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Homogeneous and heterogeneous catalyzed hydrolysis of lignin

Virginia Marie Roberts

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Chapter 1

Introduction

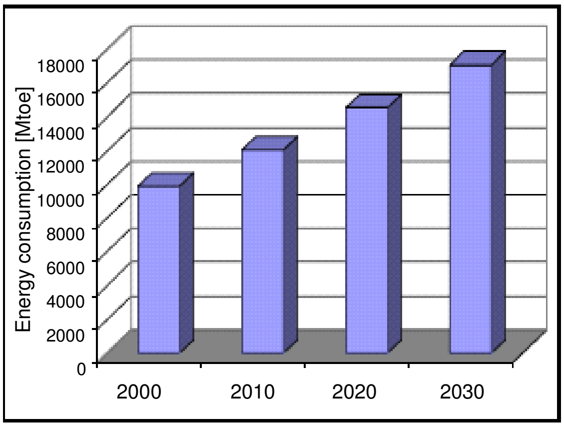
Abstract

The introduction gives a general insight on biomass utilization for energy, fuel and chemical production. Lignin is introduced, and an overview on its structure, the various methods of recovery and their effect on the properties of the obtained lignin are given. Furthermore, applications for sub – and supercritical water as a reaction medium as well as its properties and effects on reaction kinetics are described.

1 Introduction

1.1 Motivation

In January 2008, for the first time in history, the price of crude oil reached 100 dollars per barrel [1]. This value is a symbolic indicator for the decreasing availability of conventional energy sources due to the global economy growth. Particularly, there is a huge demand for resources from Less Developed Countries and Newly Industrializing Economies such as India and China. According to the *World Energy, Technology, and Climate Policy Outlook* of the European Commission, there will be a 240 % raise in the energy consumption of Asia by 2030 (based on 2000). The world total energy consumption will rise from 9,927 million tons of oil equivalent (Mtoe) to 17,100 Mtoe in the same period (Figure 1.1). As a direct consequence, the world carbon dioxide emission will be almost doubled by 2030 (Figure 1.2) [2].



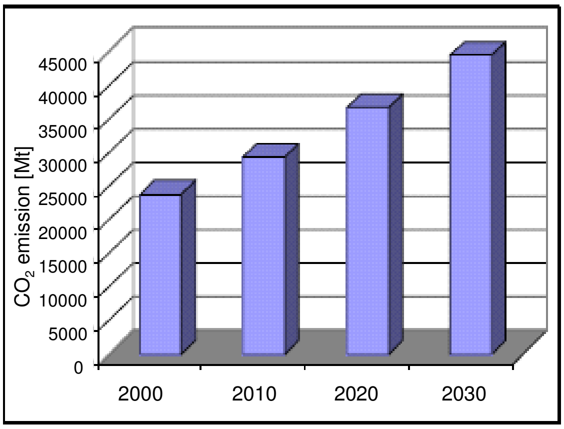


Figure 1.1: World total energy consumption [2]

Figure 1.2: World CO2 emission [2]

Since the enormous CO_2 emission is considered to be responsible for the global warming, there is a need for reducing the consumption of fossil resources. Of course, this is possible by replacing fossil fuels and using alternative energy sources like rapeseed oil, bio-ethanol, wind energy or photovoltaics. Another contribution to the reduction of the CO_2 emission is the production of energy, fuels and chemical feedstock from renewable resources like biomass. Many chemicals used by the chemical industry can be derived from biomass, potentially reducing the industry's reliance on petroleum. Therefore, there has been a growing interest in the recent years in exploring wood and other biomass materials as a source of chemicals. Out of the global annual production of biomass, 1.7-2 x 10^{11} tons only ca. 3% are used in non-food applications [3], including production of biomaterials (e.g., oils, inks, dyes, paints, detergents, biopolymers, etc.), fuels (methanol, fuel oil, and biodiesel), and biochemicals (oxyfuel additives, specialty chemicals, phenols, furfural, fatty acids, agricultural chemicals, etc.).

The principles of sustainable development were adopted in the Rio Declaration, the Agenda 21, during the Conference on Environment and Development in Rio de Janeiro organized by the United Nations [4]. In order to implement the Rio declaration, the US chemical industry prepared a Vision 2020 program [5], which gave conclusions and recommendations for the chemical industry to achieve sustainable development. In the vision 2020 catalysis report, one recommendation was to use renewable feedstock—especially cellulose and carbohydrates—as sources for valuable chemicals [5]. Goals for the chemical industry to achieve sustainable development were defined in the workshop report in July 2001 [6]. In particular, it was stated that the use of renewable raw materials should be increased by 13% until 2020. Furthermore, the EU has established a platform for sustainable chemistry demanding that 30% of the chemicals should be prepared from renewable resources by 2025 [7].

Wood biomass consists of cellulose (40–50%), lignin (16–33%), hemicelluloses (15–30%), and a variety of extractives (1–10%). Lignin represents about 20 % of terrestrial biomass and is therefore the most abundant organic material. It is predominantly utilized as secondary fuel, but has the potential to partly replace fossil carbon resources, as basis of chemical industry , due to its unique structure, comprised of the three phenyl propane units, trans-p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

1.2 Biomass

While the need for energy and raw materials is increasing world wide, environmental problems, as a result of utilizing coal, crude oil and natural gas are gaining weight. Moreover, the decline of crude oil reservoirs and the associated fear of an energy crisis make renewable resources more and more often a topic of discussion [8] [9].

Beside renewable energy sources like hydro energy and wind another important way to reduce the CO_2 emissions is the increasing use of biomass for energy- as well as for goods-production. Due to CO_2 neutrality (plants take up exactly the same amount of CO_2 during their lifetime, as the energy recovery releases) biomass has a high potential for the future.

Referring to these facts biomass has to be considered as a regenerative resource for energy and goods in detail.

Table 1.1: Disadvantages and advantages of biomass application

Advantages	Disadvantages
• Reduction of CO_2 emissions • Biomass as an energy source • Fossil fuel protection • High availability • Natural synthesis capacity reclaimable • Survival of agricultural structures • Composting ability • Biotechnology	• High subsidy requirements • Complex production, extensive cultivation effects the ecosystem • Harvest dependent quality fluctuations • Utilization spectrum restricted to applications • Complex separation of biomass • Disadvantageous C/H-ratio for basic chemicals production (ethen, propen)

Biomass is a general term for material derived from plants or from animal manure . It is produced by nature in a vast amount of $200 \cdot 10^9\ t \cdot a^{-1}$ via photosynthesis. Because it is a mixture of varying composition it is difficult to say something precise about its properties. For example the energy content of biomass varies strongly between different types (straw, softwood, hardwood ...) and depending on moisture content. The energy of biomass may be used either by combustion or by upgrading the raw material into bio fuel or other useful chemicals, as exemplary shown in Figure 1.3 [10]. The many advantages of biomass utilization have already been mentioned and are summarized in Table 1.1. Unfortunately there are also a number of disadvantages to consider. Compared to fossil fuel as closer to ready-for-use products, biomass presents costs of processing it. Compacting, chipping, shredding or cutting huge volumes of biomass is often necessary. For small biomass plants such cleaning technology may not be economically feasible. Furthermore, collection, harvesting and storing raw biomass materials is expensive, especially considering the large volumes required compared to fossil fuels. Large scale crop production will use vast areas of land and water, representing major problems, e.g. deforestation. Moreover, this land is also needed for feeding the growing population of billions of people [11].

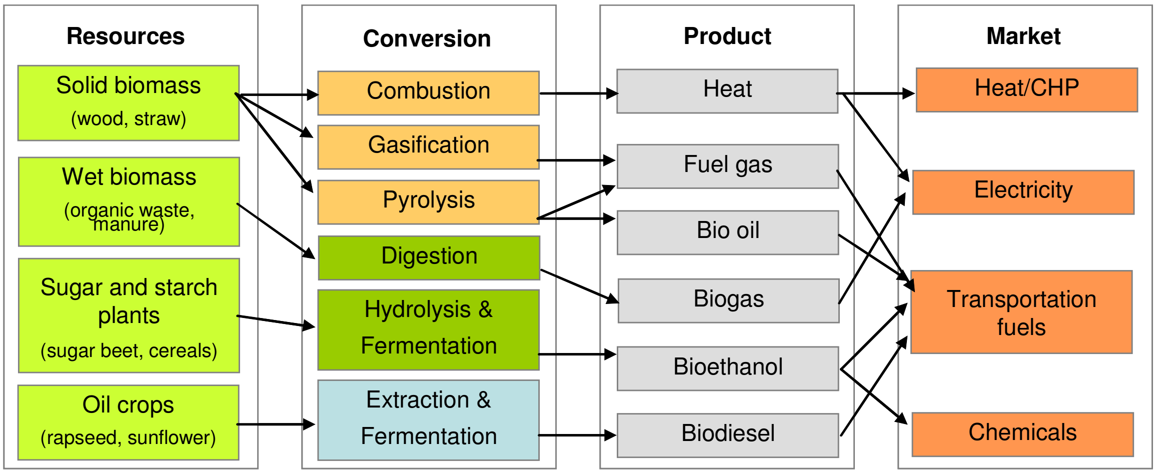


Figure 1.3: Biomass conversion routes [10]

Till now biomass is mostly used energetically by combustion, whereas a material utilization of biomass by upgrading it to defined chemicals is not a common method so far. Because of the multi component mixture it is difficult to convert biomass - like crude oil by fractionated distillation - into single well-defined products. Figure 1.3 gives an overview on the possible pathways for biomass conversion.

1.2.1 Fuels and energy production from biomass

General concepts associated with the use of biomass for the production of energy are the synthesis of common fuels, the production of heat, electricity and the production of hydrogen as a potential energy carrier in the future. For the production of gasoline, biomass is converted into synthesis gas. Synthesis gas is then transformed to motor and diesel fuel via the Fischer-Tropsch-Synthesis , to methanol via low pressure methanol synthesis [12] and to dimethyl ether as a potential diesel fuel [13]. The potential market of these bio fuels is estimated at 20 % in Germany and 30 % in Europe. Daimler-Chrysler AG in cooperation with Volkswagen AG is also active on the field of converting biomass to energy [14, 15].

The production of heat and electricity is based on the anaerobic gasification of agricultural biomass to methane that is fired in bio heating power plants. Dry biomass like wood or straw can also be fired directly in these plants. Over near-heat-networks the customers are provided with heat. The achieved output of these plants is 8.5 MW and the electricity produced is promoted by the European Union [16].

Hydrogen production from biomass is studied on model substances like glucose, sorbitol (hydrated product of glucose), glycerin (from lipolysis) and ethylene glycol (hydrogenolysis of sugars). For these purposes heterogeneous catalysts like Pt/Al_2O_3 or Raney nickel doped with Sn (SnNi) are used [17]. Reactions take place in aqueous phase at 200 °C and at 2.9 MPa. Depending on the educt, the gained gas contains from 51 to 70 mol-% hydrogen [18]. Further investigations are focusing on the application of supercritical water as reaction medium for the conversion of biomass to hydrogen, obtaining gas with 70 vol.-% hydrogen [19].

1.2.2 Chemicals production from biomass

Recently, there has been a strong political and technical focus on using biomass to produce transportation fuels [20]. Much less attention has been given to biomass as a feedstock for organic chemicals. Replacement of petroleum-derived chemicals with those from biomass will play a key role in sustaining the growth of the chemical industry.

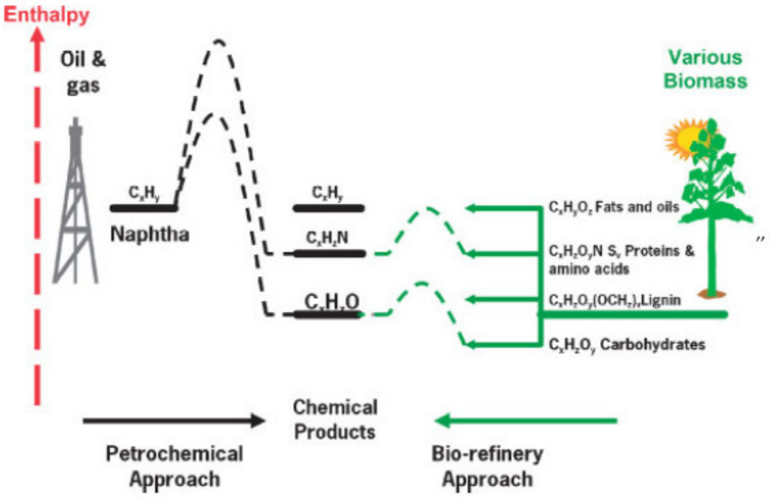


Figure 1.4: Products formed from oil and biomass [21]

Figure 1.4 shows the types of products that are produced from oil [21]. Naphtha is the general raw material for many chemical products. Olefins, such as ethylene, which contain only carbon and hydrogen, can be produced very efficiently because no major enthalpy changes have to be overcome with concomitant heat transfer. If one considers the enthalpy changes involved in the conversion of naphtha into functionalized chemical products, naphtha has a calorific value of ca. 45 GJ per tone and requires the use of additional (process) energy in the form of heat and electricity to produce a product with a significantly lower calorific value compared to the original fossil raw material. Allied with this, the process conditions at which reactions are carried out, high temperatures and pressures, as well as corrosive and toxic substrates and co-reagents are often required. Existing functionalized petrochemicals may be reduced if biomass components are used [22]. As well as this, if the structure is suitably similar to the desired product, then probably only a limited number of simple conversion steps would be required. For example, it is considered that amino acids may be suitable raw materials for the production of amines [21].

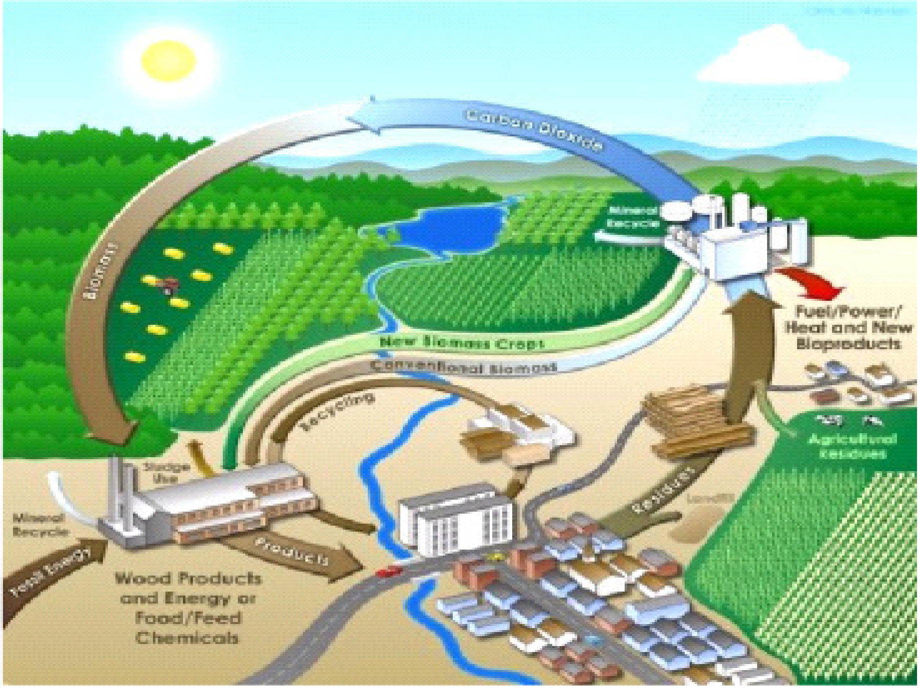


Figure 1.5: Biorefinery- and bioenergy-model [23].

Due to the chemical diversity of biomass, the production of a defined chemical substance is not trivial. Before performing a selective chemical or biochemical transformation, the used biomass has to be separated into defined substances or into a class of substances. Today, roughly 200 to 300 products are derived from oil [24]. At the beginning of this value-added chain, a petrochemical refinery separates the crude oil into different products like hydrocarbons or aromatics by rectification. Efforts have been made to develop such a value-added chain for biomass. In analogy to petrochemistry, the concept of a bio-refinery stands at the beginning of this chain Figure 1.5 [23]. By producing multiple products, a biorefinery takes advantage of the various components in biomass and their intermediates therefore maximizing the value derived from the biomass feedstock. A biorefinery could, for example, produce one or several low-volume, but high-value, chemical or nutraceutical products and a low-value, but high-volume liquid transportation fuel such as biodiesel or bioethanol. At the same time generating electricity and process heat, through combined heat and power technology, for its own use and perhaps enough for sale of electricity to the local utility. The high-value products increase profitability, the high-volume fuel helps meet energy needs, and the power production helps to lower energy costs and reduce greenhouse gas emissions from traditional power plant facilities. Although some facilities exist that can be called bio-refineries, the bio-refinery has yet to be fully realized. Future biorefineries may plan a major role in producing chemicals and materials that traditionally produced from petroleum.

Biomass differs from oil in some crucial points. First of all the physiology and the bio - chemical diversity of the components of biomass have to be specified before separating them. Such technologies are already in use when processing cellulose-, starch-, sugar- and oil-containing plants in paper mills, sugar refineries and oil mills. The basic principles are depicted in Figure 1.6. The separation of plant biomass into its principal components (i.e. biomass-precursors) and the following upgrading processes are depicted in Figure 1.7.

Given the current robust forces driving sustainable production, and available biomass conversion technologies, biomass-based routes are expected to make a significant impact on the production of bulk chemicals within 10 years, and a huge impact within 20-30 years. There is a substitution potential of 10-15 % of fossil oil-based bulk chemicals by bio-based bulk chemicals, especially for oxygenated bulk chemicals, such as ethylene glycol and propylene glycol, iso-propanol and acetone, butylene and methylethylketone and for the replacement of methyl tertiary butyl ether (MTBE) by ethyl tertiary butyl ether (ETBE) [25].

Glycerin, as a byproduct of biodiesel production, is a very favorable short-term option for the production of ethylene and propy-lene glycols. In the mid-term (10-20 years) there is clear potential for a bio-based production of ethylene, acrylic acid and N-containing bulk chemicals such as acrylonitrile, acrylamide and ε-caprolactam. Technologies involving direct isolation of aromatic building blocks from biomass, or the conversion of sugars or lignin to aromatics are still in their infancy.

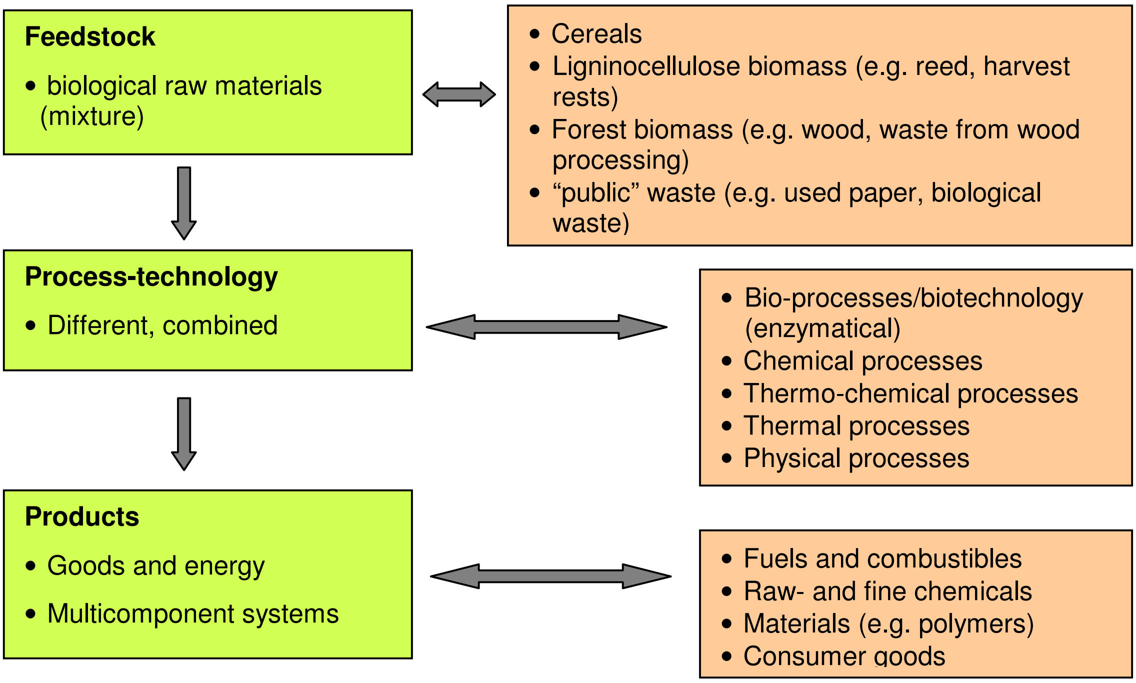


Figure 1.6: Basic principles of a bio-refinery

Biorefineries that are being started up today will form the stepping stones toward the chemicals mentioned above if we learn to upgrade their side streams [25].

One example for chemicals production from biomass is glycerol conversion. The rapid growth in the biodiesel industry, which uses chemical methods to synthesize its product, has decreased the market price of glycerol; many biodiesel production facilities now view crude glycerol as waste. Chemical companies can use this glycerol as a low-cost chemical building block. Dow Chemical Company, Huntsman Corporation, Cargill, and Archer Daniels Midland Corporation have begun, or announced plans, to chemically convert glycerol to propylene glycol [26]. Dow Chemical Company and Solvay plan to build plants that use glycerol to produce epichlorohydrin [27]. Other innovative chemical methods convert fatty acids to polymer building blocks. For example, Cargill, working with the Kansas Polymer Research Center, has developed a bio-derived polyol (BiOH) by the chemical conversion of triglyceride carboncarbon double bonds to alcohol and methoxy groups. Polyols are important precursors to numerous polyurethane materials [28]. Despite these achievements, the transition of industrial chemical production from petrochemical to biomass feedstock still faces real hurdles.

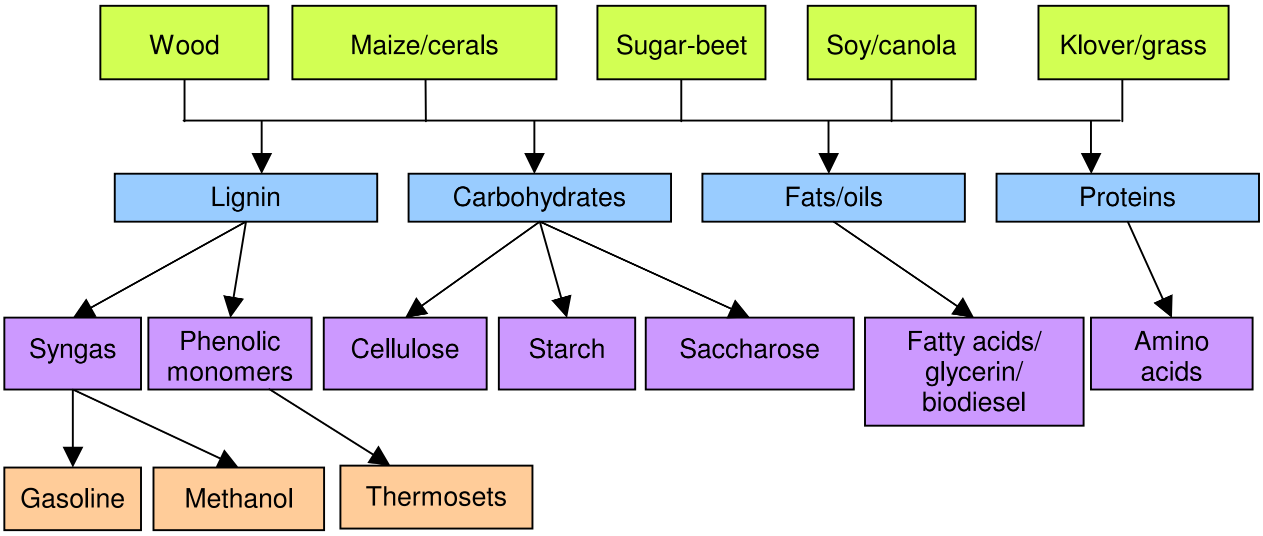


Figure 1.7: Basic separation-scheme of a bio-refinery [29].

1.3 Lignin

1.3.1 General structure of lignin

Lignin represents about 20 % of terrestrial biomass and is therefore the most abundant organic material. It is predominantly utilized as secondary fuel but its application for the production of chemicals is an issue of great economical and environmental importance. Lignin depolymerization presents a great challenge due to its reluctant structure.

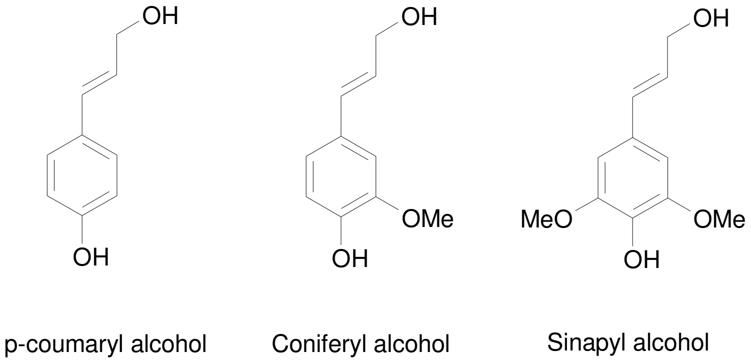


Figure 1.8: Phenylpropene units of lignin

The different lignin monomer units, trans-p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 1.8) as well as the multiplicity of bond types [30, 31] (Table 1.2) explain the heterogeneity of the molecule and the complex product distribution upon depolymerization.

Table 1.2: Overview of most frequent bond types found in lignin

Model Linkage[a]	Glasser and Glasser [32]	Erickson et al. [33]	Nimz [34]
β carbon-oxygen-4 aromatic carbon	55	49-51	65
α carbon-oxygen-4 aromatic carbon		6-8	
β carbon-5 aromatic carbon	16	9-15	6
β carbon-1 aromatic carbon	9	2	15
5 aromatic carbon- 5 aromatic carbon	9	9.5	2.3
4 aromatic carbon-oxygen- 5 aromatic carbon	3	3.5	1.5
β carbon- β carbon	2	2	5.5
β carbon- β carbon forming a furanic structure			2
α and γ carbon-oxygen- γ carbon	10		

1.3.2 Recovery of lignin

55 Million tons of lignin accumulate as a side product of the pulping process every year. With a share of 76%; the Kraft process (sulphate process) is the most significant process, followed by the Sulphite process with 8% (table y) [35]. The remaining 16% are constituted of special technologies which focus on the production of technically high quality pulp. The most important pulping processes and the resulting properties of the obtained lignin and pulp are described in the following.

Table 1.3: Global pulp production (1000 tons)

Region/country	Total pulp	Sulphate pulp	Sulphite pulp	Remaining techniques
Germany	1377	0	1023	354
Spain	1506		0	131
France	1727	1349	258	120
Finland	5916	5224	154	538
Sweden	7337	6003	749	585
Remaining Europe	4295	2759	588	948
Canada	13195	10850	1627	718
China	8894	1032		7862
USA	50775	44106	1418	5251
Remaining countries	33295	24265	4067	4963
World (total)	128317	96963	9884	21470

Kraft process

In 1878 Dahl developed the Kraft process based on the since 1854 known natron pulping process by adding alkaline sulfide and sodium sulphate. The obtained pulp had a higher quality, as the lignin was disassociated much milder. By burning the waste liquor the sodium sulphate is reduced to sodium sulphate and is fed back to the process.

Advantages of this process are that nearly all woods and grasses can be applied and the obtained pulp possesses a outstanding quality. During the process alkyl aryl ether bonds between the units are cleaved and the formed lignin cleavage products are dissolved as phenolates (Figure 1.9). The likewise dissolved SH^- ions are bound to the α-C atoms of the propane side chains and activate the alkaline hydrolysis of the alkyl aryl ether in this position. Additionally, methoxy groups are partially cleaved to form methanol, methyl mercaptan and dimethyl sulfide [36].

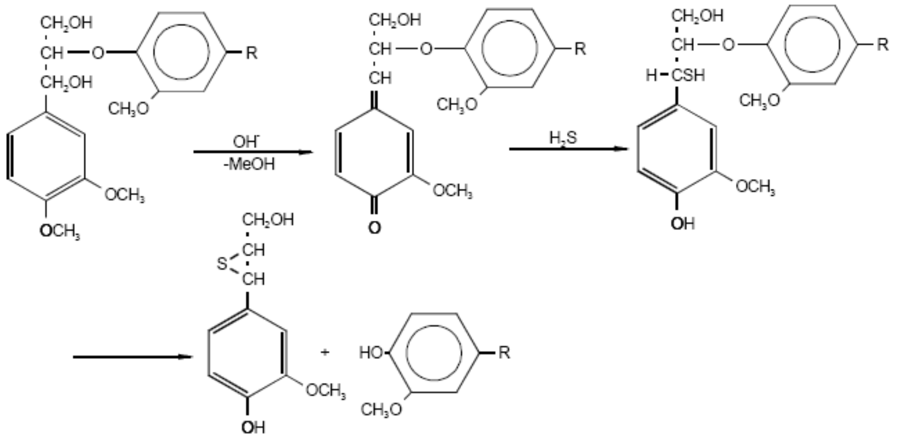


Figure 1.9: Reactions during the Kraft process for the example of the β-O-4 bond [36].

Sulphite process

In the 1866 from Tilghman developed process wood chips are cooked in solutions of hydrogen sulphites or sulphites [13]. The Sulphite process does not allow the pulping of grasses and all sorts of wood. During the process lignin is sulphonated, cleaved hydrolytically and dissolved as lignin sulphonate. The side chains of the phenyl propane units are sulphonated whereupon hydroxyl or alkyl ether groups are released (Figure 1.10). The HSO_3^- ion attacks the aliphatic ether bridges between two units, resulting in cleavage of the molecule.

A similar reaction proceeds through the influence of acids. At low pH values the lignin cleavage products condensate (repolymerization) and form a lignin like material more stable and difficult to dissolve than the initial lignin.

Soda Antrachinon process

This sulphur free process is applied to avoid the ecological damage. In contrast to the sulphur free but out-dated natron process, delignification agents, e.g. antrachinon are utilized to reduce cooking times and to increase the yield and quality of the pulp [37]. 0.5 –2 kg of antrachinone are necessary per ton of wood. The exact chemical reactions during this process are unclear, however similar pathways as during the Kraft process are assumed [38].

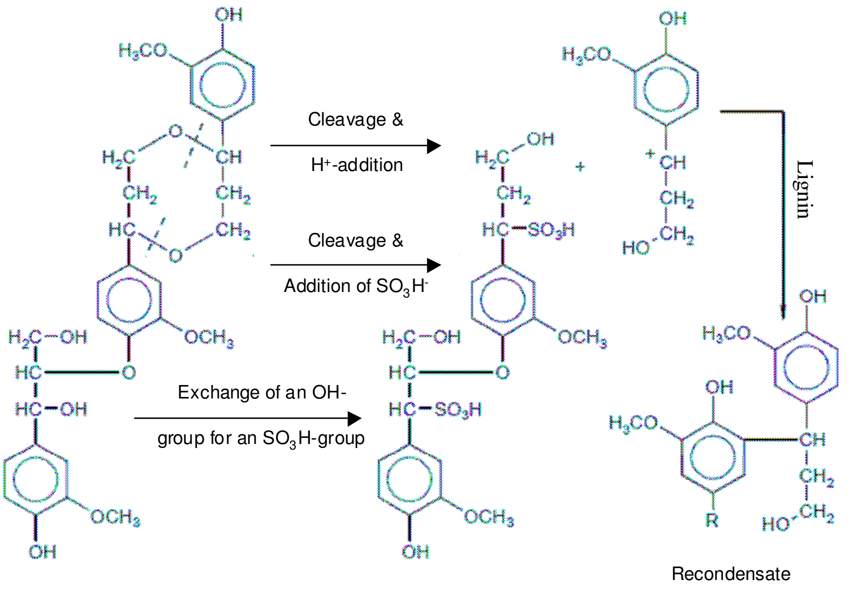


Figure 1.10: Main reactions during the sulphite process

Alcell^{TM}-process [39] [40]

Pulp is being produced sulphur free by the Alcell^{TM}-process by applying ethanol since 1989. At a temperature of 200°C and a pressure of 35 bar, wood chips are cooked three times with a ethanol/water mixture (50/50, wt./wt.). The ether bonds between the monomeric units are hereby cleaved and ethoxylated. A high quality pulp is obtained with the same properties as a pulp obtained from sulphate process. Side product of this process is the socalled Organosolv lignin, which is soluble in the prevelant solvent agents. Alcell^{TM} lignin is a dark brown powder. It has a melting point of 145°C and an average molecular weight of 1000 kg/mol.

Organocell®-process [41]

The Organocell®-process was developed 1991. It likewise operates sulphur free by applying methanol and sodium hydroxide. At a temperature of 200°C and a pressure of 35 bar, wood chips are cooked once with a methanol/water mixture (50/50, wt./wt.). Afterwards 20 wt.% NaOH are added and the cooking process is repeated [42]. During this process the ether bridges between the monomeric units are cleaved and methoxylated. Side product of this process is likewise Organosolv lignin, which is soluble in the prevelant solvent agents.

Organocell® lignin is a dark brown powder. It has a melting point of 185°C and an average molecular weight of 1000 kg/mol.

The lignin applied for this work was an Organosolv lignin. It was either purchased from Sigma-Aldrich or prepared by the ICT of the “Frauenhofer Institute Karlsruhe” by an organosolv method developed and optimized by the ICT.

The best results were obtained by extracting beech wood with a solution of ethanol and water (60:40). The mixture was then heated up to 200 °C in 150 minutes in an autoclave, and kept at this temperature for one hour. Afterwards the suspension was filtered to separate the lignin solution from the cellulose. After removing the alcohol by distillation, lignin was gained with a maximum yield of 14 %.

1.3.3 Effect of recovery method and plant origin on the properties of the isolated lignin

To create a raw material base from which both organic and polymer chemistry can produce higher processed chemicals from lignin, certain structural properties of lignin must be fulfilled. The lignin should be available in a large amount, with a constant quality, to a fair price and with the highest most possible purity and defined structure. To conduct reactions it is necessary that the lignin is soluble in organic solvents. Furthermore, a high functionality is preferable as a point of origin for chemical reactions. Disadvantages of the sulphite process are therefore obvious, as most of the aliphatic hydroxyl groups have been substituted by sulphonic acid groups. Likewise, the functionality of sulphate lignin has been reduced by the pulping process.

However, it contains more hydroxyl groups than sulphite lignin, which makes it interessting for application in the production of phenolic resins. A large disadvantage of both mentioned processes is that the recovered lignin contains sulphur, which negatively effects following reactions. Lignins from the Alcell^{TM}- and Organocell®-process contain a large amount of phenolic and aliphatic hydroxyl groups which were alylated during the recovery process. Hardwoods with a high content of syringols should be avoided, as the ortho position is a priori blocked by a methoxy group.

Table 1.4: Advantages and disadvantages of pulping processes

Recovery process	Advantages	Disadvantages
Kraft process	• High availability • Low price • High phenolic content	• Sulphurous • Contains repolymerisation product • Partially contains hemicellulosis • Mostly insoluble in organics • Low side chain functionality • Variations in quality
Sulphite process	• High availability • Low price • Polar substance, applicable as emulsifier	• Sulphurous • Contains repolymerisation product • Partially contains hemicellulosis • Mostly insoluble in organics • Low side chain functionality • Low phenolic content • Aliphatic funtionalities blocked by sulphonic acid groups
Soda antrachinon process	• High availability • Low price • Sulphur free • High aliphatic and aromatic functionality • Partially soluble in organics	• Partially contains hemicellulosis • Variations in quality • High silicate content in annual plants
Alcell^{TM}-process	• Sulphur free • Hemicellulose free • Constant quality • High solubility in organics	• Low availabiliy • High cost • Aliphatic hydroxyl and phenol groups etherified
Organocell®-process	• Sulphur free • Hemicellulose free • Constant quality • High solubility in organics	• Not available • Aliphatic hydroxyl and phenol groups etherified

Lignins from coniferes and grasses are preferable as they possess an increased amount of the monomeric unit coniferyl alcohol, in which both ortho positions are free. The choice of the recovery process and the plant origin are therefore crucial for the resulting quality. Advantages and disadvantages of the individual isolation processes are summarized in

Table 1.4.

