were suitable to facilitate the degradation of lignin to aromatic monomers in a sufficient amount. However, sulfuric acid makes the lignin more accessible for reactions, so it still has a positive effect. It must be stated that in literature it is quite common to just give the amount of volatile compounds, which also contain carbohydrate degradation products, instead of the "real" amount of aromatic monomers.[3] If also those carbohydrate derived products were accounted as "monomers", a yield of 33.5 % for Ex 12 would have been obtained.

The main aromatic monomers found:

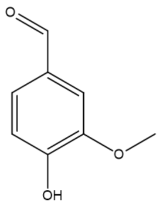

FIGURE 26: Vanillin

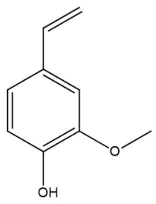

FIGURE 27: 2-Methoxy-4-vinylphenol

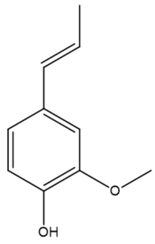

FIGURE 28 Isoeugenol

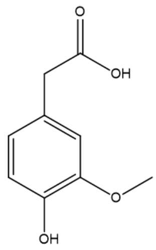

FIGURE 29: Homonvanillic acid

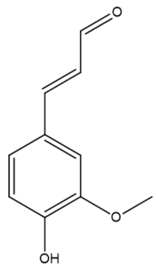

FIGURE 30: Coniferyl aldehyde

4.6.2 Yields and types of carbohydrate degradation products in oil

The exact amount of each compound and the share of carbohydrates in the oil vary a lot between the different reaction conditions. The more severe the reaction conditions, the more carbohydrate degradation products were found in the oil. Interestingly, also the composition of those products changed a lot with the severity. When sulfuric acid was used as a catalyst, exceptionally high values of ethyl levulinate and 5-ethoxymethylfurfural were produced. The equilibrium of those two compounds was shifted drastically to ethyl levulinate when stronger acid concentrations were used (1.1 vol% H_2SO_4)

TABLE 26: Carbohydrate-derived compounds in the oil

Ex	Carbohydrates in oil [g]	Carbohydrates in oil [%]	Corrected oil yield [g]
8	0.17	44.3	1.42
9	0.42	49.3	6.82
12	3.25	89	7.39
15	1.67	78.2	5.79
16	0.92	67.8	4.83

As it is shown in Table 26, the use of sulfuric acid (Ex 12, Ex 15 and Ex 16) drastically increases the amount of carbohydrate degradation products in the oil, which makes sense because it is known that glycosidic bonds are easily cleaved in acidic environments. Especially the oil produced during Ex 12 (1.1 vol% H_2SO_4) contained a lot of carbohydrate degradation products, mainly ethyl levulinate (85 % of all volatile compounds). The oils of Ex 15 and Ex 16 (both with 0.11 vol% H_2SO_4) contained 13 % and 22 % ethyl levulinate respectively. They still contain high amounts of 5-ethoxymethylfurfural with 43 % for Ex 15 and 40 % for Ex 16. As suggested before, acid catalyzes the conversion of HMF into 5-ethoxymethylfurfural – see chapter 4.6. It also catalyzed the conversion of furfural to levulinic acid (Figure 24), which can further react to ethyl levulinate with ethanol from the solvent – see chapter 4.6. As a rule of thumb, one can say that the amount of carbohydrates found in the oil correlates directly with the severity of the chosen conditions. The influence of the pH value seems to be higher than the influence of the temperature. It can also be seen, that the total amounts of carbohydrate degradation products (mainly furfurals and ethyl levulinate – see in the appendix) increase with higher temperatures. This has positive and negative aspects: On the one hand, the degradation products of hemicellulose are valuable and there are branches in the area of biomass valorization that focus on these compounds. On the other hand, it adds additional work up steps to the process, if it is desired to obtain isolated aromatic monomers. A last positive aspect is that it increases the quality of the pulp if the hemicellulose (where the bulk of the carbohydrates in the oil comes from) is already degraded. However, this should be done with minimum cellulose degradation.

4.7 Determination of the molecular size distribution of lignins via size exclusion chromatography

In order to determine the average size of the oligomeric lignin fractions (liquid oil and solid lignin), a size exclusion chromatography was performed by Dipl.-Ing. Markus Hochegger. The dissolved samples were diluted in THF to a final concentration of 0.2 mg/ml. The measurement was performed at ambient temperatures and at a flow rate of 1 ml/min.

TABLE 27: Molecular size distribution of the oil via size exclusion chromatography

Oil	Mn	Mw	PDI	Average size regarding Mn
Ex 1	707	1280	1.81	3.9
Ex 2	724	1256	1.73	4.0
Ex 3	727	1259	1.73	4.0
Ex 4	755	1325	1.75	4.2
Ex 5	752	1281	1.70	4.2
Ex 6	766	1336	1.74	4.3
Ex 7	536	881	1.64	3.0
Ex 8	545	951	1.74	3.0
Ex 9	779	1366	1.75	4.3
Ex 10	696	1296	1.86	3.9
Ex 11	728	1179	1.62	4.0
Ex 12	784	1881	2.40	4.4
Ex 13	782	1816	2.32	4.3
Ex 14	560	1534	2.74	3.1
Ex 15	607	1563	2.57	3.4
Ex 16	641	1567	2.44	3.6

Mn: Number average molar mass, Mw: Mass average molar mass, PDI: Polydispersity index

The data of the size exclusion chromatography of the oil samples (see Table 27) shows that the average molecular size (based on Mn) is around four monomeric units (Mw of coniferyl alcohol = ~180 g/mol). Low temperatures seem to have a positive effect on the size distribution i.e. it makes the average molecules in the oil smaller (see oil Ex 7 (182°C) and oil Ex 8 (190 °C)).

TABLE 28: Molecular size distribution of the solid lignin via size exclusion chromatography

Solid lignin	Mn	Mw	PDI	Average size regarding Mn
Ex 1	2091	4140	1.98	11.6
Ex 2	1687	2823	1.67	9.4
Ex 3	2179	3997	1.83	12.1
Ex 4	1813	3086	1.70	10.1
Ex 5	1904	3846	2.02	10.6
Ex 6	1773	3092	1.74	9.8
Ex 7	1832	3965	2.16	10.2
Ex 8	1718	3750	2.18	9.5
Ex 9	1799	3134	1.74	10.0
Ex 10	2227	4398	1.98	12.4
Ex 11	1954	3714	1.90	10.9
Ex 12*	2244	13307	5.93	12.5
Ex 13*	2994	15947	5.33	16.6
Ex 14*	3595	22113	6.15	20.0
Ex 15*	3466	18286	5.28	19.2
Ex 16*	3679	21675	5.89	20.4

*These values are not reliable because they were out of the linear range of the size exclusion column. We only know that the solid lignins of these experiments are bigger than the others. Mn: Number average molar mass, Mw: Mass average molar mass, PDI: Polydispersity index

The average molecular size is much higher within the solid lignin than within the oil – see Table 27 and Table 28. This absolutely matches the expectations. This fraction has an average molecular size of ~ 11 monomeric units. Unfortunately, the data from solid lignin Ex 12 – 16 are not reliable due to problems with the linear range of the used method. However, it seems that the use of acids leads to bigger molecules in the solid lignin fractions.

4.8 Overview of product yields and comparison to literature

Table 29 gives insight into the product distribution of the performed experiments and the yields of the desired oil during this master thesis. In Table 30 values and process conditions found in literature are shown and compared to the best results achieved in this master thesis. As it can be seen in Table 30, a lot of different approaches to lignin valorization exist. Most working groups still separate fractionation and depolymerization of lignin, which is often done via a preceding organosolv process. Due to its gentle process conditions it preserves the natural lignin structure and leads to less repolymerization compared to common technical processes. This makes organosolv lignin superior to e.g. kraft lignin in regards to further valorization. Some working groups also put effort in the valorization of kraft lignin because, at the moment, it is the main source of already separated lignin available, which will not change in predictable time. As it is shown in Table 29, the maximum oil yields obtained during this thesis are at ~50 wt%. If this value is compared to some values in the literature in Table 30, this is rather a mediocre yield. However, it must be stated again, that most publications in the field of lignin valorization are about the depolymerization of already separated lignin. This makes it a lot easier to work up lignin because there is no necessity anymore to also preserve the carbohydrates. In addition, a lot of the difficulties of biomass valorization origin from its complex structure, where carbohydrates and lignin are aligned in a very tangled way. If the result of the best achieved experiment of this thesis (Ex 15) with 53 % oil yield and a delignification efficiency of 88 % is compared to the published results of other groups working on ECCL, an ambivalent picture occurs. Parsell et al. achieved an oil yield of 54 % with a selectivity of 45 % dihydroeugenol and 55 % 2,6-dimethoxy-4-propylphenol respectively.[66] These values are very impressive in regards to their yield and especially their selectivity. However, Parsell did not care about carbohydrate fiber degradation because they attempted to convert the carbohydrates to ethanol enzymatically – which they achieved with a conversion efficiency of 85 %. On a first glance, ethanol and pulp are economically of similar interest with prices of ~700 €/ton (95 % purity) for ethanol and 700 – 750 €/ton for pulp; however, ethanol in this process is an end product whilst pulp is a starting product for paper making and can thus be further valorized. In the end, the big achievement of Parsell is the high selectivity in regards to lignin conversion, which they achieved with a catalytic system of Zn and Pd (10:1) nanoparticles on activated carbon. This catalytic system is quite expensive compared to the used NiO of this thesis. However, the selectivity is definitely the main task for the future of ECCL processes. Van den Bosch et al. also reported about an ECCL process with high selectivity toward monomers.[65] They achieved a yield of 50 % aromatic monomers in regards to the total lignin (the best result achieved in this master thesis was 4.3 %). This is also a very impressive value. It should, however, be stated that van den Bosch has a lower selectivity than Parsell and he also used very expensive active materials for his catalysts, namely Ru and Pt. The occurred problems with the limited conversion of NiO to Ni have been reported before in this thesis. As a last publication, the work of Rinaldi et al. should be mentioned. They developed a system that worked without molecular hydrogen but only used the solvent system 2-PrOH/water 70/30 v/v as hydrogen donor. The 2-PrOH gets converted to acetone during this process, which again can be reduced to 2-PrOH for reuse. However, the reduction of acetone to 2-PrOH also consumes hydrogen. They used Raney nickel as catalyst and achieved oil yields of up to 26 % at 180 °C for 3 h. Their obtained oil is very heterogeneous and there are some amounts of carbohydrate derived components in it, although they are not quantified (Rinaldi only speaks of the “volatile fraction” of their oil). It also should be pointed out, that all of the three other mentioned publications worked with hard wood (poplar and birch) in comparison to the used soft wood (larch) of this thesis. Hard wood lignins show less tendencies to repolymerize during processing due to their higher amount of syringyl units.

TABLE 29: Overview of the product yields of this thesis

Ex	Oil[a] [%]	Aromatic monomers [%]	Solid lignin[%]	Residual lignin in pulp [%]	Delignification efficiency[b] [%]	Pulp [g]
1	24	2.12	45.98	29.96	70.04	19.84
2	48	3.80	17.74	34.68	65.32	18.31
3	27	1.86	47.41	25.57	74.43	19.16
4	39	3.21	29.69	31.67	68.33	20.13
5	22	1.68	44.61	33.01	66.99	19.24
6	46	3.52	24.18	29.93	70.07	16.90
7	10	1.57	36.60	53.38	46.62	22.42
8	13	1.92	43.84	42.75	57.25	20.77
9	56	4.01	17.45	26.81	73.19	14.92
10	33	4.07	30.40	37.05	62.95	19.54
11	37	3.73	28.30	34.50	65.50	19.43
12	56	3.69	3.89	39.74	60.26	7.63
13	56	3.00	7.46	36.09	63.91	6.61
14	42	3.61	45.96	11.65	88.35	8.48
15	53	4.30	35.59	11.70	88.30	6.70
16	48	4.04	41.93	10.20	89.80	8.63

[a]All percentage values are given in regards to the total lignin which is the sum of oil, solid lignin and residual lignin in the pulp. [b]Comparison of the summed lignin in the oil and the solid lignin to the residual lignin in the pulp.

TABLE 30: Overview of lignin depolymerization literature

Source	Feedstock	Lignin	Solvent	Catalyst	Yield	Conditions
this study	larch sawdust	-	EtOH 75/25 v/v (350 mL s/l - 1:10))	0.11 vol%	53 % oil, 4.30 % monomers	179 °C, 40 bar H_2, 0.5 h
106	birch sawdust	catalytic hydrogenolysis lignin	MeOH (40 ml)	(0.3 g) Ru/C	50 % monomer, 20 % dimer	250 °C, 12 MPa, 3-6 h
107	birch	raw lignocellulose	ethylenglycol 100 ml	4 % Ni-30 % W_2C/AC	46 % monomer	6 MPa H_2, 4 h, 235 °C, 1000 rpm
108	poplar wood	organosolv lignin	ethylcylohexane (15 ml)	Ni/Al-SBA-15	84% conversion (saturated hydrocarbons)	7 MPa H_2, 400 rpm, 300°C, 8h
109	-	organosolv lignin	100 ml water/100 ml EtOH	0.125 g Pt/Al_2O_3, 0.58 g H_2SO_4 as co-catalyst	9 % monomers	750 rpm, 58 bar, 1.5 h, 225 °C
110	-	organosolv	MeOH	HY-zeolite	92.58 % lignin conversion, 6.02 % monomers	300 °C, 1 h

Source	Feedstock	Lignin	Solvent	Catalyst	Yield	Conditions
65	birch wood	-	MeOH	Ru/C Pd/C	50 % monomers	300 °C, 30 bar H_2
66	polar wood	-	MeOH	5 wt % ZnPd(1:0.1)/C	54 % monomers	225 °C, 34 bar H_2
3	poplar wood	-	2-PrOH 70 % v/v	Raney Nickel	26 % oil	180 °C, 3 h
111	birch sawdust	treated birch sawdust	MeOH, ethylenglycol, EtOH	Ni/C	54 % conversion	200 °C, 500 rpm, 4 MPa
112	wild cherry	-	EtOH + water 1/1 v/v	NiB+NaOH	69 % phenolic fraction, 40 % monomeric yield	H_2 130 bar, 180 °C
113	-	alcell	IPA/FA 1:1 w/w or EtOH(MeOH)/FA 1:1 w/w	Ru/C	71% oil, 10.5 % monomers	400 °C, 4 h
114	poplar wood	technical hydrolysis lignin	aqueous 5 % NaOH solution 1:8 solid/liquid	anthraquinone 0.5 wt% or no catalyst (except NaOH)	32.22 % low molecular products	180 °C, 2h

5. Conclusions

The aim of this thesis was to find suitable process conditions for the fragmentation of larch wood and the subsequent depolymerization of lignin. Therefore, 16 experiments were performed in which the effects of the catalyst, the co-catalysts, the solvent, and the conditions on an ECCL (**E**arly stage **C**atalytic **C**onversion of **L**ignin) process were investigated. A suitable solvent mixture and loading was examined i.e. an EtOH/H_2O 75/25 v/v mixture with a solid/liquid ratio of 1/10 was used as solvent. This meant that always 350 ml of the solvent mixture were used because the solid substrate loading was always 35 g of sawdust on a dry basis. The effects of hydrogen, the support material for the catalyst (kaolin) and NiO (8.2 wt% on kaolin pellets) on the process were investigated. After the first test series (210 °C, 3 h) it became apparent that hydrogen is a very potent reactant in the depolymerization of lignin. However, difficulties regarding the separation of lignin from the carbohydrates occured. This was expressed in the high yields and the morphology of the pulp and the relatively poor delignification efficiency of those experiments. The effect of the NiO catalyst and the support were investigated but both of them showed no sufficient efficiency in lignin depolymerization. Then, the effects of temperature were investigated by applying the same conditions (40 bar H_2, 3.5 g NiO loaded catalyst, 3 h) but changing the temperature (182 °C, 190 °C, 220 °C). The observed effect was, that higher temperatures give higher oil yields, leading to a stronger carbohydrate degradation, give lower solid lignin yields and higher yields of aromatic monomers. Therefore, the process works better overall with higher temperatures. Experiments with Raney nickel as a second metallic catalyst were performed to compare it to NiO. Raney nickel also showed no sufficient effect on the depolymerization of lignin. Subsequently, sulfuric acid was used as a co-catalyst for the process because it was assumed that it could help to break down glycosidic bonds and therefore make the lignin more accessible for the heterogeneous catalyst. However, the first chosen acid concentration was too high, so these experiments failed (1.1 vol% H_2SO_4, 179 °C, 3 h and 1 h, 40 bar H_2, 3.5 g catalyst). After this, the acid concentration was reduced to 0.11 %. This worked out very well and good results regarding oil yield and pulp quality were achieved. Then, the NiO catalyst was omitted and the reaction worked just as well. In the end, the reaction time could be reduced to 0.5 h whilst still delivering good results, using only H_2SO_4 as catalyst. Sulfuric acid is very potent in facilitating the separation of lignin from carbohydrates; however, it shows insufficient effect on the depolymerization of lignin, which is indicated by the low yields of monomers (maximum – 4.3 wt%) and the high yields of solid lignin (35.6 wt% - Ex 15). So, the main task for the future of this process will be to find a suitable catalyst that can survive the sulfuric acid (or another co-catalyst that enables the separation of lignin and the carbohydrates) and facilitates the depolymerization of the lignin oligomers into the solid lignin and the oil. The best results were achieved with the following conditions: 179 °C, 1 h, 0.11 vol% H_2SO_4 with yields of 53 % oil, 4.3 wt% aromatic monomers, 35.6 wt% solid lignin and 6.70 g pulp. Compared to other publications in the field of lignin valorization the oil yield of 53 % is mediocre; however, the amount of aromatic monomers is quite low. In addition the depolymerization was were unspecific and the product distribution was very broad. Parsell et al achieved an oil yield of 54 % with a selectivity of 45 % dihydroeugenol and 55 % 2,6-dimethoxy-4-propylphenol respectively.[66] However, they did not preserve the carbohydrate fibers but rather planned to enzymatically convert the carbohydrates into ethanol. Van den Bosch reported a process in which they achieved a yield of 50 % aromatic monomers using a very expensive catalytic system of Ru and Pt on carbon black.[65] Rinaldi and Ferrini performed experiments with a hydrogen donating system containing 2-PrOH/water 70/30 v/v as solvent, which also acted as hydrogen donor, and Raney nickel as catalyst. They achieved 26 % oil yield with very low selectivity.[3] The new discovery of this thesis is the combination of an organosolv process (organic solvent under acidic conditions) with an ECCL approach (molecular hydrogen, heterogeneous catalyst). Even though the heterogeneous catalysts showed no sufficient effects, the combination of sulfuric acid and hydrogen on the yields of bio-oil is very promising.

6. Outlook

The main challenge for the optimization of the process used in this thesis for the future will be to find a suitable catalyst for the enhanced depolymerization of lignin. It is especially desirable to increase the amount of aromatic monomers in the oil, which up to now, are rather a side product than the main compound. The new catalyst should be able to convert more of the solid lignin into oil and it would be beneficial if it would be possible to lower the reaction temperature/time. Thus, further catalyst screening has to be done. This probably would work best by directly using commercial catalysts because then the difficulties of the catalyst production itself would be eliminated. It is not easy to produce good catalysts; however, this is rather a technical than a scientific challenge, so commercially available ones should be of first choice. Another approach to a better catalyst functionality could be to provide a more suitable environment (i.e. more basic or more reductive). The NiO catalyst has to be reduced to metallic Ni in order to be active as a hydrogenating catalyst. The given conditions apparently were unsuitable for that. In order to determine a suitable catalyst, further analysis has to be performed (e.g. the morphology of the pellets, etc.). In addition, the process itself could be still optimized by varying the temperature, the solvent system, the pH value, the duration etc. Just because conditions were found that worked well, it does not mean that there are no better conditions available. For an assessment of the process, also the pulp quality has to be investigated. This could be done via analysis of the chain length of its fibers or other measurements. Also a different co-catalyst could be used. For instance, there is a lot of literature that uses bases instead of acids. Also a reducing acid e.g. oxalic acid could be interesting. Principally, there are no limits regarding what could be done in the future. The final goal of course would be to make valuable products of all three major streams of biomass: cellulose (pulp), hemicellulose (high value degradation products) and lignin (high value aromatics). The way to reach this goal is long and difficult but in the end, it could decrease our dependence on crude oil and therefore have beneficial impacts on the environment.

7. Appendix

MS min	List of found aromatics compound	FID min	RRfs	Reference
10.57	*cresol*	12.60	1.09	**guaiacol**
10.96	*guaiacol*	13.07	1.00	**guaiacol**
13.94	*p-cresol, 2-methoxy-*	15.94	1.26	**guaiacol**
16.18	*3',5'-dihydroxyacetophenone*	18.13	1.14	**acetovanillone**
16.32	*p-ethylguaiacol*	18.24	1.00	**p-ethylguaicol**
16.88	*monomeric aromatic compound*	18.64	1.00	**averaged**
17.32	*4-vinyl-2-methoxy-phenol*	19.15	0.94	**isoeugenol**
18.11	*chauvicol (pheno, 4-(2-propenyl)-*	19.80	0.81	**isoeugneol**
18.44	*eugenol*	20.27	1.00	**eugenol**
18.71	*dihydroeugenol*	20.52	1.00	**dihydroeugenol**
18.88	*aromatic monomer*	21.12	1.00	**averaged**
18.99	*benzene, 1-methoxy-4-methyl-*	20.69	1.07	**guaiacol**
19.37	*phenol, 4-propyl-*	21.10	0.78	**dihydroeugenol**
19.54	*vanillin*	21.29	1.00	**vanilline**
19.78	*isoeugenol cis*	21.52	1.00	**isoeugenol cis**
20.22	*2-methylresorcinol, acetate*	22.09	1.08	**acetovanillone**
20.91	*isoeugenol trans*	22.42	1.00	**isoeugenol**
21.01	*aromatic monomer*	22.61	1.00	**dihydroeugenol**
21.15	*ethyl vanillylether*	22.70	1.00	**dihydroeugenol**
21.35	*benzene, 4-ethenyl-1,2-dimethoxy*	22.84	0.91	**isoeugenol**
21.69	*acetovanillone*	23.15	1.00	**acetovanillone**
21.94	*isovanilline*	23.35	1.00	**vanilline**
22.12	*1,2-dimethoxy-4-n-propylbenzene*	23.57	0.86	**dihydroeugenol**
22.25	*monomeric aromatic compound*	23.72	1.00	**averaged**
22.57	*1-(3-hydroxy-4-methoxyphenyl)propan-2-one*	23.97	1.03	**acetovanillone**
22.62	*monomeric aromatic compound*	24.16	1.00	**averaged**
23.13	*(z)-4-(2-ethoxyethenyl)anisole*	24.42	0.89	**isoeugenol**
23.45	*monomeric aromatic compound*	24.70	1.00	**averaged**
23.55	*propiovanillone*	24.82	1.03	**acetovanillone**
23.68	*ethyl vanillate*	24.88	1.17	**acetovanillone**
23.70	*aromatic monomer*	25.45	1.00	**averaged**
24.03	*aromatic monomer*	25.67	1.00	**averaged**
24.28	*4-ethoxy-3-methoxyphenethyl alcohol*	25.86	1.00	**dihydroeugenol**
24.48	*aromatic monomer*	26.04	1.00	**averaged**
24.55	*ethyl homovanillate*	26.18	1.11	**acetovanillone**
24.65	*homovanillic acid*	26.61	1.24	**acetovanillone**
24.96	monomeric aromatic compound	26.44	1.00	**averaged**
25.21	monomeric aromatic compound	26.47	1.00	**averaged**
25.75	2-propanone,1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-	26.65	1.17	**acetovanillone**
25.91	*coniferaldehyde*	26.93	1.07	**isoeugenol**
26.38	*2-isopropyl-3,4-dimethoxybenzaldehyde*	27.34	1.05	**vanilline**
28.17	*monomeric aromatic compound*	28.20	1.00	**averaged**