1.3.4 Lignin conversion

The fact that lignin consists of phenolic components was already known in 1939, when Freudenberg et al. [43] reported that vanillin was produced from lignin by the alkali-nitrobenzene method. 1960 Kashima [44] reported the conversion of Kraft-lignin by using an iron oxide catalyst at 673 to 713 K under a hydrogen atmosphere of 19.6 MPa. He obtained light and heavy oil as well as 20 wt.-% phenol and 14 wt-% benzene. In the mid eighties, the conversion of lignin into a liquid product was studied by a large number of groups [45], usually in the presence of hydrogen and a hydrotreating catalyst. Several of theses processes were carried out in aqueous solutions near the critical point, with organic co-solvents or alkaline salts added. The goal of these experiments was to convert the lignin into phenolic or aromatic hydrocarbons. However, the products obtained were often oils or tars that were extracted with organic solvents. In 1986 and 1987, respectively, Meier et al. [46] and Faix et al. [47] examined the liquefaction of a variety of lignocellulosic feedstocks (whole woods, celluloses and lignin) in aqueous solvents at and above the critical temperature of water. Not only the produced oil was analyzed, also the feedstocks were characterized in terms of their 4-hydrox phenyl-, guaiacyl- and syringyl-contents. Johnson et al. [48] studied the hydroliquefaction of two organosolv lignins obtained from aspen in 1988. Reactions were carried out in a stirred autoclave in the presence of a palladium on carbon catalyst. The aqueous lignin suspensions were injected into the preheated autoclave to minimize the heat-up time. The lignins were converted to brown viscous oils (mostly soluble in ethyl acetate) and carbon containing gases (carbon monoxide, carbon dioxide, methane, and ethane). The highest yields (70 %) of oil were obtained after 5 to 20 minutes. At longer residence times the oil-yield decreased due to the production of gases. The apparent molecular weight distributions of the liquefied lignins were 2-3 fold smaller than the starting lignins, indicating that substantial depolymerisation had taken place. The volatile fraction of the oils contained syringols, guajacols, catechols and phenols. In 1990 Funazukuri et al. [49] carried out the liquefaction of lignin sulphonate in sub and supercritical water in a batch tube-type bomb reactor. The samples were also subjected to pyrolysis in an argon atmosphere. Much higher oil yields were obtained with supercritical water than with pyrolysis at 400 °C. Oil yield was affected by reaction time, temperature and water density. NMR analyses showed that the oil obtained at short reaction times had relatively high methoxy- and hydroxyl-group contents. In 1999 Miller et al. [50] studied the depolymerisation of Kraft- and organosolv-derived lignins by alkaline hydroxides in supercritical methanol and ethanol in rapidly heated batchmicroreactors. In KOH/ethanol at 290 °C, high conversions were realized and only 7 % of ether insoluble material remained after reaction. These high conversions were realized by extracting both the filtrate and the filter cake after acidification of the reaction mixture during the work up process. The maximum yield was reached within 15 minutes. It was shown that the strongest bases gave higher conversion. An excess of base relative to lignin monomers was required for maximum conversion. The lowering of the amount of added salt below the stoichiometric amount led to a large decrease in soluble products, indicating that stoichiometric reactions occurred. Another approach was followed by Ehara et al. [51] at the end of the last century. First buna wood was treated in supercritical water, fractioning it into a water-soluble portion, a methanol-soluble portion and methanol-insoluble residues. The study was focused on characterizing the lignin-derived products in the methanol-soluble portion and in the residue. It was found that these products had more phenolic hydroxyl groups than lignin in the original wood. Furthermore alkaline nitrobenzene oxidation analyses showed much less oxidation product in the methanol-soluble and in the methanol-residue. This indicated that the ether linkages of lignin are preferentially cleaved during supercritical water treatment. In 2003 Saisu et al. [52] examined the decomposition of lignin in supercritical water with and without phenol at 673 K. In the absence of phenol, the yield of tetrahydrofuran-insoluble products, which are claimed to be formed by polymerization and to have molecular weights higher than lignin, decreased and the molecular weight distribution of the tetrahydrofuran-soluble fraction shifted towards lower molecular weights as the water density increased. An increased water density also enhanced the lignin conversion. In the presence of phenol, the yield of the insoluble products was lower and the molecular weight distribution of the soluble products shifted towards lower weights than those in the absence of phenol. Some alkyl phenols were obtained only in the presence of phenol, because of reactions of phenol with decomposition products. These results indicate that the reaction of phenol with reactive sites occurred in supercritical water and suppressed cross-linking reactions among reactive sites of large fragments. This promoted the decomposition of lignin to lower molecular weight compounds. At the same time Okuda et al. [53] reported the depolymerisation of waste lignin (sodiumlignosulfonic acid and alkali lignin) without a catalyst in a mixture of supercritical water and *p*-cresol, without char formation. GPC confirmed that the molecular weight distribution of the original lignin shifted towards smaller molecular weight after reaction at 400 °C for 30 minutes. At higher reaction temperatures the amount of water soluble products decreased. The chemical species of the tetrahydrofuran soluble products were detected as phenol, methyl anisole, *o*-cresol and different alkyl phenols (maximum total yield of water soluble products: 10.8 % at 400 °C and 33 % at 250 °C). Further investigations with similar parameters and *p*-cresol added in 2004 also led to remarkable results [54]. Within a reaction time of four minutes, lignin, whose averagemolecular weight was $2\cdot10^3$ g·mol^{-1}, was selectively converted to a compound with a molecular weight of 214 g·mol^{-1} and identified as hydroxyphenyl-(hydroxytolyl)-methane (HPHTM) by ^{1}H and ^{13}C NMR. Its yield reached a maximum of 80 % C after 30 minutes of reaction time. Shabtai et al. [55] [56] developed a method for the base catalysed depolymerisation of lignin in supercritical water. The lignin feed was fully dispersed in a dilute alkali hydroxide solution (e.g. 2-3 wt.-% aqueous NaOH solution which showed the best activities), and subjected to base catalysed depolymerisation in a flow reactor system. In comparison to Miller et al. [57], where stoichiometric amount of salt was necessary for a significant conversion in alcohol, Shabtai *et al.* added the salt in catalytical amounts in aqueous reaction medium to obtain best results. Reactions were carried out in a temperature range between 300 and 340 °C. The optimal liquid hourly space velocity (LHSV) was found to be in the range between 0.5 and 8 h^{-1}. After reaction, the solution was acidified and the precipitate was extracted with ether. The ether phase was then evaporated to obtain the depolymerised lignin products (alkylated phenols, alkoxybenzenes, alkoxyphenols and hydrocarbons) with a maximum yield of ether and ether/water solubles of 76 wt.-%. Considerable effort has been made to characterize the lignin derived products after reaction in supercritical water (e.g. 2004 Takada et al. [58]). Here sugi wood was treated with supercritical water and fractioned into a water-soluble fraction, a methanol-soluble portion and a methanol-insoluble residue. GPC and gas chromatographic-mass spectrometric (GC-MS) analyses were performed. The GPC analysis indicated that the methanol-soluble portion contained lignin derived monomeric and dimeric products. GC-MS detected 31 products which were expected to be monomeric compounds (e.g. different guajacols, vanillin and different eugenols). Furthermore, like in the GPC analysis, dimeric compounds were detected. This clearly indicated that the products detected in the methanol-soluble portion result from the cleavage of ether linkages and propyl chains of lignin. Recently (2006) Sato et al. [59] examined the gasification of lignin biomass model compounds in the presence of magnesium oxide supported nickel catalysts (Ni/MgO) in sub- and supercritical water from 250 to 400 °C. The main gas products were methane, carbon dioxide and hydrogen. The amount of the produced gases increased with higher nickel loadings on the magnesium oxide support. The highest total gas yield in carbon basis was found to be 78 % with 20 wt.-% Ni/MgO catalyst at 400 °C and 0.3 g·cm$_{-1}$ water density. It was assumed that the metal and the support play different roles during the gasification of lignin. Sato *et al.* postulated that MgO decomposed lignin to reactive intermediates and nickel promoted reactions between intermediates and water to form gases. The yield of methane and carbon dioxide increased with increasing water density but then decreased and levelled out to constant values, which indicated that water density affected the reaction kinetics. This results of Sato et al. were confirmed by Osada [60]. Here, ruthenium catalysts supported on different substrates were used in supercritical water to study the gasification of lignin at 400 °C. Methane, carbon dioxide, hydrogen, carbon monoxide and C_2 to C_4 gases were obtained as the gaseous products. The catalytic gasification was enhanced by the increase of water density. Again it was assumed that the gasification of lignin in supercritical water proceeded through two steps. The first one is the decomposition to components of low molecular weight. The gasification of these compounds over the metal catalyst was assumed to be the second step. To prove that only the first step was enhanced by increasing the water density, experiments were carried out with 4-propyl phenol. The rate of the gasification of this molecule was not affected by water density, what clearly demonstrated that the water density only affected the first step of the gasification. The most important aspects described in this section are summarized in Table 1.5.

Table 1.5: Scientific research on decomposition of lignin

Reaction conditions / Aim of the experiment	Products / Results	References
Lignin treated with alkali-nitrobenzene	vanillin	Freudenberg *et al.* 1939 [43]
Conversion of Kraft-lignin, catalyst: iron oxide, T = 673 – 713 K, hydrogen atmosphere (19.6 MPa)	oil, phenol, benzene	Kashima 1960 [61]
1. Lignocellulosic feedstocks, aqueous solutions, $T \geq T_c$, 2. Characterisation of lignin feedstocks: hydroxyl phenyl-, guaiacyl-, syringyl-contents	oils (soluble in DCM, yield: 60 %)	Meier *et al.* 1986 [62] Faix *et al.* 1987 [63]
Organosolv lignin, SCW, $T > T_c$, catalyst : Pd/C, stirred autoclave	brown and viscous oils (yield: 70 %) , CO, CO_2, CH_4, C_2H_6	Johnson *et al.* 1988 [64]
Liquefaction of lignin in SCW, T > 400 °C	oil	Funazukuri *et al.* 1990 [65]
Different lignins in supercritical methanol or ethanol with different alkaline salts added stoichiometrically, T = 290 °C	monomer (c.a. 180 $g{\cdot}mol^{-1}$)	Miller *et al.* 1999 [66]
Characterisation of lignin derived products in methanol, obtained by treating buna wood with SCW	products have more phenolic hydroxyl groups than in lignin	Ehara *et al.* 2000 [67, 68]
Decomposition of lignin in SCW with and without addition of phenol, T = 673 K	higher water density/ phenol added →products with lower molecular weight	Saisu *et al.* 2003 [69]
Waste lignin in SCW and *p*-cresol, T > 400 °C	phenol, methyl anisole, *o*-cresol, alkyl phenoles	Okuda *et al.* 2003 [70]
Base catalysed depolymerisation of lignin in subcritical aqueous solutions, catalyst: alkali hydroxides, T = 300 – 340 °C	alkylated phenols, alkoxybenzenes, alkoxyphenols, hydrocarbons	Shabtai *et al.* 2003 [71, 72]
Lignin in SCW and *p*-cresol, T = 400 °C, residence time form 4 to 30 minutes	HPHTM (maximum yield 80 %)	Okuda *et al.* 2004 [54]
Characterisation of lignin derived products in methanol, obtained by treating sugi wood with SCW	different monomeric and dimeric compounds detected	Takada *et al.* 2004 [58]
Gasification of lignin in SCW, catalyst: Ni/MgO, T = 250 – 400 °C, variation of water density	carbon dioxide, methane, hydrogen (yield 78 %)	Sato *et al.* 2006 [73]
Gasification of lignin in SCW, catalyst: supported Ru, T = 400 °C, variation of water density	carbon dioxide, methane, hydrogen, carbon monoxide and C_2 to C_4 gases	Osada *et al.* 2006 [74]

1.4 Sub –and supercritical water

Since the end of the 1980s, research activity in the field of supercritical fluids has been growing [75]. Whether a fluid is in gas state or liquid state depends on the kinetic energy of the particles (temperature) and on the energy of intermolecular interaction. If the kinetic energy is smaller than the intermolecular interaction energy, then the fluid is a liquid.

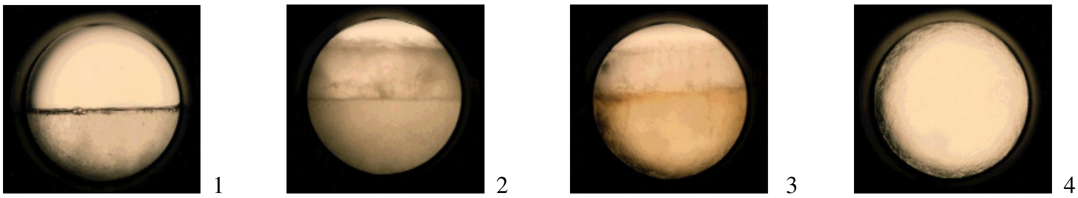


Figure 1.11: Phases of water from “normal” (1) to supercritical (4) condition

When a liquid is heated, more and more molecules migrate into the headspace, so that the density of the vapor increases, as the density of the liquid decreases. Finally a point is reached where the density of the steam is as big as the density of the liquid, so that there is no difference between both of them and the meniscus of the liquid disappears. This is illustrated in Figure 1.11.

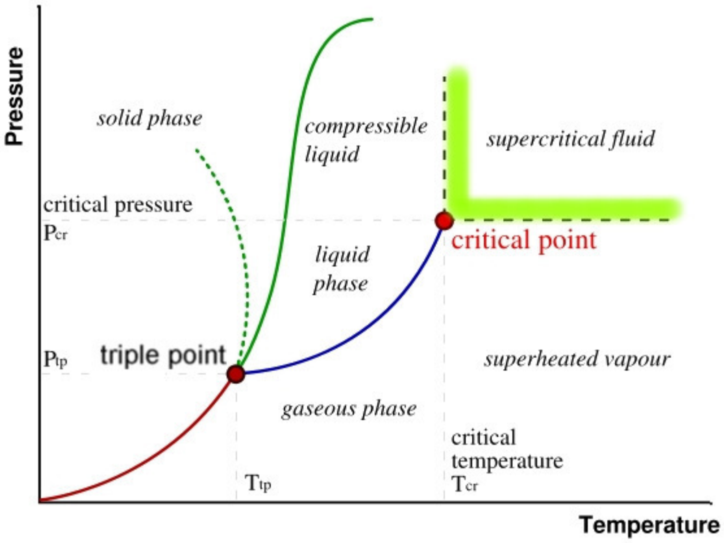


Figure 1.12: Phase diagram

The state of a substance when the temperature is higher than the critical temperature T_c and the pressure is higher than the critical pressure p_c is called supercritical (Figure 1.12). When the temperature is above T_c, the fluid is non-condensable, no matter how high the pressure is. The density of the fluid at the critical point is called critical density ρ_c and the volume of one mol of the substance at the critical temperature is called critical volume.

1.4.1 Properties of sub – and supercritical water

Because of its outstanding properties, e.g. low-priced, almost ubiquitary, non-toxic and non-combustible, water is the most important solvent. As already pointed out above, it has also remarkable properties as reaction medium and as reactant in the supercritical state. Table 1.6 presents the important physicochemical data of water as function of pressure and temperature [76].

Table 1.6: Physicochemical properties of water, as a function of temperature and pressure [76, 77].

	„normal“ water	subcritical water	supercritical water		superheated steam
T [°C]	25	250	400	400	400
p [MPa]	0.1	5	25	50	0.1
ρ [$g \cdot cm^{-1}$]	0.997	0.80	0.17	0.58	0.0003
ε	78.5	27.1	5.9	10.5	1
pK_w	14.0	11.2	19.4	11.9	---
c_p [$kJ \cdot kg^{-1} \cdot K^{-1}$]	4.22	4.86	13	6.8	2.1
η [mPas]	0.89	0.11	0.03	0.07	0.02
λ [$mW \cdot m^{-1} \cdot K^{-1}$]	608	620	160	438	55

The density ρ of supercritical water can be altered by variation of temperature and pressure continuously from high (liquid like) to low (gas like) values without phase transition.

The relative static dielectric constant ε drops form a value of 78.5 at normal standard conditions to a value of about 6 at the critical point, thus clarifying the difference in the solution properties of supercritical water in comparison with “normal” water. The reason for this relatively low value of the dielectric constant, is the reduced number of hydrogen bonds, due to density and temperature [78]. At high densities, substances with ionic bonding can be dissolved (e.g. KCl, Na_2SO_4, NaOH) whereas at low density it is possible to bring organic compounds and gases (e.g. oxygen) into solution. Thus, in the supercritical stage, water acts like a non-aqueous solvent. This is also emphasized in Figure 1.13, that shows a phase diagram of water were also the "coordinates" for different reaction types are depicted.

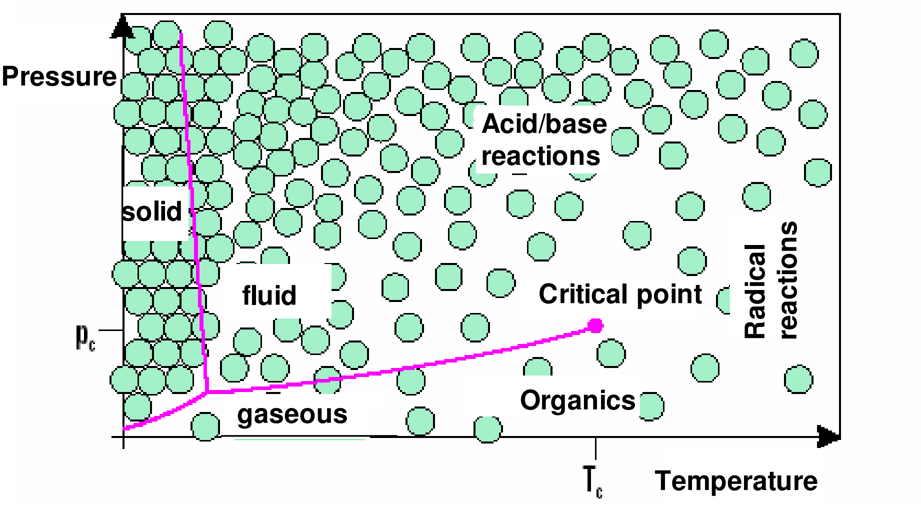


Figure 1.13: Phase diagram of water [79]

In the supercritical region water shows very high specific heat capacities c_p (e.g. 29.2 kJ·kg^{-1}·K^{-1} at 400 °C and 29 Mpa [76]), so that in the supercritical state, c_p can be varied continuously over a wide range depending on pressure and temperature. In highly exothermic reactions, such as partial oxidations in supercritical water, this could diminish the problem of hot spots.

The ionic product of water K_w is strongly dependant on density and temperature [80] (see Figure 1.14), so that this property can be used for optimizing acid/base-catalyzed reactions. At values of the pK_w lower than 14, water is more suitable as a medium for heterolytic reactions, whereas it is more suitable for homolytic reactions at $pK_w \geq 14$ [81]. However, the transition from homolytic to heterolytic cleavage is not clearly defined.

With rising temperature the dynamic viscosity η is declining at high density (collision transfer of momentum) and is increasing at low density (transitional transfer of momentum). At moderate supercritical temperatures and high density, the dynamic viscosity is only a tenth to a twentieth of its value at standard conditions [80]. This imposes advantages with regard to selectivity and space-time yield, especially in the case of heterogeneously catalyzed reactions, in which the overall reaction rate is often limited by mass transfer to and from the active centers [82].

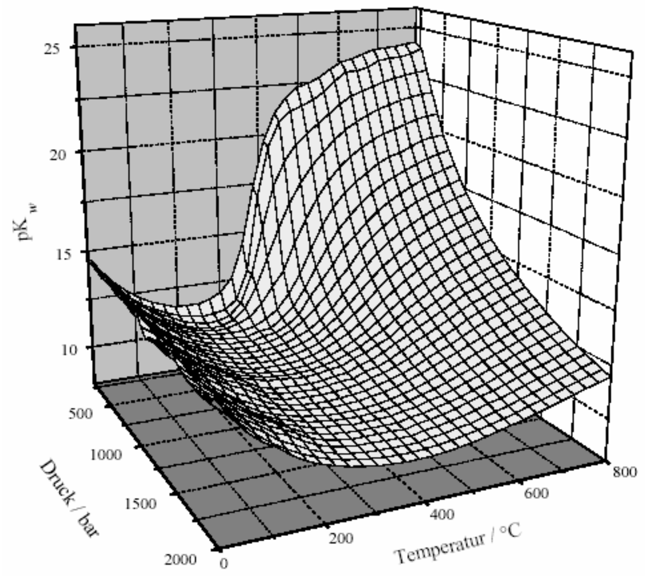


Figure 1.14: Pressure and temperature dependence of the pK_w [83].

The attribution of a physical effect for the cause of the course of a chemical reaction in supercritical water is complicated, because all physical properties are strongly depending on temperature and pressure. Water does not have only the role of a solvent. It can also act as a reactant or as a catalyst [84, 85, 86. Thermodynamic data for pure water are available in a wide range of pressures and temperatures {Haar, 1984 #434, 87]. However, besides a few analyzed binary systems there is a lack of data for aqueous multicomponent systems. Especially the lack of data on pressure- and temperature-dependant specific volumes needs to be emphasized. These values that can only be obtained by means of many experiments allow the exact determination of residence times in continuously operated reactors.

Figure 1.15 shows the density, the relative dielectric constant and the ionic product of water as a function of temperature at 25 and at 55MPa.

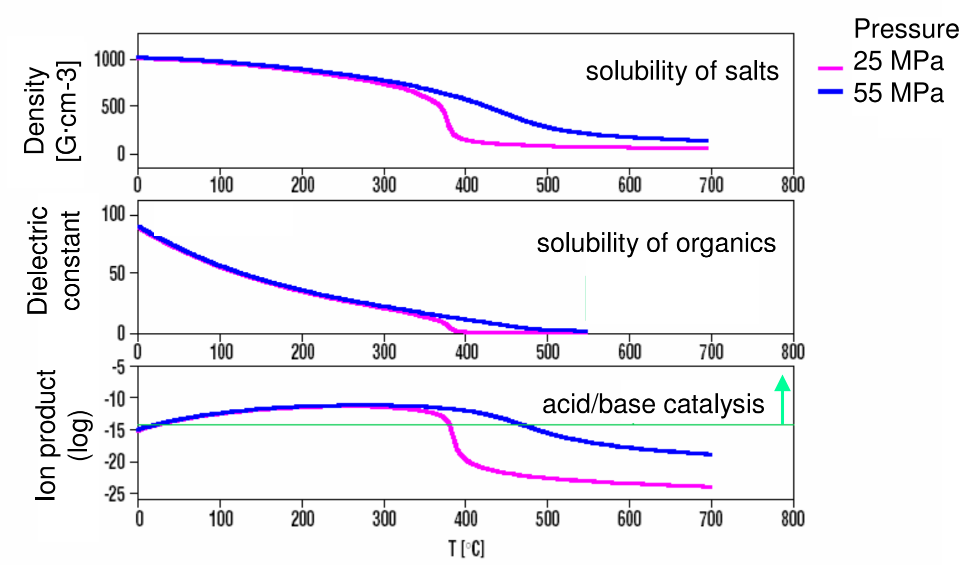


Figure 1.15: Density, relative dielectric constant and ionic product of water as function of temperature at 250 and 550 bar [78]

1.4.2 Overview on applications of sub –and supercritical water

Research in the field of supercritical fluids is on the rise since the 1980's. Especially investigations of supercritical water and its applications have been growing in more recent times [82] and the understanding of the fundamental chemistry has increased strongly over the past decade.

With the relatively good dissolving properties for organic substances and gases, reactions can take part in one phase and therefore relatively high conversions and selectivities can be achieved. Apart from that, the economic aspects of the technique and the ecology of the procedure are to mention, because water as a solvent or reaction medium is low-priced, non-toxic, non-combustible and readily available and in addition to that expensive and energy-consuming separation methods can be avoided by using sc-water.

Many research papers appeared which investigate the supercritical water oxidation (SCWO) to transform organic waste into simple, nonhazardous compounds [88-90]. Yesodharan et. al. came to the conclusion that the application is especially recommended for the disposal of hazardous waste like explosives and propellants, halogenated organics, chemical weapons and miscellaneous organic wastes [88].

Supercritical water is likewise used for the processing of biomass [48, 91]. The main problem in the past was, that biomass is wet containing up to 95% water and therefore, it has to be dried for the classical gas-phase gasification or liquefaction process. This causes high costs and can be avoided by using sub- and supercritical water [92].

Due to the properties and the advantages of sc-water, there is a wide range of potential application areas. First of all - because of the good dissolving power of sc-water - it is possible to conduct the oxidation e.g. of waste in one homogenous phase with water as solvent. Thus almost complete conversions and no by-product results. The process is particularly suitable if harmful substances already are in aqueous solution like e.g. industrial sewage. Another application area is the use of sc-water as a reactant for example for the gasification of biomass or coal [60, 93]}. In this case high yields of hydrogen are reached, because half of the hydrogen comes from the water and furthermore the wet biomass has not been dried before. In addition to that, sc-water as a reactant can be used for the recycling of plastics, so that the created monomers can be used as raw material for new reactions [94, 95]. Because the dissolving power of water for organic compounds disappears when cooling down the product, the hydrophobic organic components are separated automatically form the water-phase. So the costs for separation operations like distillation can be economized. The last application area to be mentioned here results from the fact, that the ionic product can be adjusted over a wide range so that reactions take part, which normally demand acid- or base-catalysis. This renders, primarily in technical important reactions like hydrolysis, rearrangements, assembling of carbon-carbon-bonds and condensation reactions, the addition of acids and bases unnecessary and once more the costs can be reduced [79].

Despite all the advantages there are still some problems concerning these techniques, mainly regarding supercritical water oxidation (SCWO). The high temperatures and pressures as well as the presence of corrosive ions like chloride, fluoride, sulfate and phosphate and additional high concentrations of oxygen and extreme pH-values lead to a very high corrosive behavior. Therefore, corrosion resistant reactors have to be applied [82, 96].

The following table shows successful examples for the treatment of waste water in technical scale (up to 630 °C, 32 MPa, flow rate 10 $kg\cdot h^{-1}$, 20 $kg\cdot h^{-1}$ air) [97].

Another obstacle in applying water under super critical conditions is the poor solubility of salts in this media. This has lead to reactor concepts where the deposition of salt does not occur. An example is the transpiring wall reactor [97] developed at the "Institut für Technische Chemie" of the "Forschungszentrum Karlsruhe".

Table 1.7: Examples for waste water treated in a tubular reactor (160-280 bar, reaction time 10-60 s) [97]. (TOC (total organic carbon): Amount of carbon in form of organic compounds)

Waste water from:	TOC $[mg \cdot L^{-1}]$	Conversion [%]	Temperature [°C]	Salt [wt.%]
Pharmaceutical industry	1000	86	450	1
	7000	83	30	1
	20000	97	550	3
Chemical industry	23000	99.9	550	---
	450	99.98	550	---
Paper mill	2000	98	450	0.1
	2000	99	500	0.1
	11000	97	500	0.2
Clarification plant	1000	85	500	< 0.1
	630	98	550	0.1
	5400	99	550	0.1

1.4.3 Reaction kinetics in supercritical fluids

Due to the high compressibility of supercritical fluids, pressure plays an important role when carrying out chemical reactions in these media. Besides temperature and concentration, the rate constant k_x is highly affected by the pressure. This is illustrated by equation 1-1 [98], where $\Delta V^{\neq}$ is the molar volume of activation, which, accordingly to the transition state theory, is interpreted as the difference between the partial molar volumes of the transition state and the sums of the partial volumes of the reactants at the same temperature and pressure.

$$\left(\frac{\partial \ln k_x}{\partial p} \right)_{T,x_i} = \frac{-\Delta V^{\neq}}{RT} \qquad (1\text{-}1)$$

with: rate constant (k_x), pressure [Pa] (p), molar volume of activation $[m^3 mol^{-1}]$ ($\Delta V^{\neq}$), general gas constant $[8,3145\ Jmol^{-1}K^{-1}]$ (R), absolute temperature [K] (T)

Nevertheless, this interpretation of the volume of activation should be treated with caution when having a look at complex reactions or reactions in supercritical fluids. In these cases $\Delta V^{\neq}$ should be considered only as a formal fitting parameter for quantitatively describing the pressure dependence. For supercritical reactions the value of the volume of activation is often high, so that considerable changes of the rate constant can be achieved here [99].

Usually the volume of activation is split into two terms (equation 1-2 [100]). The first term $\Delta V^{\neq}_1$ is an expression of the difference of the molecular size of the reactants and the transition state (intrinsic or reaction-specific term). The second term $\Delta V^{\neq}_2$ gives information about the interaction between the reactants and the solvent molecules (extrinsic or solvent-specific term).

$$\Delta V^{\neq} = \Delta V_1^{\neq} + \Delta V_2^{\neq} \tag{1-2}$$

For common solutions both terms are approximately the same, whereas in supercritical fluids the second term often predominates and hence determines the pressure dependence of the kinetics. The intrinsic part of the volume of activation is in the magnitude of ±30 cm^3mol^{-1} [101]. Reactions in supercritical fluids are decisively influenced by these solvent-specific interactions and their uncommon solution properties.

Like normal fluids, supercritical fluids also show the effect known as “clustering“ or “cage” effect, i.e. the physical properties in the neighborhood of a dissolved particle are fundamentally different from the average value for the solution. This cluster formation, occurring increasingly near the critical point, leads to a local increase in density, whereas the involved cluster molecules are in a dynamic equilibrium with the solvent molecules. A local reduction of the density around dissolved particles is also possible [102]. In terms of reaction kinetics, this behavior can become apparent in different ways, so each case has to be considered separately on the basis of the theory of collisions in solutions [103]. In diffusion-controlled reactions, the rate can be increased in the fluid phase by a reduction in viscosity and the increased diffusion of the reactants associated with it. Yet barriers to diffusion can also arise due to the cage effect [104].

Because of the fact that the diffusion coefficient of supercritical fluids is declining with increasing pressure, a kinetic controlled reaction can become diffusion controlled by raising the pressure. Therefore, in reaction networks where only a few steps are diffusion controlled the selectivity can be influenced by adjusting the diffusion coefficient [105]. Figure 1.16 and Figure 1.17 illustrate the dependence of the density and the self-diffusion coefficient of water in dependence of temperature and pressure.

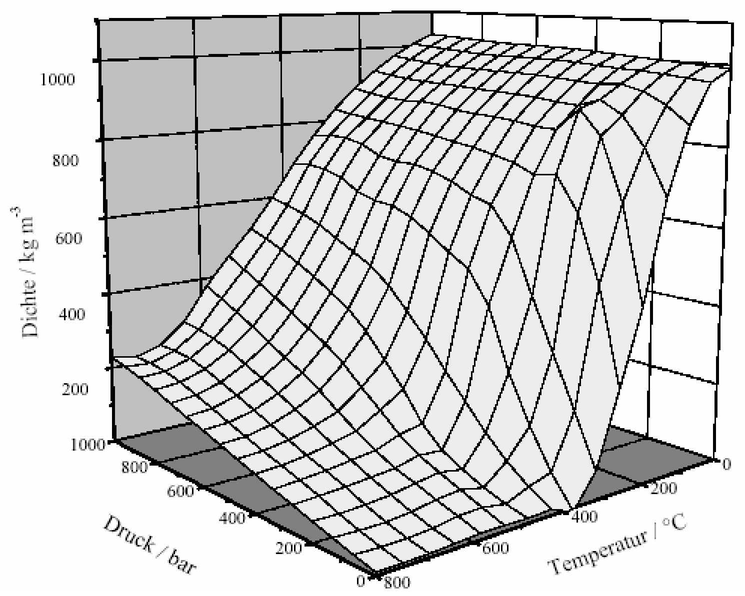


Figure 1.16: Pressure and temperature dependence of the density ρ of water [106].

The rate of a reaction is also determined by the probability of the decomposition of the activated complex, i.e. energy transfer from the activated complex to the reaction medium. Due to the high mobility of the particles and a high density at the same time, this energy transfer is favored in supercritical fluids [107].

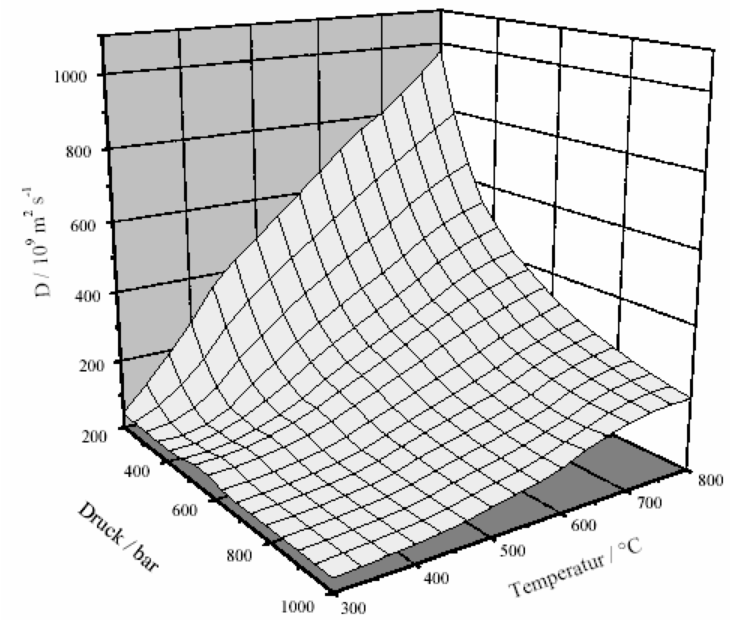


Figure 1.17: Pressure and temperature dependence of the self-diffusion coefficient of water [108].

According to quantum mechanical calculations, water molecules in a supercritical state are involved in breaking chemical bonds by significantly reducing the activation barrier [100]. Particularly the aggregation of water molecules leads to complex molecules with many energetically occupied degrees of freedom. The energy of these molecules is now available to the activated complex [109].

The lowering of the activation barrier is especially important for kinetic controlled reactions. Here the reactants pass a maximum of the potential energy. This maximum is equal to the activated complex $C^{\neq}$.

$$A + B \rightleftharpoons C^{\neq} \longrightarrow P \qquad (1\text{-}3)$$

According to the transition-state theory, the activated complex is formed out of a rapid, antecedent equilibrium and leads to the product P, following a reaction of first order [110]. The difference in the potential energy of the educts and the transition state is the activation energy. This activation barrier is influenced by the solvent, as it determines the potential energy of the reactants. The effect on a reaction by changing the solvent is shown in Figure 1.18, with G^R_I being the Gibbs energy of the reactants in solvent I and G^R_{II} being the Gibbs energy of the reactants in solvent II. The difference in the Gibbs energy of the reactants in both solvents (G^R_I - G^R_{II}) is denoted as $\Delta G^R_{I\rightarrow II}$. For the activated complex, the Gibbs energy can be written as: $\Delta G^{\neq}_{I\rightarrow II} = (G^{\neq}_I - G^{\neq}_{II})$.

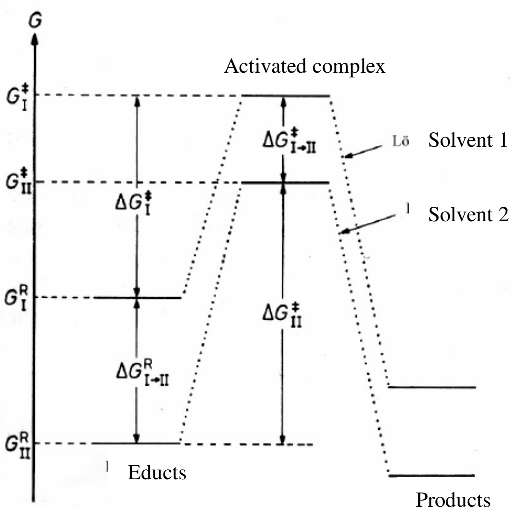


Figure 1.18: Gibbs energy diagram for a chemical reaction in two different solvents [111].

The change of the activation energy is given by:

$$\Delta\Delta G^{\neq} = \Delta G_I^{\neq} - \Delta G_{II}^{\neq} = \left(\Delta G_I^{\neq} - \Delta G_I^{R}\right) - \left(\Delta G_{II}^{\neq} - \Delta G_{II}^{R}\right). \qquad (1\text{-}4)$$

This expression can be simplified by writing:

$$\Delta\Delta G^{\neq} = \Delta G_{I\to II}^{\neq} - \Delta G_{I\to II}^{R}\,. \qquad (1\text{-}5)$$

Quantitatively this effect is described by equation 1-6:

$$\ln k = \ln k_0 - \frac{1}{RT}\left(\Delta G_{A,solv} + \Delta G_{B,solv} - \Delta G_{(AB)^{\neq},solv}\right). \qquad (1\text{-}6)$$

Especially the dielectric constant of the solvent plays an important role, because it changes with pressure and temperature (Figure 1.19) and thus leads to a variation of the rate.

The dissolving capacity of a fluid is dependent on its density, the higher the density, the higher the dissolving power. Furthermore polar solvents with a high dielectric constant are capable of dissolving polar substances. Non-polar solvents (low dielectric constant) on the other hand dissolve non-polar substances. Under normal conditions, water is a polar solvent dissolving polar substances like salts. As mentioned above, the dielectric constant and therefore the solubility are highly affected by a change in pressure and temperature.

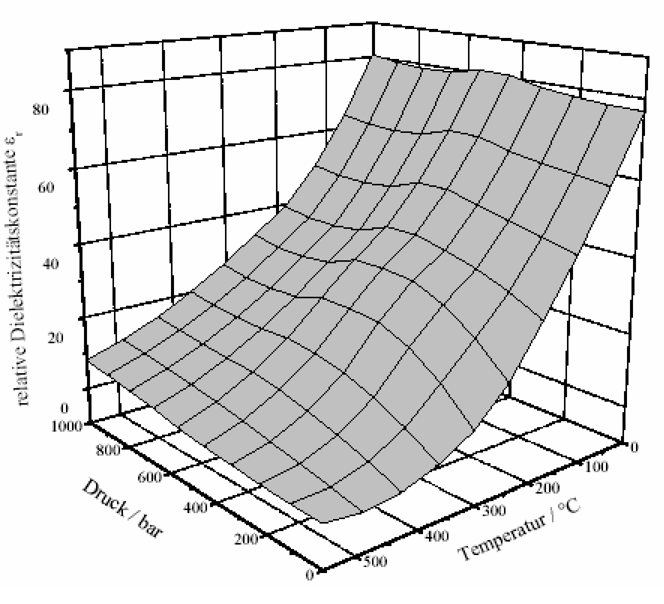


Figure 1.19: Pressure and temperature dependence of the relative permittivity ε_r of water [106].

Studies on the solubility of sodium sulfate and sodium carbonate in sub - and supercritical water [75] show how salt solubility decreases with temperature and decreasing density of the solvent. Khan et al. report that the solubility of sodium carbonate in subcritical water decreases from approximately 10 to 1 wt.% when increasing the temperature from 320 to 370°C [75]. With declining density of the solvent after passing the critical point the solubility is drastically reduced. At high temperatures (600 °C), high solubility can be realized at high pressures/densities (up to 60 MPa).

1.5 Scope of the thesis

The application of lignin in industrial processes, with the aim to produce organic intermediates such as phenolic derivatives or thermosets like phenolic resins, has not been realized so far. Lignin depolymerization in various solvents and by application of acids and bases has been a subject of research for a long time [54, 56, 112¸ Xin M., 2005 #359, 113]. However, up to now, a continuous process producing phenolic derivatives of high quality (high value chemicals) and in significant amounts has not been developed. The difficulties herein, lie in the extremely high thermal stability of the polymer, as well as in controlling a selective bond cleavage into the phenolic monomers. Therefore, the aim of this work was to optimize reaction engineering and to develope a processing concept for the hydrothermal lignin conversion. Furthermore, this work represents a fundamental investigation towards characterization of the reaction products from the catalytic and non-catalytic hydrothermal lignin depolymerization. The intention in this context was to follow a totally new synthetic route. Applying high pressures and water as a solvent, formation of tar should be suppressed and cleavage into small products preferred.

The large amount of various products known from lignin depolymerization reactions give rise to the challenge of developing an economically and ecologically reasonable process to produce phenolic compounds with a high selectivity by appropriate choice of pressure, temperature, reaction time, concentration and catalytic system.

A general insight on biomass and more especially lignin utilization for energy, fuel and chemical production is given in chapter 1. Lignin is introduced and an overview on its structure, the various methods of recovery and their effect on the properties of the obtained lignin are given. Furthermore, applications for sub – and supercritical water as a reaction medium as well as its properties and effects on reaction kinetics are described.

Chapter 2 explains the continuous setup as well as the batch autoclaves and the tumbling oven used for the high pressure experiments. The GC methods for analyzing the probe molecules and the low molecular lignin cleavage products are likewise described.

In chapter 3 the results from the experiments with model compounds representing the various bonds in lignin are presented and discussed. Emphasis is given to the influence of reaction conditions and additives on the different reaction pathways possible.

The developed work up procedure to separate and recover the lignin cleavage products is described in chapter 4. Furthermore, the effect of operation conditions on oil yield and monomer selectivity are shown, and a mechanism for the base catalyzed depolymerization of lignin is suggested and discussed.

Chapter 5 covers the phenomenon of lignin repolymerization and shows how it can successfully be suppressed by the addition of an appropriate blocking agent.

Chapter 6 summarizes the most important results and conclusions.

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Chapter 2

Experimental Section

Abstract

The experimental section describes the continuous setup as well as the batch autoclaves and the tumbling oven used for the high pressure experiments. The methods of product analysis are likewise described and examples are given. The applied chemicals, work up procedures, other methods of product analysis and catalysts preparation will be explained in the corresponding chapters.

2 Experimental

2.1 Autoclaves and tumbling oven

For the experiments conducted in batch mode autoclaves with a total volume of 5.6 mL (*High Pressure Technology*) were applied. As can be seen in Figure 2.1, each autoclave is equipped with a valve, to release and possibly generated gaseous products after reaction. These products were collected in an attached syringe to determine the volume. Likewise, the valve was used for filling the reaction with hydrogen for hydro processing experiments.

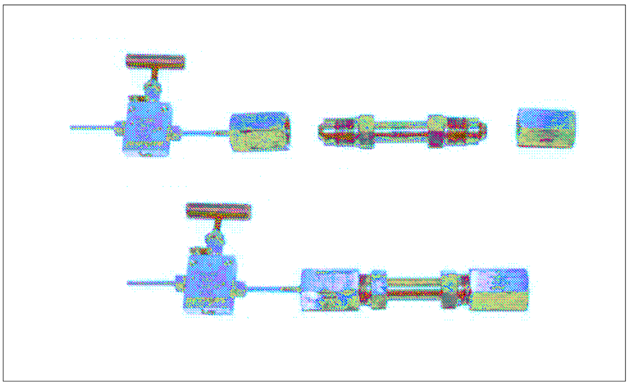

Figure 2.1: Tube autoclaves with high pressure valve

The filled autoclaves were set in an aluminum block oven for uniform heating. The oven was closed with an aluminum lid and tumbled to ensure a thorough mixing of the reaction mixture. The tumbling oven is depicted in Figure 2.2. After the reaction time had elapsed the autoclaves were removed from the oven and quenched to room temperature with water.

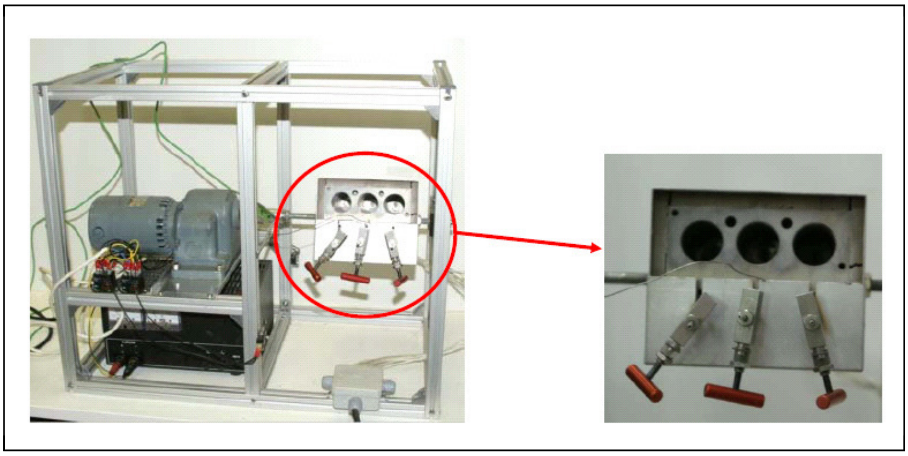

Figure 2.2: Aluminum tumbling oven with tube autoclaves

2.2 Continuous set ups

Experiments were conducted in stainless steel flow continuous reactors. For the initial experiments a tube reactor with a total volume of 0.87 mL was chosen. The reaction mixtures were fed to the reactor with a HPLC pump [*Gilson*, 307 pump]. The temperature was monitored by a controller [*Eurotherm*, 2416 controller] and the pressure was adjusted via a regulator [*Swagelok*]. After exiting the reaction zone the product mixture was expanded to atmospheric pressure and collected for work up before product analysis was conducted. To realize experiments at residence times shorter than one minute, a reactor with a total volume of 8 mL was necessary. For this system a second flow of preheated water was fed to the reactor by a second HPLC pump. Both flows were allowed to mix right before entering the reactor. The scheme of the set up is depicted in the following figure.

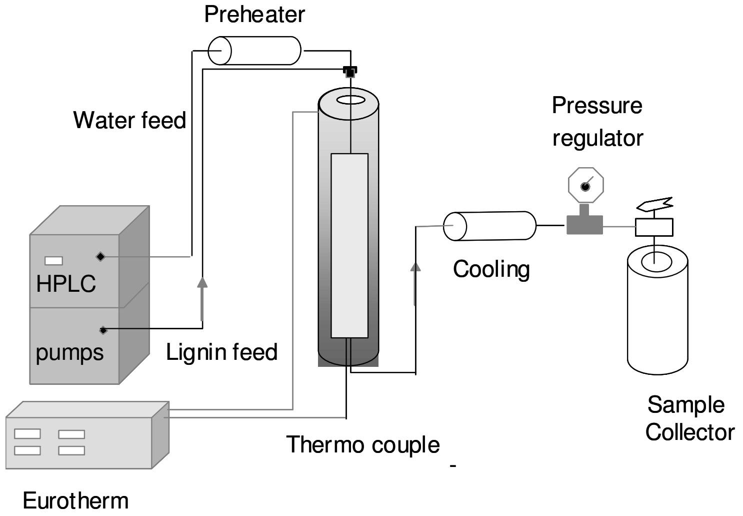

Figure 2.3: Continuous set up with water pre-heater and cooler

2.3 Product Analysis

GC/MS and GC/FID measurements were applied to detect and quantify the lignin model compounds as well as all lignin cleavage products of relatively low molecular weight. A "Shimadzu" GCMS – QP 20105 gas chromatograph-mass spectrometer (column: HP 5 crosslinked 5 % PhME Siloxane 30·0.32 mm·0.25 µm) with a second column linked to a FID detector was here for applied. The data was processed with "GCMS solution" software provided by Shimadzu.

The reaction solutions were transferred into 50 ml calibrated metering flasks and leveled with acetone (model compounds) or ethyl acetate (lignin experiments).

Table 2.1: GC methods applied for model compound and lignin experiments

Model Compound experiments	Lignin experiments
Column oven temperature: 50°C	Column oven temperature: 50°C
Injection temperature: 300°C	Injection temperature:280°C
Injection mode: Split	Injection mode: Split
Pressure: 28.8 kPa	Pressure: 28.8 kPa
Total flow: 23.9 mL/min	Total flow: 23.9 mL/min
Column flow: 1.9 mL/min	Column flow: 1.9 mL/min
Linear velocity: 50 cm/sec	Linear velocity: 50 cm/sec
Purge Flow: 3 mL/min	Purge Flow: 3 mL/min
Split ratio: 10	Split ratio: 10
High Pressure Injection: off	High Pressure Injection: off
Oven temperature program:	Oven temperature program:

Rate	Temp. [°C]	Hold time [min]	Rate	Temp. [°C]	Hold time [min]
-	50	0.0	-	50	0.0
20	300	7.5	10	120	5.0
			10	280	8.0
			10	300	2.0

The concentration of the reactant model compounds as well as the low molecular products was determined by calibrating the peak area with acetone or ethyl acetate solutions of known concentration of these compounds. The GC methods developed and used for the product analysis are shown in Table 2.1.

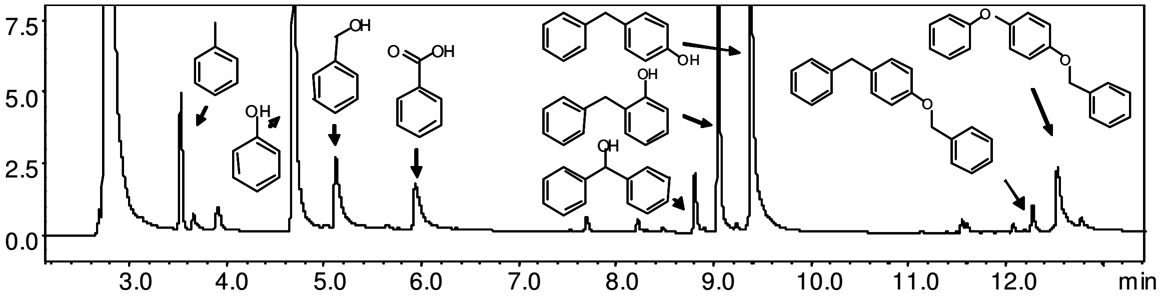

Figure 2.4: Typical GC/FID spectra of product mixture obtained from hydrothermal treatment of benzyl phenyl ether.

Table 2.2: Retention times of calibrated model compounds and products from model compound experiments

Compound	**Chemical formula**	**Retention Time [min]**
Benzene	C_6H_6	3.14
Toluene	C_7H_8	3.55
Ortho-xylol	C_8H_{10}	4.24
Guaiacol	$C_7H_8O_2$	5.51
Veratrol	$C_8H_{10}O_2$	5.83
Diphenyl ethet	$C_{12}H_{10}O$	7.54
Phenol	C_6H_6O	4.71
Benzylalkohol	C_7H_8O	5.15
Benzyl phenyl ether	$C_{13}H_{12}O$	8.5
Diphenylcarbinol	$C_{13}H_{12}O$	8.88
2-benzylphenol	$C_{13}H_{12}O$	9.10
4-benzylphenol	$C_{13}H_{12}O$	9.46
4-methoxy biphenyl	$C_{13}H_{12}O$	8.98
4-hydroxy biphenyl	$C_{12}H_{10}O$	9.25
Biphenyl	$C_{12}H_{10}$	7.4
Phthalan	C_8H_8O	5.5
Eugenol	$C_{10}H_{12}O_2$	7.2
Diphenyl methane	$C_{13}H_{12}$	7.69
Anisole	C_7H_8O	4.35
o-cresol	C_7H_8O	5.19
p-cresol	C_7H_8O	5.31
o-ethyl phenol	$C_8H_{10}O$	5.74
p-ethyl phenol	$C_8H_{10}O$	5.93
o-isoprop-phenol	$C_9H_{12}O$	6.14
p-isoprop-phenol	$C_9H_{12}O$	6.32

Figure 2.4 shows a typical GC/FID spectra of product mixture obtained from hydrothermal treatment of benzyl phenyl ether. The model compounds, main products, their structures and retention times are summarized in Table 2.2.

Table 2.3: Retention times of calibrated lignin cleavage products

Compound	**Chemical formula**	**Retention Time [min]**
Syringol	$C_8H_{10}O_3$	14.14
Syringyl aldehyde	$C_9H_{10}O_4$	19.29
3, 5-dimethoxy-4-hydroxy acetophenone	$C_{10}H_{12}O_4$	20.18
4-methyl-syringol	$C_9H_{12}O_3$	16.11
Guaiacol	$C_7H_8O_2$	7.89
Vanillin	$C_8H_8O_3$	15.21
4-hydroxy-3methoxy phenylacetone	$C_{10}H_{12}O_3$	17.53
Ortho-methoxy-catechol	$C_7H_8O_3$	11.66
Catechol	$C_6H_6O_2$	9.95
Veratrol	$C_8H_{10}O_2$	8.79
4-methyl-catechol	$C_7H_8O_2$	12.41

Table 2.3 gives an overview on the main monomeric products obtained from base catalyzed depolymerization, their chemical formula and their retention times.

Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was measured to determine the product distribution of the product oil and to detect high molecular compounds formed during the experiments with the lignin model compounds. Therefore, solutions of approximately 10 wt.% oil in H_2O/acetonitrile (1:1) with 1 wt.% trifluoroacetic acid were prepared. The mixture was placed in an ultrasonic bath for 15 min. From this suspension 2 µl were deposited on a sample holder. LDI-TOF mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer equipped with a N_2 laser ($\nu = 337$ nm) operating at a pulse rate of 3 Hz. The ions were accelerated with pulsed ion extraction after delay of 50 ns by a voltage of 28.5 kV. The analyzer was operated in reflection mode, and the ions were detected using a micro channel-plate detector. Prior to measurement the mass spectrometer was calibrated with a polystyrene standard.

LDI-TOF/MS was applied to determine the molecular weight distribution of the oil obtained from lignin depolymerization. From the measured spectra conclusions on the ratio of monomers to oligomers were made and the composition of the different oils was compared.

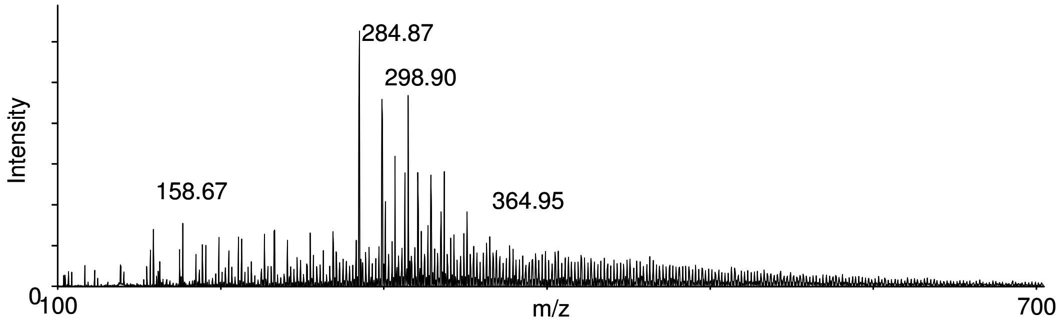

Figure 2.5: LDI/TOF spectra of a product oil obtained from base catalyzed depolymerization.

For example, from the spectra in Figure 2.5 it can be concluded that the oil consists of monomers and dimers. Intensities in the range up to 180 g/mol (average molecular weight for a syringol derivative) are relatively low, therefore, dimeric compounds are predominant. Above 360 g/mol (trimers) intensities decrease, indicating a low amount of trimers.

Chapter 3

A study on the hydrothermal treatment of lignin model compounds

Abstract

As to the complexity and diversity of the lignin structure, model compounds were selected to investigate the behavior of lignin in sub-and supercritical water. Six compounds were chosen, namely diphenyl ether, benzyl phenyl ether, diphenyl methan, eugenol, 4-methoxy biphenyl und phthalan to represent the most frequent occuring bond types in lignin. The influence of solvent density on the pyrolysis and hydrolysis of the compounds was studied. The influence of solutions of Li-, Na- and K-carbonate differs depending on reaction conditions and thus solvent properties like density and dielectric constant. At high temperatures, as applied for DPE conversion alkali carbonates catalyze the reaction, whereas at lower temperatures hydrolysis is suppressed and pyrolysis enhanced. This chapter also covers a study on the suitability of applying alcohols as reaction solvents.

3 A study on the hydrothermal treatment of lignin model compounds

3.1 Introduction

Freudenberg [1] and Nimz [2] both worked on determining the structure of lignin and suggested up to 25 diffent types of bonds in the molecule. Even today, analytical studies are being done to determine the lignin structure. Table 3.1 gives an overview of the most frequent bond types found in softwood lignin.

Table 3.1 Overview of most frequent bond types found in lignin [3], [4]

Model Linkage[a]	Glasser and Glasser [5]	Erickson et al. [6]	Nimz [7]
β carbon-oxygen-4 aromatic carbon	55	49-51	65
α carbon-oxygen-4 aromatic carbon		6-8	
β carbon-5 aromatic carbon	16	9-15	6
β carbon-1 aromatic carbon	9	2	15
5 aromatic carbon- 5 aromatic carbon	9	9.5	2.3
4 aromatic carbon-oxygen- 5 aromatic carbon	3	3.5	1.5
β carbon- β carbon	2	2	5.5
β carbon- β carbon forming a furanic structure			2
α and γ carbon-oxygen- γ carbon	10		
α carbon-β carbon	11		2.5
β carbon –6 aromatic carbon	2	4.5-5	
6 aromatic carbon-5 aromatic carbon	1-5		
1 aromatic carbon-oxygen-4 aromatic carbon			
1 aromatic carbon-5 aromatic carbon			
Total	118-123	85.5-96	99.8

Due to the complexity and diversity of the lignin structure probe molecules were applied to investigate the behaviour of lignin in sub-and supercritical water. Six compounds were chosen, namely diphenyl ether, benzyl phenyl ether, diphenyl methan, eugenol, 4-methoxy biphenyl und phthalan to represent the most frequent occuring bond types in lignin. Besides, C-C bonds lignin contains a row of different ether bonds. The ether bond found most frequently is the aromatic methoxy group. Therefore, two probe molecules containing a methoxy group were chosen, eugenol and 4-methoxy biphenyl. Furthermore, a large share of phenyl propane units are linked to each other by ether bonds. Some of these are aryl-aryl ethers as in diphenyl ether, while most are aryl-alkyl ether bonds, as in benzyl phenyl ether.

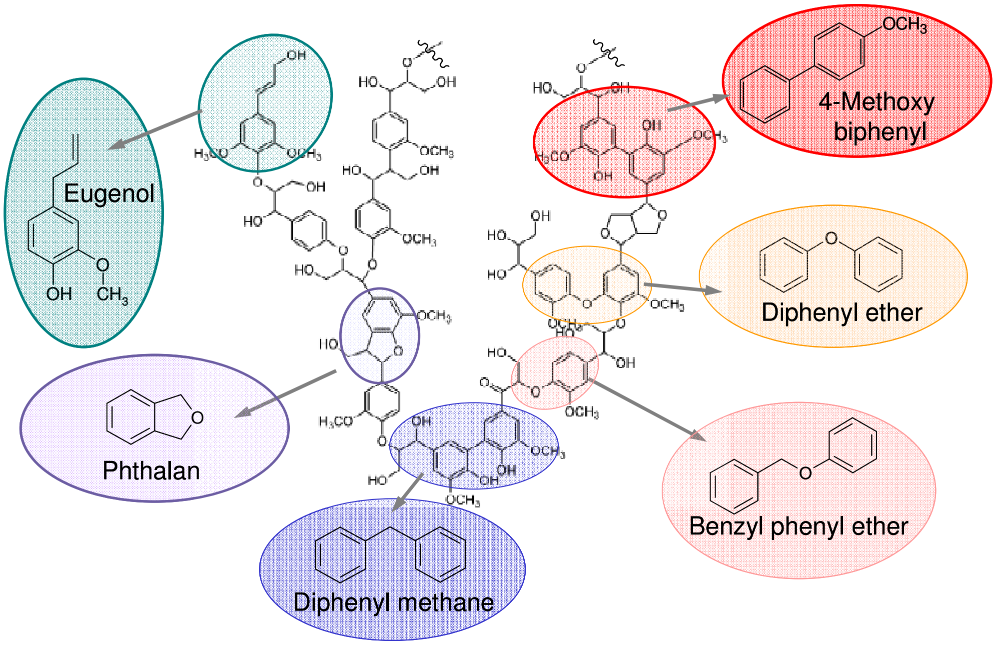

Figure 3.1: **Selection of probe molecules**

Additionally to dipenyl and benzyl phenyl ether, phthalan was chosen to represent the ether bond in the phtalan subunits of lignin. The aromatic components however can also directly be linked by C(aryl)-C(aryl) bonds, as in 4-methoxy biphenyl or by C(aryl)-C(alkyl) bonds, for example methylen bridges as in diphenyl methan. Eugenol was also chosen as a probe molecule due its large similarity to the lignin component coniferyl alkohol. In this chapter effects of temperature, reaction time, density, solvent and the application of alkali carbonate salts as well as supported K_2CO_3 on conversion and product distribution of the selected probe molecules is described.

The cleavage of lignin model compounds in sub-and supercritical water has been intensively discussed in literature, as it is easier to analyze the reactions of small and well defined molecules. This section is divided into three parts, according to the different bond types: phenyl alkyl ethers, carbon-carbon bonds and aryl-aryl ether bonds.

3.1.1 Phenyl alkyl ethers

In 1988 Afifi *et al.* [8] studied the aromatic methoxy linkage in anisole under high temperatures and pressures, close or exceeding supercritical conditions. Emphasis was put on the pyrolytic pathways in presence and absence of a hydrogen donor solvent (tetralin). It was found that at high tetralin to anisole ratios, the most abundant products are phenol and toluene (4:1). When reacting only anisole in hydrogen or argon atmosphere, a broad variety of products (benzene, cresols and polymer in addition to phenol and toluene) was found. In both cases, evidence was provided for a free radical initiation with the initiating step being the thermolysis of the methyl-oxygen linkage leading to methyl and phenoxy radicals. However, the propagation steps involved the phenoxymethyl radical which appeared to be able to invert the oxygen aryl linkage in favour of the aryl carbon linkage through a long lived spiranic oxiran radical intermediate, thus explaining benzaldehyde and benzyl alcohol formation. Nelson [9] studied the alkaline cleavage of 2-phenoxy-1-phenyl-1-propanol with electron donating and withdrawing groups on the phenoxy ring. It was demonstrated that organic free radicals occur during the thermolysis of lignin model compounds. Townsend *et al.* [10] examined the reactions of heteroatom-containing model compounds in water over a range of reduced water densities of $0 < \rho w < 2.1$ g·cm-3. Dibenzyl ether (DBE), phentyl phenyl ether (PPE), guajacol, benzyl phenyl ether and other compounds underwent parallel pyrolysis and hydrolysis. Furthermore, detailed kinetic analysis of the reactions of DBE, PPE and guajacol were presented. It was found that hydrolysis proceeded through a transition state that is more polar than the reactants. The selectivity towards the hydrolysis products increased with the water loading as the correlating higher dielectric constant stabilizes the polar hydrolysis transition state over the less polar reactants.

Some preliminary studies were conducted by Aoyama *et al.* [11] in 1991 on the degradation of guajacylglycerol-β-aryl ether and other lignin model compounds in organic solvent systems (e.g. ethanol/water or 2-butanone/water). Di- or trivalent inorganic salts (aluminium chloride, aluminium sulphate, ferric chloride, ferric sulphate and stannic chloride) were employed as a Lewis acid in the temperature range between 140 and 170 °C and with reaction time up to 60 minutes. The results indicated that the employed lignin model compounds were susceptible to degradation in organic solvent systems in the presence of one of these salts. Stannic chloride was found to be the most suitable catalyst for the degradation of the guajacylglycerol-β-aryl ether to different phenols substituted with alkyl- and methoxy-groups. The kinetics of dibenzyl ether hydrothermolysis in hot compressed water was investigated in a continuous tubular reactor system by González *et al.* [12]. The pressure was varied form 22.5 to 36.2 MPa in a temperature range from 325 to 390 °C, whereas the water to DBE ratio was held constant. The thermal scission of DBE yielded equimolar amounts of benzaldehyde and toluene. The rate constant for the thermolysis in supercritical water decreased with water density. Furthermore, benzyl alcohol was produced by DBE reversible hydrolysis, catalyzed by free protons from water dissociation. As the dielectric constant was raised, the reaction rates for pyrolysis were lowered, but the equilibrium shifted towards the formation of benzyl alcohol, which is more polar than DBE. The low dipole moment strength of the transition state complex was further supported by the negative effect of the ionic strength (varied by addition of a small concentration of NaCl) on the rate constant for DBE hydrolysis.

In this study we selected benzyl phenyl ether (BPE) to represent the most frequent bond type in lignin. Unlike the aryl aryl type ether bond as in diphenyl ether, aryl alkyl ethers are already cleaved in subcritical water. The conversion of aryl alkyl ether compounds can proceed following two different reaction mechanisms. This is also the case for BPE. The reaction pathways as well as an excerpt of possible products for the treatment of BPE in subcritical water are depicted in Figure 3.2. The ionic pathway, namely hydrolysis leads to the formation of benzyl alcohol and phenol (reaction 1). A radical mechanism, where the ether bond is cleaved in a homolytic manner generates a phenoxy and a benzyl radical species. Being highly reactive these can recombine either with hydrogen to give phenol and toluene or can recombine among themselves, with BPE or with the hydrolysis products (reaction 2 & 3). In this case dimers, trimers, and higher molecular compounds are formed.

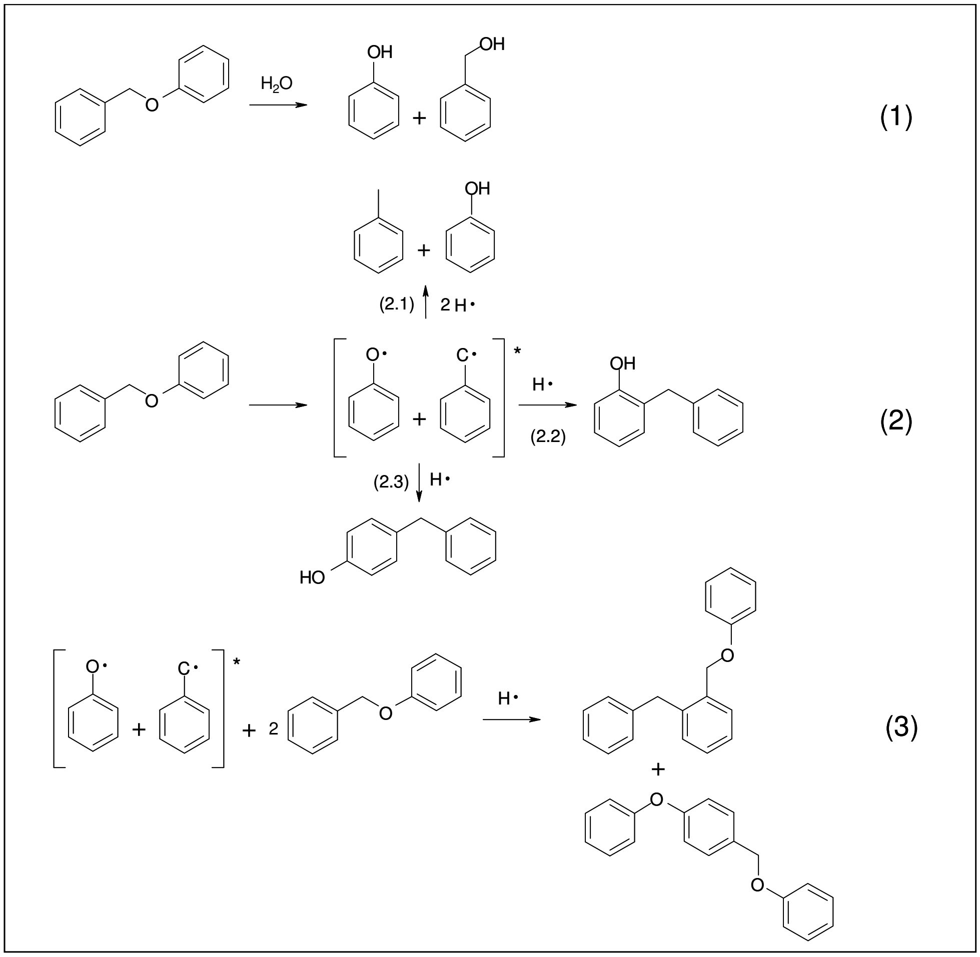

Figure 3.2: Ionic and radical mechanism pathway with possible recombination products [13]

The presented products are only exemplary and many other consecutive products can be formed. Huppert et al. studied the influence of solvent density and salts (NaCl, $CaCl_2$ and $FeCl_3$) on the conversion of the aryl-alkyl ether guaiacol in supercritical water [14]. It was found that the reaction of guaiacol in supercritical water proceeds via parallel pyrolysis and hydrolysis pathways. However, since the transition state for hydrolysis is more polar than its reactants, selectivity towards hydrolysis can be increased by enhancing the ionic properties of the water. This was realized by either adding the mentioned salts or by increasing the solvent density. As a result reaction conditions are shifted from gaslike to liquidlike, where it is reasonable to expect ionic reaction pathways. Unlike for NaCl, however, critical amounts of $CaCl_2$ and $FeCl_3$ were found. Above these values a further salt addition did not have an effect on the hydrolysis rate. Huppert et al. assigned this effect to the formation of a two phase system, due to the different solubility of the salts.

Yokoyama et al. came to the same conclusion when investigating the thermolysis of BPE in sub- and supercritical water [13]. The effect of density on the selectivity was found to be greater in supercritical water than in subcritical water and it was found, that an increased density not only favors hydrolysis but also reactions like hydrogen abstraction and radical recombination. Also Miller et al. studied hydrothermal treatment of BPE [15]. Experiments were conducted in KOH/ethanol at 290°C for 1 hour and yielded a 30% conversion. Major products were phenol and ethoxymethyl benzene. Benzyl alcohol and benzene propanol were also detected in small amounts. It was therefore concluded that solvolysis, and hence an ionic mechanism dominates over a free radical mechanism under the given conditions.

Here, we present the influence of temperature; residence time and applied alkali carbonate (lithium-, sodium- and potassium carbonate) on BPE conversion and product distribution in subcritical water.

3.1.1 Carbon-carbon bonds

The work of Townsend *et al.* [10] also dealt with model compounds without any heteroatoms. At the same reaction conditions as the ethers, 1,3-diphenylpropane and 1,2-diphenylethane underwent only pyrolysis, giving toluene and styrene as major products. In 1994 Katritzky *et al.* [16] studied the reactions of some benzenoid hydrocarbons in supercritical water, 15 % aqueous formic acid and 15 % aqueous sodium formate at 460 °C. For each substrate, a solution in cyclohexane at 460 °C was also examined in order to distinguish thermolytic (mainly radical) reactions from the ionic reactions in the aqueous systems. Most substrates showed significant change within 1 h, only biphenyl and 1,1'-binaphthyl were essentially unreactive. 1-benzylnaphthalene underwent only slow thermolysis, whereas 1-benzyltetralin underwent rapid homolysis in all media. Cyclohexylbenzene and –naphthalene showed similar trends in all media. The conversion rates for the n-alkyl-substituted aromatics were noticeably higher than those for the cyclohexyl-substituted aromatics. Biaryl linkages were also the scope of the research of Siskin *et al.* and Katritzky *et al.* [17] in 1995. They found that many biaryls (also biaryls containing heteroatoms), even though unreactive in supercritical water at 460 °C, undergo bond cleavage and heteroatom removal under reducing conditions in supercritical water. The major hydrocarbon products were benzene and naphthalene and their C1 to C4 alkylated derivates. After sufficient reaction time heteroatoms were always removed. Tagaya *et al.* investigated the decomposition of model compounds such as prepolymers (e.g. phenol trimers) and substituted diphenyl methanes to their monomers in water at temperatures from 300 to 430 °C in 10 mL tubing bomb reactors [18]. The decomposition reactions were accelerated by addition of alkali salts such as Na_2CO_3. However unsubstituted diphenyl methane was not converted. One year later the group reported a direct oxygen supply from supercritical water [19]. This was confirmed by the production of benzophenone from diphenyl methane in $H_2{}^{18}O$ at 430°C. In 2001 Tagaya *et al.* published data on cleavage reactions of bis(hydroxyphenyl)methanes in sub- and supercritical water under an argon atmosphere, again showing, that the methylen bond is only cleaved when phenolic compounds are used [20].

3.1.2 Aryl-aryl ethers

To investigate the behaviour of the aryl-aryl ether bond in sub-and supercritical water diphenyl ether (DPE) was chosen. As calculated (Figure 3.3), the hydrolysis of DPE to phenol is thermodynamically not limited and should proceed completely above 120°C, when applying a pressure of 250 bar and a water to DPE ratio of 35.

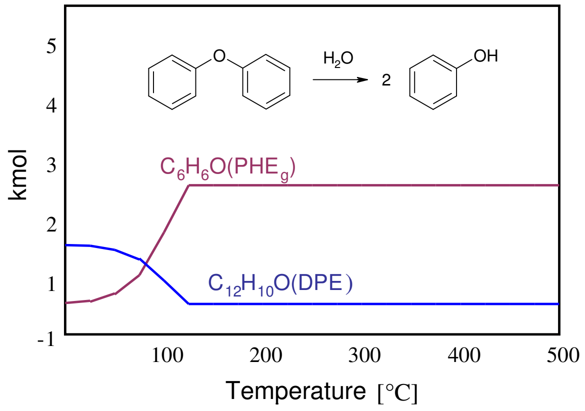

Figure 3.3 Thermodynamic data for the hydrolysis of DPE to phenol

In spite of this, literature reports only of insignificant DPE conversions below temperatures of 460°C and four hours of reaction time. Katritzky *et al.* also examined reactions of compounds with linkages of the diphenyl ether type [16]. They found that dibenzofuran was unreactive under the reaction conditions (see section on carbon-carbon bonds above). Diphenyl ether underwent base catalyzed hydrolysis to phenol (32.9 % yield) in aqueous sodium carbonate (15 %) at 460 °C for one hour. The base catalyzed mechanism proposed by Katritzky *et al.* is shown in Figure 3.4 and starts with a nucleophilic attack of a hydroxide anion on the diphenyl ether to give the intermediate shown below. The intermediate is then decomposed to phenolate and finally protonated.

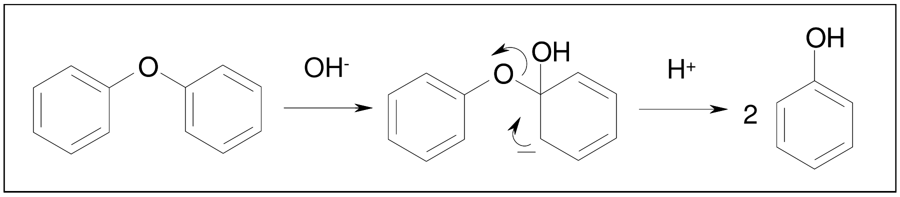

Figure 3.4: Base catalyzed hydrolysis of DPE in supercritical water [16]

The conversion of DPE in supercritical water can proceed following two different reaction mechanisms (Figure 3.5). The ionic pathway, namely hydrolysis leads to the formation of 2 mol phenol for each mol of converted DPE (reaction 1). A radical mechanism, where the ether bond is cleaved in a homolytic manner generates phenoxy radical and phenyl radical species (reaction 2). These can recombine with hydrogen to form phenol and benzene or undergo recombination with themselves, DPE, phenol or intermediates leading to dimers such as 4-hydroxy biphenyl (reaction 3) or even higher molecular compounds, e.g. phenoxy biphenyl (reaction 4).

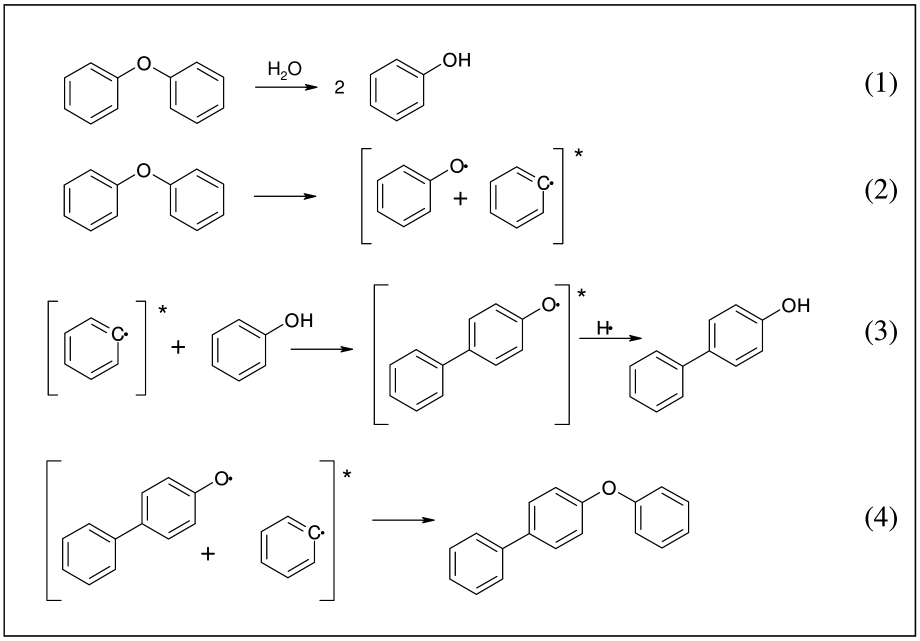

Figure 3.5: Ionic and radical mechanism pathway with possible recombination products

1999 Penninger *et al.* carried out reactions on diphenyl ether in supercritical water at 415 to 480 °C [21]. At low water density (0 to 0.3 g·cm-3), the conversion of DPE decreased gradually with an increase of density. The found products were typical for radical-type polycondensation reactions (e.g. diphenyl, phenyl diphenyl ether, phenoxy diphenyl). At water densities greater than 0.3 g·cm-3 these products vanished, the conversion of diphenyl ether increased and phenol as sole reaction product was formed, indicating ionic hydrolysis as the governing chemistry. Furthermore a proton catalyzed mechanism for the hydrolysis of diphenyl ether was proposed. It was postulated, that the protons needed for the reaction were initially generated by the self dissociation of water, a reaction strongly enhanced by density at supercritical temperatures reaching values comparable to those of liquid water at ambient temperatures [22]. The next step of the reaction was the protonation of DPE followed by a decomposition into phenol and phenyl-cation that reacted with water giving a second phenol molecule and a proton. The proton can then re-enter the reaction cycle. One year later Penninger *et al.* used dilute solutions of NaCl in supercritical water, in concentrations from 0 to 3.1 wt.-%, for the hydrolysis of diphenyl ether [23]. The reaction rate at 430 °C and at a water density of 0.46 $g{\cdot}cm^{-3}$ sharply decreased with incremental addition of salt. But an increase of the rate was observed with continued addition of salt reaching a value almost twice that of the rate in absence of salt when the salt concentration was 3.1 wt.-%. The decrease of the rate was attributed to the formation of the ion pair $H^+ Cl^-$. The excess of Cl^- ions arisen from ionic dissociation of NaCl captured the protons generated by self-dissociation of water. This was confirmed by calculations of the ionic dissociation equilibria. It was reported that the formation of protonated DPE, as a critical intermediate species in the chemistry of the earlier postulated SN_1 mechanism, competes with the ion pair for protons and is consequently restrained. The effect of higher salt concentrations was explained by the prevailing of a new mechanism, due to the Lewis acid/base behaviour of Na^+ and Cl^- ions in supercritical water. It was supposed that charge transfer in the water cluster surrounding these ions generated H^+ and OH^- ions in the outer hydration shells of the clusters forming an active species for the diphenyl ether hydrolysis. The rate of hydrolysis, according to this Lewis acid/base theory, was predicted to be proportional to the square root of the salt concentration in the super critical water reaction medium, which was also confirmed experimentally. Diphenyl ether was efficiently hydrolyzed into phenol (up to 50 mol%) by Varga *et al.* [24]. The group used Lewis acids, such as boron trifluoride and $Ni(BF_4)_2$, in supercritical water at 380 °C. The observed side reactions were reported to be insignificant and BF_3 was found to be nearly twice as effective, than HBF_4 under the same conditions. Cleavage of diphenyl ether in supercritical organic solvents as 2,2,2-trifluoroethanol and trifluoroacetic acid with BF_3 at 250°C, was less successful and accompanied by Friedel-Crafts side reactions. However, slightly more than 25 mol% of diphenyl ether were cleaved to phenyl trifluoroacetate in supercritical trifluoroacetic acid with equimolar BF_3 at 250 °C. Shibasaki *et al.* tried to optimize the conditions for the cleavage of ether linkages between two aryl substituents [25]. Conversion of dinaphthyl ether to naphthol was attained by the reaction in water with basic additives added at 430 °C. During the reaction in supercritical water no production of naphthalene was observed, so that chemical participation of water was suggested. Also diphenyl ether was decomposed into phenol (maximum yield 72.6) in supercritical water with 10 mmol/mL Na_2CO_3 added at 430 °C for 3 hours. Furthermore, cleavages of 1,4-diphenoxy benzene and *p*-phenoxy phenol were also confirmed.