Ex 1 #	**FID min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**Monomers c [mg/mL]**	**Monomers total mass [mg]**
1	12.602	4396	0.521%	cresol	**1.096**	7.27E-07	0.02	1.17
2	13.074	22003	2.607%	guaiacol	**1.00**	7.27E-07	0.11	5.33
3	15.945	8128	0.963%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.05	2.49
4	18.246	5305	0.628%	p-ethylguaiacol	**1.00**	6.12E-07	0.02	1.08
5	19.159	71924	8.521%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.37	18.63
6	19.823	2872	0.340%	chauvicol	**0.81**	8.24E-07	0.01	0.64
7	20.276	37039	4.388%	eugenol	**1.00**	6.17E-07	0.15	7.61
8	20.574	2080	0.246%	dihydroeugenol	**1.00**	5.63E-07	0.01	0.39
9	21.120	4923	0.583%	phenol, 4-propyl-	**0.78**	5.63E-07	0.01	0.72
10	21.298	112385	13.314%	vanillin	**1.00**	8.59E-07	0.64	32.19
11	21.523	7207	0.854%	cis-isoeugenol	**1.00**	8.24E-07	0.04	1.98
12	22.428	153292	18.161%	trans-isoeugenol	**1.00**	8.24E-07	0.84	42.09
13	22.618	19593	2.321%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.07	3.68
14	23.155	17897	2.120%	acetovanillone	**1.00**	7.02E-07	0.08	4.19
15	23.970	25608	3.034%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.12	6.16
16	24.703	4838	0.573%	aromatic monomer	**1.00**	6.95E-07	0.02	1.12
17	24.888	21754	2.577%	ethyl vanillate	**1.17**	7.02E-07	0.12	5.93
18	26.178	4741	0.562%	ethyl homovanillate	**1.11**	7.02E-07	0.02	1.23
19	26.614	83940	9.944%	homovanillic acid	**1.24**	7.02E-07	0.49	24.28
20	26.939	211925	25.107%	conifer aldehyde	**1.07**	8.24E-07	1.24	62.10
21	27.343	22245	2.635%	2-isopropyl-3,4-dimethoxybenzaldehyde	**1.05**	8.59E-07	0.13	6.67
	sum of	corrected	areas:	844095			sum [g]	0.23
				v oil = 50 mL, g oil = 3.3399, dilution factor = 6.67			[%] of oil	6.88

Ex 2 **#**	**FID** **min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**Monomers** **c [mg/mL]**	**Monomers** **total mass [mg]**
1	12.603	7605	0.804%	cresol	**1.09**	7.27E-07	0.07	3.34
2	13.073	47295	5.000%	guaiacol	**1.00**	7.27E-07	0.38	18.97
3	15.937	18133	1.917%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.18	9.19
4	18.251	30001	3.172%	p-ethylguaiacol	**1.00**	6.12E-07	0.20	10.13
5	19.158	76715	8.110%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.66	32.88
6	19.806	3300	0.349%	chauvicol	**0.81**	8.24E-07	0.02	1.21
7	20.276	42564	4.500%	eugenol	**1.00**	6.17E-07	0.29	14.47
8	20.526	8436	0.892%	dihydroeugenol	**1.00**	5.63E-07	0.05	2.62
9	21.120	8837	0.934%	phenol, 4-propyl-	**0.78**	5.63E-07	0.04	2.15
10	21.296	83256	8.802%	vanillin	**1.00**	8.59E-07	0.79	39.45
11	21.522	16106	1.703%	cis-isoeugenol	**1.00**	8.24E-07	0.15	7.32
12	22.428	236924	25.048%	trans-isoeugenol	**1.00**	8.24E-07	2.15	107.63
13	22.617	27873	2.947%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.17	8.66
14	23.154	36751	3.885%	acetovanillone	**1.00**	7.02E-07	0.28	14.22
15	23.967	25816	2.729%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.21	10.27
16	24.699	10040	1.061%	aromatic monomer	**1.00**	6.94E-07	0.08	3.85
17	24.886	20544	2.172%	ethyl vanillate	**1.17**	7.02E-07	0.19	9.27
18	25.713	18398	1.945%	aromatic monomer	**1.00**	6.94E-07	0.14	7.05
19	26.176	4064	0.430%	ethyl homovanillate	**1.11**	7.02E-07	0.03	1.75
20	26.609	72617	7.677%	homovanillic acid	**1.24**	7.02E-07	0.69	34.75
21	26.936	139532	14.751%	conifer aldehyde	**1.07**	8.24E-07	1.35	67.65
22	27.340	11087	1.172%	2-isopropyl-3,4-dimethoxybenzaldehyde	**1.05**	8.59E-07	0.11	5.50
sum	of	corrected	areas:	945893			sum [g]	0.41
				v oil = 50 mL, g oil = 5.5175, dilution factor = 11.03			[%] of oil	7.47

Ex 3 #	**FID min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**Monomers C [mg/mL]**	**Monomers total mass [mg]**
1	12.605	1507	0.246%	Cresol	1.09	7.27E-07	0.01	0.48
2	13.073	14401	2.348%	guaiacol	1.00	7.27E-07	0.08	4.18
3	15.942	4324	0.705%	p-cresol, 2-methoxy-	1.26	7.27E-07	0.03	1.59
4	18.192	3883	0.633%	3',5'-dihydroxyacetophenone	1.14	7.02E-07	0.02	1.24
5	18.245	3067	0.500%	p-ethylguaiacol	1.00	6.12E-07	0.01	0.75
6	19.157	56526	9.216%	4-vinyl-2-methoxy-phenol	0.94	8.24E-07	0.35	17.53
7	19.827	1362	0.222%	chauvicol	0.81	8.24E-07	0.01	0.36
8	20.278	21650	3.530%	eugenol	1.00	6.17E-07	0.11	5.33
9	21.296	88610	14.446%	vanillin	1.00	8.59E-07	0.61	30.38
10	22.427	95273	15.533%	trans-isoeugenol	1.00	8.24E-07	0.63	31.31
11	22.615	14763	2.407%	2,4-dihydroxypropiophenone	1.00	5.63E-07	0.07	3.32
12	23.153	13216	2.155%	acetovanillone	1.00	7.02E-07	0.07	3.70
13	23.967	18781	3.062%	1-(3-hydroxy-4-methoxyphenyl)propan-1-one	1.03	7.02E-07	0.11	5.41
14	24.700	3516	0.573%	aromatic monomer	1.00	6.94E-07	0.02	0.97
15	24.888	16617	2.709%	ethyl vanillate	1.17	7.02E-07	0.11	5.42
16	26.174	4132	0.674%	ethyl homovanillate	1.11	7.02E-07	0.03	1.28
17	26.615	60210	9.816%	homovanillic acid	1.24	7.02E-07	0.42	20.84
18	26.935	175537	28.619%	conifer aldehyde	1.07	8.24E-07	1.23	61.57
19	27.342	15995	2.608%	2-isopropyl-3,4-dimethoxybenzaldehyde	1.05	8.59E-07	0.11	5.74
	sum of corrected areas			613369			sum [g]	0.20
				v oil = 50 mL, g Oil = 3.9962, dilution factor = 7.98			[%] of oil	5.04

FID #	Ex 4 min	Area	% of total	Compound	RRf	Rf	Monomers C [mg/mL]	Monomers total mass [mg]
1	12.606	7896	0.874%	cresol	**1.00**	7.27E-07	0.06	2.80
2	13.075	45482	5.032%	guaiacol	**1.00**	7.27E-07	0.32	16.11
3	15.940	15567	1.722%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.14	6.97
4	18.250	29167	3.227%	p-ethylguaiacol	**1.00**	6.12E-07	0.17	8.70
5	19.159	60632	6.709%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.46	22.95
6	20.277	40761	4.510%	eugenol	**1.00**	6.17E-07	0.24	12.24
7	20.531	4945	0.547%	dihydroeugenol	**1.00**	5.63E-07	0.03	1.36
8	21.123	6415	0.710%	phenol, 4-propyl-	**0.78**	5.63E-07	0.03	1.38
9	21.298	93231	10.315%	vanillin	**1.00**	8.59E-07	0.78	39.02
10	21.523	17661	1.954%	cis-isoeugenol	**1.00**	8.24E-07	0.14	7.09
11	22.428	226261	25.034%	trans-isoeugenol	**1.00**	8.24E-07	1.82	90.77
12	22.619	27392	3.031%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.15	7.52
13	23.153	26425	2.924%	acetovanillone	**1.00**	7.02E-07	0.18	9.03
14	23.399	2416	0.267%	benzaldehyde, 3-hydroxy-4-methoxy-	**1.00**	8.59E-07	0.02	1.01
15	23.574	2797	0.309%	1,2-dimethoxy-4-n-propylbenzene	**0.86**	5.63E-07	0.01	0.66
16	23.729	2846	0.315%	aromatic monomer	**1.00**	6.94E-07	0.02	0.96
17	23.969	27968	3.095%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.20	9.83
18	24.698	9034	1.000%	monomeric aromatic compound	**1.00**	6.94E-07	0.06	3.06
19	24.889	21533	2.383%	ethyl vanillate	**1.17**	7.02E-07	0.17	8.58
20	26.042	2830	0.313%	aromatic monomer	**1.00**	6.94E-07	0.02	0.96
21	26.179	3982	0.441%	ethyl homovanillate	**1.11**	7.02E-07	0.03	1.51
22	26.606	66548	7.363%	homovanillic acid)	**1.24**	7.02E-07	0.56	28.12
23	26.937	150234	16.622%	conifer aldehyde	**1.07**	8.24E-07	1.29	64.32
24	27.345	8611	0.953%	2-isopropyl-3,4-dimethoxybenzaldehyde	**1.05**	8.59E-07	0.08	3.78
sum	of	corrected	areas:	903802			sum [g]	0.35
				v oil = 50 mL, g oil 4.8557, dilution factor = 9.74			[%] of oil	7.18