3.2 Experimental

The experiments were carried out in stainless steel autoclaves at temperatures ranging from 270 and 400°C and with varying densities depending on the probe molecule. The density/pressure was adjusted by the amount of the reactor content, while the molar ratio of water/probe molecule and weight ratio probe molecule/catalyst was held constant. For the kinetic studies of DPE and BPE, experiments were conducted with 3 wt. % catalyst, and 10 wt. % DPE and 5wt.% BPE, respectively. For these experiments the density in the autoclaves was adjusted to a value of 0.9 g/cm³. The reactors were set in a preheated alumina block which was tumbled to ensure thorough mixing. An initial heat up time of 30 min was allowed to elapse before the reaction time was recorded. After the reaction, the autoclaves were quenched to room temperature with water. The autoclaves were rinsed with acetone and the collected washings were combined with the reactor content. This homogeneous solution was transferred into a 50 ml calibrated metering flask and leveled with further acetone. The reaction products were identified by GC/MS and quantified by GC/FID-analysis (column: HP 5 cross linked 5 % PhME Siloxane 30·0.32 mm·0.25 µm). The concentration of the reactants as well as the products was determined by calibrating the peak area with acetone solutions of known concentration of these compounds. The supported catalysts were prepared by incipient wetness impregnation, calcined at 550°C, and characterized by XRD, AAS, BET and TPD.

3.3 Results

3.3.1 Kinetic investigation of DPE and BPE

Diphenyl ether

Initial exploratory experiments at 400°C, a density of 0.5 g/cm³and with 0.5 g catalysts of various acidic and basic strengths showed phenol yields to be larger than 2% only when basic catalysts were applied. The most promising results were found for ZrO_2 supported K_2CO_3. The yield of phenol increased with the K_2CO_3 loading as can be seen in Figure 3.6.The figure shows that phenol selectivity in all cases is low. Other products found in the reaction mixture are of higher molecular nature, e.g. 1, 2-diphenoxybenzol and phenoxy bipheny. Their formation will be discussed later on. Additionally, gas formation is observed. Penninger et al. have shown that increasing the initial water loading and therefore the ion product of the solvent shifts the reaction towards the ionic pathway giving rise to higher yields of the hydrolysis product [21]. Therefore, the influence of density on phenol selectivity was investigated. The results are shown in Figure 3.7.

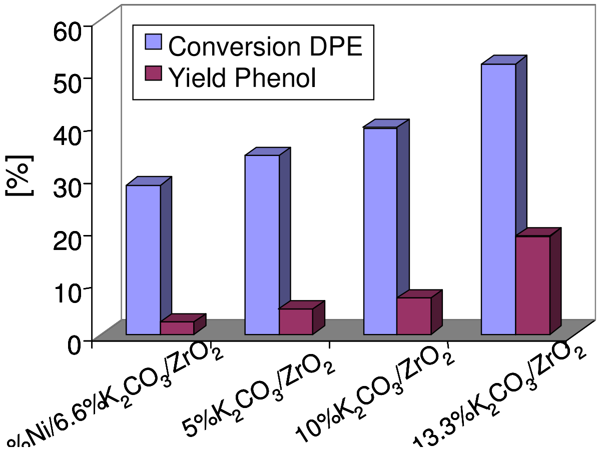

Figure 3.6: Increasing phenol yield with increasing basicity of the catalyst. Experiment conducted for 60 min at 400°C and 0.5 g/cm³. in discussion pyrolysis products

The figure shows that while DPE conversion decreases, phenol yield increases, enhancing phenol selectivity dramatically up to 100% and yielding 30 % phenol for a density of 0.9

g/cm^3. Gas formation is fully suppressed at this density. Therefore, the following experiments were conducted with an initial reactor loading corresponding to a density of 0.9 g/cm^3.

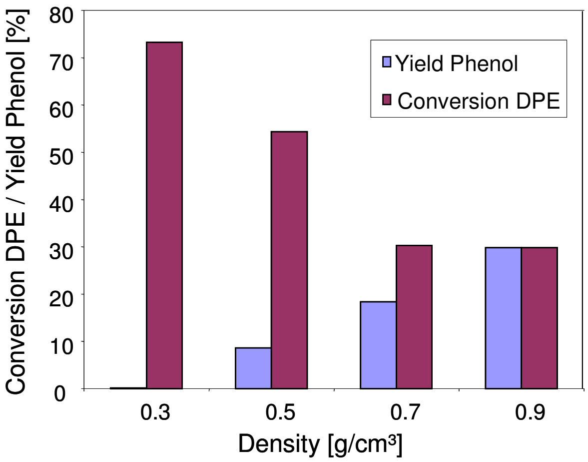

Figure 3.7 : Influence of density on phenol selctivity at 400°C with 3 wt. % of 10 mol% K_2CO_3/ZrO_2

The figure shows that while DPE conversion decreases, phenol yield increases, enhancing phenol selectivity dramatically up to 100% and yielding 30 % phenol for a density of 0.9 g/cm^3. Gas formation is fully suppressed at this density. Therefore, the following experiments were conducted with an initial reactor loading corresponding to a density of 0.9 g/cm^3.

Table 3.2 : Product distribution of DPE conversion with Li_2CO_3, Na_2CO_3 and K_2CO_3 at 400°C and 0.9 g/cm^3

Salt	DPE	Phenol	Mono alkyl phenols	Xanthene & Xanthene carboxylic acid	4-Hydroxy biphenyl	Trimers	Higher Molecular compounds
Li_2CO_3	16.4	53.7	6.9	0.9	3.7	10.1	8.3
Na_2CO_3	15.4	50.3	4.3	0.5	5.1	11.7	12.7
K_2CO_3	14.2	69.7	14.4	1.5	0	0	0.2

Trimers: Sum of 1, 1-biphenyl-2-phenoxy ether and 1,2-Diphenoxy-Benzol

To investigate the kinetics of the reaction and to test if the catalytic effect of the supported material merely results from the impregnated salt, time dependent experiments were conducted with lithium, sodium, and potasium carbonate as well as with the supported catalyst. For this, 3 wt. % catalyst and 10 wt. % DPE were applied. The best phenol yield, i.e., 73% was obtained with K_2CO_3.- Figure 3.8 clearly shows that K_2CO_3 also achieves the highest phenol selectivity of 100%. Na_2CO_3 and Li_2CO_3 achieve selectivities of only 59 and 64%

respectively. The total product spectra are summarized in Table 3.2. Among the side products, only those having a relatively low molecular mass, such as the trimers 1, 1-biphenyl-2-phenoxy ether, could be identified via GC-MS analysis. Larger molecules are not eluted from the column. Therefore we have defined the gap between BPE conversion and the total yield of all GC-MS detected products as higher molecular compounds in Table 3.2.

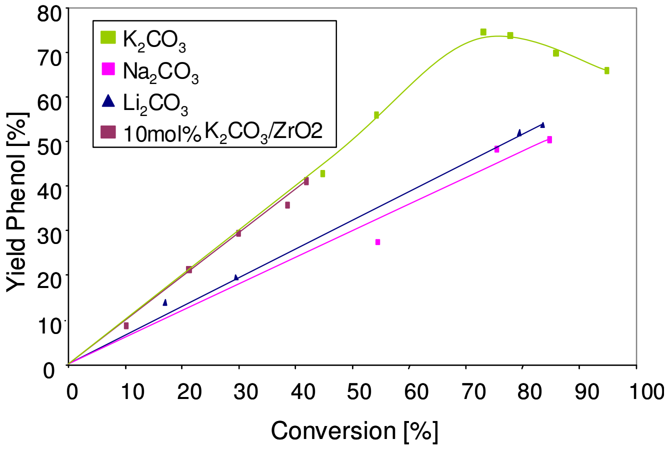

Figure 3.8: Phenol yields for different carbonates and supported catalyst at 400°C and 0.9 g/cm³.

Comparison of the unsupported K_2CO_3 with the ZrO_2 supported K_2CO_3 catalyst reveals that after 420 min reaction time the supported catalyst has reached only 42 % conversion, while the salt has already reached 95 % conversion. Unlike for the reaction with the supported catalyst where phenol selectivity is 100 % at all times, selectivity is 100 % up to a conversion of 73 % and then begins to decrease for the salt.

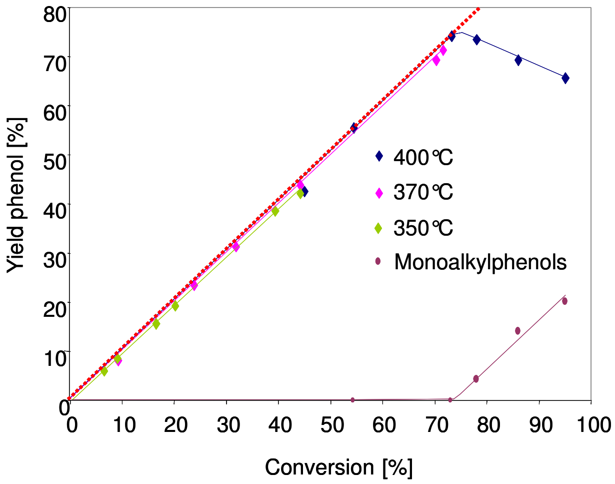

Figure 3.9: Phenol selectivities for 3 wt. % K2CO3 at different temperatures.

The decrease of phenol selctivity for K_2CO_3 above 73% conversion and at 400°C does not result from the formation of high molecular compounds such as di – and trimers which are found for lower densities and partially for the other carbonates, but is associated with the appearance of mono alkyl phenols. Figure 3.9 shows the increasing yield of these compounds simultaneously to the decreasing phenol selectivity. At lower temperatures, phenol selectivities are almost 100% for all catalysts.

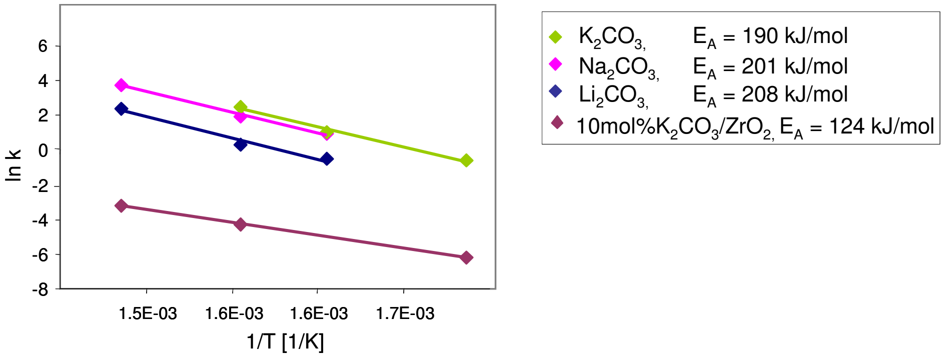

Figure 3.10 : Activation energies for the supported and unsupported catalysts.

To determine the reaction order the integral approach was applied. For the reactions with an alkali carbonate, the reaction is of second order regarding DPE. In the case of the supported catalyst, a reaction order of zero was determined. The reaction rates were obtained from the slopes of the graphs. The Arrhenius plot in Figure 3.10 yields the activation energies for the various catalysts. Among the alkali carbonates the Arrhenius plot reveals the smallest activation energy for K_2CO_3 with a value of 190 kJ/mol. Lithium and sodium carbonate have similar activation energies in the range of 201-208 kJ/mol. DPE conversion has the smallest activation energy for the supported catalyst (124 kJ/mol), however the pre-exponential factor is 8-9 magnitudes lower than those for the salts. Therefore reaction rates for DPE conversion with the supported salt are only larger for very low initial DPE concentrations (Figure 3.11).

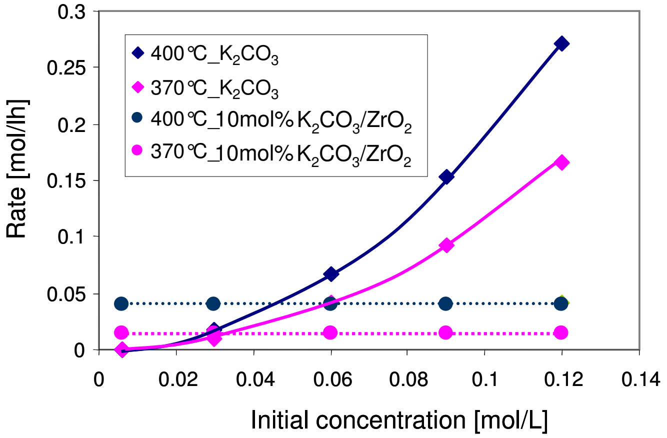

Figure 3.11: Calculated rates of DPE conversion with K_2CO_3 and ZrO_2 supported K_2CO_3 at 370 and 400°C.

Benzyl phenyl ether

Without the addition of Li_2CO_3, Na_2CO_3 or K_2CO_3, BPE is immediately converted at 350 and 370°C (Figure 3.12). At 320°C, conversion has reached 96% after 30 min and at 270°C, 240 min are necessary for the conversion to proceed to 91%. Figure 3.13 shows the effect of the alkali carbonates on BPE conversion from 270 to 350°C. The data points are for a reaction time of 60 min. We observed that up to a 320°C BPE conversion is strongly reduced by the presence of the salts.

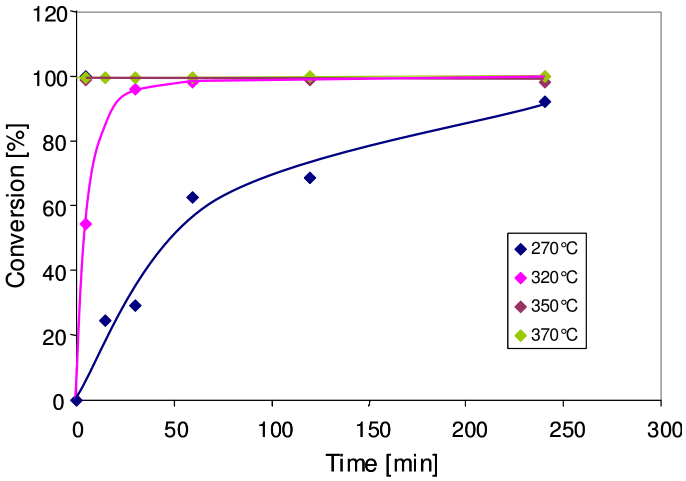

Figure 3.12: BPE conversion with reaction time in the absence of a base additive for different temperatures.

Beyond this temperature conversion is 100% in all cases. It should be noted that the inhibiting effect of the carbonates increases in the sequence Li > Na > K. Table 3.3 summarizes the products detected for the reaction of BPE at 270°C after 60 min reaction time without a carbonate added. BPE is converted to 62.9%. The yields of toluene, the dimers (diphenyl carbinol, 2-benzyl phenol and 4-benzyl phenol) and the trimers (1-benzyl-2-phenoxymethyl-benzene and 1-phenoxy-4-phenoxlmethyl-benzene) are all relatively low at 270°C.

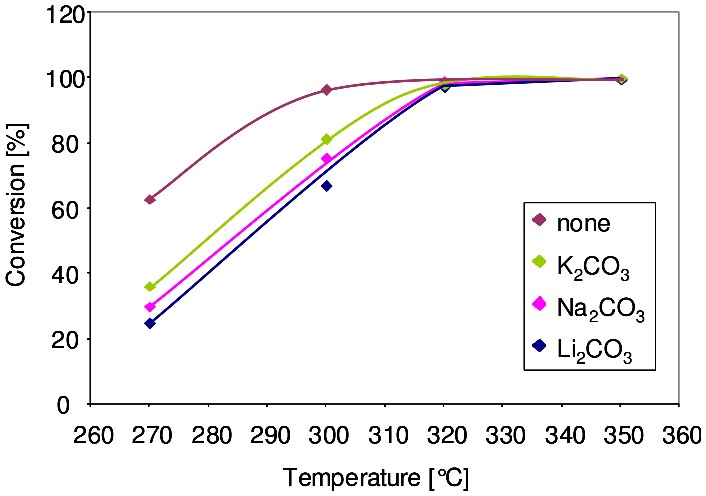

Figure 3.13: Influence of alkali carbonates on BPE conversion from 270-350°C after 60 min

Phenol and benzyl alcohol however are both formed with a yield of 40%. Higher molecular compounds which preferably are formed at higher temperatures and longer reaction times could not be detected via GC/MS due to their high boiling points. Although their formation was confirmed by MALDI-TOF/MS measurements, quantification was not possible so that these products were not accounted for in the carbon balance. However, the yield of these products can be estimated by the deviation of the carbon balance closure.

Table 3.3: Product spectrum after 60 min of BPE conversion at 270°C in absence of a salt

Phenol [mol%]	Benzyl alcohol [mol%]	Toluene [mol%]	Dimers [mol%]	Trimers [mol%]	Higher molecular [mol%C]
40.4	39.6	0.4	4.1	0.4	18

The carbon balance of the reaction without an additive is plotted against the temperature in Figure 3.14. As mentioned above, the balance was calculated merely from the yields of products and unconverted BPE detected by the GC. The balance is not satisfactory and deviation clearly increases with temperature. An explanation for this will be given in the discussion part.

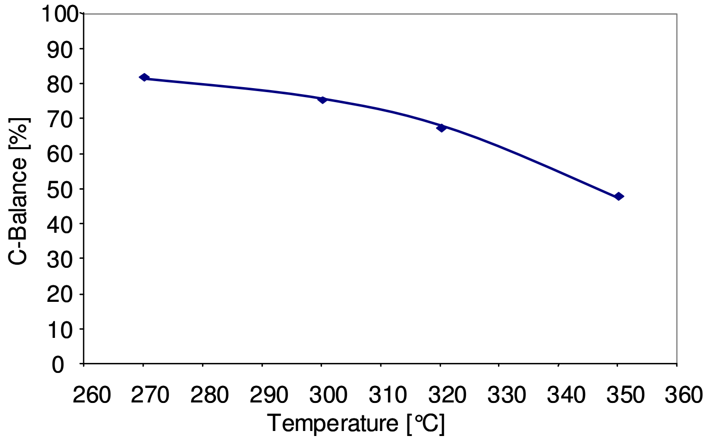

Figure 3.14: Carbon balance with temperature for BPE conversion without an alkali carbonate.

Figure 3.16 shows the main product distribution with time at 320°C without an alkali carbonate. The term "consecutive products" summarizes the dimeric products as well as the trimers. Traces of further products were detected by the GC, but could not be identified. At 320°C the yields of the hydrolysis products phenol and benzyl alcohol reach a maximum after 30 min reaction time and then decrease with time, while the consecutive products increase and the toluene yield is basically stable. This suggests the formation of consecutive products at least partially from the hydrolysis products. Comparison of the yields of the hydrolysis products after 60 min at 270°C (Table 3.1) and 320°C (Figure 3.15) shows that the temperature increase has an enhancing effect, however at 320°C phenol and benzyl alcohol are not detected in equivalent amounts as expected for a pure hydrolysis reaction.

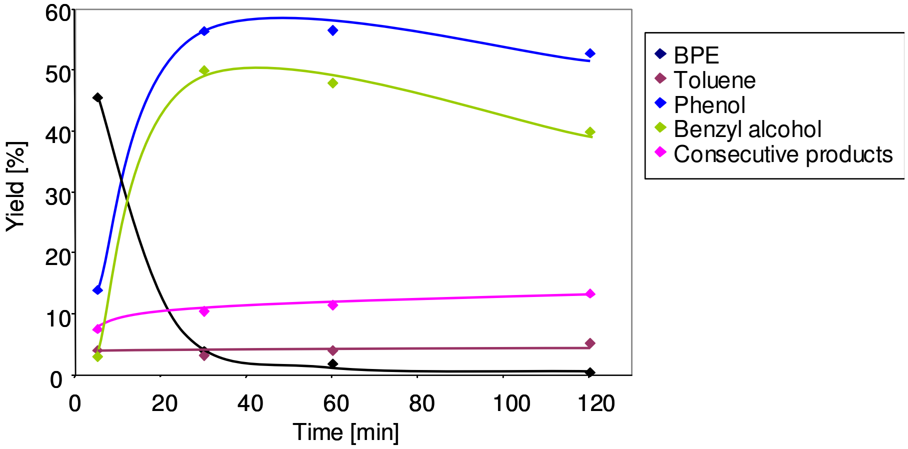

Figure 3.16*:* BPE conversion and product distribution at 320°C without an alkali carbonate.

Figure 3.17 shows the product distribution with time for the same conditions but in the presence of K_2CO_3. Comparison of the graphs in Figure 5 and 6 clearly show the effect of the salt. While the yields of toluene and consecutive products are enhanced by the salt, the formation of the hydrolysis products phenol and benzyl alcohol is reduced. Furthermore, the amounts of the hydrolysis products diverge strongly.

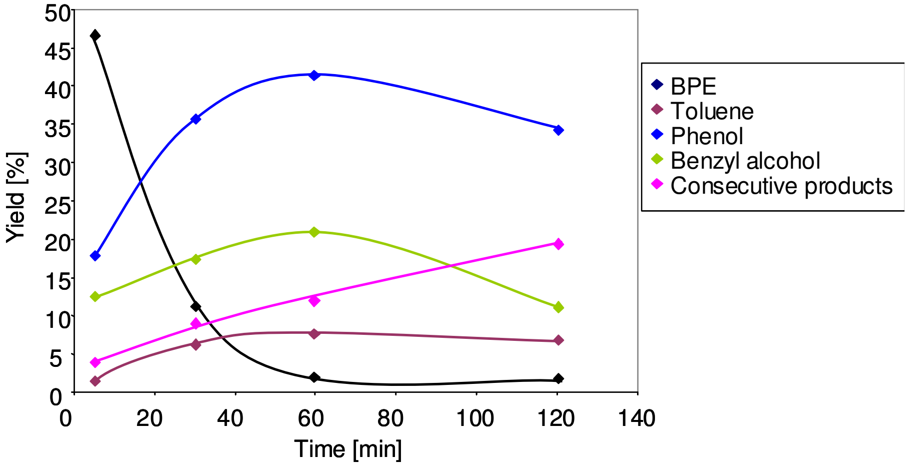

Figure 3.17: BPE conversion and product distribution at 320°C with 3 wt.% K_2CO_3.

Assuming that phenol is formed only by hydrolysis, this would mean that at 320°C 50% of benzyl alcohol has already been degraded after 60 min. However, under these conditions 8% toluene has likewise been formed meaning that phenol is not only being formed via a hydrolysis pathway.

The results show that benzyl alcohol is very unstable and lower temperatures as well as short residence times must be applied to achieve high yields of the hydrolysis products.

This statement can be supported by the diagrams in Figure 3.18, where only the yields of phenol and benzyl alcohol with time are depicted for the conversion of BPE with 3 wt% K_2CO_3 at 270, 320, 350 and 370°C.

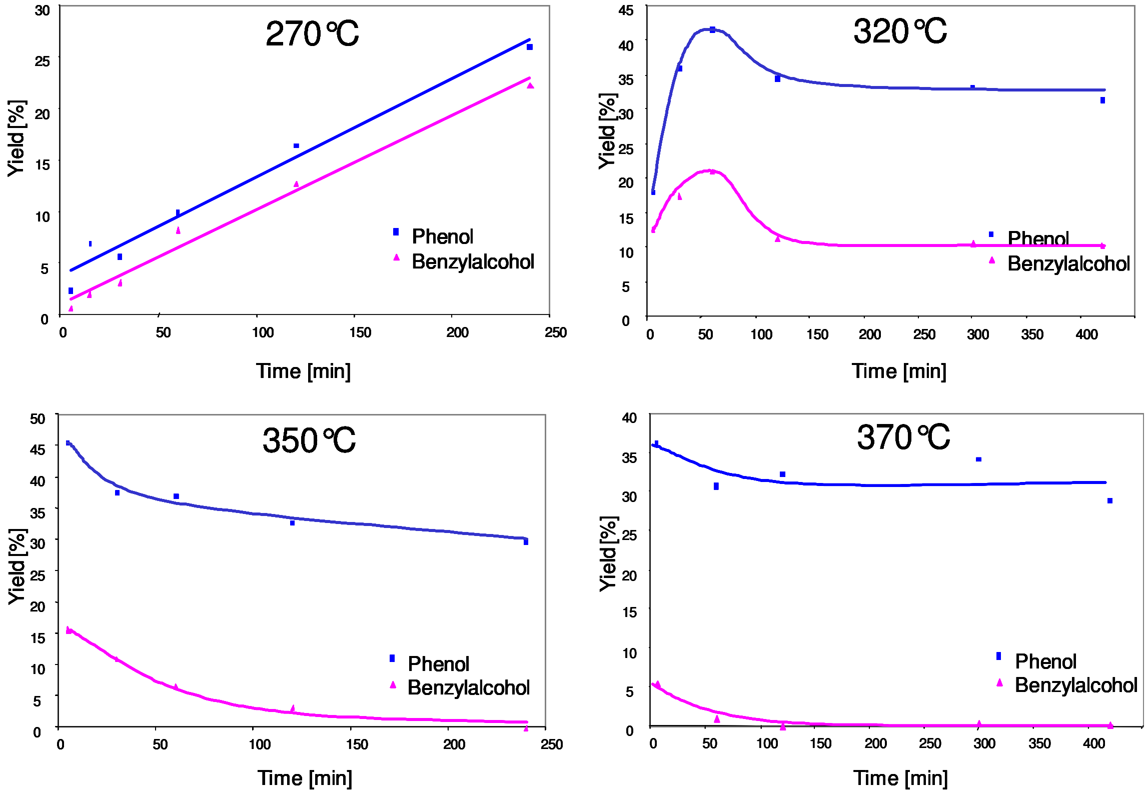

Figure 3.18: Effect of increasing temperature with time on yield of hydrolysis products with the addition of 3wt.% K_2CO_3.

The yields of benzyl alcohol and phenol are similar and increase over the entire reaction time up to 22 and 26% for a temperature of 270°C. At 320°C yields of the hydrolysis products are initially similar but drift apart with time, although still increasing and reaching a value of 21 and 42% after 60 min. Afterwards yields decrease and become stable after 120 min at an average yield of 11 and 32% for benzyl alcohol and phenol respectively. Increasing the reaction temperature to 350°C accelerates the reaction to the extent that the hydrolysis products are already being degraded after 5 min. A further increase to 370°C yields only 0,3% benzyl alcohol after 120 min. Figure 3.18 does not only show the expected increase in reaction rate with elevated temperature but also the instability of the hydrolysis products especially benzyl alcohol with temperature. For reasons of clarity the yields of phenol and benzyl alcohol will be summarized as the yield of hydrolysis products in the following. Figure 3.19 shows the effect of Li_2CO_3, Na_2CO_3 or K_2CO_3 on the yields of hydrolysis products after 60 min at different temperatures. In each case a maximum yield is reached between 300 and 320°C. At 270°C the carbonates show a strong inhibiting effect on BPE hydrolysis, decreasing with basicity. At this temperature the yield is reduced from 80 to 18 % in the presence of K_2CO_3. In the case of Na_2CO_3 and Li_2CO_3, yields have been reduced to 11 and 2 %, respectively. An increase in temperature to 320°C only has a small impact in the absence of a carbonate.

However, in the presence of an alkali carbonate the yield of hydrolysis products is strongly increased at 320°C and the influence of the cation has changed. After 60 min Na_2CO_3 yields 81 % of hydrolysis product and K_2CO_3 and Li_2CO_3 yield 63 and 56 %, respectively. Hydrolysis decreases above 320°C in all cases. This can be attributed to a consecutive reaction of these products, especially benzyl alcohol. Values for the reaction with and without carbonate converge with temperature. At 350°C both the yields for the reactions with a carbonate as well as without lie in a range of 43 to 54%.

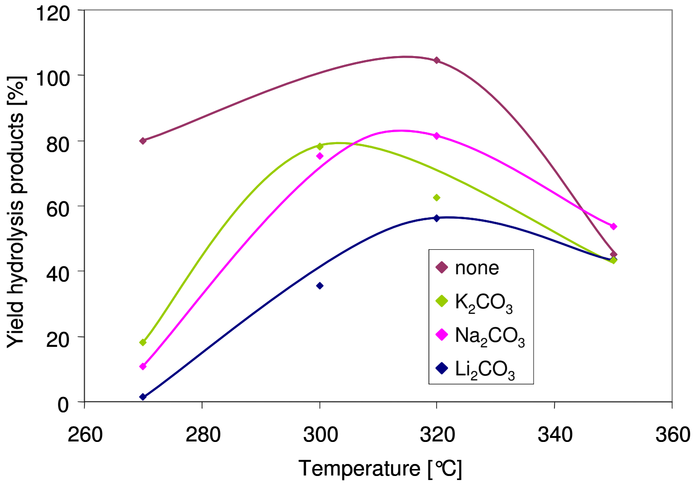

Figure 3.19: Effect of Temperature and carbonate on the yield of hydrolysis products (sum of phenol and benzyl alcohol).

Applying the integral approach, we have found that the treatment of BPE in subcritical water is of first order regarding BPE. Table 3.4 summarizes the rate constants obtained by this method.

Table 3.4: Rate constants for different temperatures

Additive	Rate constant (270°C) [x10^{-3}]	Rate constant (300°C) [x10^{-3}]	Rate constant (320°C) [x10^{-3}]
None	13	34.0	106
Li_2CO_3	7.5	20.0	84.6
Na_2CO_3	6.7	25.0	78.0
K_2CO_3	7.5	28.0	67.0

As expected from the previous results, the rate constants of BPE conversion with alkali salts at 270°C are lower than without an additive and very similar among each other. The rate constant is decreased by approximately 50%. With a temperature increase to 300 °C the rates for BPE conversion in the presence of a salt start converging towards the rate obtained in pure water. At 320°C, where the product distribution has been shifted from the hydrolysis products phenol and benzyl alcohol to toluene and higher molecular consecutive products, rates are 70-80% of the rate without an additive and increase as following $K_2CO_3 < Na_2CO_3 < Li_2CO_3$.

3.3.2 Density effects on conversion and product distribution

In this context density is defined as the total mass of the reactants divided by the reactor volume. Experiments were carried out at 400°C and with 0.5 g 10wt% K_2CO_3/ZrO_2. The influence of density on DPE treatment was already presented in the foregoing paragraph and will therefore be neglected here.

Benzyl phenyl ether

BPE experiments were carried out at 400°C, 2wt. %BPE, 0,5g 10wt% K_2CO_3/ZrO_2 and 40 min reaction time. Figure 3.20shows the effect of density increase from 0,2 auf 0,8 g/cm³ on product distribution.

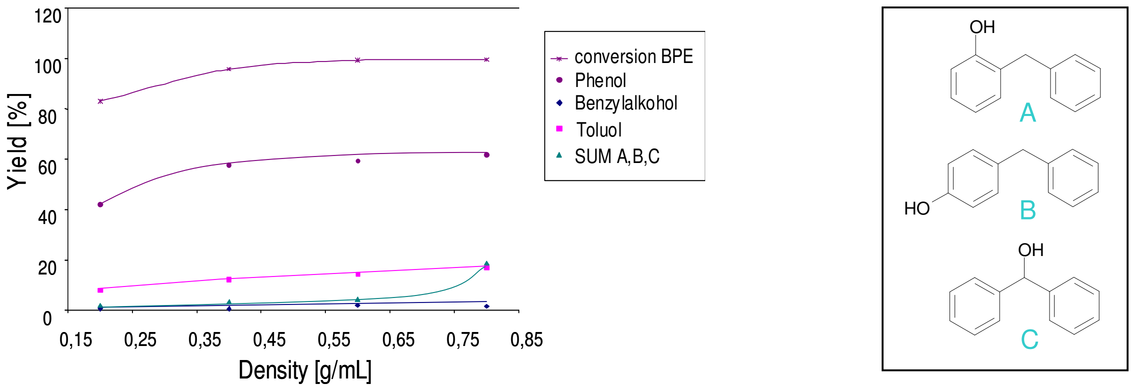

Figure 3.20: Effect of density on product distribution.

Conversion is increased from 82 ($\varphi = 0.2\ \mathrm{g/cm^3}$) to 100% ($\varphi = 0.8\ \mathrm{g/cm^3}$). The yield of hydrolysis products is increased in the same manner from 42 to 63%. However at a temperature of 400°C mainly phenol accounts for the hydrolysis products as the thermally instable benzyl alcohol is degraded at these temperatures. Interestingly, the yields of 2-and 4-benzyl phenol as well as diphenyl carbinol (SUM A,B,C) increase from 4 to 18% with a density increase from 0.6 to 0.8 g/cm^3.

4- Methoxybiphenyl

The C-C bond between the two aromatic rings is not cleaved at temperatures up to 400°C and when applying the 10wt.% K_2CO_3/ZrO_2 catalyst. At 400°C not only the hydrolysis product 4-hydroxy biphenyl was formed but also pyrolysis products like 2 –methyl -4-hydroxybiphenyl were found. Figure 3.21 shows the increase in 4-hydroxy biphenyl with density. The yield of 4-hydroxy biphenyl increases 7% at a density of 0.5g/cm^3 to 18% at 0.9g/cm^3.

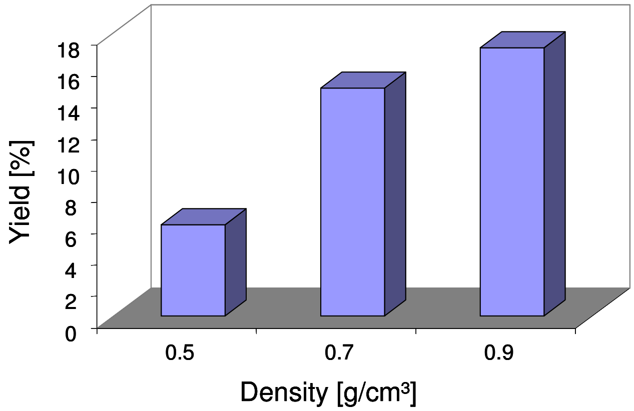

Figure 3.21: Einfluss der Dichte auf die Ausbeute an 4-Hydroxybiphenyl bei 400°C und 0,5g 10wt%K_2CO_3/ZrO_2.

Eugenol und Phthalan

At 400°C both compounds are converted 90-100% independent of the density. A very broad product spectrum is observed, however none of the expected hydrolysis products. The only indication for hydrolysis is the detection of methanol, which increases with density while 4-hydroxy biphenyl decreases.

Diphenylmethan

Under the applied conditions (400°C and 0.5 g 10wt.% K_2CO_3/ZrO_2) diphenyl is not converted at any of the applied densities. When increasing the temperature to 500°C, yields of benzene and toluene < 5% are detected.

3.3.3 Alcoholysis versus Hydrolysis

To implement a continuous process of lignin hydrolysis, lignin must be brought into solution to be able to feed it to the reactor. Organosolv lignin is only soluble in alkaline media and alcohols. Therefore the effect of methanol, ethanol and their aqueous solutions on the conversion of the DPE and BPE was investigated.

Results of DPE conversion are summarized in Table 3.5. We see that the presence of an alcohol has a strongly diminishing effect on DPE conversion and no hydrolysis products are formed.

Table 3.5: Influence of methanol, ethanol and their aqueous solutions on DPE conversion at 400°C, ρ= 0,9g/cm³, 0,5g 10wt%K_2CO_3/ZrO_2, wt%(H_2O/alcohol) = 50 and a reaction periode of 1h. For the fields marked red the autoclaves were not quenched after the reaction

	Pure MeOH	MeOH/H_2O	EtOH/H_2O	EtOH/H_2O	sc-water	
	1wt% DPE		n(H_2O/DPE) = 35	n(H_2O+EtOH/DPE) = 35	n(H_2O/DPE) = 35	
					13,3wt% K_2CO_3/ZrO_2	3wt% K_2CO_3
Conversion DPE [%]	7,5	9,7	4	2	30-35	46,6
Conversion Alcohol [%]	36	19	57	70		
Yield Phenol [%]	0	0	0	0	26-30	42

The table also shows that alcohol itself is being converted during the reaction. Figure 3.22 shows a comparison of the gas chromatograms of the products obtained from the conversion of BPE in sc-water, methanol and a water/ethanol mixture of 50/50 wt.%.

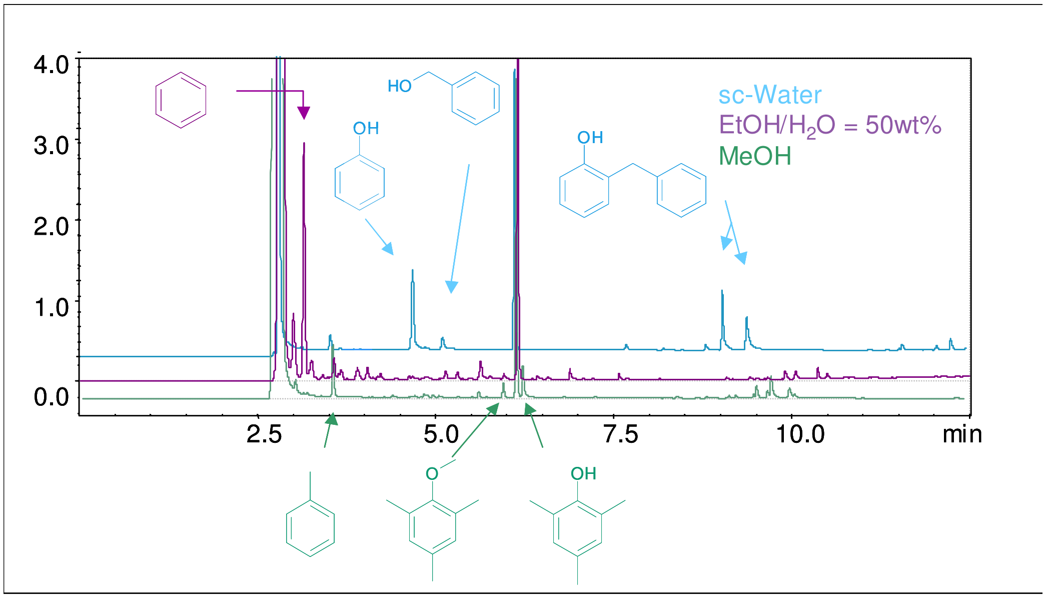

Figure 3.22: Gas chromatograms of products obtained in various solvents.

Only in the case of BPE conversion in water are hydrolysis products observed in significant amounts. In methanol and the water/ethanol mixture hydrolysis is suppressed and merely pyrolysis products are obtained. Also we find that the alcohol is reacting with BPE or intermediate BPE products, as in 2-, 4-, 6-trimethyl anisole.

3.4 Discussion

3.4.1 Diphenyl ether and benzyl phenyl ether

Diphenyl ether

Both acid and base catalyzed mechanisms have been proposed for the hydrolysis of DPE. Penninger et al. proposed the formation of a protonated DPE molecule which then decomposes to form phenol [21]. However Katritzky et al. assume a base catalyzed mechanism where the aromatic C1 atom is attacked by a hydroxyl ion [16]. The results of the catalyst screening, where significant phenol yields were only found for basic materials and yields increased with basicity, support Katritzky´s assumption. Furthermore, temperature programme desorption experiments with CO_2 and NH_3 confirmed the basicity of the ZrO_2 supported K_2CO_3 materials.

The large increase in phenol selectivity with density dependent pressure can be attributed to several factors. First, according to the principle of *Le Chatelier* gas formation is supressed with increasing pressure and in fact at a density of 0.9 g/cm³ gaseous products were not formed.

Also, with increasing density the influence of the cage effect becomes stronger. The cage effect describes how properties of a molecule are affected by its surroundings. Wu et al. described the density effect on the pyrolysis of benzyl phenyl ether and found the same results [26].

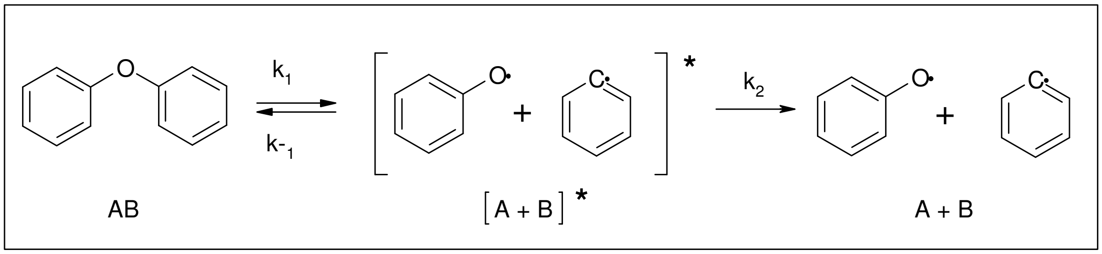

Figure 3.23: Homolytic cleavage of DPE to an encountered pair [A + B]* (k1), reassociation to AB (k-1) and dissociation to A + B.

Figure 3.23 illustrates a sequence of steps where the initially formed radicals are trapped as a pair in the solvent cage [A + B]* and the overall reaction from AB to A + B can only be realized if the initially formed radical pair is able to diffuse apart. High densities increase the solvent cage strength, as intermolecular interaction becomes stronger. Consequently the k_{-1} rate for recombination to AB increases. Thus, the yield of products formed by a radical pathway is decreased.

Furthermore, auto-protolysis is enhanced with density, giving rise to higher concentrations of OH^- and H_3O^+-ions and therefore increasing acid/base type catalytic properties of the system, while at lower densities the reaction mechanism is shifted towards a radical pathway. Therefore, we can conclude that the many side products found at lower densities are formed by a radical mechanism, where the ether bond is cleaved in a homolytic manner. Among all additives, K_2CO_3 gives the best results regarding phenol formation. We assume that this can be assigned to the fact that it is the salt with the highest solubility. However, at conversions above 71%, phenol is degraded and mono alkyl phenols are formed. Anitescu et al. have described the formation of such products from biphenyl under similar conditions, where hydroxy biphenyl is an intermediate [27]. As mentioned above, hydroxy biphenyl is also a side product in our reaction system.

Comparison of the supported and unsupported K_2CO_3 shows that the phenol formation rate is largest for the unsupported salt, however high yields of phenol (42% after 420min) can likely be achieved with a tenfold less of K_2CO_3 when supported. Figure 3.24 compares the rates of DPE conversion for the pure salt and K_2CO_3 supported on ZrO_2 normalized with respect to the applied K_2CO_3 amount. At 400°C and an initial concentration of 0.06 mol/l DPE the rate is approximately ten times higher for K_2CO_3 supported on ZrO_2.

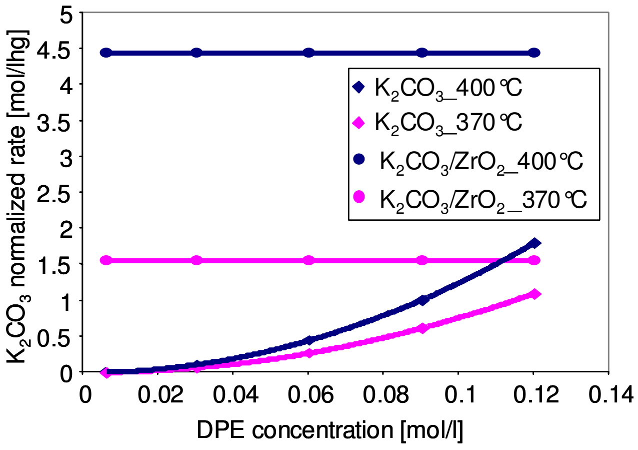

Figure 3.24: K_2CO_3 normalized rates of DPE conversion with K_2CO_3 and ZrO_2 supported K_2CO_3 at 370 and 400°C.

Figure 3.25 shows the X-ray diffraction patterns of calcined (550°C) ZrO_2 and the supported catalyst. ZrO_2 shows a predominantly monoclinic phase. However, the same sample when impregnated with 10wt.% K_2CO_3 leads to predominantly cubic phase. Furthermore, the BET surface area increases from 81 to 125 m²/g, upon impregnation.

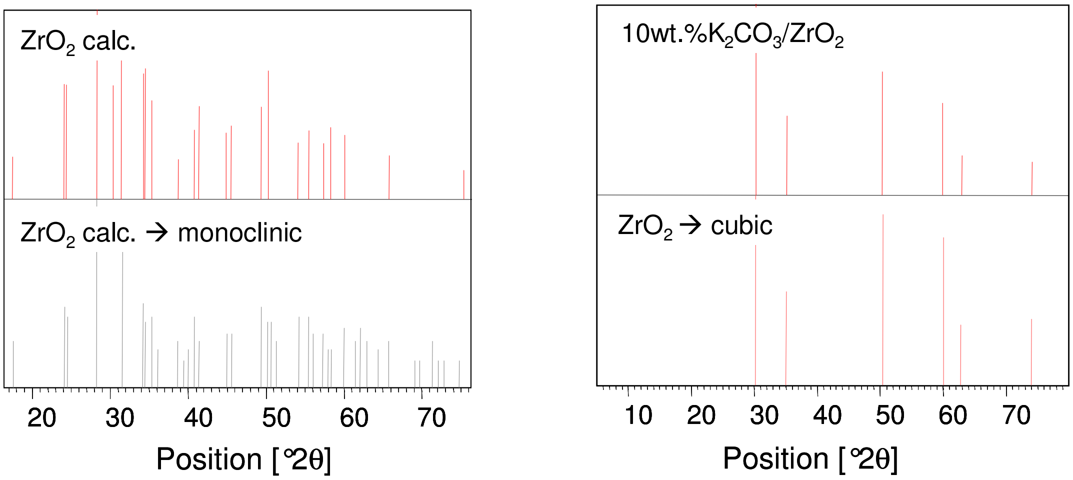

Figure 3.25: X-ray diffraction patterns of ZrO_2 and 10 wt.% K_2CO_3/ ZrO_2

These results suggest a migration of the salt into the zirconia lattice. It is known that in water the surface of metal oxide possesses hydroxyl groups (base site) and oxy-acid groups (acid site) due to the dissociative adsorption of water. According to Shimizu [28], hydroxyl groups exist on a metal oxide surface up to a value of about 13 of electro negativity (defined by Sanders) of the metal ion, while oxy-acid group exist over a value of 13. The electro negativity of the metal ion in ZrO_2 is 8.1 and thus, the surface is rich of hydroxyl groups. The incorporation of very low electro negative potassium in the lattice increases the amount further. Since we are working with a surplus of water we consider that water is activated as hydroxyl groups on the metal oxide surface and therefore propose the following mechanism (figure 3.25) for phenol formation.

The aromatic C1 atom in DPE is attacked by a hydroxyl group on the catalyst surface forming a spacious anionic DPE adduct. Upon release, the phenolate ion abstracts a proton from the neighboring hydroxyl group, forming phenol.

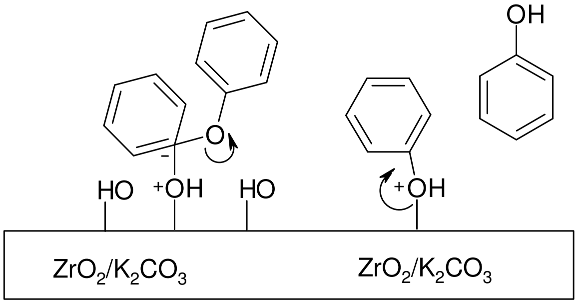

Figure 3.25: Mechanism for the formation of phenol from DPE in the presence of 10 wt.% K_2CO_3/ ZrO_2

This also explains why the pre-exponential factor is much lower than for the alkali carbonates, as not all active sites can be accessed due to the dimension of the DPE adduct.

Valyashko et al. investigated the solubility of salts in supercritical water and devided them into two different types. K_2CO_3 is classified as a high solubilty salt, which means that its solubility increases with temperature, while Li_2CO_3 and Na_2CO_3 are low solubility salts. Their solubility decreases in water with temperature above 100°C [29]. Under the conditions applied, the solubility of Na_2CO_3 is 1.2 wt.% according to Khan et al. [30]. As Li_2CO_3 belongs to the same type of salt, we can conclude that these salts are only partially dissolved in our system and are influencing the reaction both homogeneously and heterogeneously, while K_2CO_3 is completely dissolved and catalyzes only homogeneously. This may explain the lower phenol selectivity of Li_2CO_3 and Na_2CO_3 [29].

Benzyl phenyl ether

The results have shown that the ether bond in BPE is not as stable as the aryl aryl ether bond [31]. In comparison, it can be cleaved under relatively moderate thermal conditions and short reaction times. In the absence of an alkali carbonate BPE is converted to 100% after very short reaction times at 350°C Figure 3.12. Hence, the aryl-alkyl ether bond is much easier cleaved than the aryl-aryl ether bond as in diphenyl ether (DPE) [10, 16, 21, Penninger, 2000 #83, 32]. The approximately 100 kJ/mol higher C-O bond energy in DPE results from the sp^2 hybridization of the C atom.

At 270°C the yields of toluene, dimers and trimers are low (Table 3.3). Only the hydroylsis products phenol and benzyl alcohol are formed in large amounts and to the same extent (40%). Therefore, it can be concluded that hydrolysis is the main reaction pathway at low temperatures. The ionization constant of water is maximized at 250°C where it is three orders of magnitude higher than at room temperature. Therefore, subcritical water can itself act as a catalyst for reactions which normally require addition of an acid or base catalyst. The decrease of phenol and especially benzyl alcohol with time and with temperature increase can be attributed to consecutive reactions forming toluene, 2- and 4- benzyl phenol and higher molecular compounds [13]. This is supported by the increasingly non-satisfactory carbon balance with temperature and by MALDI-TOF/MS measurements.

The formation of 2-benzyl phenol is shown in Figure 3.26.

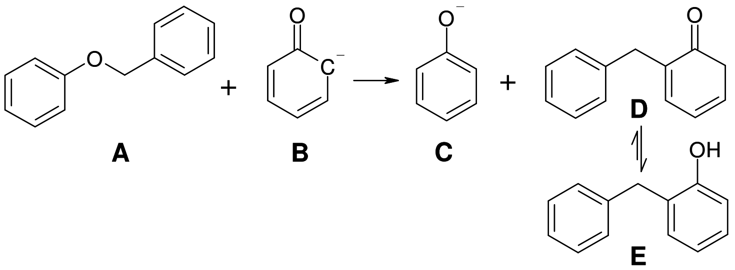

Figure 3.26: Formation of 2-benzyl phenol via a carbanion

Phenolate ions present in the alkaline media are likewise stabilized by delocalization of the charge. Due to resonance stabilization, the phenolate ion also exists as a carbanion with a negative charge in ortho – or para position of the phenolic hydroxyl group [33]. The carbanion (B) attacks BPE (A) at the polarized aliphatic C-atom forming a phenolate and 2-benzyl-cyclohexa-2, 4-dienone (D). Under the applied conditions the keton is more stabile in its enol form and rearranges to 2-benzyl phenol (E).

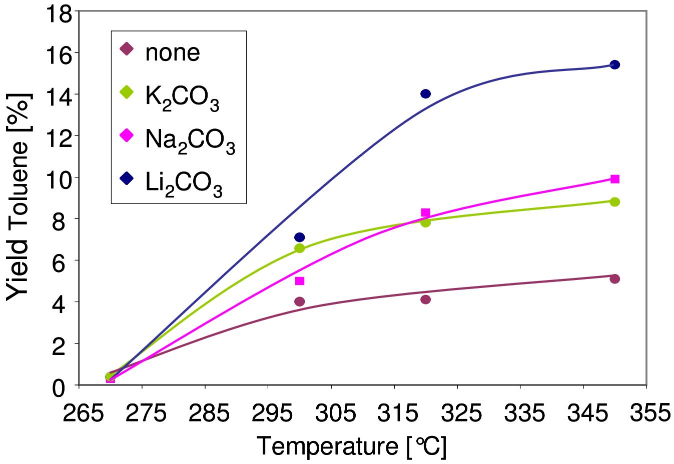

Figure 3.27: Effect of alkali carbonates on toluene yield after 60 min of reaction time

Figure 3.27 shows the effect of applied carbonates on toluene yield with increasing temperature. According to literature [13] and shown in Figure 3.2, toluene is claimed to be formed via homolytic cleavage of the ether bond and subsequent hydrogen abstraction of the formed benzyl radical. Our results, however, show that the addition of a salt strongly influences toluene formation. In the presence of a carbonate, toluene yields are vastly increased and, among the carbonates increase with charge density of the cation. In case of a homolytic cleavage the cation should not have an effect on toluene yield. Therefore, it is concluded that toluene is formed via an ionic mechanism, where the cation forms an adduct with the BPE ether bond. As a consequence, the ether bond is polarized and heterolytic cleavage is faciliated compared to toluene formation in the absence of a salt.

Figure 3.28shows both mechanisms, hydrolysis (top) and the proposed mechanism for toluene formation (bottom). It is suggested that toluene is formed via a hydride assisted heterolytic cleavage of the ether bond.

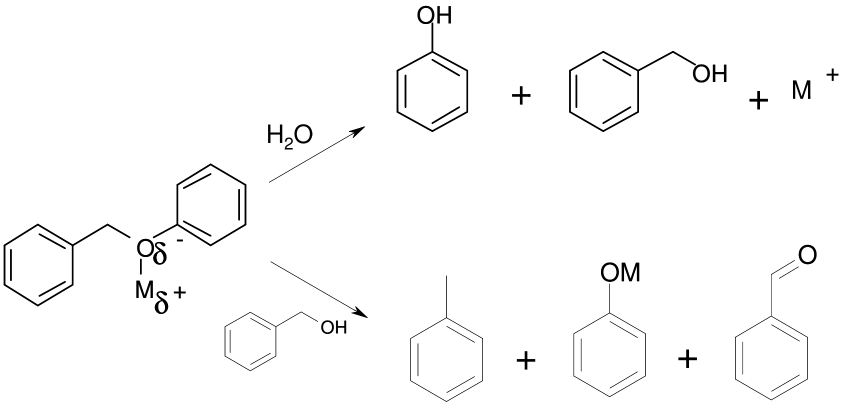

Figure 3.28: BPE-cation adduct and concurrent ionic reaction pathways

The necessary hydride ions are provided by benzyl alcohol which is oxidized to benzaldehyde. Benzaldehyde was not detected in our studies, but is known to be formed from dibenzyl ether under hydrothermal conditions [12]. Small amounts of benzene detected, indicate that benzaldehyde is decarbonylated and was therefore not detected.

The rsults show that, depending on the temperature, the presence of alkali carbonate has two different effects on product distribution. As the experiments were conducted under subcritical conditions we must account for a two phase like system with the following rate equation for hydrolysis:

$$r = A_1k_1[BPE]_1\,[H_2O]_1 + A_2k_2[BPE]_2\,[H_2O]_2 \qquad (1)$$

where A_1 is the amount of the salt rich aqueous phase and A_2 the amount of the organic phase.

Obviously, hydrolysis takes place in the aqueous phase. Addition of a salt to the system increases the polarity of the solvent, reducing solubility of BPE in the aqueous phase. Consequently, phase separation is increased in the presence of a salt. $[BPE]_1$ is diminished and thus, the hydrolysis rate is strongly reduced, as seen in figure 7. Although $[BPE]_2$ is increased the reactant (water) availability in the organic phase is poor.

Torry et al. describe the same effect of salt addition on hydrolysis of dibenzyl ether and benzyl phenyl amine [34].

The general increase in toluene yield in the presence of an alkali carbonate can be ascribed to the same effect. The concentration $[BPE]_2$ in the organic phase is increased, where hydrolysis can not proceed. In this phase the salt is not dissolved and should not have an effect. However, in the aqueous phase the salt enhances the reaction of the remaining BPE by formation of an intermediate cationic BPE structures as in figure 11 and therewith weakens the ether bond.

With increasing temperature hydrolysis rates with and without an alkali carbonate converge. In the range of temperatures applied (270 – 370°C), the dielectric constant decreases almost independently of the pressure. The declining influence of the added salts on the yield of hydrolysis products with temperature can, therefore, be explained by their reduced solubility. Khan et al. report that the solubility of sodium carbonate in subcritical water decreases from approximately 10 to 1 wt.% when increasing the temperature from 320 to 370°C [12].

3.4.2 Density effects on conversion and product distribution

According to Penninger *et al.* [21], the density ρ_w corresponding pressure p can be calculated with equation 2:

$$p = c_T \cdot T \cdot \rho_w \qquad (3.2),$$

where c_T·[J·g-1·K-1] is the temperature dependent coefficient. The variation of the pressure with the density at 400 °C is presented in Figure 3.29.

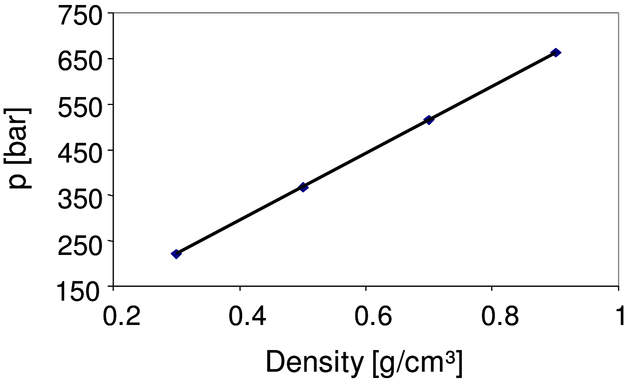

Figure 3.29: Density corresponding pressure for 400°C

The pressure changes from 220 bar (ρ_w = 0.3 g/cm³) to 660 bar (ρ_w = 0.9 g/cm³). As already pointed out in chapter 1, pressure determines many properties of supercritical water. The ionic product of water K_w is strongly dependant on density and temperature. The pK_w of supercritical water changes from 19.4 at 250 bar to about 10 at 600 bar. This has serious effects on the reaction type. Therefore this property can be used for optimizing acid/base-catalyzed reactions. At pK_w values lower than 14, water is more suitable as a medium for heterolytic reactions, whereas it is more suitable for homolytic reactions at $pK_w \geq 14$. The transition from homolytic to heterolytic cleavage is not clearly defined; however the reults clearly show a shift from a pyrolytic to an ionic reaction pathway with density. Another enhancing effect on hydrolysis results from the increased dielectric constant at high pressures. Hydrolysis proceeds through a transition state that is more polar than the reactants [14]. The selectivity towards the hydrolysis products is therefore also increased with the water loading as the correlating higher dielectric constant stabilizes the polar hydrolysis transition state over the less polar reactants.

Furthermore, pyrolysis is suppressed at high densities due to the “cage” effect. Like normal fluids, supercritical fluids also show the effect known as “clustering“ or “cage” effect, i.e. the physical properties in the neighborhood of a dissolved particle are fundamentally different from the average value for the solution. High densities increase the solvent cage strength, as intermolecular interaction becomes stronger. Consequently, recombination of radicals formed from a homolytic bond cleavage becomes more likely. Thus, the yield of products formed by a radical pathway is decreased. The influence of the “cage” effect on pyrolysis is described in more detail in the foregoing paragraph (DPE).

Figure 3.20 however shows an increase in the pyrolysis products diphenyl carbinol, 2-and 4-benzyl phenol with density. Taking the C-balance into account we find an increase with density, meaning that the total amount of non-detectable, high molecular pyrolysis products is larger at low densities. Just as for DPE and BPE we find increased yields of hydrolysis products with density for 4-methoxy biphenyl, eugenol and phthalan. The main pathway for eugenol and phthalan at a temperature of 400°C however is pyrolysis as these compounds are much more reactive.

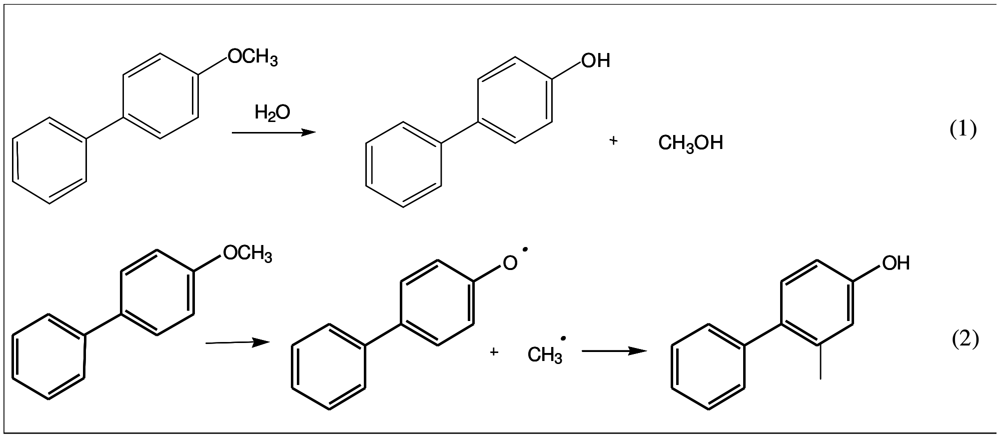

Figure 3.30: Hydrolytic and pyrolytic pathways for the conversion of 4- methoxy biphenyl.

Figure 3.30 shows the different pathways for the main products of 4- methoxy biphenyl conversion at 400°C with 10 wt.% K_2CO_3/ ZrO_2.

As expected density shows no effect on the conversion of diphenyl methane to toluene and benzene as it is not an ionic mechanism.

3.4.3 Alcoholysis versus hydrolysis

The results show that the application of alcohols and alcohol/water solutions as solvents is unsuitable. Reason here fore are an inhibition of hydrolysis and an enhancement of pyrolysis. In addition to this the product spectrum is further increased by reaction of the alcohol with the probe molecules. It should also be noted that a large amount of the alcohol is gasified. These results are in good agreement with literature. Yokoyama et al. came to the same conclusion when investigating the thermolysis of BPE in sub- and supercritical water as well as in sc-methanol [13]. They found that both pyrolysis and hydrolysis occurred in subcritical and supercritical water, but only pyrolysis occurred in methanol. Miller et al. studied hydrothermal conversion of BPE [35] in KOH/ethanol at 290°C for 1 hour. Major products were phenol and ethoxy methyl benzene meaning that ethanol acts not only as a solvent but also takes part in the reaction.

3.5 Conclusion

We have shown that for all probe molecules containing an ether bond both pyrolysis and hydrolysis can take place under the applied conditions. By increasing the density it is possible to enhance the hydrolytic pathway. In the case of the very stable aryl-aryl ether DPE, an increase in density even enhances hydrolysis up to a phenol selectivity of 100%.

Furthermore, application of 3 wt.% lithium, potassium or sodium carbonate catalyzes DPE conversion so that significant yields of phenol can be obtained already at 350°C. Phenol yields are highest for K_2CO_3. However, when K_2CO_3 is supported on ZrO_2 significant yields of phenol and a phenol selectivity of 100% can be achieved with much smaller amounts of the carbonate. We ascribe this to the increased amount of hydroxyl groups in the system, due to the dissociative absorption of water on the metal oxide carrier. In contrast hereto alkali carbonates have a totally different effect on BPE conversion in subcritical water. If hydrolysis is the preferred reaction pathway, the reaction should be conducted in the absence of an alkali carbonate. We ascribe this to the different properties of the solvent and thus different solubilities of the salts at the applied conditions. The highest selectivity towards the hydrolysis products is obtained for 320°C and a reaction time of 60 min. At higher temperatures and residence times the yields of phenol and especially benzyl alcohol decrease and higher molecular compounds are formed. The application of alkali carbonates diminishes BPE hydrolysis and accelerates catalytic cracking via a carbenium ion due to the increased polarity of water and the formation of an intermediate metal-BPE adduct. The C-C bonds in diphenyl methane and 4- methoxy biphenyl could not be cleaved at 400°C and in the presence of 10wt.% K_2CO_3/ZrO_2. We have also shown that the application of alcohols and alcohol/water solutions as solvents is unsuitable, as hydrolysis is inhibited and pyrolysis enhanced. In addition to this, the product spectrum is further increased by reaction of the alcohol with the probe molecules.

As, the largest fraction of bonds in lignin are of the aryl-alkyl ether type, the BPE investigations give us the most valuable results. We therefore conclude that the applied temperatures for lignin conversion should not exceed 320°C. Above this temperature hydrolysis products are degraded and form higher molecular pyrolysis products. In addition to moderate temperatures high densities/pressures are advantageous for hydrolysis.

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Chapter 4

Elaboration of an optimized work up procedure for the BCD process

Abstract

Hydrothermal depolymerization of lignin yields a wide product spectrum. Products consist not only of the monomeric lignin building blocks, but to a large extent of oligomers and polymers. However, when the aim of lignin depolymerization is the production of chemicals, a high monomeric content is desirable. A novel work up procedure for hydrothermal lignin depolymerization is presented, which yields a product oil consisting predominantly of monomers and dimers. The properties of the oil can be tailored by selective extraction. A variety of solvents were investigated for this purpose and the results presented.

4 Elaboration of an optimized work up procedure for the BCD process

4.1 Introduction

Lignin depolymerization presents a great challenge due to its reluctant structure. The different lignin monomer units (Figure 4.1) as well as the multiplicity of bond types (Table 4.1) explain the heterogeneity of the molecule and the complex product distribution. Beside the phenolic monomers a large amount of oligomeric coumpounds are obtained upon hydrothermal treatment. These compounds are dimers and trimers, but also higher molecular oligomers. So far comparison of product yields between different research groups is difficult due a number of different work up procedures. The yield of product oil and also its quality can differ strongly due to variations in the work up process.

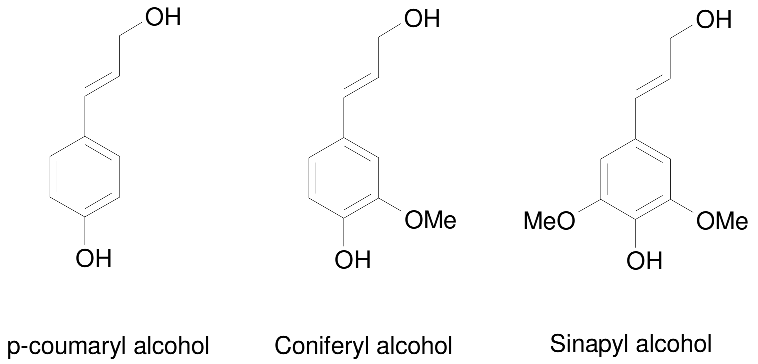


Figure 4.1: Phenylpropene units of lignin

Regarding lignin conversion to produce high valuable chemicals, oil with a relatively defined average molecular weight is desirable. The quality of oil increases with its content of monomeric compounds. Phenolic compounds are of high preferrability as the aromatic hydroxyl group allows electrophilic substitution of the aromatic ring and is an outstanding initiation site for further functionalisation.

In general, the first work up step after hydrothermal lignin treatment is acidification of the reaction mixture. This step is to regain unconverted lignin. However, beside unconverted lignin, coke and predominantly oligo– and polymeric products are present in the precipitate. More hydrophilic compounds with lower molecular weights, mainly monomers and dimers remain predominantly in the filtrate. One possibility found in literature is to only extract the filter cake and express the success of depolymerization in terms of unconverted lignin (solids remaining after extraction) [1, 2]. Obviously, in this manner lignin conversions are high but the oil obtained has a high oligomer content and is of low quality. Furthermore, the unconverted lignin is not seperated from possibly formed coke.

Table 4.1: Overwiev of most frequent bond types found in lignin

Model Linkage[a]	Glasser and Glasser [3]	Erickson et al. [4]	Nimz [5]
β carbon-oxygen-4 aromatic carbon	55	49-51	65
α carbon-oxygen-4 aromatic carbon		6-8	
β carbon-5 aromatic carbon	16	9-15	6
β carbon-1 aromatic carbon	9	2	15
5 aromatic carbon- 5 aromatic carbon	9	9.5	2.3
4 aromatic carbon-oxygen- 5 aromatic carbon	3	3.5	1.5
β carbon- β carbon	2	2	5.5
β carbon- β carbon forming a furanic structure			2
α and γ carbon-oxygen- γ carbon	10		
α carbon-β carbon	11		2.5
β carbon –6 aromatic carbon	2	4.5-5	
6 aromatic carbon-5 aromatic carbon	1-5		
1 aromatic carbon-oxygen-4 aromatic carbon			
1 aromatic carbon-5 aromatic carbon			
Total	118-123	85.5-96	99.8

[a] Linkage per C_9 unit

Other groups extract both the filter cake and the filtrate. In this case high yields of oil are obtained [6-9]. The quality of oil has improved compared to the first work up procedure as it contains a higher amount of monomers. However, it has a broad product and molecular weight distribution and is disadvantageous as a source of high valuable chemicals. A further work up method is to recover products and unconverted lignin in tetrahydrofuran (THF) and then separate into THF soluble and THF insoluble products [10, 11]. In the case of Organosolv lignin, which is THF soluble, the THF insoluble products are defined as coke and separated from the products and unconverted lignin in this way. Yet, the whole product spectrum and the unconverted lignin remain in the THF soluble fraction, making it impossible to draw conclusions on conversion or yield. When THF insoluble, but water soluble sodium lignosulfonic acid and alkali lignins are applied, coke and unconverted lignin can be seperated by washing the THF insolubles with water [11]. However, the THF soluble fraction again consists of the complete product spectrum and is comparable to the low quality oil obtained when extracting both filtrate and filter cake after precipitation.

The most two frequent approaches for hydrothermal lignin treatment found in literature are the depolymerization in supercritical water, and below the supercritical state in alkaline media. This later process is referred to as “base catalyzed depolymerization” (BCD). From 1997 the National Renewable Energy Laboratory, the University of Utah and Sandia National Laboratory have been working together on a process for converting lignin into a blending component for gasoline [2]. The process developed consists of two steps, where the first is a base catalyzed depolymerization followed by a hydroprocessing step. When an excess of NaOH was used relative to lignin monomers, only 8% insoluble material remained after treatment at 330 °C for one hour, and only 15% insoluble material remained after a one hour treatment at 290 °C. However, the work up procedure applied by these research groups comprises extraction of both the filtrate and the filter cake as mentioned above. The fraction of oil obtained only from extraction of the monomer rich filtrate reveals a yield of merely 22 wt.%. The oil obtained from extraction of the filter cake however contains primarily oligomers [7].

As the aim of our research is the production of high valuable chemicals, we here suggest an optimized work up procedure, where an oil is obtained, containing merely monomers and dimers, the main products of interest. The procedure also allows the separation of coke from unconverted lignin and high molecular lignin units. Furthermore, we have elaborated a selection of extracting agents which allow tailoring the properties of the oil, by selectively extracting compounds with desired functionalities.

4.2 Experimental

The experiments were carried out discontinuously in stainless steel tube autoclaves at 300°C and a reaction time of 40 min. Organosolv lignin was purchased from Sigma Aldrich. The autoclaves were filled with 5 mL of a 10 wt.% lignin/ 4 wt.% NaOH aqueous solution. The reactors were set in a preheated alumina block which was tumbled to ensure thorough mixing. After the reation, the autoclaves were quenched to room temperature with water. The reactor contents and water washings were combined.

The continuous experiments (conducted by the ICT Karlsruhe) were carried out in a pilot plant with a maximum temperature of 400°C and a maximum pressure of 300 bar. Figure 4.2 shows the flow diagram of the pilot plant. Two types of organosolv lignin were used; a purchased one from Sigma Adlrich and a self manufactured one. The continuous experiments were all conducted with a concentration of 2.5 wt.% lignin in 0.5 wt.% NaOH at 250 bar. The reaction times varied between 30 seconds and 15 minutes and reaction temperatures between 250°C and 350°C were applied.

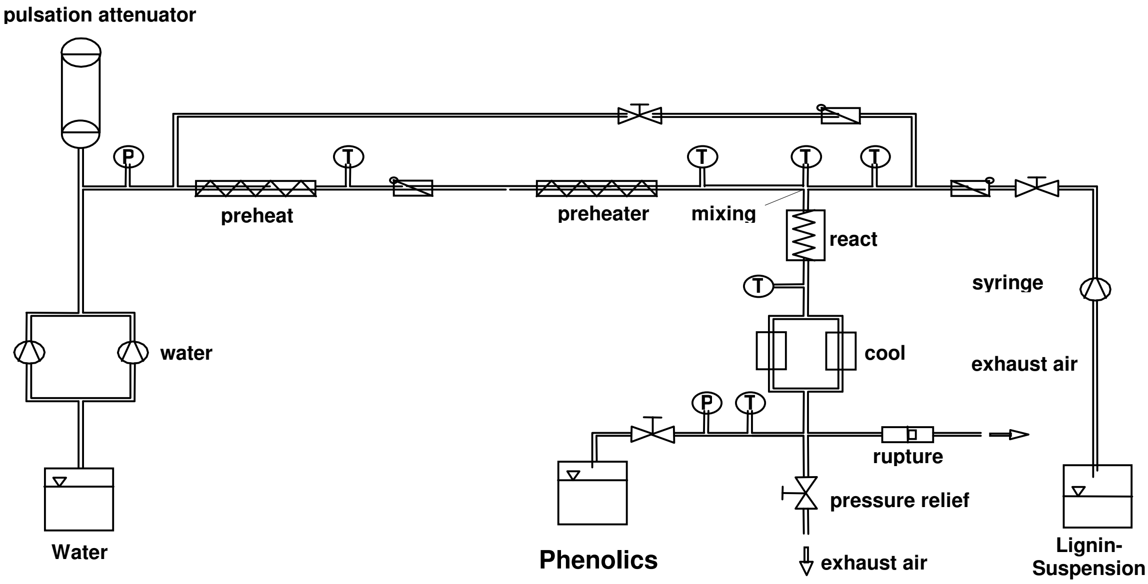


Figure 4.2: Flow scheme of the continuous working setup

The work up procedure of all experiments was the same, and is described in the following. The monomeric reaction products were identified by GC/MS and quantified by GC/FID-analysis using a “Shimadzu” GCMS – QP 20105 gas chromatograph-mass spectrometer (column: HP 5 crosslinked 5 % PhME Siloxane). For this purpose the oil was dissolved in ethyl acetate, transfered into a 50 ml calibrated metering flask and leveled with further ethyl acetate. The concentration of the main monomeric products was determined by calibrating the peak area with ethyl acetate solutions of known concentration of these compounds. Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was employed to determine the molecular weight distribution of the product oil. Therefore, solutions of approximately 10 wt.% oil in H_2O/acetonitrile (1:1) with 1 wt.% trifluoroacetic acid were prepared. LDI-TOF mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer. The lignin and products were analyzed for their carbon content, employing a CHN analysis.