FID #	Ex 5 min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	12.599	5024	0.606%	cresol	**1.09**	7.27E-07	0.02	1.08
2	13.070	22680	2.736%	guaiacol	**1.00**	7.27E-07	0.09	4.43
3	15.939	6727	0.811%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.03	1.66
4	19.154	74216	8.952%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.31	15.51
5	20.274	31015	3.741%	eugenol	**1.00**	6.17E-07	0.10	5.14
6	21.296	125351	15.120%	vanillin	**1.00**	8.59E-07	0.58	28.96
7	22.423	139869	16.871%	isoeugenol (phenol, 2-methoxy-4-(1-propenyl)-	**1.00**	8.24E-07	0.62	30.97
8	22.613	22165	2.673%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.07	3.36
9	23.150	22175	2.675%	acetovanillone	**1.00**	7.02E-07	0.08	4.18
10	23.965	28129	3.393%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.11	5.46
11	24.698	5033	0.607%	monomeric aromatic compound	**1.00**	6.94E-07	0.02	0.94
12	24.886	22364	2.697%	ethyl vanillate	**1.17**	7.02E-07	0.10	4.92
13	26.173	4523	0.545%	ethyl homovanillate	**1.11**	7.02E-07	0.02	0.95
14	26.603	56013	6.756%	homovanillic acid	**1.24**	7.02E-07	0.26	13.06
15	26.937	243459	29.365%	conifer aldehyde	**1.07**	8.24E-07	1.15	57.54
16	27.337	20323	2.451%	monomeric aromatic compound	**1.00**	6.94E-07	0.08	3.79
sum	of	corrected	areas:	829065			sum [g]	0.18
				v oil = 50 mL, g oil = 2.6907, dilution factor = 5.3763			[%] of oil	6.76

Ex 6 #	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	13.069	37953	4.173%	guaiacol	**1**	7.27E-07	0.29	14.68
2	15.936	16773	1.844%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.16	8.20
3	18.243	29884	3.286%	p-ethylguaiacol	**1**	6.12E-07	0.19	9.73
4	19.154	67053	7.373%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.55	27.72
5	19.800	5021	0.552%	chauvicol	**0.81**	8.24E-07	0.04	1.78
6	20.270	37492	4.122%	eugenol	**1**	6.17E-07	0.25	12.30
7	20.520	7728	0.850%	dihydroeugenol	**1**	5.63E-07	0.05	2.32
9	21.294	89129	9.800%	vanillin	**1**	8.59E-07	0.81	40.74
10	21.517	17402	1.913%	isoeugenol	**1**	8.24E-07	0.15	7.63
11	22.424	230787	25.376%	isoeugenol	**1**	8.24E-07	2.02	101.13
12	22.612	26519	2.916%	2,4-dihydroxypropiophenone	**1**	5.63E-07	0.16	7.95
13	23.148	29437	3.237%	acetovanillone	**1**	7.02E-07	0.22	10.99
14	23.570	3020	0.332%	aromatic monomer	**1**	6.94E-07	0.02	1.12
15	23.723	4841	0.532%	aromatic monomer	**1**	6.94E-07	0.04	1.79
16	23.965	28871	3.175%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.22	11.08
17	24.696	10240	1.126%	monomeric aromatic compound	**1**	6.94E-07	0.08	3.78
18	24.880	22505	2.475%	ethyl vanillate	**1.17**	7.02E-07	0.20	9.79
19	26.606	71575	7.870%	homovanillic acid	**1.24**	7.02E-07	0.66	33.03
20	26.932	150469	16.545%	conifer aldehyde	**1.07**	8.24E-07	1.41	70.36
21	27.337	8118	0.893%	aromatic monomer	**1**	6.94E-07	0.06	3.00
22	29.002	8020	0.882%	aromatic monomer	**1**	6.94E-07	0.06	2.96
sum	of	corrected	areas:	909455			sum [g]	0.38
				v oil = 50 mL, g oil = 5.3007, dilution factor = 10.64			[%] of oil	7.21

Ex 7 #	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	12.599	8991	0.479%	cresol	**1.09**	7.27E-07	0.02	0.83
2	13.072	24018	1.279%	guaiacol	**1.00**	7.27E-07	0.04	2.02
3	15.935	10016	0.534%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.02	1.06
4	18.241	5583	0.297%	p-ethylguaiacol	**1.00**	6.12E-07	0.01	0.39
5	19.156	110899	5.907%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.20	9.95
6	19.805	12370	0.659%	chauvicol	**0.81**	8.24E-07	0.02	0.95
7	20.276	66757	3.556%	eugenol	**1.00**	6.17E-07	0.10	4.75
8	21.122	3525	0.188%	phenol, 4-propyl-	**0.78**	5.63E-07	0.00	0.18
9	21.297	185715	9.893%	vanillin	**1.00**	8.59E-07	0.37	18.42
10	21.519	10154	0.541%	cis-isoeugenol	**1.00**	8.24E-07	0.02	0.97
11	22.429	285148	15.189%	trans-isoeugenol	**1.00**	8.24E-07	0.54	27.11
12	22.613	30265	1.612%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.04	1.97
13	22.710	10783	0.574%	ethyl vanillylether	**1.00**	5.63E-07	0.01	0.70
14	23.155	16859	0.898%	acetovanillone	**1.00**	7.02E-07	0.03	1.37
15	23.725	8866	0.472%	aromatic monomer	**1.00**	6.94E-07	0.01	0.71
16	23.966	29620	1.578%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.05	2.47
17	24.695	7920	0.422%	aromatic monomer	**1.00**	6.94E-07	0.01	0.63
18	24.885	26321	1.402%	ethyl vanillate	**1.17**	7.02E-07	0.05	2.48
19	25.923	15339	0.817%	aromatic monomer	**1.00**	6.94E-07	0.02	1.23
20	26.175	17150	0.914%	ethyl homovanillate	**1.11**	7.02E-07	0.03	1.54
21	26.289	65068	3.466%	homovanillic acid	**1.24**	7.02E-07	0.13	6.52
22	26.439	31400	1.673%	aromatic monomer	**1.00**	6.94E-07	0.05	2.52
23	26.466	65069	3.466%	2-isopropyl-3,4-dimethoxybenzaldehyde	**1.05**	8.59E-07	0.14	6.76
24	26.653	20159	1.074%	2-propanone,1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-	**1.17**	7.02E-07	0.04	1.90
25	26.945	460705	24.540%	conifer aldehyde	**1.07**	8.24E-07	0.93	46.74
26	27.342	329812	17.568%	aromatic monomer	**1.00**	6.94E-07	0.53	26.43
sum	of	corrected	areas:	1877333			sum [g]	0.17
				v oil = 50 mL, g oil = 1.154, dilution factor = 2.31			[%] of oil	14.78

Ex 8 # 	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	6.056	169218	5.718%	ethyl lactate	NA	NA	NA	NA
2	6.467	114253	3.860%	furfural	NA	NA	NA	NA
3	6.955	29814	1.007%	2-furanmethanol	NA	NA	NA	NA
4	7.168	23370	0.790%	acetol acetate	NA	NA	NA	NA
5	7.938	13988	0.473%	furan-2,5-diol	NA	NA	NA	NA
6	8.096	34762	1.175%	ethyl-2-ethoxybutyrate	NA	NA	NA	NA
7	8.633	55221	1.866%	ethanol, 2,2-diethoxy-	NA	NA	NA	NA
8	8.960	15326	0.518%	2(3h)-furanone, 5-methyl-	NA	NA	NA	NA
9	9.586	32163	1.087%	1-methoxy-but-3-en-2-ol	NA	NA	NA	NA
10	10.040	19351	0.654%	4-oxobutyric acid, ethyl ester	NA	NA	NA	NA
11	10.624	2854	0.096%	4-methyl-2-hepten	NA	NA	NA	NA
12	10.765	7793	0.263%	1h-pyrrole-2-carboxaldehyde	NA	NA	NA	NA
13	11.053	92646	3.130%	aliphatic)	NA	NA	NA	NA
14	11.174	14907	0.504%	aliphatic	NA	NA	NA	NA
15	11.274	46282	1.564%	corylone (hydroxy-3-methyl-3-cylopenten-1-one)	NA	NA	NA	NA
16	11.590	6299	0.213%	butane, 1-ethoxy-	NA	NA	NA	NA
17	11.723	21377	0.722%	ethyl 2-methylbuta-2,3-dienoate	NA	NA	NA	NA
18	12.027	1739	0.059%	furanous aliphatic	NA	NA	NA	NA
19	12.237	37597	1.270%	ethyl levulinate	NA	NA	NA	NA
20	12.596	13001	0.439%	furanous aliphatic	NA	NA	NA	NA
21	12.760	11239	0.380%	aliphatic	NA	NA	NA	NA
22	12.923	18585	0.628%	3-furancarboxylic acid, methyl ester	NA	NA	NA	NA
23	13.069	37420	1.264%	guaiacol	**1.00**	7.27E-07	0.09	4.31
24	13.169	4920	0.166%	2-cyclopenten-1-one, 3-ethyl-2-hydroxy	NA	NA	NA	NA
25	13.385	6112	0.207%	aliphatic	NA	NA	NA	NA
26	13.505	9140	0.309%	aliphatic	NA	NA	NA	NA
27	13.690	10518	0.355%	maltol	NA	NA	NA	NA

28	13.858	4904	0.166%	furanous aliphatic	NA	NA	NA	NA
29	14.105	4236	0.143%	3-octanol	NA	NA	NA	NA
30	14.546	8138	0.275%	ethanone, 1-cyclohexyl-	NA	NA	NA	NA
31	14.612	11543	0.390%	3-ethoxy .gamma. butyrolactone	NA	NA	NA	NA
32	14.756	25913	0.876%	aliphatic	NA	NA	NA	NA
33	14.930	38757	1.310%	4-hydroxy-6-methyl2h-pyran-2-one	NA	NA	NA	NA
34	15.166	9073	0.307%	aliphatic	NA	NA	NA	NA
35	15.369	27881	0.942%	aliphatic	NA	NA	NA	NA
36	15.938	26437	0.893%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.08	3.84
37	16.430	6757	0.228%	aliphatic	NA	NA	NA	NA
38	16.560	10581	0.358%	aliphatic	NA	NA	NA	NA
39	17.067	116257	3.928%	hydroxy methyl furfural	NA	NA	NA	NA
40	17.130	80089	2.706%	aliphatic	NA	NA	NA	NA
41	17.358	7267	0.246%	cryptone	NA	NA	NA	NA
42	17.449	77240	2.610%	aliphatic	NA	NA	NA	NA
43	17.799	4082	0.138%	aliphatic	NA	NA	NA	NA
44	17.920	10851	0.367%	diethyl hydroxybutanedioate	NA	NA	NA	NA
45	18.240	15400	0.520%	p-ethylguaiacol	**1.00**	6.12E-07	0.03	1.49
46	18.468	6691	0.226%	aliphatic	NA	NA	NA	NA
47	18.766	5740	0.194%	aliphatic	NA	NA	NA	NA
48	18.955	8312	0.281%	5-acetoxymethyl-2-furaldehyde	NA	NA	NA	NA
49	19.153	119254	4.029%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.29	14.67
50	19.319	5451	0.184%	aliphatic	NA	NA	NA	NA
51	19.560	14511	0.490%	furanous compound	NA	NA	NA	NA
52	19.812	10099	0.341%	chavicol	**0.81**	8.24E-07	0.02	1.06
53	20.273	68758	2.323%	eugenol	**1.00**	6.17E-07	0.13	6.71
54	20.539	11337	0.383%	phenol, 2-propyl	**0.78**	5.63E-07	0.02	0.79
55	20.789	3863	0.131%	aliphatic	NA	NA	NA	NA
56	20.978	2649	0.089%	aliphatic	NA	NA	NA	NA
57	21.128	5097	0.172%	1,4-benzenediol, 2-methoxy-	**1.00**	6.94E-07	0.01	0.56

58	21.298	184261	6.226%	vanillin	**1.00**	8.59E-07	0.50	25.05
59	21.518	11956	0.404%	cis-isoeugenol	**1.00**	8.24E-07	0.03	1.56
60	22.032	3307	0.112%	aliphatic	NA	NA	NA	NA
61	22.159	4240	0.143%	aliphatic	NA	NA	NA	NA
62	22.426	279596	9.447%	trans-isoeugenol	**1.00**	8.24E-07	0.73	36.44
63	22.614	19665	0.664%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.04	1.75
64	22.707	5792	0.196%	aromatic monomer	**1.00**	6.94E-07	0.01	0.64
65	23.098	7026	0.237%	aromatic monomer	**1.00**	7.02E-07	0.02	0.78
66	23.150	30308	1.024%	acetovanillone	**1.00**	7.02E-07	0.07	3.37
67	23.309	3245	0.110%	undeterminable		NA	NA	NA
68	23.393	5722	0.193%	aromatic monomer	**1.00**	6.94E-07	0.01	0.63
69	23.724	10179	0.344%	aromatic monomer	**1.00**	6.94E-07	0.02	1.12
70	23.966	35177	1.189%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.08	4.02
71	24.391	8461	0.286%	undeterminable		NA	NA	NA
72	24.511	2735	0.092%	aromatic monomer	**1.00**	6.94E-07	0.01	0.30
73	24.695	9459	0.320%	aromatic monomer	**1.00**	6.94E-07	0.02	1.04
74	24.885	29774	1.006%	ethyl vanillate	**1.17**	7.02E-07	0.08	3.85
75	25.943	23443	0.792%	ethyl homovanillate	**1.11**	7.02E-07	0.06	2.89
76	26.289	153449	5.185%	homovanillic acid	**1.24**	7.02E-07	0.42	21.07
77	26.608	22104	0.747%	aromatic monomer	**1.00**	6.94E-07	0.05	2.43
78	26.663	6452	0.218%	3,5-dimethoxy cinnamic acid	**1.00**	6.94E-07	0.01	0.71
79	26.729	14696	0.497%	aromatic monomer	**1.00**	6.94E-07	0.03	1.61
80	26.939	405984	13.718%	conifer aldehyde	**1.07**	8.24E-07	1.13	56.48
81	27.337	85499	2.889%	aromatic monomer	**1.00**	6.94E-07	0.19	9.40
		sum of corrected areas:		2959594			sum [g]	0.21
				v oil = 50 mL, g oil = 1.581, dilution factor = 3.16			[%] of oil	13.19

Ex 9 **#**	**FID** **min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**Monomers** **c [mg/mL]**	**Monomers** **total mass [mg]**
1	6.056	160028	10.451%	ethyl lactate	NA	NA	NA	NA
2	6.476	31283	2.043%	furfural	NA	NA	NA	NA
3	6.913	945	0.062%	2-furanmethanol	NA	NA	NA	NA
4	6.958	16714	1.092%	2-butanone	NA	NA	NA	NA
5	7.172	13143	0.858%	acetol acetate	NA	NA	NA	NA
6	7.519	842	0.055%	aliphatic	NA	NA	NA	NA
7	7.814	1503	0.098%	aliphatic	NA	NA	NA	NA
8	7.943	1897	0.124%	aliphatic	NA	NA	NA	NA
9	8.095	30144	1.969%	ethyl-2-ethoxybutyrate	NA	NA	NA	NA
10	8.631	15620	1.020%	2,5-hexanedione	NA	NA	NA	NA
11	8.978	2474	0.162%	2(3h)-furanone, 5-methyl-	NA	NA	NA	NA
12	9.164	2344	0.153%	furanous compound	NA	NA	NA	NA
13	9.505	2101	0.137%	furanous compound	NA	NA	NA	NA
14	9.592	13387	0.874%	5-methyl-2-furfural	NA	NA	NA	NA
15	9.761	1369	0.089%	aliphatic	NA	NA	NA	NA
16	10.039	13986	0.913%	4-oxobutyric acid, ethyl ester	NA	NA	NA	NA
17	10.544	1255	0.082%	4-methyl-2-hepten	NA	NA	NA	NA
18	10.619	4553	0.297%	4-heptanol	NA	NA	NA	NA
19	10.706	1900	0.124%	aliphatic	NA	NA	NA	NA
20	11.056	18228	1.190%	aliphatic	NA	NA	NA	NA
21	11.177	7966	0.520%	aliphatic	NA	NA	NA	NA
22	11.273	71737	4.685%	corylone (hydroxy-3-methyl-3-cylopenten-1-one)	NA	NA	NA	NA
23	11.719	7945	0.519%	ethyl 2-methylbuta-2,3-dienoate	NA	NA	NA	NA
24	11.810	2259	0.148%	aliphatic	NA	NA	NA	NA
25	12.085	6945	0.454%	furancarbonic acid-(2)-ethylester	NA	NA	NA	NA
26	12.237	40383	2.637%	ethyl levulinate	NA	NA	NA	NA
27	12.603	7429	0.485%	cresol	1.09	7.27E-07	0.09	4.27
28	12.779	1759	0.115%	3-furancarboxylic acid, methyl ester	NA	NA	NA	NA

29	12.931	2456	0.160%	aliphatic	NA	NA	NA	NA
30	13.069	53549	3.497%	guaiacol	1.00	7.27E-07	0.56	28.08
31	13.387	4643	0.303%	aliphatic	NA	NA	NA	NA
32	13.512	3282	0.214%	aliphatic	NA	NA	NA	NA
33	13.697	5694	0.372%	maltol	NA	NA	NA	NA
34	13.861	10357	0.676%	2-cylopenten-1-one, 3ethyl-2-hydroxy-	NA	NA	NA	NA
35	14.546	11127	0.727%	ethanone, 1-cyclohexyl-	NA	NA	NA	NA
36	14.628	4407	0.288%	3-ethoxy .gamma. butyrolactone	NA	NA	NA	NA
37	14.758	2163	0.141%	aliphatic	NA	NA	NA	NA
38	14.931	21661	1.415%	4-hydroxy-6-methyl2h-pyran-2-one	NA	NA	NA	NA
39	15.166	13865	0.906%	aliphatic	NA	NA	NA	NA
40	15.518	4298	0.281%	butanedioic acid, diethyl ester	NA	NA	NA	NA
41	15.930	25396	1.659%	p-cresol, 2-methoxy-	1.26	7.27E-07	0.34	16.83
42	16.558	10809	0.706%	aliphatic	NA	NA	NA	NA
43	16.824	51484	3.362%	hydroxy methyl furfural	NA	NA	NA	NA
44	17.127	34580	2.258%	aliphatic	NA	NA	NA	NA
45	17.201	22314	1.457%	cryptone	NA	NA	NA	NA
46	17.397	31747	2.073%	aliphatic	NA	NA	NA	NA
47	17.443	20348	1.329%	aliphatic	NA	NA	NA	NA
48	17.526	9740	0.636%	aliphatic	NA	NA	NA	NA
49	17.717	2968	0.194%	aliphatic	NA	NA	NA	NA
50	17.800	2402	0.157%	aliphatic	NA	NA	NA	NA
51	17.918	4557	0.298%	diethyl hydroxybutanedioate	NA	NA	NA	NA
52	18.246	45854	2.995%	p-ethylguaiacol	1.00	6.12E-07	0.40	20.24
53	18.768	2772	0.181%	aliphatic	NA	NA	NA	NA
54	19.154	38022	2.483%	4-vinyl-2-methoxy-phenol	0.94	8.24E-07	0.43	21.31
55	19.560	4537	0.296%	aliphatic	NA	NA	NA	NA
56	20.272	34531	2.255%	eugenol	1.00	6.17E-07	0.31	15.35
57	20.520	11221	0.733%	dihydroeugenol	1.00	5.63E-07	0.09	4.56
58	21.292	78386	5.119%	vanillin	1.00	8.59E-07	0.97	48.58

59	21.516	17676	1.154%	cis-isoeugenol	1.00	8.24E-07	0.21	10.50
60	22.423	181662	11.864%	trans-isoeugenol	1.00	8.24E-07	2.16	107.92
61	22.612	20640	1.348%	2,4-dihydroxypropiophenone	1.00	5.63E-07	0.17	8.39
62	23.151	25519	1.667%	acetovanillone	1.00	7.02E-07	0.26	12.91
63	23.570	2749	0.180%	aromatic monomer	1.00	6.94E-07	0.03	1.38
64	23.963	26134	1.707%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	1.03	7.02E-07	0.27	13.60
65	24.696	10336	0.675%	aromatic monomer	1.00	6.94E-07	0.10	5.18
66	24.882	14775	0.965%	ethyl vanillate	1.17	7.02E-07	0.17	8.72
67	26.175	3540	0.231%	ethyl homovanillate	1.11	7.02E-07	0.04	1.99
68	26.603	58495	3.820%	homovanillic acid	1.24	7.02E-07	0.73	36.60
69	26.732	11433	0.747%	undeterminable	NA	NA	NA	NA
70	26.931	105327	6.879%	confer aldehyde	1.07	8.24E-07	1.34	66.78
71	28.169	3588	0.234%	aromatic monomer	1.00	6.94E-07	0.04	1.80
sum	of	corrected	areas:	1531186			sum [g]	0.43
				v oil = 50 mL, g oil = 7.24 dilution factor = 14.42			[%] of oil	6.00