Oil yield was calculated as following:

$$OilYield[wt.\%] = \frac{m(oil)}{m(lignin_{applied})} \cdot 100 \qquad \textbf{(1)}$$

4.3 Results

Figure 4.1 shows a scheme for the elaborated work up procedure. The extraction agent depends on the desired product spectrum and will be discussed in detail later on. The first step is the acidification of the reaction mixture.

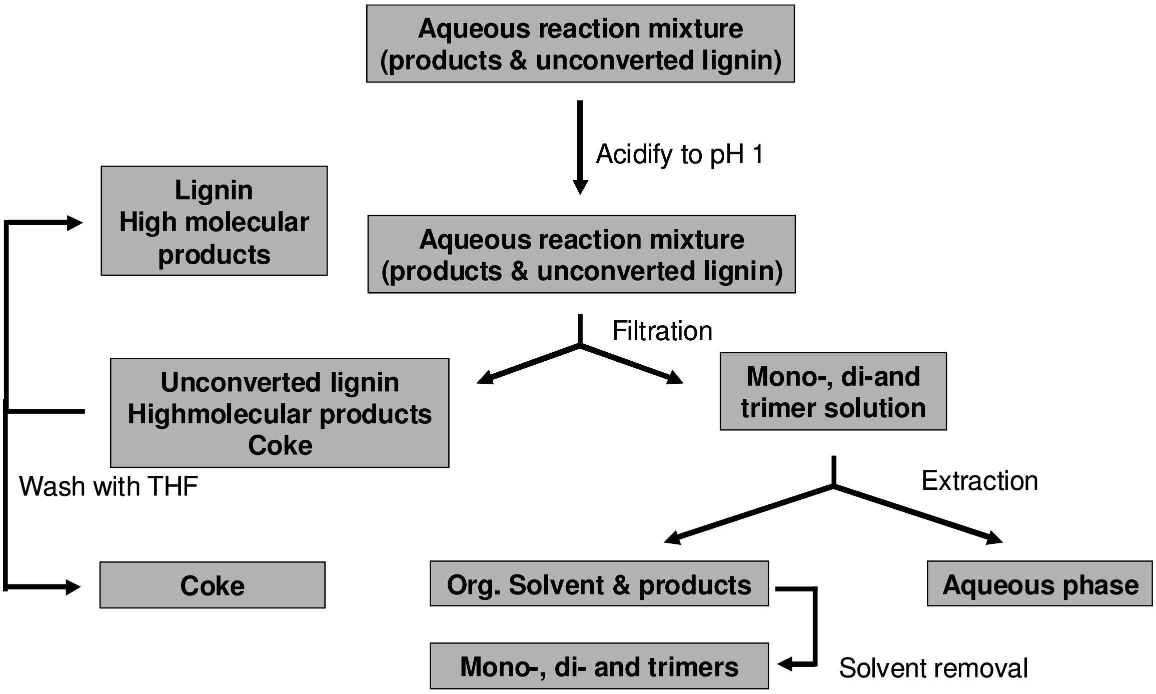


Figure 4.3: Elaborated work up scheme to improve oil quality

However, if a heterogeneous catalyst was applied during the reaction, it should first be removed by filtration of the aqueous reaction mixture. Then the mixture is acidified with HCl to a pH value of 1. This results in the precipitation of unconverted lignin and high molecular lignin cleavage units. The unconverted lignin would also precipitate at higher pH values, however Table 4.2 shows that an increasing amount of oil is extracted with decreasing pH. To determine the extent of extracted products depending on the pH value, the reaction mixture was repeatingly extracted with decreasing pH.

Table 4.2 shows that at a pH of 5 only 76 wt.% of the total oil was extracted. When increasing acidity to lower pH values and extracting the reaction mixture the oil yield increased. A maximum oil yield was obtained at a pH value of 1.

Table 4.2: Influence of pH on the extent of oil extraction

Temperature [°C]	Pressure [bar]	Residence time [sec]	Reaction mixture [wt.%]	pH	Weight oil [g]	Oil yield [wt.%]
350	250	600	2.5% Lignin 0.5% NaOH	5	2.91	16.3
				3	0.77	4.3
				1	0.15	0.8

After adjustment of the pH, the solids were removed from the suspension by filtration, dried and weighed. The unconverted lignin as well as the precipitated oligomers were retrieved from the filter cake by washing with THF, while possibly formed coke remained behind. The acidic filtrate was then repeatedly extracted with an organic solvent to obtain the lignin cleavage products. The choice of extraction solvent depends on the future application and, therefore, on the desired properties of the oil. Table 4.4 compares the monomeric compounds obtained from extraction with the following agents: Ethyl acetate (EA), methylene chlorid, methyl isobutyl ketone (MIBK) and toluene. We see that the applied extracting agent has a strong effect on the total content of monomers in the oil. Furthermore, the nature of the extracted monomers can be selected, depending on the choice of extracting agent. The term unknown compounds refers to products with a boiling point too high to be analyzed via GC and are assumed to be di-and trimers. The monomers are classified into groups depending on their functionalities and the corresponding yields are summarized in the following table. Extracting with toluene, an oil was obtained with only a small amount of oligomers (33.4 %). The majority (88 %) of monomers are mono – and dimethoxy phenols (guaiacol, syringol and their derivatives). The affinity of toluene towards catecholic compounds is very low (2.4 %).

The same trend is observed for methylen chloride, yet to a smaller extent. Ethyl acetate and methyl isobutyl ketone likewise show very similar extraction behaviors among each other. In contrast to methylen chloride and toluene, these solvents show a high affinity towards catecholic compounds (16.8 and 14.9 % respectively), while only 23.6 and 20 % of mono and dimethoxy phenolic compounds are extracted.

After extraction the solvent is removed with a rotor vapour to obtain the product oil. Unconverted lignin can be regained by washing the filter cake with tetrahydrofuran. Lignin is dissolved during this procedure while coke is insoluble and can be removed by filtration.

Apart from the oil, other lignin derived products are found in the aqueous phase containing hydrophilic compounds (ethanol, methanol and heavier hydrophilic aromatics) that were not extracted during the separation procedure.

Methanol is formed from hydrolysis of the methoxy groups on the aromatic rings, forming methanol and *o*-hydroxy phenolic compounds, while ethanol is likely to originate from the partially hydroxyl substituted alkyl side chains. An indication here for, is that only traces of alkylated monomers were detected in our studies.

Gas and coke are also formed from lignin, but solely above 320°C. A small amount of product is lost during the work up procedure in the form of a gas, which is liberated upon acidification of the reaction mixture.

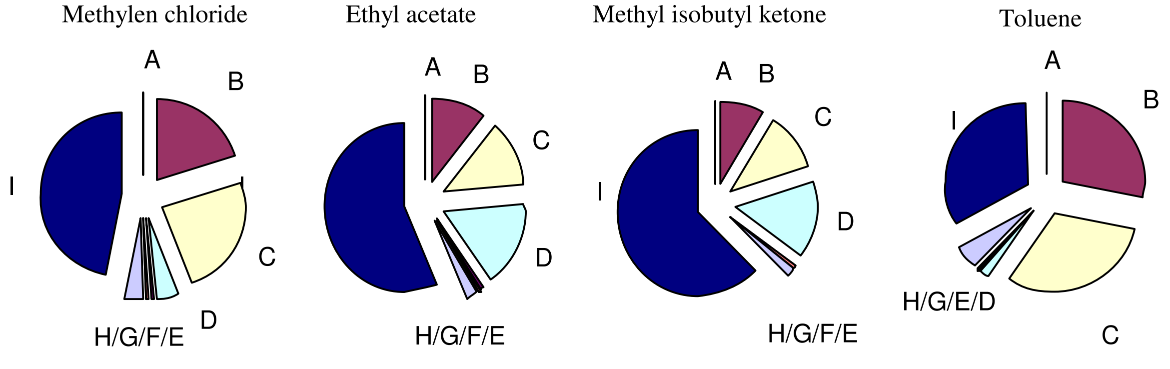
Table 4.3: Mass balance over products obtained from 10 wt.% lignin and 4 wt.%NaOH at 300°C

Products	Yield [wt.%]
Unconverted lignin	80.2
Oil	11.5
Products in water phase	7.7
Total	99.4

The gas was verified as CO_2 by passing it into a $Ba(OH)_2$ solution and forming barium carbonate. CO_2 is dissolved in the reaction solution or present as sodium carbonate, which is liberated upon acidification [12, 13]. The low amount of CO_2 liberation observed upon acidification of the product mixture is in agreement with the satisfactory mass balance and shows that the amount is negligible.

Yields presented in the table are based on weight percent. CHN analysis of the lignin before and after treatment yielded 65.7 and 70.9 wt.% carbon, respectively. Thus, lignin undergoes a structural modification during the reaction. The carbon content of the oil obtained by extraction is 62.2 wt.%, while that of the oil obtained by water removal of the aqueous phase is only 47.7 wt.%.

Table 4.4: Comparison of compounds obtained by extraction of a product mixture from continuous lignin depolymerization experiment when extracting with methylene chloride, ethyl acetate, methyl isobutyl ketone or toluene.

	Compounds in wt.% in respect to oil weight			
	Methylen chloride	Ethyl acetate	Methyl isobutyl ketone	Toluene
Phenol [A]	0.3	0.2	0.2	0.2
Guaiacol & mono methoxy phenols [B]	20.2	10.9	9.1	27.8
Syringol & dimethoxy phemols [C]	23.4	12.7	10.9	31.1
o-hydroxy phenol derivatives [D]	4.6	16.5	14.7	2.1
m-hydroxy phenol derivatives [E]	0.4	0.3	0.2	0.3
Benzene & 1, 2, 3, triol derivatives [F]	0.5	0.7	0.6	0.0
Alkyl phenols [G]	0.3	0.2	0.2	0.4
Di- and trimethoxy alkyl benzenes & alkyl benzenes [H]	3.2	1.7	1.6	4.8
Unknown compounds [I]	47.1	56.9	62.5	33.4
				

4.4 Discussion

To obtain high quality oil, consisting merely of monomers and dimers, we recommend only the filtrate to be extracted. Figure 4.4 shows a LDI-TOF/MS spectrum of the oil obtained by extracting the filtrate from a batch experiment. After the reaction, the product mixture was worked up as described above and extracted with ethyl acetate. The average weight of monomeric compound is considered to be 180 g/mol. The LDI spectrum shows that the main product distribution is below 350 g/mol and the highest intensity is found for 210 g/mol. Therefore, we have obtained high quality oil containing primarily mono - and dimers.

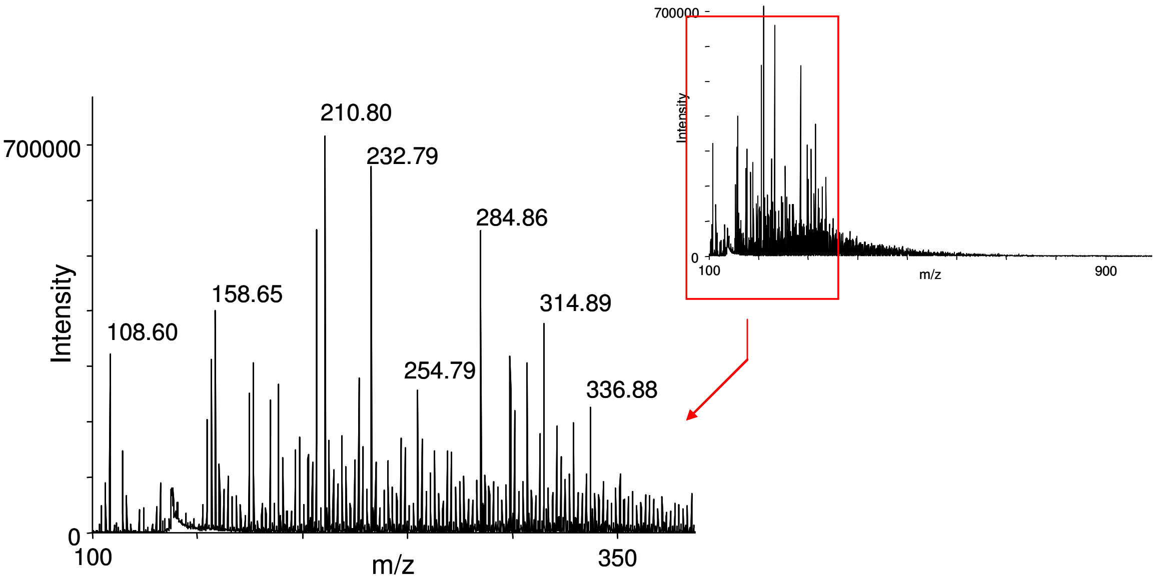


Figure 4.4: LDI-TOF spectrum of oil obtained from extraction with ethyl acetate

Figure 4.5 shows the LDI-TOF/MS spectrum obtained from extraction of the corresponding filter cake with diethyl ether as described in literature [6-9]. We see that the fraction of monomers is much lower than in the oil obtained from extracting merely the filtrate. Moreover, the total product distribution is shifted towards higher molecular weights with the highest intensity found at 326 g/mol.

Thus, oil received by extracting both the filtrate and the filter cake posseses a wider product distribution with a much higher content of di- and trimers.

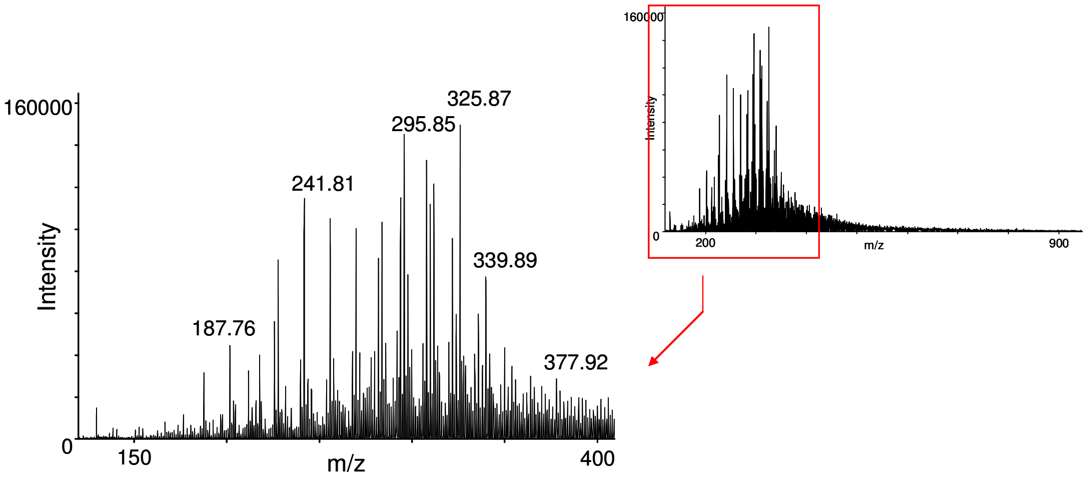


Figure 4.5: LDI spectrum of filter cake extracted with diethyl ether

From Table 4.4 we have seen that the fraction of monomers in the oil as well as the property of the oil (functionalities of monomers) can be adjusted by choosing an appropriate extracting agent. The highest content of monomers in the oil (66.7%) is achieved with toluene, where 58.9 wt.% of the oil consists of mono – and dimethoxy phenols as guajacol and syringol. The total amount of monomers found in the oil decreases in the sequence: Toluene > methylene chloride > EA > MIBK. Methylen chloride also shows a high affinity towards mono – and dimethoxy phenols (43.6 wt.% of the oil). Only low yields of these compounds are found when extracting with ethyl acetate and MIBK, while yields of ortho-hydroxy phenolic compounds are 3-8 times higher than for touluene and methylene chloride. If the main criterion however, is to achieve a high monomer yield from extraction, independent of the type of monomer or the remaining oligomeric content in the oil, MIBK and EA yield the best results.

Table 4.5: Comparison of oil yield, monomer yield and monomer content obtained from extraction for a selection of agents. Yields are normalized with respect to toluene.

	Toluene	CH_2Cl_2	EA	MIBK
Yield Oil	1	1.3	2.6	3.1
Monomer Content	66.6	52.9	43.1	37.5
Yield Monomers	1	1.03	1.69	1.75

The monomer yields obtained from extraction with toluene and methylen chloride are 41-43 % lower. If high yields of oil are demanded regardless of monomer and oligomer content, MIBK is the extraction agent to choose, as the extracted oil yield is 3.1 times higher than for toluene. These results are summarized in Table 4.5. The yields are normalized with respect to toluene.

4.5 Conclusion

Hydrothermal depolymerization of lignin yields a wide product spectrum. Products consist not only of the monomeric lignin building blocks, but to a large extent of oligomers and polymers. However, when the aim of lignin depolymerization is the production of chemicals a high monomeric content is desirable. The elaborated work up procedure presented here, allows separation of monomers and oligomers from unconverted lignin and polymeric products by acidification of the reaction mixture in the first process step. A maximum amount of products is extracted if the product solution is acidified to a pH of 1.

It was shown that following this procedure a product oil is obtained consisiting mainly of monomers and dimers, which is of great interest for chemical production. Further, by washing the filter cake with THF, unconverted lignin can be separated from coke and regained.

A selection of extracting agents was elaborated, which allow either maximizing oil yield or monomer yield, and tailoring the properties of the oil, by selectively extracting compounds with desired functionalities.

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Chapter 5

On the mechanism of base catalyzed depolymerization of lignin

Abstract

The products of base catalyzed liquid phase hydrolysis of lignin depend markedly on the operation conditions. Varying temperature, pressure, catalyst concentration and residence time the yield of monomers and oligomers from depolymerized lignin can be adjusted It is shown for the first time that monomers of phenolic derivatives are the sole primary products of base catalyzed hydrolysis and that oligomers form subsequently. Oligomerization reactions lead to the frequently observed di,-tri- and tetramers of these phenols.

5 On the mechanism of base catalyzed depolymerization of lignin

5.1 Introduction

The interest in lignin has been growing steadily over the last decade. Lignin constitutes about 20 % of terrestrial biomass and is, therefore, the most abundant organic material. The different lignin monomer units (*p*-coumaryl alcohol, coniferyl- and sinapyl alcohol) as well as the multiplicity of bond types, illustrate the heterogeneity of the molecule [1-3]. Three general routes for lignin conversion exist: (i) gasification to produce syngas [4, 5], (ii) production of biooil through pyrolysis or liquefaction [6, 7] and (iii) hydrolysis to produce monomer and/or oligomer units [8, 9] The first two routes demand severe conditions, while hydrolysis is comparatively mild. Hydrolysis of cellulose, the other main constituent of biomass, can effectively be realized with high monomer yields. The hydrolysis of lignin however, remains a great challenge due to its recalcitrant structure.

So far, studies on the reaction routes of lignin depolymerisation have lead to different conclusions. An investigation on the reactivity of phenoxy linkages in lignin showed that between 200 and 400°C bonds between aromatic units are cleaved, of which the β-O-4 ether bond (Figure 5.1) is the weakest [10]. Decomposition chemistry becomes more complex at higher temperatures as secondary reactions occur, and recombination of carbon centered radicals leads to the formation of strong carbon-carbon bonds and thus coke and tar formation. Li et al. proposed an acidolysis of the β-O-4 ether bond as the dominant reaction during hydrothermal lignin treatment [11]. The organic acids catalyzing the process are hereby generated during the treatment. It is stated that repolymerization takes place simultaneously with acidolysis and that both reaction pathways posses the same intermediate state, namely a carbenium ion, generated at the α carbon atom. The ether bond in the intermediate can then either be cleaved (depolymerization) or be attacked by an adjacent aromatic ring forming a stable carbon-carbon bond (repolymerization). McDonough et al. [12] propose that during alkaline organosolv delignification processes deprotonated hydroxyl groups in α–position of the β-O-4 ether bond serve as nucleophile in displacing the neighboring aroxy substituent by forming an oxirane ring. The oxirane is then opened by addition of a hydroxide ion forming a glycol grouping.

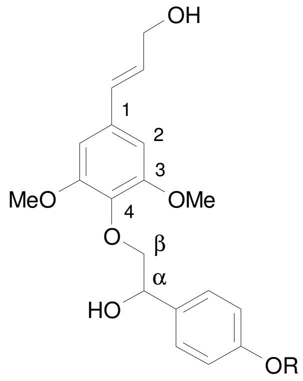


Figure 5.1: Fragment of lignin with β-O-4 ether bond

Britt et al., studied the pyrolysis of β-alkyl aryl ethers with dispersed acid catalysts to investigate the relative rates of ionic reactions versus free-radical reactions in thermal depolymerisation of lignin [13]. Their results suggest that the thermal degradation of lignin principally follows a free radical reaction pathway. Depolymerization of lignin in supercritical water was studied by Man et al. [14]. They consider hydrolysis and dealkylation to occur, generating reactive low molecular weight fragments as formaldehyde and phenolic compounds. Literature on lignin depolymerization does not only show that many different mechanistic models of lignin depolymerization and the resulting reactive intermediates exist, but also outline clear limitations to lignin depolymerization. No matter to which conditions lignin is exposed, if work up procedures are comparable, each approach to depolymerize its structure does not exceed yields of approximately 20 -23 wt.% of product oil [8, 15-17].

The two most frequent approaches for hydrothermal lignin treatment document in literature are the depolymerization in supercritical water [8, 18], and below the supercritical state in alkaline media [19, 20, 21, 22]. The latter process is referred to as “base catalyzed depolymerization” (BCD). Recently, a process for converting lignin into a blending component for gasoline has been explored [21]. It consists of two steps, i.e., a base catalyzed depolymerization followed by a hydroprocessing step. Lignin conversions of up to 92 % have been claimed, but the work up procedure applied comprises extraction of both the filtrate and the filter cake after acidification and precipitation. The fraction of oil obtained only from extraction of the monomer rich aqueous phase again led to yields of merely 22 wt.%. The filter cake, in turn, contains primarily oligomers [23].

The work we present here is based on the BCD process mentioned above, aiming not to convert lignin to biofuels or gasoline additives, but to produce high value phenolic chemicals, preferably monomers. To achieve this, understanding of the mechanism of lignin depolymerization is essential. Here, we report the effects of operation conditions, i.e., lignin/NaOH weight ratio, lignin concentration, temperature, pressure and residence time, on oil yield and monomer selectivity of the oil. Moreover, kinetic studies on products formation and an attempt to understand the mechanism for lignin depolymerization are presented.

5.2 Experimental

Experiments were conducted in stainless steel flow continuous reactors. For the initial experiments a tube reactor with a total volume of 0.87 cm^3 was chosen. Organosolv lignin obtained from Sigma Aldrich was applied for all experiments. Lignin depolymerization was performed in an aqueous basic solution with lignin/NaOH weight ratios varying from 2.5 to 5. The reaction mixtures were fed to the reactor with a HPLC pump [*Gilson*, 307 pump]. To investigate the effect of lignin concentration, the lignin/NaOH weight ratio was kept constant at a 2.5, while the concentration of lignin was varied between 2.5 and 10 wt.%. The temperature (240-340°C) was set by means of a Eurotherm, 2416controller and the pressure (250-315bar) was adjusted via a regulator [*Swagelok*]. After exiting the reaction zone the product mixture was expanded to atmospheric pressure and collected for work up before product analysis was conducted. To realize experiments at residence times shorter than 1 min, a reactor with a total volume of 8 cm^3 was necessary. For this system a second flow of preheated water was fed to the reactor by a second HPLC pump. Both flows were allowed to mix right before entering the reactor. The scheme of the set up is depicted in Figure 5.2.

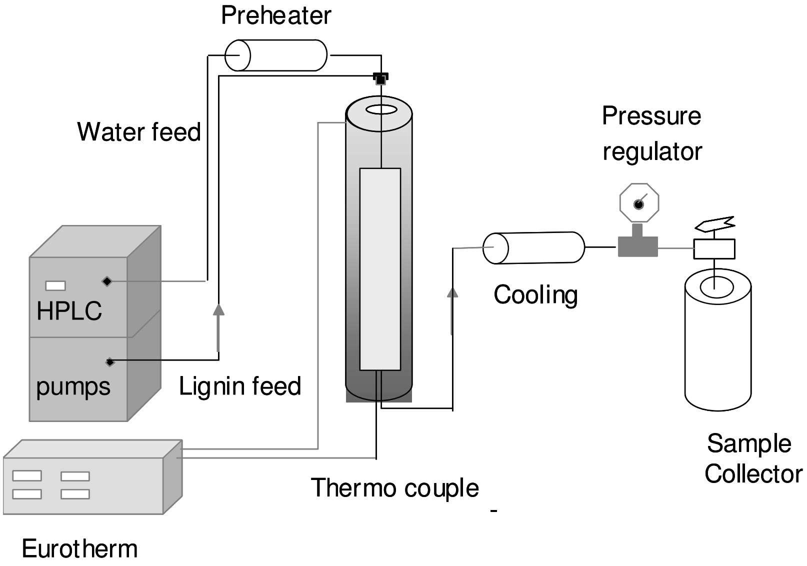


Figure 5.2: Continuous set up with water preheater and cooler

A scheme of the work up procedure is shown in Figure 5.3. The reaction mixture is first acidified with HCl to a pH value of 1. This results in the precipitation of unconverted lignin and high molecular lignin cleavage units. After adjusting the pH, the solids are removed from the suspension by filtration, dried and weighed. The unconverted lignin as well as the precipitated oligomers can be retrieved from the filter cake by washing with THF while possibly formed coke remains behind. The acidic filtrate is then repeatedly extracted with ethyl acetate to obtain the formed monomers, dimers and trimers. After extraction ethyl acetate is removed and dark brown oil is received which is dried overnight at 60°C before being weighed. Lignin conversion, oil yield, and monomer yield as well as selectivity are calculated as following:

$$LigninConversion[wt.\%] = \frac{\lfloor m(lignin_{applied}) - m(lignin_{THFwashedFiltercake})\rfloor}{m(lignin_{applied})} \cdot 100 \qquad \textbf{(1)}$$

$$Yield\,\mathrm{Pr}\,oduct[wt.\%] = \frac{m(product)}{m(lignin_{applied})} \cdot 100 \qquad \textbf{(2)}$$

Beside the products contained in the oil, coke and gaseous products formed at elevated temperatures, ethanol, methanol and some organic products remain in the aqueous phase during extraction. A small amount of product, i.e., CO_2 dissolved in water or present as sodium carbonate is lost as it is liberated during the acidification step.

The monomeric reaction products were identified by GC/MS and quantified by GC/FID-analysis using a “Shimadzu” GCMS – QP 20105 gas chromatograph-mass spectrometer (column: HP 5 crosslinked 5 % PhME Siloxane). For this purpose the oil was dissolved in ethyl acetate, transferred into a 50 ml calibrated metering flask and leveled with further ethyl acetate. The concentration of the main monomeric products was determined by calibrating the peak area with ethyl acetate solutions of known concentration of these compounds.

Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was employed to determine the molecular weight distribution of the product oil. Therefore, solutions of approximately 10 wt.% oil in H_2O/acetonitrile (1:1) with 0.1 wt.% trifluoroacetic acid were prepared. LDI-TOF mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer. The lignin and products were analyzed for their carbon content, employing CHN analysis.

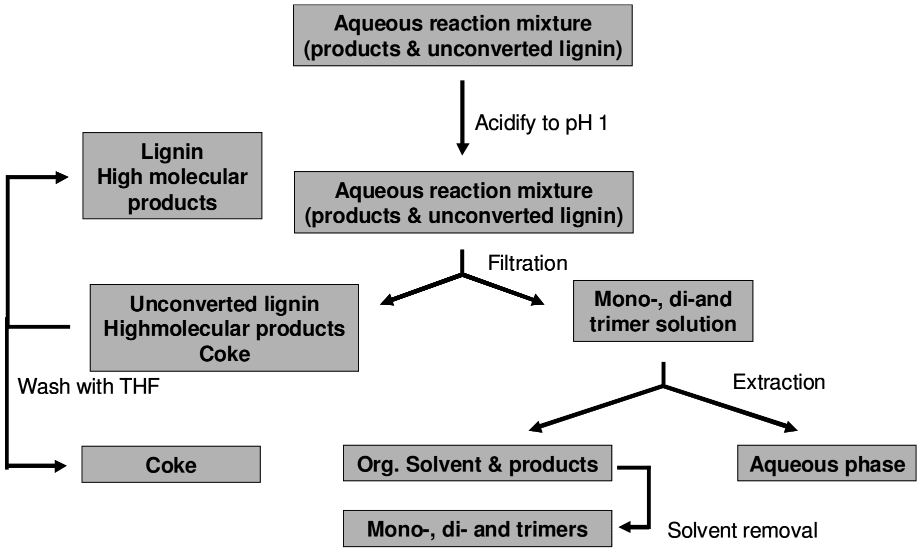


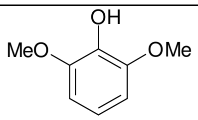
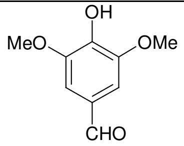
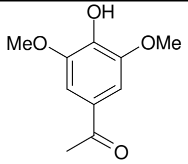
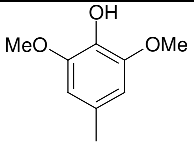
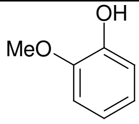
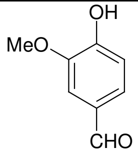
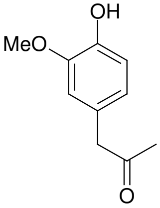
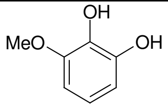
Figure 5.3: Separation sequence for product and lignin recovery

Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was employed to determine the molecular weight distribution of the product oil. Therefore, solutions of approximately 10 wt.% oil in H_2O/acetonitrile (1:1) with 0.1 wt.% trifluoroacetic acid were prepared. LDI-TOF mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer. The lignin and products were analyzed for their carbon content, employing CHN analysis.

5.3 Results

The main product obtained from the base catalyzed depolymerisation of lignin is dark viscous oil. LDI-TOF/MS measurements show that it contains both monomers and oligomers. Table 5.1 summarizes the main monomeric components and their composition in an oil, obtained from 5 wt.% lignin and 2 wt.% NaOH at 300°C and 250 bar. The monomers were identified by GC/MS and quantified by GC/FID to belong to syringyl and guaiacyl compounds. Syringol and its derivatives represent the largest fraction with 82% at a residence time of 2.5 min. Apart from the oil, other lignin derived products are found in the aqueous phase containing hydrophilic compounds (ethanol, methanol and heavier hydrophilic aromatics) that were not extracted during the separation procedure.

Table 5.1: Concentration of various components in the monomeric fraction of an oil obtained from lignin depolymerization at 300°C, 250 bar and a residence time of 2.5 min (lignin 5 wt.%, NaOH 2 wt.%).

Monomer	**Chemical formula**	**Structure**	**Conc. [wt.%]**
Syringol	$C_8H_{10}O_3$		40.9
Syringyl aldehyde	$C_9H_{10}O_4$		18.0
3, 5-dimethoxy-4-hydroxy acetophenone	$C_{10}H_{12}O_4$		16.3
4-methyl-syringol	$C_9H_{12}O_3$		6.7
Guaiacol	$C_7H_8O_2$		10.5
Vanillin	$C_8H_8O_3$		3.5
4-hydroxy-3methoxy phenylacetone	$C_{10}H_{12}O_3$		2.3
Ortho-methoxy-catechol	$C_7H_8O_3$		1.6

After water removal from the aqueous phase, NaOH is isolated by dissolving the organics in acetone and filtration of the suspension. Removal of acetone yields a second fraction of oil having a lower viscosity than the first. The compounds remaining in the aqueous phase after extraction were found to be ethanol and methanol as well as heavier hydrohpilic aromatic compounds. NMR measurements of this oil show that no aliphatic compounds are present. The main NMR peaks can be assigned to aromatic protons, methoxy groups and aldehyde groups. Additionally, large amounts of hydroxy and phenolic protons explain the high hydrophilicity of these compounds. The yield of the products remaining in the aqueous phase increases with temperature. At 320°C 10.7 wt.% were found in comparison to 7.7 wt.% at 300°C. Bergstrom reports 15.4 wt.% water soluble products (methanol, ethanol and propanol) from base catalyzed lignin depolymerisation [24]. Methanol is formed by hydrolysis of the methoxy groups on the aromatic rings, forming methanol and *o*-hydroxy phenolic compounds, while ethanol is likely to originate from the partially hydroxyl substituted alkyl side chains. An indication here for, is that only traces of alkylated monomers were detected in our studies.

Gas and coke are also formed from lignin, but solely above 320°C. A small amount of product is lost during the work up procedure in the form of a gas, which is liberated upon acidification of the reaction mixture. The gas was verified as CO_2 by passing it into a $Ba(OH)_2$ solution and forming barium carbonate. CO_2 is dissolved in the reaction solution or present as sodium carbonate, which is liberated upon acidification [15]. The low amount of CO_2 liberation observed upon acidification of the product mixture is in agreement with the satisfactory mass balance and shows that the amount is negligible.

Yields presented in the table are based on weight percent. CHN analysis of the lignin before and after treatment yielded 65.7 and 70.9 wt.% carbon, respectively. Thus, lignin undergoes a structural modification during the reaction. The carbon content of the oil obtained by extraction is 62.2 wt.%, while that of the oil obtained by water removal of the aqueous phase is only 47.7 wt.%.

Table 5.2: Mass balance over products obtained from 10 wt.% lignin and 4 wt.%NaOH at 300°C and 250 bar .

Products	Yield [wt.%]
Unconverted lignin	80.2
Oil	11.5
Products in water phase	7.7
Total	99.4

The base catalyzed depolymerization of lignin was realized by the addition of NaOH. The effect of residence time on oil yield was investigated at 300°C and 250 bar. A 10 wt.% lignin, 4 wt.% NaOH solution was used for this purpose. The results are shown in Figure 5.4. We find that the oil yield increased up to 23 wt.% for a residence time of 4.2 min.

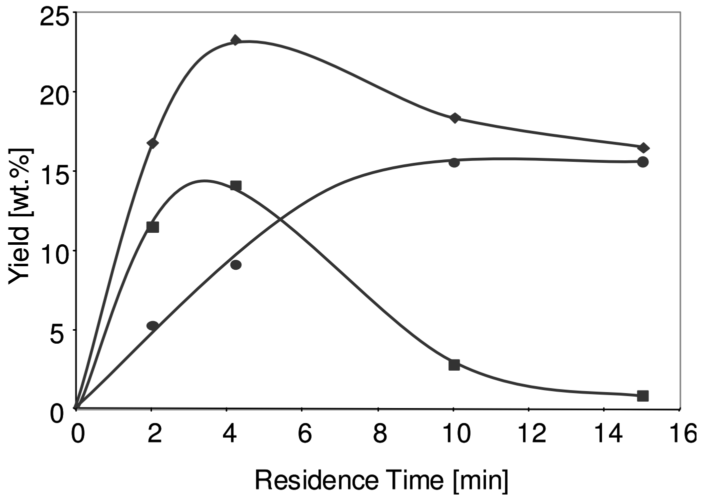


Figure 5.4: Oil yield dependence on residence time at 300°C and 250 bar, for a 10 wt.% lignin/ 4 wt.% NaOH solution (♦ oil, ● oligomers, ■ monomers).

Beyond this residence time yields declined. Separation of the total oil yield in monomer and oligomer yield shows that oil formation is a consecutive reaction where the monomers are the primary products. Polymerization of the monomers leads to the formation of oligomeric compounds. At a residence time of 15 min the obtained oil is comprised mainly of oligomers.

Experiments regarding temperature dependence of the reaction were conducted under the same conditions, but with a constant residence time of 4.4 min. Temperature was increased from 240 to 340°C. While lignin conversion increased almost monotonously with temperature, the gap between conversion and oil yield increased exponentially. Only at low temperatures the selectivity for oil formation was 100 %. At the highest temperature used (340°C), only one third of the converted lignin remained in the organic phase as oil. The major part is transformed to coke, hydrophilic organics in the aqueous phase and gaseous products. A maximum oil yield of 23 wt.% was reached at 300°C. At this temperature the oil is comprised of 72 % oligomers and 28 % monomers. With increaseing temperatures oil yield declines due to the formation of the side products mentioned above.

The influence of NaOH concentration on the yield of the oil, oligomer and monomer yield is depicted in Figure 5.6. Experiments were conducted with 10 wt.% lignin at 320°C, 250 bar and a residence time of 4.4 min.

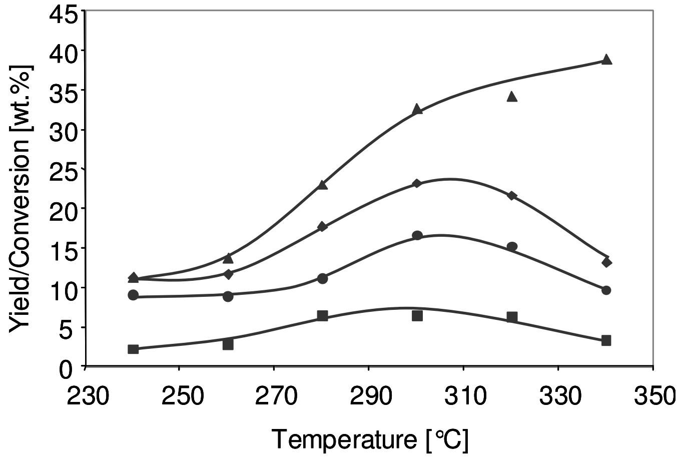


Figure 5.5: Temperature effect on oil yield and lignin conversion at 250 bar and a residence time of 4.4 min for a 10 wt.% lignin/ 4 wt.% NaOH solution (▲ conversion, ♦ oil, ● oligomers, ■ monomers).