Ex 10	FID						Monomers	Monomers
#	**min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**c [mg/mL]**	**total mass [mg]**
1	12.600	15459	1.042%	cresol	**1.09**	7.27E-07	0.10	4.91
2	13.069	21701	1.463%	guaiacol	**1.00**	7.27E-07	0.13	6.30
3	15.929	29914	2.017%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.22	10.97
4	18.246	147642	9.957%	p-ethylguaiacol	**1.00**	6.12E-07	0.72	36.06
5	19.154	24996	1.686%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.16	7.75
6	19.801	5444	0.367%	chauvicol	**0.81**	8.24E-07	0.03	1.45
7	20.273	23220	1.566%	eugenol+4-hydroxybenzaldehyde	**1.00**	6.17E-07	0.11	5.71
8	20.521	250209	16.873%	dihydroeugenol	**1.00**	5.63E-07	1.12	56.24
9	21.116	1995	0.135%	phenol, 4-propyl-	**0.78**	5.63E-07	0.01	0.35
10	21.292	42717	2.881%	vanillin	**1.00**	8.59E-07	0.29	14.64
11	21.518	41349	2.788%	cis-isoeugenol	**1.00**	8.24E-07	0.27	13.59
12	22.428	450977	30.413%	trans-isoeugenol	**1.00**	8.24E-07	2.96	148.21
13	22.614	3614	0.244%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.02	0.81
14	23.151	21954	1.480%	acetovanillone	**1.00**	7.02E-07	0.12	6.15
15	23.568	5245	0.354%	1,2-dimethoxy-4-n-propylbenzene	**0.86**	5.63E-07	0.02	1.02
16	23.723	7021	0.473%	aromatic monomer	**1.00**	6.94E-07	0.04	1.95
17	23.965	32153	2.168%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	0.19	9.26
18	24.693	39727	2.679%	aromatic monomer	**1.00**	6.94E-07	0.22	11.01
19	24.816	25101	1.693%	propiovanillone	**1.03**	7.02E-07	0.14	7.23
20	25.859	19023	1.283%	4-ethoxy-3-methoxyphenethyl alcohol	**1.00**	5.63E-07	0.09	4.29
21	26.485	238489	16.083%	homovanillic acid	**1.24**	7.02E-07	1.65	82.55
22	26.931	13372	0.902%	aromatic monomer	**1.07**	8.24E-07	0.09	4.69
23	27.335	10953	0.739%	aromatic monomer	**1.00**	6.94E-07	0.06	3.03
24	28.196	10587	0.714%	aromatic monomer	**1.00**	6.94E-07	0.06	2.93
Sum	of	corrected	areas:	1482858			Sum [g]	0.44
				v oil = 50 mL, g oil = 4.00 g, dilution factor = 7.98			[%] of oil	11.04

Ex 11	FID						Monomers	Monomers
#	**min**	**Area**	**% of total**	**Compound**	**RRf**	**Rf**	**c [mg/mL]**	**total mass [mg]**
1	12.592	17548	1.420%	cresol	**1.09**	7.27E-07	0.13	6.31
2	13.068	38752	3.136%	guaiacol	**1.00**	7.27E-07	0.25	12.73
3	15.930	32676	2.645%	p-cresol, 2-methoxy-	**1.26**	7.27E-07	0.27	13.57
4	18.241	130539	10.565%	p-ethylguaiacol	**1.00**	6.12E-07	0.72	36.11
5	19.151	35325	2.859%	4-vinyl-2-methoxy-phenol	**0.94**	8.25E-07	0.25	12.40
6	19.814	1792	0.145%	chauvicol	**0.81**	8.24E-07	0.01	0.54
7	20.271	15823	1.281%	eugenol	**1.00**	6.17E-07	0.09	4.41
8	20.517	151965	12.299%	dihydroeugenol	**1.00**	5.63E-07	0.77	38.68
9	21.112	2671	0.216%	phenol, 4-propyl-	**0.78**	5.63E-07	0.01	0.53
10	21.293	41124	3.328%	vanillin	**1.00**	8.59E-07	0.32	15.97
11	21.515	8412	0.681%	cis-isoeugenol	**1.00**	8.24E-07	0.06	3.13
12	22.418	125729	10.176%	trans-isoeugenol	**1.00**	8.24E-07	0.94	46.79
13	22.610	8167	0.661%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.04	2.08
14	22.703	1967	0.159%	ethyl vanillylether	**1.00**	5.63E-07	0.01	0.50
15	22.841	10992	0.890%	benzene, 4-ethenyl-1,2-dimethoxy-	**0.91**	8.24E-07	0.07	3.73
16	23.147	19509	1.579%	acetovanillone	**1.00**	7.02E-07	0.12	6.19
17	23.960	21169	1.713%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.028E-07	0.14	6.90
18	24.164	5486	0.444%	aromatic monomer	**1.00**	6.95E-07	0.03	1.72
19	24.690	21651	1.752%	aromatic monomer	**1.00**	6.95E-07	0.14	6.79
20	24.815	7149	0.579%	propiovanillone	**1.03**	7.02E-07	0.05	2.33
21	24.879	6870	0.556%	ethyl vanillate	**1.17**	7.02E-07	0.05	2.54
22	25.859	188746	15.276%	4-ethoxy-3-methoxyphenethyl alcohol	**1.00**	5.63E-07	0.96	48.25
23	26.430	282999	22.904%	homovanillic acid	**1.24**	7.02E-07	2.22	110.94
24	26.929	41654	3.371%	aromatic monomer	**1.07**	8.24E-07	0.33	16.55
25	27.334	12017	0.973%	aromatic monomer	**1.00**	6.94E-07	0.08	3.77
26	28.192	4847	0.392%	aromatic monomer	**1.00**	6.94E-07	0.03	1.52
Sum	of	corrected	areas:	1235578			Sum [g]	0.40
				v oil = 50 mL, g oil = 4.52, dilution factor = 9.04			[%] of oil	8.96

Ex 12 #	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	6.061	18593	0.380%	ethyl lactate	NA	NA	NA	NA
2	6.485	33855	0.692%	furfural, 2-hydroxy	NA	NA	NA	NA
3	7.812	1620	0.033%	glycerine	NA	NA	NA	NA
4	8.098	8395	0.172%	butanoic acid, 2-hydroxy-, ethyl ester	NA	NA	NA	NA
5	8.637	8339	0.171%	hexandione	NA	NA	NA	NA
6	9.313	31710	0.649%	gamma valerolactone	NA	NA	NA	NA
7	9.650	5559	0.114%	3-methyl-2-cylopenten-1-one	NA	NA	NA	NA
8	10.043	5665	0.116%	4-oxoxbutyric acid, ethyl ester	NA	NA	NA	NA
9	10.203	7198	0.147%	pentanoic acid, 4-oxo- methyl ester	NA	NA	NA	NA
10	10.404	1886	0.039%	furanous compound	NA	NA	NA	NA
11	10.537	998	0.020%	2-cyclopenten-1-one,2,2-dimethyl	NA	NA	NA	NA
12	10.972	2153	0.044%	4-heptanol	NA	NA	NA	NA
13	11.277	70663	1.445%	1,2-cyclopentanedione, 3-methyl-	NA	NA	NA	NA
14	11.660	15430	0.316%	2-cyclopenen-1-one, 2,3-dimethyl	NA	NA	NA	NA
15	12.065	36291	0.742%	2-furancarboxylic acid, ethyl ester	NA	NA	NA	NA
16	12.307	3749209	76.677%	ethyl levulinate	NA	NA	NA	NA
17	12.638	4677	0.096%	m-cresol	1.09	7.27E-07	0.080	3.99
18	12.817	3556	0.073%	3-octanone	NA	NA	NA	NA
19	12.928	40996	0.838%	aliphatic compound	NA	NA	NA	NA
20	13.076	40048	0.819%	guaiacol	1.00	7.27E-07	0.62	31.20
21	13.262	14180	0.290%	1-methylethyl 3-actylpropanoate	NA	NA	NA	NA
22	13.384	10659	0.218%	furanous compound	NA	NA	NA	NA
23	13.774	10056	0.206%	furanous compound	NA	NA	NA	NA
24	13.868	15093	0.309%	5-ethylcyclopentanone	NA	NA	NA	NA
25	14.275	7114	0.145%	2(3h)-furanone, 5-methyl-	NA	NA	NA	NA
26	14.503	19645	0.402%	furanous compound	NA	NA	NA	NA
27	14.902	18718	0.383%	furanous compound	NA	NA	NA	NA
28	15.518	4343	0.089%	butanedioic acid, diethyl ester	NA	NA	NA	NA

29	15.915	3886	0.079%	furanous compound	NA	NA	NA	NA
30	16.433	15121	0.309%	ethanone, 1-(2-furanyl)-	NA	NA	NA	NA
31	16.840	6693	0.137%	furanous compound	NA	NA	NA	NA
32	17.100	22111	0.452%	furanous compound	NA	NA	NA	NA
33	17.366	5892	0.120%	furanous compound	NA	NA	NA	NA
34	17.782	30082	0.615%	undetermined	NA	NA	NA	NA
35	18.301	68078	1.392%	3-vinyl-2-cylopenten-1-ol	NA	NA	NA	NA
36	18.907	12027	0.246%	undetermined	NA	NA	NA	NA
37	19.125	10488	0.214%	aromatic monomer	1.00	6.94E-07	0.16	7.80
38	19.925	8987	0.184%	cyclohexanol, 4-methyl-	NA	NA	NA	NA
39	20.070	13486	0.276%	aromatic monomer	1.00	6.94E-07	0.20	10.04
40	20.314	4419	0.090%	dihydrocarvone	NA	NA	NA	NA
41	20.417	14250	0.291%	2,5-dimethyl-3-ethylfuran	NA	NA	NA	NA
42	20.688	12942	0.265%	aromatic monomer	1.00	6.94E-07	0.19	9.63
43	20.983	6274	0.128%	4,4-dimethylcyclohexadienone			0	0
44	21.099	6071	0.124%	benzene, 1-methoxy-4-methyl-	1.07	7.27E-07	0.10	5.05
45	21.292	25103	0.513%	vanillin	1.00	8.59E-07	0.46	23.11
46	22.086	2857	0.058%	2-methylresorcinol, acetate	1.08	7.02E-07	0.05	2.31
47	22.134	4122	0.084%	furanous compound			0	0
48	22.382	4520	0.092%	trans-isoeugenol	1.00	8.24E-07	0.08	3.99
49	23.148	4659	0.095%	acetovanillone	1.00	7.02E-07	0.07	3.50
50	23.188	3680	0.075%	undetermined	NA	NA	NA	NA
51	23.482	6184	0.126%	aromatic monomer	1.00	6.94E-07	0.09	4.60
52	23.566	9565	0.196%	1,2-dimethoxy-4-n-propylbenzene	0.86	5.63E-07	0.10	4.97
53	23.877	30398	0.622%	aromatic monomer	1.00	6.94E-07	0.45	22.62
54	23.968	219011	4.479%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	1.03	7.02E-07	3.39	169.32
55	24.329	13803	0.282%	aromatic monomer	1.00	6.94E-07	0.21	10.27
56	24.870	21844	0.447%	aromatic monomer	1.00	6.94E-07	0.33	16.25
57	25.218	6383	0.131%	aromatic monomer	1.00	6.94E-07	0.09	4.75
58	25.275	7650	0.156%	ethyl vanillate	1.17	7.02E-07	0.13	6.71