An increase of the NaOH concentration has a clear positive effect on oil and monomer yield, but in different ways. While monomer yield increases linearly, the formation of oil increases strongly with NaOH concentration up to a value of 2.5 and then only slightly continues increasing. Oligomer formation behaves similarly but reaches a plateau of approximately 15 wt.% above a NaOH conentration of 2.5 wt.%.

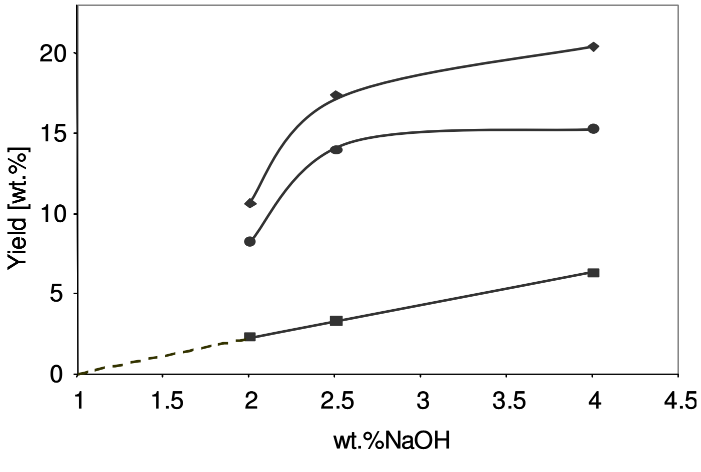


Figure 5.6: Influence of NaOH concentration on product yield with 10 wt.% lignin at 320°C, 250 bar and a residence time of 4.4 min (♦ oil, ● oligomers, ■ monomers).

An important criterion to determine the success of lignin depolymerization and the quality of the obtained oil is the monomer content. Figure 5.7 compares the LDI-TOF spectra of the oils obtained from the solutions with a NaOH concentration of 2.5 and 4. The product spectrum for the 2.5 solution covers a molecular weight range from approximately 100 to 400 g/mol while intensities are highest in the range of 100 to 350 g/mol. The solution with the higher lignin content generated a product spectrum shifted to molecular weights up to 570 g/mol and much lower intensities in the molecular weight range of monomeric products (< 180 g/mol).

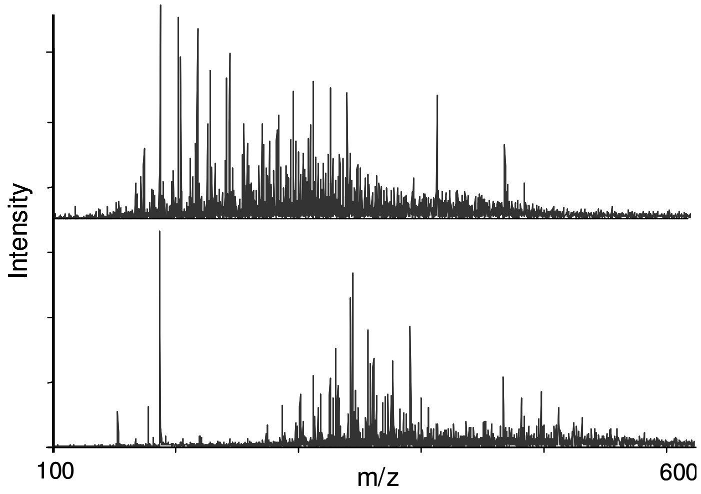


Figure 5.7: Comparison of LDI TOF spectra obtained from oil with NaOH concentrations of 2.5 (top) and 4 (bottom).

To obtain high yields of high quality oil (maximum of low molecular weight products) and at the same time assure a fully homogeneous lignin solution, further experiments were conducted with a constant lignin/NaOH weight ratio of 2.5.

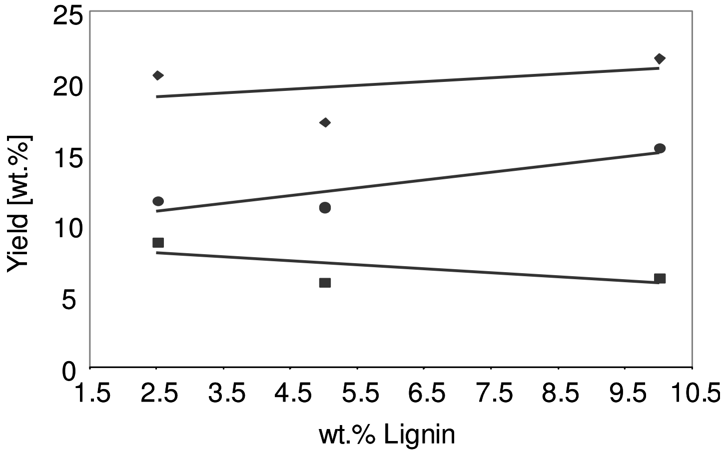


Figure 5.8: Effect of lignin weight pertcentage on oil yield and monomer selectivity at 320°C, 250 bar, 4.4 min residence time and a lignin/NaOH weight ratio of 2.5, (♦ oil, ● oligomers, ■ monomers).

Figure 5.8 shows the effect of lignin concentration on the product yields in the range from 2.5 to 10 wt.%. The oil yield was hardly influenced by the lignin content, while a clear trend is observed for monomer and oligomer yields. The highest Monomer yield of 9 wt.% was obtained for lignin solution of 2.5 wt.% and gradually decreases with higher lignin concentrations. Oligomer yield, however reaches its highest value of 15 wt.% at 10 wt.% lignin. Lignin conversion declined modestly from 40 to 34 % when increasing lignin content from 2.5 to 10 wt.% (not shown).

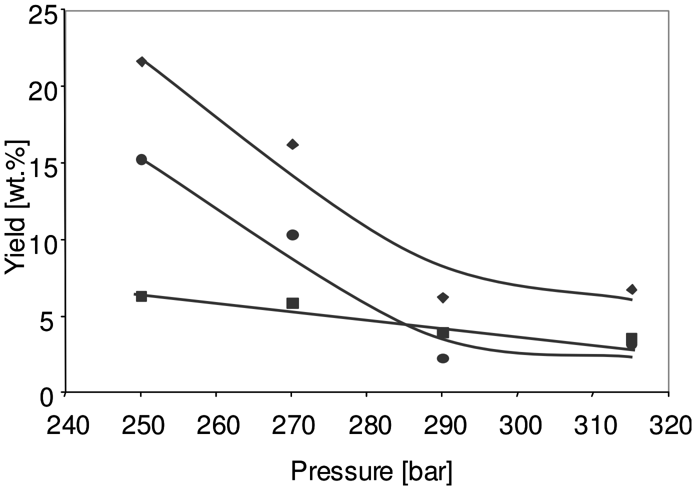


Figure 5.9: Influence of pressure on product yields 320°C, 4.4 min residence time, wt.(lignin/NaOH) = 2.5 and 10wt.% lignin (♦ oil, ● oligomers, ■ monomers).

To investigate the influence of pressure on the product yields experiments were conducted with 10 wt.% lignin, 4 wt.% NaOH at 320°C, a residence time of 4.4 min and pressure from 250 to 315 bar. Figure 5.9 shows that pressure increase had a negative effect on oil yield. It should be noted, however, that oligomer formation was suppressed much stronger than oligo fromation, which decreased from 15 to 3 wt.% with a pressure increase of 250 to 315 bar.

As compiled in Table 5.1, the monomers produced were mainly syringol, guaiacol and their derivatives. To explore the effect of severity (residence time/ temperature) on monomer distribution, the yields of the main monomeric products are plotted against residence time in Figure 5.10 and temperature in Figure 5.11. These experiments were conducted in the 8 cm³ tube reactor.

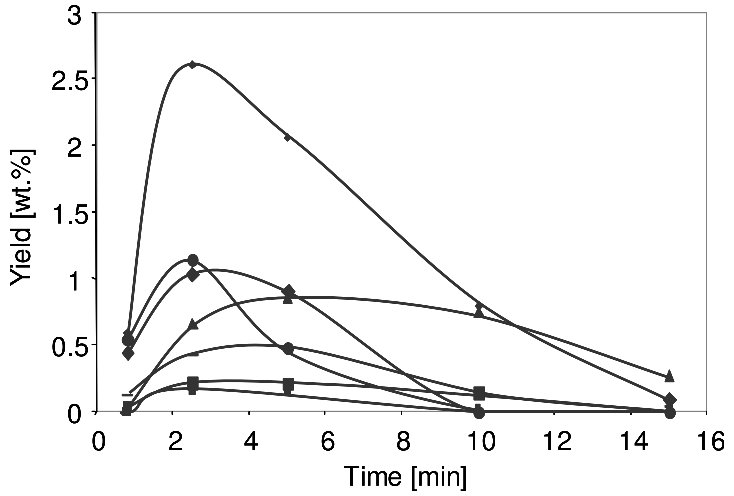


Figure 5.10: Monomer yields with time, 5 wt.% lignin, 2 wt.% NaOH, 250 bar and 300°C, (• syringol, ♦ 3,5-dimethoxy-4-hydroxyacetophenon, ● syringyl aldehyde, ▤ 4-methyl syringol, ▲ guaiacol, ■ 4-hydroxy-3-methoxy phenylaceton, ■ vanillin).

Low yields of other products, such as phenol, catechol, methyl catechol, *ortho*-methoxy catechol and veratrol were likewise detected, but for reasons of clarity are not included in the following figures. Syringol and its derivatives reached a maximum in concentration after 2.5 min and then decreased. Guaiacol compounds needed more severe conditions to be formed and were first detected after 2.5 min. The highest total monomer yield of 11 wt. % was reached at a residence time of 2.5 min. Syringol and its derivatives account for 93 % of the monomeric fraction under these conditions.

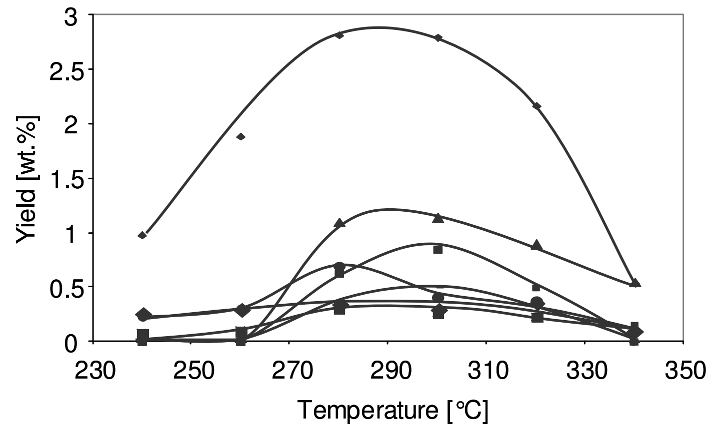


Figure 5.11: Monomer yields with temperature, 10 wt.% lignin, 4 wt.% NaOH, 250 bar and 4.4 min residence time, (• syringol, ♦ 3,5-dimethoxy-4-hydroxyacetophenon, ● syringyl aldehyde, ▤ 4-methyl syringol, ▲ guaiacol, ■ 4-hydroxy-3-methoxy phenylaceton, ■ vanillin).

Not only short residence times, but also low temperatures favor the formation of syringylic compounds (Figure 11). Experiments with a 10 wt.% lignin/ 4 wt.% NaOH solution at 250 bar and a residence time of 4.4 min showed that the only products present in significant amounts between 240°C and 260°C are syringol and its derivatives. Only at 280°C guaiacol and its derivatives were detected.

5.4 Discussion

Mechanism of lignin depolymerization

Literature suggests that lignin is comprised of up to 14 different bond types [1-3]. The majority of these bonds however are ether bonds. The most frequent ether bond is the β-O-4 bond shown in Figure 5.1 It belongs to the group of the aryl-alkyl ether bonds, which can be cleaved in subcritical water without a catalyst. In contrast, aryl aryl ether bonds are very stable, and likewise, carbon-carbon bonds between aromatic lignin units need more severe conditions to be broken. To facilitate the investigation of the different bond types in lignin a series of model compounds was selected and treated hydrothermally in the absence and the presence of base catalysts [25] [26]. The results showed that C-C bonds (aryl-aryl bonds and methylene bridging bonds) are not cleaved up to temperatures of 400°C. The aryl-aryl ether bond can only be cleaved beneath 400°C when applying an appropriate base catalyst. The aryl-alkyl ether bond, however, is readily cleaved above 270° C. Relating these findings to the base catalyzed depolymerization of lignin, it is concluded that among the bonds connecting the aromatic units predominantly aryl-alkyl ether bonds, specifically the β-O-4 ether bond will be cleaved under the conditions applied.

It is suggested that, during base catalyzed depolymerization of lignin, cleavage of the β-O-4 ether bond takes place heterolytically via the formation of a sodium phenolate derivative and a carbenium ion like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and, thus, polarizing the ether bond (see Figure 5.12). Consequently, the negative partial charge of the oxygen is increased and the energy necessary for heterolytic bond cleavage is reduced.

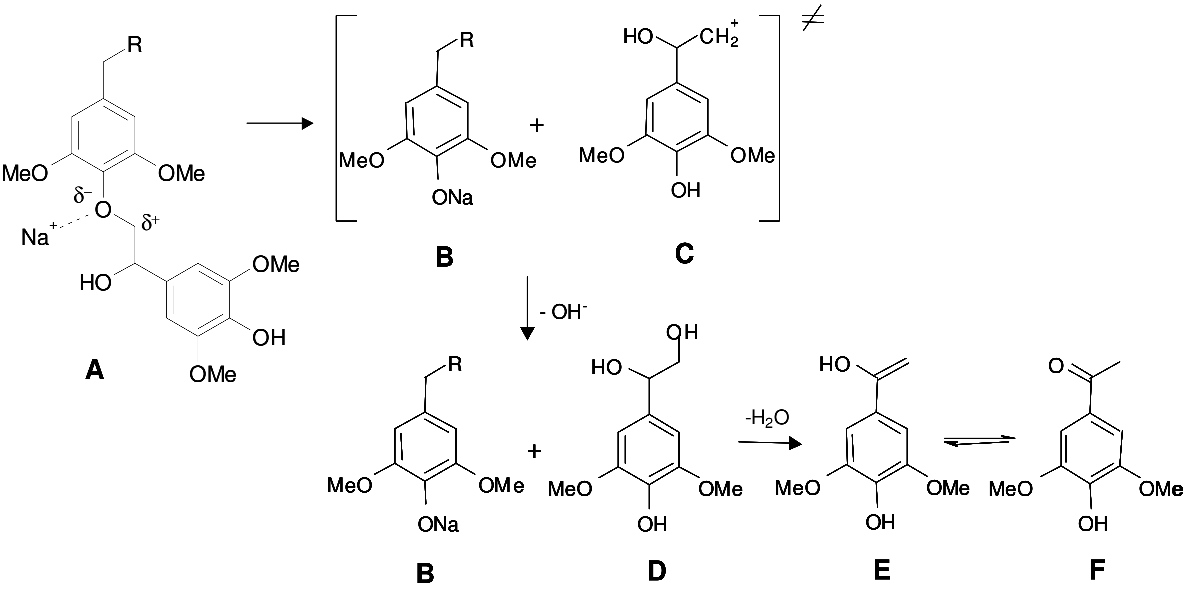


Figure 5.12: Cleavage of the β-O-4 bond and formation of syringyl derivatives

Figure 5.12 shows the formation of 3, 5-dimethoxy-4-hydroxyacetophenon (F), one of the main monomeric components at short residence times. In the first step heterolytic cleavage of the polarized ether bond (A) forms a natrium phenolate (B) and a carbenium ion in a transition state (C). Under the basic conditions applied, the carbenium ion is instantly neutralized by addition of a hydroxide ion, forming a glycolic grouping (D). Water is eliminated from the glycol group generating an enol (E) which rearranges to a keton forming 3, 5-dimethoxy-4-hydroxyacetophenon (F). If the α-carbon is not hydroxylated, an ethyl alcohol substituted syringol is formed, which is dealkylated and the main component syringol is obtained.

Even though the carbenium is a transition state and is immediately neutralized, its formation is determined by its reactivity. The reactivity of the formed carbenium ion depends on the capability of the substituents to disperse the positive charge (resonance stability). The presence of directional orbitals can account for its stability; thus, a carbon atom with available atomic p orbitals is an adequate option for charge delocalization. Therefore, the nature of the substituent is crucial for the stability of a particular carbenium ion. The π aromatic system would be excellently suited for charge delocalization. Appropriate substituents of the aromatic ring can further delocalize the positive charge and enhance stability of the carbenium ion. This is the case for a methoxy group in ortho position to the cleaved ether bond. In this position the resonance (+R) interaction of the methoxy group by far compensates for its inductive (-I) effect.

Thus, the formation of the carbenium ion from a syringylic unit (two methoxy groups) is energetically preferred as the transition state is more stable than for a carbenium ion of guaiacylic nature (one methoxy group). In both cases the carbenium ion rapidly rearranges to a tertiary carbenium species and is resonance stabilized by the aromatic system. However, as shown below, neighbouring methoxy groups expand the electron delocalization and further stabilize the carbenium intermediate.

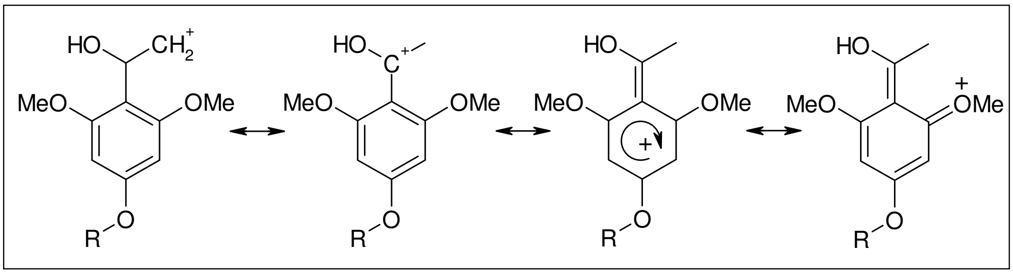


Figure 5.13: Resonance structures of methoxy substituted benzyl carbenium ions

The heterolytic ether bond cleavage via a carbenium ion also explains the findings compiled in Figure 5.10 and Figure 5.11. According to the Bell-Evans-Polanyi theory products with stabilized transition structures are formed preferably. As guaiacyl species contain only one methoxy group, they are kinetically unfavourable and are formed at a slower rate compared to syringyl derivatives (Figure 5.10).

Furthermore, the higher potential energy of the guaiacylic carbenium ion leads to higher energies necessary for the formation of guaiayclic compounds (Figure 5.11), and therefore explains why it is formed at higher temperatures than the guaiacyl derivatives.

The present results show that parallel to the heterolytic cleavage of the β-O-4 ether bond, dealkylation of side chains and hydrolysis of methoxy groups occurs and becomes more dominant under conditions of higher severity. Simultaneously, recombination of the highly reactive lignin cleavage products competes with depolymerization.

Mechanism of monomer oligomerization

The results show that monomer formation is limited by consecutive oligomerization reactions. Addition and condensation reactions of the highly reactive phenolic and catecholic monomers limit lignin depolymerization. Phenolate ions present in the alkaline media are likewise stabilized by delocalization of the charge. Due to resonance stabilization, the phenolate ion also exists as a carbanion with a negative charge in ortho – or para position of the phenolic hydroxyl group [12]. An example for such an oligomerization reaction is the aldol addition shown in Figure 5.14. Addition of the carbanion species (G) to the keton species (H) will, therefore, induce facile formation of carbon-carbon bonds (I) between these compounds.

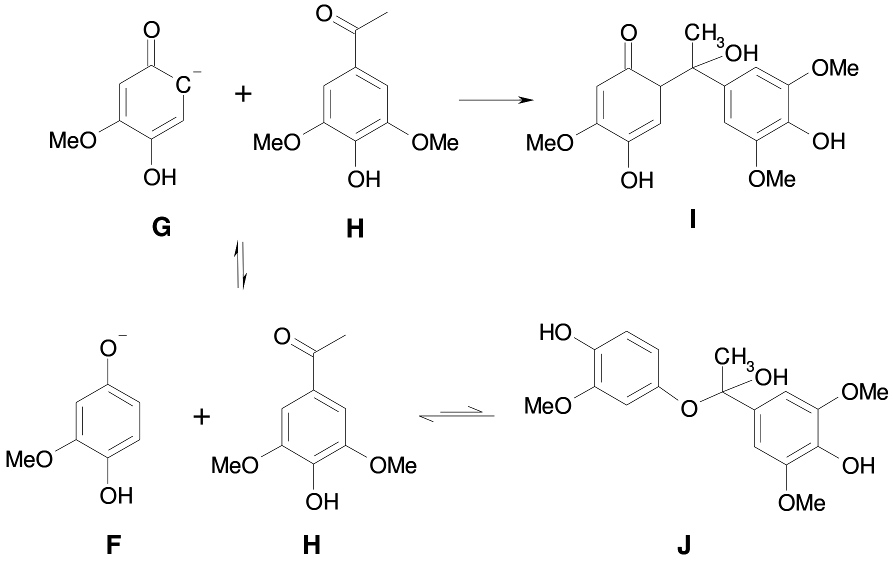


Figure 5.14: Repolymerization reaction between a phenolate and a carbenium ion

Less likely, however also possible, is that the phenolate ion (F) attacks the carbenium ion (J) forming a new aryl-alkyl ether bond. As has been shown, these ether bonds are not very stable and can be cleaved under the present conditions so that the equilibrium of this reaction lies on the side of the reactants.

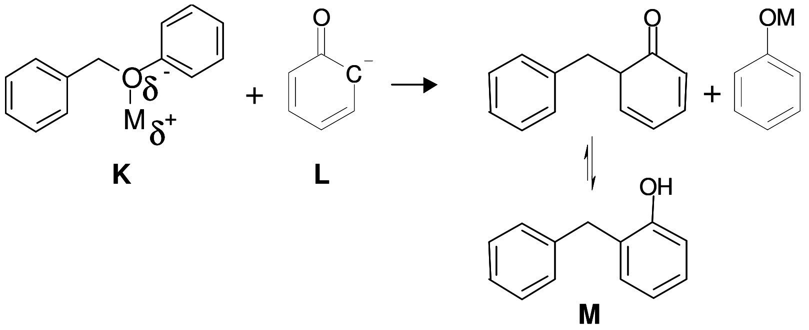


Figure 5.15: Formation of 2- benzyl phenol via a carbanion

This is what we had expected in accordance with previous investigations on hydrothermal treatment of lignin model compounds. A study on benzyl phenyl ether (K), which represents the most frequent bond type in lignin, the aryl-alkyl ether bond, had shown a maximum yield of hydrolysis products between 300 and 320°C [25]. Beyond 320°C yields dropped vastly and higher molecular compounds were formed due to polymerization reactions of the monomers.

In the case of benzyl phenyl ether (K), oligomerization was likewise initiated by a carbanion (L) formed from the main hydrolysis product phenolate. Figure 5.15 shows the formation of the two main side products 2-benzyl phenol (M) and 4-benzyl phenol. This confirms the formation of carbon-carbon bonds initiated by a carbanion species.

Oligomerization and polymerization reactions are also confirmed by the fact that the material regained after washing the filter cake with THF, (defined as “unconverted lignin”) shows a different chemical composition (5.2 wt.% higher carbon content) than the original lignin and yields only 2 wt.% additional product oil when used again as feed for hydrolysis.

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Influence of reaction conditions on lignin depolymerization and sequential polymerization

The yield of product oil obtained from base catalyzed depolymerization of lignin goes through a maximum with both residence time and temperature and decreases with pressure. Oil yields peak at 300°C, a residence time of 4.2 min and 250 bar. The highest yield of 23.3 wt.% oil was obtained from a 10 wt.% lignin/ 4 wt.% NaOH aqueous solution under these conditions. This is in agreement with Miller et al. [21], who found less insoluble products (unconverted lignin) with decreasing lignin/NaOH ratios. The products in this oil have molecular masses below 350 g/mol. As the estimated molecular mass of a syringol unit is estimated to be 175 g/mol, the products consist primarily of monomers and dimers. When the NaOH concentration was decreased to 2.5 wt.% the product oil contained oligomers up to the weight of tetramers. As shown in Figure 5.6 monomer yield is proportional to the concentration of available NaOH (Na^+ cations). However, extrapolation of the monomer yield reveals that approximately 1 wt.% NaOH is necessary to initiate hydrolytic conversion.

In part this “excess” NaOH is needed to convert the hydroxyl groups of phenolic and catecholic compounds into the alcoholate. This process reduces internal hydrogen bonding between the hydroxyl groups [27] and increases the solubility of lignin. The ratio of Na^+ to oxygen atoms in lignin corresponds to eight oxygen molecules per Na^+ atom used, before hydrolysis is being catalyzed in line with the average concentration of free Na^+ cations. It can be speculated that the reduction of the internal hydrogen bonds enhances also the accessibility of the ether bonds and facilitates the cleavage of phenolic monomers of lignin.

NaOH does not play an active role in the mechanism of oligomer formation. However, oligomer formation depends on NaOH concentration in terms of solubility, as the formation of a carbanion is only possible if the hydroxyl group is deprotonated. Figure 4 illustrates that at a NaOH concentration of 2.5 wt.% oligomer yield reaches a plateau indicating that oligomerization is not longer limited by the low solubility of reactants.

In Figure 5.8 is seen that monomer yields slightly increase with lignin dilution while oligomer yields decrease simultaneously. This is what we expect for a consecutive reaction where oligomers are secondary products. This becomes more clear when refering to monomer concentrations. With an increase in initial lignin concentration, monomer concentration rises. Consequently, the rate for oligomer formation is enhanced. This is in agreement with Vigneault et al., who observed a decrease of monomer yield with increasing lignin concentrations [15].

At present, the negative effect of pressure on lignin depolymerization is not clear. Yet, a possible explanation for the decrease in monomer yield could be the solvent cage effect. With increasing pressure the density of the solvent increases, intermolecular interactions are enhanced and the influence of the cage effect becomes stronger [28]. According to the cage effect theory the initially formed ion pair is trapped in the solvent cage $[A^{+}+B^{-}]^{*}$ and the overall reaction from AB to $A^{+}+B^{-}$ can only be realized if the initially formed ion pair is able to diffuse apart. High densities increase the solvent cage strength, as intermolecular interaction becomes stronger. Referring to the β-O-4-bond cleavage, this means that the formed phenolate and the carbenium ion can not diffuse apart and are more likely to recombine and regenerate the reactant. This effect is predominantly observed in super critical water, but has been invoked for reactions in subcritical water to rationalize the change in the reaction pathways with the change in the solvent or with increasing water density [29].

In the same way oligomer formation could be suppressed as the solvent cage would hinder the natrium phenolate ion pair to diffuse and thus suppresses the formation of a carbanion.

5.5 Conclusions

We have shown that the depolymerization of lignin to monomeric compounds is limited by consecutive addition and condensation reactions of the phenolic monomers to oligomers. The formation of monomers from base catalyzed hydrolysis is proportional to the

NaOH concentration in the aqueous solution. However, an excess of NaOH is necessary to initiate hydrolysis. The “excess” NaOH is needed to convert the hydroxyl groups of phenolic and catecholic compounds into the alcoholate. This process reduces internal hydrogen bonding between the hydroxyl groups [27] and increases the solubility of lignin. It can be speculated that the reduction of the internal hydrogen bonds enhances also the accessibility of the ether bonds and facilitates the cleavage of phenolic monomers of lignin.

It is suggested that, during base catalyzed depolymerization of lignin, cleavage of the β-O-4 ether bond takes place heterolytically via the formation of a sodium phenolate derivative and a carbenium ion like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and, thus, polarizing the ether bond. Syringol and its derivatives are preferentially formed due to the stabilization of the carbenium ion transition state by the substituted methoxy groups.

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Chapter 6

Boric acid as a capping agent to suppress oligomerization reactions during hydrothermal lignin treatment

Abstract

The inhibition of concurrent oligomerization reactions during hydrothermal lignin depolymerization is an important issue to enhance product yields. Applying boric acid as a capping agent to suppress addition and condensation reactions of primarily formed products significantly increases lignin depolymerization. Combination of base catalyzed lignin hydrolysis with the addition of boric acid shifts the product distribution to lower molecular weight and further increases products yields.

6 Boric acid as an additive to suppress repolymerization reactions during hydrothermal lignin treatment

6.1 Introduction

Lignin is a vastly abundant but underutilized polymer. Due to its composition of phenyl propane units, it is a potentially rich source of phenolic compounds. If suitably depolymerized, lignin has the potential to be a suitable gasoline additive or diesel fuel when hydro treated. Literature research on lignin depolymerization however, shows that there are limitations to the process. No matter to which condition lignin is exposed, each approach to depolymerize its structure does not yield more than approximately 20-25 wt.% of a product oil containing monomers and dimers. This boundary can be attributed to the repolymerization of the highly reactive lignin cleavage products, forming coke and a lignin like material, which is defined as unconverted lignin. Yet CHN analysis of the unconverted lignin shows a different chemical composition (5.2 wt.% higher carbon content) than the original lignin and yields only 2 wt.% additional product oil when retreated [1]. The mechanism of repolymerization is so far unclear although assumptions have been made in literature [1-5].

To increase the yield of product oil from hydrothermal lignin treatment repolymerization has to be limited. Many attempts have been made hereunto by stabilizing the intermediate products, yet with little success.

In the following, we will give a general literature review, introducing the theory behind these attempts, and will then introduce a new technique which inhibits repolymerization to such an extent, that higher yields of product oil can be obtained.

Ionic and radical mechanisms have been proposed for repolymerization. Xin et al [2] consider hydrolysis and dealkylation to occur, generating reactive low molecular weight fragments as formaldehyde and phenolic compounds. Polymerization of these compounds then takes place by cross-linking of the formaldehyde with the phenolic units. Others assume the formation of stable C-C bonds by condensation of the reactive structures primarily formed by ether hydrolysis [3-5].

Li et al. [6] propose depolymerization and repolymerization to take place simultaneously and that both reaction pathways posses the same intermediate state, namely a carbenium ion, generated at the α carbon atom.

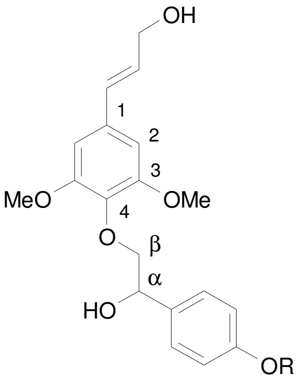


Figure 6.1: The β-O-4 ether bond in lignin

Considering an ionic mechanism, attempts to prevent unfavorable repolymerization, are commonly the addition of a capping or blocking agent. 2003 Saisu *et al.* examined the decomposition of Organosolv lignin, which is tetrahydrofuran (THF) soluble, in supercritical water with and without phenol at 400°C. In the absence of phenol, the yield of THF insoluble products, which were claimed to be formed by repolymerization and to have molecular weights higher than lignin, decreased [7]. The distribution of the THF-soluble products shifted to lower molecular weights, due to prevention of repolymerization of cleavage products. However, yields exceeding 21.6 wt.% were not achieved and a series of alkyl phenols were formed which were not obtained in the absence of phenol. Okuda *et al.* reported the depolymerization of lingo sulfonic acid (THF-insoluble) in a mixture of supercritical water and *p*-cresol [wt.(p-cresol/lignin) = 25/1] [8].. Information on the yield of obtained monomeric and dimeric product oil is not given but gel permeation chromatography (GPC) confirmed that the molecular weight distribution of the original lignin shifted towards smaller molecular weight after reaction at 400 °C for 30 minutes and that the formation of coke was decreased from 13.9 to 0.8 wt% by adding p-cresol to the water. Lora *et al.* studied the conversion of dioxane soluble aspen milled wood lignin at 170 °C and a pH of 3.5 with three different additives (2-naphthol, resorcinol, *p*-hydroxybenzoic acid). By separating into dioxane insoluble (DI) and soluble fractions, it was found that in the absence of an additive the lignin first depolymerized remaining soluble and then repolymerized to become insoluble [9]. When adding 2-naphthol, the formation of DI lignin was avoided. GPC studies showed that just as phenol and p-cresol, 2-naphthol acted as a blocking agent, preventing polymerization effectively by reacting with lignin fragments. Yields of product oil are not given. Man *et al.* compared the effect of phenol as an inhibitor of lignin polymerization to that of benzene in supercritical conditions [2]. In a phenol-water mixture at 400 °C, the formation of coke was reduced to 12 wt.%, while a mixture of benzene and water did not block polymerization. On examining steam treatment of aspen wood and lignin, Li *et al.* investigated the competition between depolymerization and repolymerization of lignin in the presence of blocking agents. Addition of 2-naphthol was revealed to inhibit the polymerization most effectively [10].

Repolymerization of lignin cleavage products has also been claimed to follow a radical pathway [11, 12]. Dorrestjin reports that weak phenoxylic bonds inside the lignin matrix start to cleave and thereby initiate radical reactions. Subsequently, recombination of radical moieties may lead to the formation of new carbon-carbon bonds [12]. Therefore, a further attempt to suppress polymerization of lignin cleavage products is the application of an external hydrogen-donor source to reduce the radical concentration by reacting the radical moieties with hydrogen.

Dorrestjin et al. studied the depolymerisation of lignin to mono phenolic compounds in mixtures of 9,10-dihydroanthracene and dioxane between 227 and 377°C [13]. The highest yield of mono phenolic compounds (7 wt.%) was achieved applying Organosolv lignin in a weight ratio of dioxane to 9,10-dihydroanthracene of 1:1 and 352°C. Tetralin was used as a hydrogen donor solvent in studies on lignin hydrogenolysis conducted by Sugita [14] and Thring [15]. In contrast to Dorrestijin these experiments were conducted in a hydrogen atmosphere additionally to the hydrogen donor solvent. Thring summarizes the detected monomeric products (phenol-, syringyl-, guaiacyl- and catechol derivatives as well as aldehydes) and obtained a maximum yield of approx. 7 wt.% for a reaction time of 60 min at 390°C and with a nickel-tungsten catalyst. Sugita investigated the effect of $FeCl_3$ and $ZnCl_2$ and found a maximum total yield of 24 wt% products obtained from extraction of the acidic fraction in a temperature range of 400-420°C and with $FeCl_3$.

6.2 Experimental

The experiments were carried out in stainless steel autoclaves with a volume of 5.6 mL at 270°C to 360°C and reaction times from 20-60 min. Organosolv lignin purchased from Sigma Aldrich was applied for all experiments. The reactors were filled with 0.1g lignin, 0.2g boric acid and 3.7 mL bi distilled water. To determine the effect of boric acid concentration, the weight ratio boric acid to lignin was varied from 0.5 to 2. For the experiments with NaOH, weight ratios of NaOH to boric acid were varied from 0.5 to 1.25. Base catalyzed depolymerisation experiments (BCD) were conducted under the same conditions with 5 mL of a 10 wt.% lignin/4 wt.% NaOH aqueous solution. The reactors were set in a preheated alumina block which was tumbled to ensure thorough mixing. After the reaction, the autoclaves were quenched to room temperature with water. The autoclaves were rinsed with water and the collected washings were combined with the reactor content. A scheme of the further work up procedure is shown in Figure 6.2. The reaction mixture is first acidified with HCl to a pH value of 1. This results in the precipitation of unconverted lignin and high molecular lignin cleavage units. After adjusting the pH, the solids are removed from the suspension by filtration, dried and weighed. The unconverted lignin as well as the precipitated oligomers can be retrieved from the filter cake by washing with tetrahydrofuran while possibly formed coke remains behind. The acidic filtrate is then repeatedly extracted with ethyl acetate to obtain the formed products. After extraction ethyl acetate is removed a dark brown oil is received which is dried overnight at 60°C before being weighed.

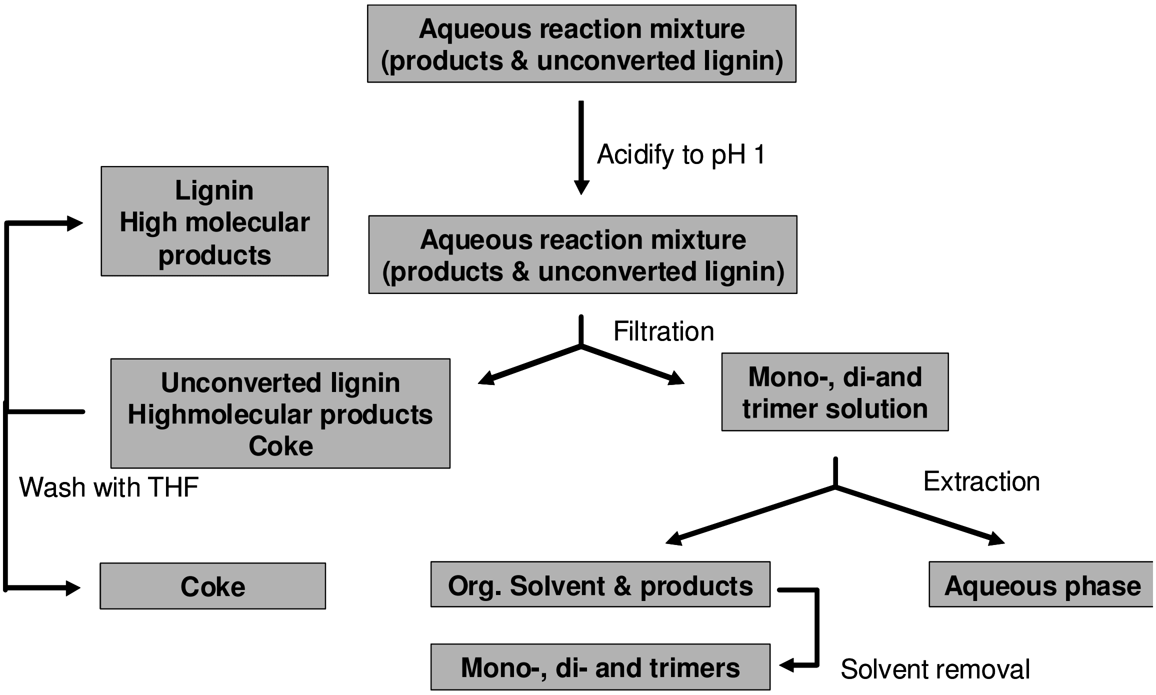


Figure 6.2: Separation sequence for product and lignin recovery

Beside the products contained in the oil, as well as the coke and gaseous products formed at elevated temperatures, ethanol and acetic acid are also generated and remain in the aqueous phase during extraction. A small amount of product, namely CO_2 that was dissolved in the water or present as sodium carbonate is lost as it is set free during the acidification step.