59	25.449	3186	0.065%	aromatic monomer	1.00	6.94E-07	0.05	2.37
60	25.674	2783	0.057%	aromatic monomer	1.00	6.94E-07	0.04	2.07
61	25.702	3819	0.078%	aliphatic compound	NA	NA	NA	NA
62	25.860	12724	0.260%	4-ethoxy-3-methoxyphenethyl alcohol	1.00	5.63E-07	0.15	7.71
63	25.997	1712	0.035%	aromatic monomer	1.00	6.94E-07	0.03	1.27
64	26.041	6458	0.132%	aromatic monomer	1.00	6.94E-07	0.10	4.81
65	26.156	4896	0.100%	aromatic monomer	1.00	6.94E-07	0.07	3.64
66	26.446	3805	0.078%	benzeneacetic acid, 4-hydroxy-3-methoxy-	1.00	6.94E-07	0.06	2.83
67	26.614	19157	0.392%	7-benzofuranol,2,3-dihydro-2,2-dimethyl	1.00	6.94E-07	0.29	14.25
68	26.805	2334	0.048%	aromatic monomer	1.00	6.94E-07	0.03	1.74
69	26.930	6125	0.125%	aromatic monomer	1.00	6.94E-07	0.09	4.56
70	27.165	2610	0.053%	aromatic monomer	1.00	6.94E-07	0.04	1.94
71	27.281	566	0.012%	aromatic monomer	1.00	6.94E-07	0.01	0.42
72	27.326	210	0.004%	aromatic monomer	1.00	6.94E-07	0.003	0.16
73	27.389	1188	0.024%	ethanedione, di-2-furanyl	NA	NA	NA	NA
74	27.554	690	0.014%	undetermined	NA	NA	NA	NA
75	27.625	180	0.004%	aromatic monomer	1.00	6.94E-07	0.003	0.13
76	27.700	1747	0.036%	aromatic monomer	NA	NA	NA	NA
77	27.859	4942	0.101%	aromatic monomer	1.00	6.94E-07	0.07	3.68
78	27.921	165	0.003%	aromatic monomer	1.00	6.94E-07	0.002	0.12
79	27.955	115	0.002%	aromatic monomer	1.00	6.94E-07	0.002	0.09
80	28.030	2351	0.048%	aromatic monomer	1.00	6.94E-07	0.03	1.75
81	28.084	94	0.002%	aromatic monomer	1.00	6.94E-07	0.001	0.07
82	28.158	5533	0.113%	undetermined	NA	NA	NA	NA
83	28.290	509	0.010%	aromatic monomer	1.00	6.94E-07	0.008	0.38
84	28.352	2381	0.049%	aromatic monomer	1.00	6.94E-07	0.04	1.77
85	28.507	2534	0.052%	aromatic monomer	1.00	6.94E-07	0.04	1.89
86	28.612	698	0.014%	aromatic monomer	1.00	6.94E-07	0.01	0.52
87	28.675	603	0.012%	aromatic monomer	1.00	6.94E-07	0.01	0.45
88	28.796	2208	0.045%	aromatic monomer	1.00	6.94E-07	0.03	1.64

89	28.912	397	0.008%	undetermined	NA	NA	NA	NA
90	28.971	1683	0.034%	undetermined	NA	NA	NA	NA
91	29.003	3971	0.081%	undetermined	NA	NA	NA	NA
sum	of	corrected	areas	620979170			sum [g]	0.400392621
				v oil = 50 mL, g oil = 10.64, dilution factor = 21.43			% of oil	3.761921777

Ex 13 **#**	**FID** **min**	**Area**	**% of total**	**Compounds**	**RRf**	**Rf**	**Monomers** **c [mg/mL]**	**Monomers** **total mass [mg]**
1	13.072	21289	4.006%	guaiacol	**1.00**	7.27E-07	0.31	15.48
2	20.687	9997	1.881%	aromatic monomer	**1.00**	6.94E-07	0.14	6.94
3	20.982	4701	0.904%	aromatic monomeric compound	**1.00**	6.94E-07	0.07	3.26
4	21.060	10480	1.972%	monomeric aromatic compound	**1.00**	6.94E-07	0.15	7.28
5	21.291	29056	5.468%	vanillin	**1.00**	8.59E-07	0.50	24.97
6	22.089	1607	0.302%	2-methylresorcinol, acetate	**1.08**	7.02E-07	0.02	1.22
7	22.607	14760	2.778%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	0.17	8.32
8	23.152	10099	1.901%	acetovanillone	**1.00**	7.02E-07	0.14	7.09
9	23.567	6018	1.132%	1,2-dimethoxy-4-n-propylbenzene	**0.86**	5.63E-07	0.06	2.92
10	23.876	19022	3.580%	monomeric aromatic compound	**1.00**	6.94E-07	0.26	13.21
11	23.964	176923	33.295%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	2.55	127.67
12	24.324	17167	3.231%	monomeric aromatic compound	**1.00**	6.94E-07	0.24	11.92
13	24.884	72681	13.678%	ethyl vanillate	**1.00**	5.63E-07	0.82	41.12
15	25.669	7510	1.413%	aromatic monomer	**1.00**	6.94E-07	0.10	5.22
16	25.858	6596	1.241%	4-ethoxy-3-methoxyphenethyl alcohol	**1.00**	5.63E-07	0.07	3.73
17	26.041	13612	2.562%	aromatic monomer	**1.00**	6.94E-07	0.19	9.45
18	26.154	9197	1.731%	ethyl homovanillate	**1.11**	7.02E-07	0.14	7.17
19	26.424	14264	2.684%	monomeric aromatic compound	**1.00**	6.94E-07	0.20	9.91
20	26.612	16551	3.115%	homovanillic acid	**1.24**	7.02E-07	0.29	14.36
21	26.805	4477	0.843%	monomeric aromatic compound	**1.00**	6.94E-07	0.06	3.11
sum	of	corrected	areas:	531378			sum [g]	0.33
				v oil = 50 mL, g oil = 8.91, dilution factor = 20.00			% of oil	3.65

Ex 14 #	FID min	Area	% of total	Compound	RRfs	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	13.067	12549	1.248%	guaiacol	1.00	7.27E-07	0.11	5.26
2	15.934	914	0.091%	p-cresol, 2-methoxy-	**1.09**	7.27E-07	0.01	0.42
3	18.132	5978	0.595%	3',5'-dihydroxyacetophenone	**1.14**	7.02E-07	0.06	2.76
4	18.224	7899	0.786%	p-ethylguaiacol	**1.00**	6.12E-07	0.06	2.79
5	18.643	21490	2.138%	aromatic monomer	**1.00**	6.94E-07	0.17	8.61
6	19.140	1670	0.166%	4-vinyl-2-methoxy-phenol	**0.94**	8.24E-07	0.01	0.75
7	19.817	1025	0.102%	chauvicol (pheno, 4-(2-propenyl)-	**0.81**	8.24E-07	0.01	0.39
8	20.259	33086	3.291%	eugenol	**1.00**	6.17E-07	0.24	11.77
9	20.546	7161	0.712%	dihydroeugenol	**1.00**	5.63E-07	0.05	2.33
10	20.701	6156	0.612%	aromatic monomer	**1.00**	6.94E-07	0.05	2.47
11	21.049	2119	0.211%	aromatic monomer	**1.00**	6.94E-07	0.02	0.85
12	21.130	2665	0.265%	phenol, 4-propyl-	**0.78**	5.63E-07	0.01	0.68
13	21.290	73766	7.338%	vanillin	**1.00**	8.59E-07	0.73	36.57
14	21.520	1179	0.117%	cis-isoeugenol	**1.00**	8.24E-07	0.01	0.56
15	22.418	6553	0.652%	trans-isoeugenol	**1.00**	8.24E-07	0.06	3.11
17	22.612	272650	27.123%	2,4-dihydroxypropiophenone	**1.00**	5.63E-07	1.77	88.62
18	23.149	4956	0.493%	acetovanillone	**1.00**	7.02E-07	0.04	2.01
19	23.355	4977	0.495%	benzaldehyde, 3-hydroxy-4-methoxy-	**1.00**	8.59E-07	0.05	2.47
20	23.564	5492	0.546%	1,2-dimethoxy-4-n-propylbenzene	**0.86**	5.63E-07	0.03	1.54
21	23.822	9380	0.933%	monomeric aromatic compound	**1.00**	6.94E-07	0.08	3.76
22	23.962	164396	16.354%	1-(3-hydroxy-4-methoxyphenyl)propan-2-one	**1.03**	7.02E-07	1.37	68.44
23	24.424	10615	1.056%	(z)-4-(2-ethoxyethenyl)anisole	**0.89**	8.24E-07	0.09	4.48
24	24.887	73753	7.337%	ethyl vanillate	**1.17**	7.02E-07	0.70	34.81
25	25.211	1742	0.173%	aromatic monomer	**1.00**	6.94E-07	0.01	0.70
26	25.421	5411	0.538%	aromatic monomer	**1.00**	6.94E-07	0.04	2.17
27	25.675	15516	1.543%	aromatic monomer	**1.00**	6.94E-07	0.12	6.22
28	25.873	8238	0.819%	4-ethoxy-3-methoxyphenethyl alcohol	**1.00**	5.63E-07	0.05	2.69
29	26.025	6909	0.687%	aromatic monomer	**1.00**	6.94E-07	0.06	2.77

30	26.171	29045	2.889%	ethyl homovanillate	**1.11**	7.02E-07	0.26	13.06
31	26.378	62486	6.216%	homovanillic acid)	**1.24**	7.02E-07	0.63	31.28
32	26.928	78965	7.855%	conifer aldehyde	**1.07**	8.24E-07	0.80	40.05
33	27.381	3451	0.343%	aromatic monomer	**1.05**	8.59E-07	0.04	1.79
34	27.506	14736	1.466%	aromatic monomer	**1.00**	6.94E-07	0.12	5.90
sum	of	corrected	areas:	1005246			sum [g]	0.39
				v oil = 50 mL, g oil = 5.75 dilution factor = 11.54			% of oil	6.82

Ex 15 #​	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	6.459	356055	8.816%	furfural	NA	NA	NA	NA
2	6.978	2077	0.051%	methyl ethyl ketone	NA	NA	NA	NA
3	7.201	7424	0.184%	4-ethoxy-2-butanone	NA	NA	NA	NA
4	8.282	36122	0.894%	2,5-hexandione	NA	NA	NA	NA
5	8.438	117836	2.918%	2(3h)-furanone, 5-methyl-	NA	NA	NA	NA
6	8.950	25481	0.631%	5-methyl-2-furfural	NA	NA	NA	NA
7	9.588	24210	0.599%	1-(furan-2-yl)propan-1-one	NA	NA	NA	NA
8	10.295	2119	0.052%	ethanol, 2,2-diethoxy-	NA	NA	NA	NA
9	11.276	14937	0.370%	2(3h)-furanone, 5-ethyldihydro-5-methyl-	NA	NA	NA	NA
10	11.952	17373	0.430%	2-propylfuran-2-ol	NA	NA	NA	NA
11	12.245	768079	19.017%	ethyl levulinate	NA	NA	NA	NA
12	12.526	4607	0.114%	furanous compound	NA	NA	NA	NA
13	12.699	3768	0.093%	4,5-dimethyl-2-formylfuran	NA	NA	NA	NA
14	12.922	33154	0.821%	furancarboxylic acid, methyl ester	NA	NA	NA	NA
15	13.067	12541	0.311%	guaiacol	1.00	7.27E-07	0.14	6.77
16	13.266	3656	0.091%	1-methylethyl 3-acetylpropanoate	NA	NA	NA	NA
17	13.499	3102	0.077%	furanous compound	NA	NA	NA	NA
18	13.740	2380	0.059%	2-furanmethanol	NA	NA	NA	NA
19	14.280	1853	0.046%	furanous compound	NA	NA	NA	NA
20	14.437	3784	0.094%	n-butyl ether	NA	NA	NA	NA
21	14.930	23118	0.572%	4-hydroxy-6-methyl2h-pyran-2-one	NA	NA	NA	NA
22	15.709	20123	0.498%	carbohydrate compound	NA	NA	NA	NA
23	16.429	39080	0.968%	1-(furan-2-yl)ethanone	NA	NA	NA	NA
24	16.596	1549	0.038%	furanous compound	NA	NA	NA	NA
25	16.857	1622666	40.176%	5-ethoxymethyl furfural	NA	NA	NA	NA
26	17.834	15974	0.396%	furanous compound	NA	NA	NA	NA

27	18.129	5678	0.141%	3',5'-dihydroxyacetophenone	1.14	7.02E-07	0.07	3.38
28	18.214	13458	0.333%	ethylguaiacol	1.00	6.12E-07	0.12	6.12
29	18.640	23082	0.571%	aromatic monomer	1.00	6.94E-07	0.24	11.90
30	19.499	6270	0.155%	undetermined	NA	NA	NA	NA
31	20.259	26661	0.660%	furanous compound	NA	NA	NA	NA
32	20.539	9017	0.223%	eugenol	1.00	6.17E-07	0.08	4.13
33	20.703	6472	0.160%	aromatic monomer	1.00	6.94E-07	0.07	3.34
34	21.124	12125	0.300%	phenol, 4-propyl-	0.78	5.63E-07	0.08	3.97
35	21.290	54938	1.360%	vanillin	1.00	8.59E-07	0.70	35.06
36	22.409	5937	0.147%	aromatic monomer	1.00	6.94E-07	0.06	3.06
37	22.490	3398	0.084%	trans-isoeugenol	1.00	8.24E-07	0.04	2.08
38	22.610	230744	5.713%	2,4-dihydroxypropiophenone	1.00	8.24E-07	2.82	141.15
39	23.146	4028	0.100%	acetovanillone	1.00	7.02E-07	0.04	2.10
40	23.350	4679	0.116%	aromatic monomer	1.00	8.59E-07	0.06	2.99
41	23.566	6624	0.164%	1,2-dimethoxy-4-n-propylbenzene	0.86	5.63E-07	0.05	2.39
42	23.821	11506	0.285%	1h-inden-1-one, 2,3-dihydro-3,3,5,6-tetramethyl-	1.00	6.94E-07	0.12	5.93
43	23.963	199840	4.948%	1-(3-hydroxy-4-methoxyphenyl) propan-2-one	1.03	7.02E-07	2.14	107.08
44	24.333	4400	0.109%	2-(4-hydroxy-3-methoxyphenyl) acetic acid methyl ester	1.00	6.94E-07	0.05	2.27
45	24.421	9913	0.245%	(z)-4-(2-ethoxyethenyl)anisole	0.89	8.24E-07	0.11	5.39
46	24.752	7126	0.176%	aromatic monomer	1.00	6.94E-07	0.07	3.67
47	24.885	83615	2.070%	benzoic acid, 4 hydroxy-3-methoxy-ethyl ester	1.17	7.02E-07	1.02	50.79
48	25.679	9421	0.233%	aromatic monomer	1.00	6.94E-07	0.10	4.86
49	25.873	6289	0.156%	undetermined	NA	NA	NA	NA
50	26.035	4595	0.114%	di-alpha,4-dihydroxy-3-methoxyphenylaceetic acid	1.00	6.94E-07	0.05	2.37
51	26.167	18226	0.451%	homovanillic acid	1.24	7.02E-07	0.23	11.74
52	26.294	3051	0.076%	aromatic monomer	1.00	6.94E-07	0.03	1.57
53	26.416	16024	0.397%	aromatic monomer	1.00	6.94E-07	0.17	8.26
54	26.499	4652	0.115%	vanillic acid methyl ester	1.24	7.02E-07	0.06	3.00

55	26.616	5928	0.147%	aliphatic	NA	NA	NA	NA
56	26.727	18022	0.446%	aliphatic	NA	NA	NA	NA
57	26.797	3851	0.095%	homovanillic acid methyl ester	1.24	7.02E-07	0.05	2.48
58	26.927	41934	1.038%	aromatic monomer	1.00	6.94E-07	0.43	21.63
59	27.503	10859	0.269%	methyl homovanillate	1.24	7.02E-07	0.14	7.00
sum	of	corrected	areas	4038841			sum [g]	0.47
				v oil = 50 ml, g oil =7.46, dilution factor = 14.85			[%] of oil	6.25

Ex 16 # 	FID min	Area	% of total	Compound	RRf	Rf	Monomers c [mg/mL]	Monomers total mass [mg]
1	6.459	323278	10.928	furfural	NA	NA	NA	NA
2	8.650	1847	0.062	2,5-hexandione	NA	NA	NA	NA
3	8.960	12121	0.41	2(3h)-furanone, 5-methyl-	NA	NA	NA	NA
4	9.588	14359	0.485	5-methyl-2-furfural	NA	NA	NA	NA
5	10.295	2502	0.085	ethanol, 2,2-diethoxy-	NA	NA	NA	NA
6	10.954	920	0.031	pentane, 1,1-diethoxy-	NA	NA	NA	NA
7	11.280	4888	0.165	2(3h)-furanone, 5-ethyldihydro-5-methyl-	NA	NA	NA	NA
8	11.734	707	0.024	furancarbonic acid-(2)-ethylester	NA	NA	NA	NA
9	12.013	3013	0.102	furanous compound	NA	NA	NA	NA
10	12.232	334533	11.308	ethyl levulinate	NA	NA	NA	NA
11	12.526	3910	0.132	furanous compound	NA	NA	NA	NA
12	12.704	2367	0.08	1,4-benzenediol, 2-methyl-	1.09	7.27E-07	0.02	1.09
13	12.916	27719	0.937	furancarboxylic acid, methyl ester	NA	NA	NA	NA
14	13.067	10580	0.358	guaiacol	1.00	7.27E-07	0.09	4.44
15	13.261	1935	0.065	1-methylethyl 3-acetylpropanoate	NA	NA	NA	NA
16	13.499	7882	0.266	furanous compound	NA	NA	NA	NA
17	13.737	1912	0.065	2-furanmethanol	NA	NA	NA	NA
18	14.433	2083	0.07	n-butyl ether	NA	NA	NA	NA
19	14.934	16017	0.541	4-hydroxy-6-methyl-pyran-2-one	NA	NA	NA	NA
20	15.336	784	0.026	carbohydrate compound	NA	NA	NA	NA
21	15.706	19614	0.663	carbohydrate compound	NA	NA	NA	NA
22	15.970	3136	0.106	carbohydrate compound	NA	NA	NA	NA
23	16.429	23575	0.797	carbohydrate compound	NA	NA	NA	NA
24	16.594	1584	0.054	carbohydrate compound	NA	NA	NA	NA
25	16.844	1058961	35.796	5-ethoxymethyl furfural	NA	NA	NA	NA
26	17.364	34102	1.153	carbohydrate compound	NA	NA	NA	NA
27	17.852	12454	0.421	ethanol, 2,2-diethoxy-	NA	NA	NA	NA
28	18.130	4836	0.163	carbohydrate compound	NA	NA	NA	NA

29	18.231	8829	0.298%	ethylguaiacol	1.00	6.12E-07	0.06	3.12
30	18.638	20963	0.709%	aromatic monomer	1.00	6.94E-07	0.17	8.40
31	19.136	6948	0.235%	2-methoxy-4-vinylphenol	0.94	8.24E-07	0.06	3.12
32	19.497	8689	0.294	aliphatic	NA	NA	NA	NA
33	20.184	9076	0.307	furanous compound	NA	NA	NA	NA
34	20.259	21566	0.729	aliphatic	NA	NA	NA	NA
35	20.542	3434	0.116%	eugenol	1.00	6.17E-07	0.02	1.22
36	20.705	2630	0.089%	aromatic monomer	1.00	6.94E-07	0.02	1.05
37	21.124	8625	0.292%	phenol, 4-propyl-	0.78	5.63E-07	0.04	2.19
38	21.287	65109	2.201%	vanillin	1.00	8.59E-07	0.65	32.28
39	21.943	1932	0.065	aliphatic	NA	NA	NA	NA
40	22.419	7630	0.258%	trans-isoeugenol	1.00	8.24E-07	0.07	3.63
41	22.612	341501	11.544%	2,4-dihydroxypropiophenone	1.00	8.24E-07	3.25	162.30
42	23.149	3676	0.124%	acetovanillone	1.00	7.02E-07	0.03	1.49
43	23.347	7273	0.246%	benzaldehyde, 3-hydroxy-4-methoxy-	1.00	8.59E-07	0.07	3.61
44	23.562	6138	0.207%	1,2-dimthoxy-4-n-propylbenzene	0.86	5.63E-07	0.03	1.72
45	23.821	7425	0.251%	aromatic monomer	1.00	6.94E-07	0.06	2.97
46	23.960	161187	5.449%	1-(3-hydroxy-4-methoxyphenyl) propan-2-one	1.03	7.02E-07	1.34	67.10
47	24.342	3534	0.119%	2-(4-hydroxy-3-methoxyphenyl) acetic acid methyl ester	1.00	6.94E-07	0.03	1.42
48	24.417	11131	0.376%	(z)-4-(2-ethoxyethenyl)anisole	0.89	8.24E-07	0.09	4.70
49	24.750	5976	0.202%	aromatic monomer	1.00	6.94E-07	0.05	2.39
50	24.883	70216	2.374%	ethyl vanillate	1.17	7.02E-07	0.66	33.14
51	25.421	3865	0.131%	methyl homovanillate	1.00	6.94E-07	0.03	1.55
52	25.671	11826	0.400%	aromatic monomer	1.00	6.94E-07	0.09	4.74
53	25.872	4163	0.141%	aromatic monomer	1.00	6.94E-07	0.03	1.67
54	26.028	2444	0.083%	alpha,4-dihydroxy-3-methoxyphenylaceetic acid	1.00	6.94E-07	0.02	0.98
55	26.168	37686	1.274%	homovanillic acid	1.24	7.02E-07	0.38	18.86
56	26.374	7167	0.242%	aromatic monomer	1.00	6.94E-07	0.06	2.87
57	26.382	8823	0.298%	aromatic monomer	1.24	7.02E-07	0.09	4.42
58	26.442	4146	0.140%	aromatic monomer	1.00	6.94E-07	0.03	1.66

59	26.533	3147	0.106	aliphatic	NA	NA	NA	NA
60	26.610	1954	0.066	aliphatic	NA	NA	NA	NA
61	26.727	28285	0.956	aliphatic	NA	NA	NA	NA
62	26.796	3573	0.121%	aromatic monomer	1.24	7.02E-07	0.04	1.79
63	26.926	91940	3.108%	aromatic monomer	1.17	7.02E-07	0.87	43.39
64	27.503	17481	0.591%	aromatic monomer	1.24	7.02E-07	0.18	8.75
65	27.898	2129	0.072%	aromatic monomer	1.00	6.94E-07	0.02	0.85
66	28.245	1219	0.041%	aromatic monomer	1.00	6.94E-07	0.01	0.49
67	28.326	5435	0.184%	benzendiol, 4-(1,1 -dimethylethyl)-	1.00	6.94E-07	0.04	2.18
68	29.002	7962	0.269%	aromatic monomer	1.00	6.94E-07	0.06	3.19
				sum of corrected areas: 2958351			sum [g]	0.44
				v oil = 50 mL, g oil = 5.76, dilution factor = 11.54			[%] of oil	7.62

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