The monomeric reaction products were identified by GC/MS and quantified by GC/FID-analysis using a "Shimadzu" GCMS – QP 20105 gas chromatograph-mass spectrometer (column: HP 5 crosslinked 5 % PhME Siloxane 30). For this purpose the oil was dissolved in ethyl acetate, transferred into a 50 ml calibrated metering flask and leveled with further ethyl acetate. The concentration of the main monomeric products was determined by calibrating the peak area with ethyl acetate solutions of known concentration of these compounds.

Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was employed to determine the product distribution of the product oil. Therefore, solutions of approximately 10 wt.% oil in H_2O/acetonitrile (1:1) with 1 wt.% trifluoroacetic acid were prepared. LDI-TOF mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer.

6.3 Results

To inhibit repolymerization of the highly reactive intermediate products and obtain increased yields of product oil, boric acid was added to the reaction system. The effect of boric acid concentration on product oil yield was investigated at 300°C and a reaction time of 40 min. These resulting oil yields, as well as those obtained under the same conditions in the presence of a base catalyst (10 wt.% lignin/4 wt.% NaOH) and without a catalyst are shown in Figure 6.3.

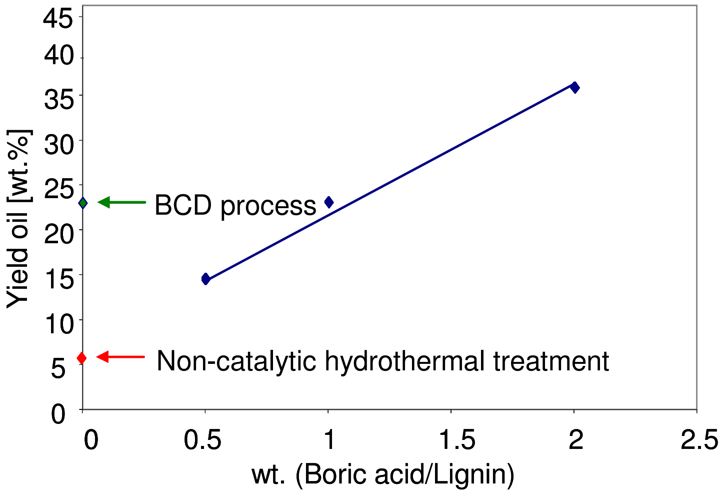


Figure 6.3: Effect of weight ratio boric acid/lignin and comparison to non-catalytic hydrothermal treatment and base catalyzed depolymerization.

It is clearly shown, that by adding even small amounts of boric acid to the system, oil yields are dramatically increased (15 wt.%) compared to the non-catalyzed system under the same conditions (6 wt.%). At a boric acid/lignin weight ratio of 1, the oil yield is equivalent to that obtained from the base catalyzed reaction. A significant increase to 36 wt.% is achieved at a weight ratio of two. Therefore, the following experiments were conducted with a boric acid/lignin weight ratio of 2.

Figure 6.4 shows the dependence of oil yields on reaction time in the presence of boric acid at 300°C.

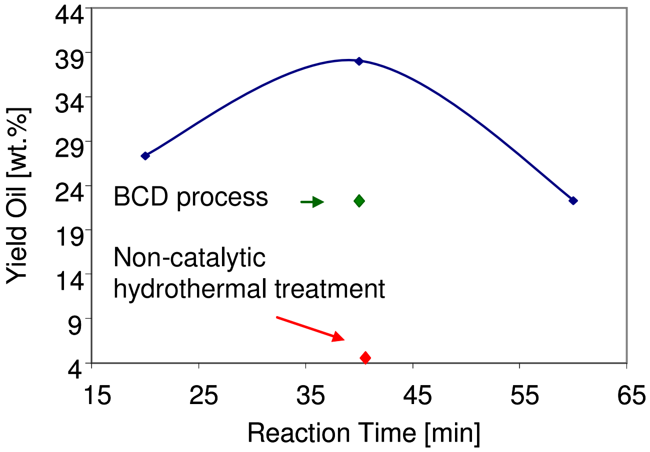


Figure 6.4: Effect of reaction time on oil yield in the presence of boric acid at 300°C, wt.(boric acid/lignin) = 2.

A maximum oil yield of 36 wt.% is reached after 40 min and then drops markedly. This trend is also known from the base catalyzed depolymerization (BCD) of lignin and can be ascribed to the repolymerization of highly reactive intermediate products and will be discussed in more detail further on. The oil yield of 25-26 wt.% represents a maximum. At longer reaction times, higher temperatures and lignin/NaOH ratios yields decrease for the BCD process (Roberts, 2008 – lignin paper).

The effect of temperature on lignin depolymerization in the presence of boric acid is shown in Figure 6.5. The oil yield of 36 wt.% is also a maximum regarding temperature. Again, the same temperature dependence was found for the BCD process, where oil yields likewise peak at 300°C. Therefore, a temperature of 300°C and a reaction time of 40 min were applied for further experiments.

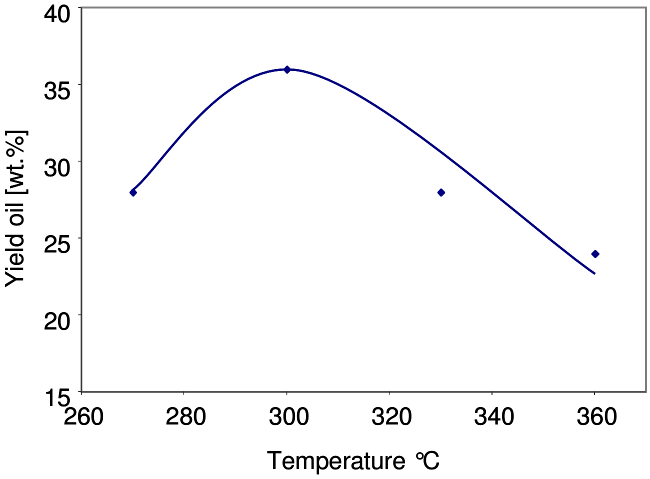


Figure 6.5: Temperature dependence of oil yield from lignin depolymerization in the presence of boric acid after a reaction time of 40 min.

Table 6.1 summarizes the main monomeric compounds and their composition in oil obtained from the BCD process after 40 min. There are three main groups of compounds, namely syringyl, guajacyl and catecholic compounds. Catechol and its derivatives represent the largest fraction with 64 % under these conditions. GC-MS analysis of the product oil obtained from lignin depolymerization in the presence of boric acid shows that hardly any monomers are present in the oil. The total yield of monomers sums up to approximately 1 wt.% of the initial lignin.

To detect higher molecular compounds LDI-TOF/MS spectra of the two oils were measured and compared. The spectra are shown in Figure 6.6. The product spectrum of the BCD oil covers a molecular weight range from approximately 100 to 400 g/mol while intensities are highest in the range of 100 to 350 g/mol. The average weight of a monomeric syringyl derivative is considered to be 180 g/mol. Therefore, we have obtained high quality oil containing primarily mono- and dimers.

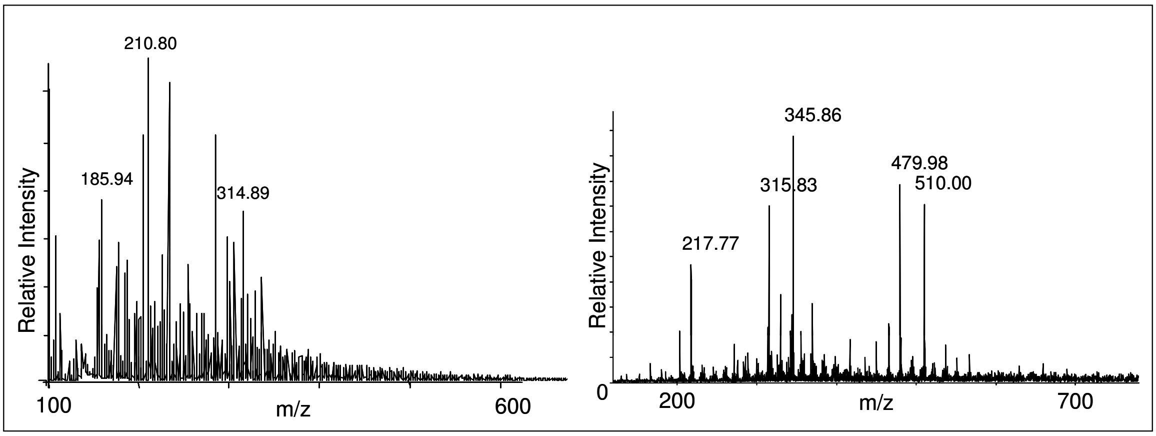
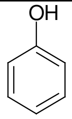
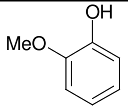
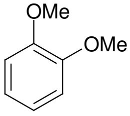
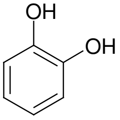
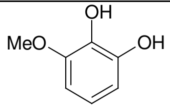
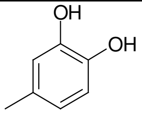
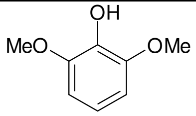
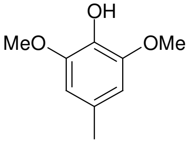
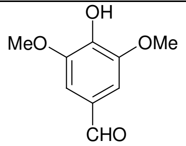
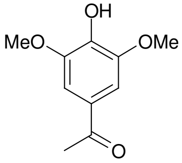


Figure 6.6: **LDI**-TOF spectra of the oil obtained from the BCD process (left) and in the presence of boric acid (right).

Table 6.1: Concentration of various components in the monomeric fraction of an oil obtained from the BCD process at 300°C a residence time of 40 min (lignin 10 wt.%, NaOH 4 wt.%)

Monomer	**Chemical formula**	**Structure**	**wt.% concentration**
Phenol	C_6H_6O		1.0
Guaiacol	$C_7H_8O_2$		10.5
Veratrol	$C_8H_{10}O_2$		1.8
Catechol	$C_6H_6O_2$		33.7
Ortho-methoxy-catechol	$C_7H_8O_3$		24.2
4-methyl catechol	$C_7H_8O_2$		6.6
Syringol	$C_8H_{10}O_3$		8.8
4-methyl syringol	$C_9H_{12}O_3$		2.1
Syringyl aldehyde	$C_9H_{10}O_4$		2.6
3,5-dimethoxy-4-hydroxy acetophenone	$C_{10}H_{12}O_4$		8.8

The LDI-TOF spectrum of the oil obtained in the presence of boric acid shows a clear shift to higher molecular compounds. High intensities are found for oligomers up to molecular weight of 510 g/mol. The quantity of monomers has strongly declined, but product distribution is more defined with a smaller amount of different compounds.

To investigate the effect of the pH on the reaction system with boric acid, NaOH was added. Table 6.2 shows the oil yields for varying the NaOH/boric acid weight ratios from 0 to 1.25. The results show that for the experiments conducted at pH values of 13 and 13.3 oil yields have clearly increased in comparison to the experiment without NaOH.

Table 6.2: Effect of NaOH adjusted pH on the yield of oil at 300°C and 30 min, wt.(boric acid/lignin)=2

Experiment	wt.(NaOH/boric acid)	pH	Yield oil [wt.%]
1	0	3.5	36
2	0.50	9.6	29
3	0.75	13.0	52
4	1.00	13.3	47
5	1.25	13.4	29

A maximum yield of 52 wt.% oil is obtained for a NaOH/boric acid weight ratio of 0.75. At higher ratios the yield declines. However, even at a ratio of 1.25 the yield is still larger than for the BCD process. Surprisingly, at the buffer point of the boric acid/NaOH sytem (pH = 9.6), the oil yield is decreased to 29 wt.%.

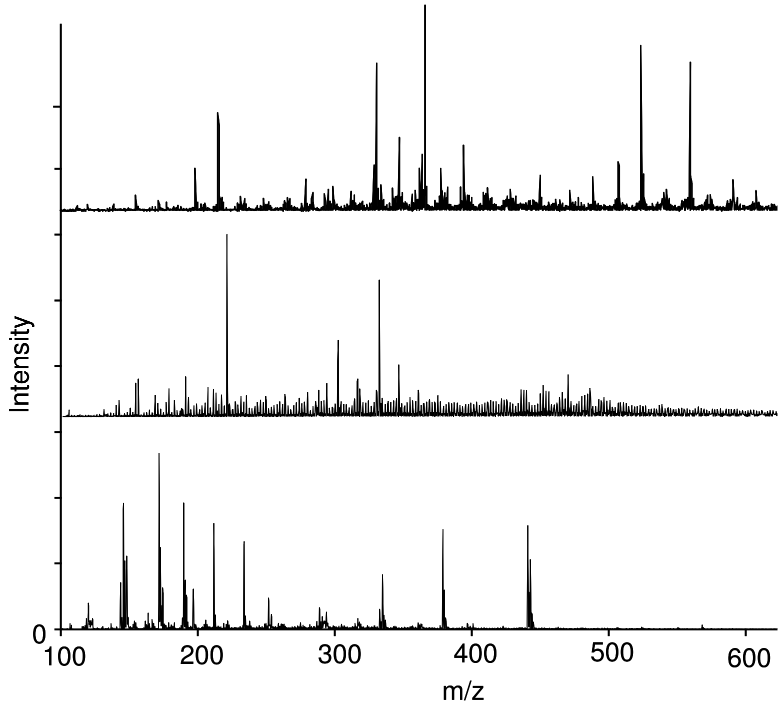


Figure 6.7: LDI-TOF spectrum of oil obtained from experiment with varying NaOH/boric acid ratios at 300°C and 40 min reaction time (top: NaOH/boric acid = 0, middle: NaOH/boric acid = 0.75, bottom: NaOH/boric acid = 1.25).

The LDI-TOF spectra of the oils obtained from the experiments with varying NaOH/boric acid weight ratios (Table 6.2: experiments 1, 3 and 5) are shown in Figure 6.7. With compounds in the range of 150 to 500 g/mol, the oil obtained with from experiment 3 has a narrower molecular weight distribution than the oil obtained from the experiment with only boric acid (experiment 1). Also, in comparison to the oil obtained in the presence of boric acid the monomer fraction (up to 180 g/mol) in the oil has increased. This trend is even more pronounced when the NaOH/boric acid ratio is increased to 1.25 (experiment 5). In this case, the product distribution has become more defined and the monomeric fraction in the oil has further increased. In general, it is observed that with an increasing amount of NaOH the molecular weight distribution is shifted towards lower molecular products, increasing the monomeric fraction of the oil.

It should be noted that only the relative intensities among peaks of one spectrum can be compared but not of two different spectra.

6.4 Discussion

Lignin can be depolymerized via acid and base catalyzed hydrolysis of the ether linkages abundant in its structure. The products of base catalyzed hydrolysis are compiled in Table 6.1, indicating that the initial products formed are substituted derivatives of phenol and catechol [1]. It has been indeed shown that in the early stages of reaction such monomers have been found, which condense via an aldol addition route in the later stages of the reaction [1]. The monomer concentration is proportional to the concentration of NaOH in the aqueous solution, i.e., it is proportional to the activity of the Na^+ cations.

It is important to note at this point that an excess of NaOH is necessary to initiate hydrolytic conversion. In part this “excess” lignin is needed to convert the hydroxyl groups of phenolic and catecholic compounds into the alcoholate. This process reduces internal hydrogen bonding between the hydroxyl groups [16] and increases the solubility of lignin. The ratio of Na^+ to oxygen atoms in lignin corresponds to eight oxygen molecules per Na^+ atom used, before hydrolysis is being catalyzed in line with the average concentration of free Na^+ cations. It can be speculated that the reduction of the internal hydrogen bonds enhances also the accessibility of the ether bonds and facilitates the cleavage of phenolic monomers of lignin.

In contrast to the basic, the acidic environment even enhances the degree of internal hydrogen bonding. As a consequence, the possibility of the acid catalyzed cleavage of ether bonds is reduced compared to the base catalyzed. Thus, in acid catalyzed hydrolysis the fragments produced are larger (dimers to tetramers) than in the base catalyzed route [1].

For both cases the formed primary products undergo facile addition and condensation reactions leading to higher molecular weight products [1]. The solubility of these secondary products as well as the reactivity towards catalytic hydrolysis is significantly lower than that of the reacting lignin.

We decided, therefore, to block the reactions, by capping the phenolic hydroxy groups with boric acid forming strongly coordinated boric acid esters (see Figure 6.8). The esterification is shown conclusively by ^{1}H NMR spectra of the products indicating that phenolic groups are reacted nearly quantitivaley. The results show that increasing the concentration of boric acid increases the yield of such products proportionally (see Figure 6.3). The finding that capping the phenolic hydroxyl groups suffices to prevent oligomerization strongly suggests that the phenolic hydroxyl groups are the most important active groups involved in the addition and condensation reactions [1, 17].

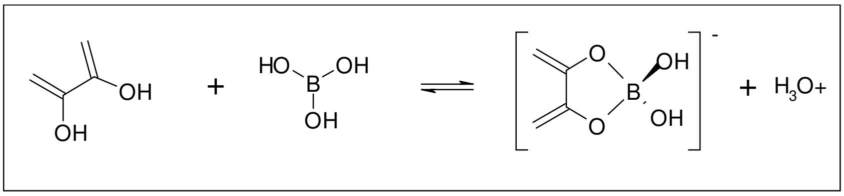


Figure 6.8: Formation of mono esters with cis-diols

While the increase in yield by adding boric acid was impressive, the consisitency of the filter cake was even more surprising. The product distribution of the filter cake and the oil was very similar. In consquence, extraction of the filter cake more than doubled the yield of usable products, pushing the yield in oligomers to 85 wt.%, without changing the product distribution.

The question now arises whether or not the hydrolysis of lignin to oligomers can also be modified in a way that preferentially monomeric units are being formed. For this purpose NaOH catalyzed hydrolysis was combined with the addition of boric acid. The combination of the two indeed shifts product distribution to lower molecular weights (see Figure 6.9) and the monomeric fraction in the oil is increased proportionally to the NaOH concentration. This is in agreement to the increase of monomer yield with NaOH concentration in the absence of boric acid [17].

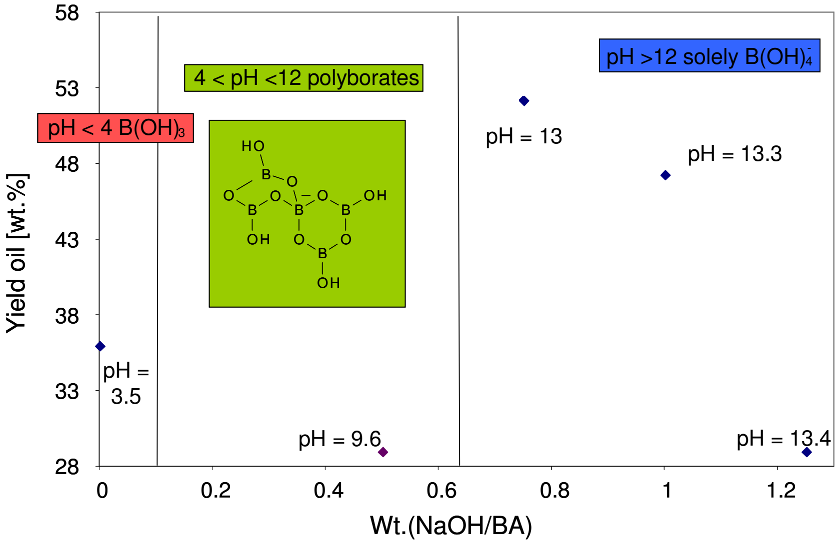


Figure 6.9: Effect of pH on oil yields and existing structure of boric acid

The combination of the two processes also has a strong effect on the total yield of formed products, depending on the applied NaOH/boric acid weight ratio (see Table 6.2). A synergistic effect of NaOH and boric acid was found at weight ratios of NaOH/boric acid of 0.75 to 1. In this range, product yield was increased up to 52 wt.%. However, at lower and higher weight ratios less products are formed than in the mere presence of boric acid. This is related to the structure of boric acid in the aqueous solution, which is determined by the pH value [18] and shown in Figure 6.9. At a pH lower 4 boric acid exists as $B(OH)_3$ and readily reacts with hydroxy groups to form boric acid esters. This also applies to pH values larger 12. In this case boric acid is existent as borate $B(OH)_4^-$ and can likewise act as a capping agent to hinder condensation and additon reactions of the primarily formed products. The reduction of product yield at very high NaOH concentrations is attributed to the competing effect of a high OH^- concentration in the aqueous solution reducing the probability of ester formation. At pH values in the range of 4 to 12, polyborates exist predominantly in solution, and are less prone to react with phenolic and catecholic compounds. This explains the reduced product yield of 29 wt.% at a NaOH/boric acid weight ratio of 0.5 (pH = 9.6).

6.5 Conclusion

The inhibition of concurrent oligomerization reactions during hydrothermal lignin depolymerization is important to enhance product yield from lignin depolymerization. Boric acid has shown to be an excellent capping agent forming esters with phenolic OH groups. Note that this indirectly also shows that the phenolic OH groups are key to these secondary oligomerization rections. The acid catalyzed hydrolysis route is concluded to produce larger fragments as primary products, because the stabilization of intermolecular hydrogen bonding in lignin reduces the steric accessibility of ether groups for hydrolysis. In consequence, dimers to tetramers are the most abundant products when boric acid is present as catalyst and capping agent. With this approach 85% of lignin can be utilized in a single reaction step. The product composition can be shifted to monomeric products by addition of appropriate concentration of NaOH. The results indicate that lignin can be successfully converted into chemically viable tailored phenolic building blocks.

6.6 References

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Chapter 7

Summary

7.1 Summary

While the need for energy and raw materials is increasing world wide, environmental problems, as a result of utilizing coal, crude oil and natural gas are gaining weight. The decline of crude oil reservoirs and the associated fear of an energy crisis make renewable resources more and more a topic of discussion. Due to its “CO_2 neutrality”, biomass has a high potential for the future and has to be considered as a regenerative resource for energy and chemical production.

Lignin is a vastly abundant, but underutilized polymer. Due to its composition of phenyl propane units, it is a potentially rich source of phenolic compounds for chemical production. If suitably depolymerized, lignin further has the potential to be utilized as gasoline additive or diesel fuel when hydro treated.

Three general routes for lignin conversion exist: (i) gasification to produce syngas, (ii) production of biooil through pyrolysis or liquefaction and (iii) hydrolysis to produce monomer and/or oligomer units. The first two routes demand severe conditions, while hydrolysis is comparatively mild. Hydrolysis of lignin however, remains a great challenge due to the extremely high thermal stability of the polymer, as well as in the difficulty of controlling a selective bond cleavage into the phenolic monomers. The aim of this work was therefore, to optimize reaction engineering and to develope a processing concept for hydrothermal lignin conversion. Further, this work represents a fundamental investigation towards characterization of the reaction products from catalytic hydrothermal lignin depolymerization.

Due to the complexity and diversity of the lignin structure, model compounds were applied to investigate the behaviour of lignin in sub-and supercritical water. Six compounds were chosen, namely diphenyl ether, benzyl phenyl ether, diphenyl methan, eugenol, 4-methoxy biphenyl und phthalan to represent the most frequent occuring bond types in lignin. The results are summarized and discussed in chapter 3. It was shown that, in all model compounds, the ether bond is cleaved both by pyrolysis and hydrolysis under the applied conditions. Product distribution, however, can be influenced by adjusting the density of the solvent. An increase in density shifts the reaction route towards an ionic pathway and the formation of hydrolysis products is enhanced. For the very stable aryl-aryl ether bond in DPE, a 100 % selectivity towards the hydrolysis product phenol is achieved at high densities in supercritical water. By addition of alkali carbonates operation temperature for DPE conversion is reduced from over 400°C to 350°C. Phenol yields are highest for K_2CO_3.

However, when K_2CO_3 is supported on ZrO_2 significant yields of phenol and a phenol selectivity of 100% can be achieved with much smaller amounts of the carbonate. We ascribe this to the increased amount of hydroxyl groups in the system, due to the dissociative absorption of water on the metal oxide carrier. In contrast, alkali carbonates show an inhibiting effect on BPE hydrolysis in subcritical water at low temperatures (270-300°C). This is related to a change in solvent properties by addition of the carbonate. As the polarity of water is increased in the presence of a salt, phase separation is enhanced and hydrolysis reduced.

The C-C bonds in diphenyl methane and 4- methoxy biphenyl are not cleaved below 400°C and in the presence of 10wt.% K_2CO_3/ZrO_2. It was further shown that the application of alcohols and alcohol/water solutions as solvents is unsuitable, as hydrolysis is inhibited and the product spectrum broadens due to reaction of the model compounds with the solvent.

Relating these findings to the base catalyzed depolymerization of lignin, it is concluded that among the bonds connecting the aromatic units, predominantly aryl-alkyl ether bonds, specifically the β-O-4 ether bond, will be cleaved under the conditions applied. Consequently, beside the phenolic monomers a large amount of oligomeric coumpounds are obtained upon hydrothermal treatment. These compounds are dimers and trimers, but also higher molecular oligomers.

Composition of the product oil differs strongly depending on the work up process, but so far, a standard procedure has not been published. When lignin depolymerization aims towards the production of chemicals, a high monomeric content of the product oil is desirable. Therefore, a novel work up procedure for hydrothermal lignin depolymerization was elaborated and is presented in chapter 4. The suggested work up yields a high value product oil consisting predominantly of monomers and dimers. Furthermore, a variety of solvents were investigated which allow tailoring the properties of the oil by selective extraction.

The products of base catalyzed liquid phase hydrolysis of lignin depend markedly on the operation conditions. Varying temperature, pressure, catalyst concentration and residence time the yield of monomers and oligomers from depolymerized lignin can be adjusted. These results, as well as a concluded mechanism for the base catalyzed depolymerization are presented in chapter 5. It is shown that the depolymerization of lignin to monomeric compounds is limited by consecutive addition and condensation reactions of the phenolic monomers to oligomers. The formation of monomers from base catalyzed hydrolysis is proportional to the NaOH concentration in the aqueous solution. However, an excess of NaOH is necessary to initiate hydrolysis. The "excess" NaOH is needed to convert the hydroxyl groups of phenolic and catecholic compounds into the alcoholate. This process reduces internal hydrogen bonding between the hydroxyl groups and increases the solubility of lignin. It can be speculated that the reduction of the internal hydrogen bonds enhances also the accessibility of the ether bonds and facilitates the cleavage of phenolic monomers of lignin.

It is suggested that, during base catalyzed depolymerization of lignin, cleavage of the β-O-4 ether bond takes place heterolytically via the formation of a sodium phenolate derivative and a carbenium ion like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and, thus, polarizing the ether bond. Syringol and its derivatives are preferentially formed due to the stabilization of the carbenium ion transition state by the substituted methoxy groups.

As mentioned above, the formed primary products from lignin hydrolysis undergo facile addition and condensation reactions leading to higher molecular weight products. The inhibition of concurrent oligomerization reactions during hydrothermal lignin depolymerization is, thus, important to enhance product yield from lignin depolymerization. We decided, therefore, to block the reactions, by capping the phenolic hydroxy groups with boric acid forming strongly coordinated boric acid esters. The obtained results are presented in chapter 6. Boric acid has shown to be an excellent capping agent forming esters with phenolic OH groups. Note, that this indirectly also shows that the phenolic OH groups are key to these secondary oligomerization rections. The acid catalyzed hydrolysis route is concluded to produce larger fragments as primary products, because the stabilization of intermolecular hydrogen bonding in lignin reduces the steric accessibility of ether groups for hydrolysis. In consequence, dimers to tetramers are the most abundant products when boric acid is present as catalyst and capping agent. With this approach 85% of lignin can be utilized in a single reaction step. The product composition can be shifted to monomeric products by addition of appropriate concentration of NaOH. These results indicate that lignin can be successfully converted into chemically viable tailored phenolic building blocks.

7.2 Zusammenfassung

Aufgrund des weltweit zunehmenden Verbrauchs an Energie und Rohstoffen wachsen die aus der Nutzung von Kohle, Rohöl und Erdgas resultierenden Umweltprobleme. Die zur Neige gehenden Erdölressourcen und die damit verbundene Angst einer drohenden Energiekrise rücken erneuerbare Rohstoffe zunehmend in den Fokus des Interesses auf Seiten von sowohl Energielieferanten als auch -verbrauchern. Aufgrund ihrer „CO_2-Neutralität“, besitzt Biomasse ein hohes Zukunftspotential und muß als Rohstoff für erneuerbare Energie und die Herstellung von Feinchemikalien berücksichtigt werden.

Aufgrund seiner hohen Bioverfügbarkeit und gleichzeitig noch geringen Nutzung handelt es sich bei Lignin um ein kommerziell interessantes Polymer. Seine Zusammensetzung aus Phenylpropan-Untereinheiten macht Lignin zu einer potentiellen Ausgangsverbindung für die Herstellung phenolischer Verbindungen in der chemischen Industrie.

Des Weiteren kann es, nach Depolymerisation und Hydrierung, als Grundstoff für die Gewinnung von Benzinadditiven und Dieselbrennstoffen dienen. Hierbei können drei verschiedene Varianten zur Behandlung des Rohmaterials unterschieden werden: (i) Vergasung zur Synthesegas-Herstellung, (ii) Herstellung von Bioöl durch Pyrolyse respektive Verflüssigung und (iii) Hydrolyse zur Gewinnung von Monomeren und niedermolekularen Oligomeren.

Bei den ersten beiden Verfahren werden harsche Bedingungen benötigt, während die Hydrolyse vergleichsweise mild ist. Durch die extrem hohe Strukturstabilität und die Schwierigkeit einer selektiven Spaltung in Monomere stellt die Hydrolyse von Lignin jedoch immer noch eine große Herausforderung dar.

Ziel dieser Arbeit war es daher, einerseits ein Verfahrenskonzept für die hydrothermale Ligninumsetzung zu entwickeln und andererseits die Prozeßbedingungen zu optimieren. Zusätzlich beinhaltet diese Arbeit eine umfassende Charakterisierung der gewonnen Produkte.

Lignin besitzt eine sehr komplexe und vielfältige Struktur. Es wurden daher Modellverbindungen eingesetzt, um das Verhalten von Lignin in sub- und überkritischem Wasser zu untersuchen. Sechs Verbindungen wurden gewählt, um die häufigsten Bindungsarten im Lignin abzubilden: Diphenylether, Benzylphenylether, Diphenylmethan, Eugenol, 4-Methoxybiphenyl und Phthalan. Die Ergebnisse sind in Kapitel 3 zusammengefasst und diskutiert. Es wurde gezeigt, dass in allen Verbindungen die Etherbrücken sowohl über einen radikalischen als auch einen ionischen Mechanismus umgesetzt werden. Die Ausbeuten an Hydrolyseprodukten, die über einen ionischen Mechanismus gebildet werden, lassen sich jedoch deutlich mit der Dichte erhöhen. Bei hohen Dichten wird für die DPE-

Umsetzung in überkritischem Wasser sogar eine 100 %ige Selektivität zum Hydrolyseprodukt Phenol erreicht. Ohne Katalysator findet unterhalb von 460°C keine DPE-Umsetzung statt. Durch die Zugabe von Lithium-. Natrium- und Kalium-Carbonat erzielt man bereits ab 350°C signifikante Ausbeuten an Phenol. Die Selektivität ist dabei für K_2CO_3 am höchsten.

Ebenfalls hohe Ausbeuten und Selektivitäten lassen sich mit weitaus kleineren Mengen an K_2CO_3 erreichen, wenn dieses auf ZrO_2 geträgert wurde. Dies wird auf die höhere Konzentration von Hydroxylgruppen durch die dissoziative Absorption von Wasser auf dem Metalloxidträger zurückgeführt.

Im Gegensatz dazu hemmt die Zugabe von Alkalicarbonaten die Hydrolyse von BPE in subkritischem Wasser bei niedrigen Temperaturen (270-300°C). Diese Beobachtung wird mit einer Veränderung der Lösungsmitteleigenschaften durch Zugabe der Salze in Verbindung gebracht. Das Salz verursacht eine erhöhte Polarität des Wassers, wodurch eine Phasentrennung begünstigt und somit die Hydrolyse gehemmt wird.

Die C-C-Bindung zwischen den aromatischen Einheiten im 4-Methoxybiphenyl sowie die Methylenbrücke im Diphenylmethan lassen sich unter den verwendeten Bedingungen, auch nicht bei Zugabe von ZrO_2 geträgertem K_2CO_3, spalten. Es wurde weiterhin gezeigt, dass Alkohole als Lösungsmittel ungeeignet sind. Gründe hierfür sind vor allem eine Hemmung der Hydrolyse, aber auch ein Rückgang der Selektivität an Hydrolyseprodukten durch die Formation einer weitaus breiteren Produktpalette. Zudem wird ein Großteil des Alkohols vergast.

Aus den Experimenten mit Lignin-Modellverbindungen lässt sich folgern, dass bei der basenkatalysierten Lignin-Hydrolyse vorwiegend die Aryl-Alkyl Etherbindungen, insbesondere die β-O-4 Bindungen, gespalten, und neben Monomeren auch ein großer Anteil Oligomere erhalten wird.

Die Zusammensetzung des gewonnen Produktöls hängt dabei stark von der Aufarbeitung ab. Bisher publizierte Verfahren weichen stark voneinander ab und liefern Öle mit hohem Oligomeranteil. Zielt die Lignin-Hydrolyse jedoch auf die Chemikaliengewinnung ab, so ist ein hoher Anteil von Monomeren erforderlich. Eine Aufarbeitungsmethode, die ein hochwertiges Öl liefert, bestehend aus vorwiegend Monomeren und Dimeren, konnte im Rahmen dieser Arbeit erfolgreich entwickelt werden und wird in Kapitel 4 beschrieben. Zudem wurde eine Reihe verschiedener Lösungsmittel untersucht, die durch selektive Extraktion ein Abstimmen der Produkteigenschaften erlauben.

Die aus der basenkatalysierten Ligninhydrolyse gewonnen Produkte hängen stark von den Reaktionsbedingungen ab. Monomer- und Oligomerausbeute lassen sich durch Variation der Temperatur, des Drucks, der Katalysatorkonzentration und der Verweilzeit einstellen. Die Ergebnisse der hierzu durchgeführten Experimente sowie der daraus folgende Reaktionsmechanismus für die basenkatalysierte Depolymerisierung finden sich in Kapitel 5.

Es konnte gezeigt werden, dass die Depolymerisierung zu monomeren Produkten durch Folgereaktionen wie Additions – und Kondensationsreaktionen der Monomere limitiert ist.

Die Bildung der Monomere ist dabei proportional zur NaOH-Konzentration der wässrigen Lösung. Ein Überschuß an NaOH ist jedoch nötig um die Hydroxylgruppen der Phenol- und Catecholverbindungen in das entsprechende Alkoholat zu überführen und somit die Monomerbildung zu initiieren. Dadurch wird die Anzahl intramolekularer Wasserstoffbrückenbindungen (WBB) reduziert und die Löslichkeit des Moleküls erhöht. Es wird angenommen, dass die Reduktion der intramolekularen WBB die Zugänglichkeit der Etherbrücken erhöht und dadurch die Depolymerisierung in Monomere erleichtert wird.

Kinetische Untersuchen deuten auf eine heterolytische Spaltung der β-O-4 Etherbrücke hin. Dabei wird ein Natriumphenolat und ein Carbeniumartiger Übergangszustand gebildet, der sofort durch ein Hydroxidion neutralisiert wird. Na^+ katalysiert dabei die Spaltung durch Polarisierung der Lignin Etherbrücken. Syringolverbindungen werden bei der basenkatalysierten Ligninhydrolyse bevorzugt gebildet, da im Übergangszustand das Carbeniumion durch die erhöhte Anzahl der Methoxygruppen stabilisiert wird.

Wie bereits erwähnt, reagieren die Primärprodukte der Ligninhydrolyse durch Addition und Kondensation zu Oligomeren weiter. Um die Ausbeute an Spaltprodukten zu erhöhen, muß die Oligomerisierung folglich unterdrückt werden. Die Reaktion von Borsäure mit Alkoholen zu Borsäureestern ist bekannt. Wir haben deshalb beschlossen, Folgereaktionen der Primärprodukte durch Blockierung der phenolischen Hydroxygruppen mit Borsäure zu verhindern. Die erhaltenen Ergebnisse werden in Kapitel 6 vorgestellt.

Borsäure hat sich durch ihre Fähigkeit zur Ausbildung von Estern mit phenolischen Hydroxylgruppen, als hervorragendes Reagenz zur Unterdrückung der Oligomerisierung erwiesen. Die Ergebnisse lassen darauf schließen, dass die säurekatalysierte Hydrolyse durch Stabilisierung der intramolekularen WBB im Lignin die Zugänglichkeit der Ethergruppen reduziert und deshalb zu höhermolekularen Produkten führt. Folglich erhält man in Anwesenheit von Borsäure vorwiegend Dimere bis Tetramere. Mit diesem Verfahren erhält man in einem einzigen Reaktionsschritt eine 85%ige Ausbeute an Hydrolyseprodukten. Durch Zugabe geeigneter Mengen NaOH läßt sich die Produktzusammensetzung zu einem höheren Monomeranteil verschieben.

Im Rahmen dieser Arbeit konnte gezeigt werden, dass die Lignin Depolymerisierung zu wertvollen, industriell nutzbaren phenolischen Verbindungen realisierbar ist.

8 Curriculum vitae

Virginia Marie Roberts was born in Landstuhl, Germany on December 1st, 1978. She visited the Gymnasium Wiesloch untill September 1993 and then moved with her parents to Augsburg, where she visited the Holbein Gymnasium. 1998 she graduated and received her Abitur (general qualification for university entrance). In the same year she took up chemistry studies at the Technische Universität München, majoring in biochemistry. In 2004, Virginia Roberts joined the group of Johannes Lercher (Chair for technical chemistry II) for her Diploma thesis entitled “Mechanistic studies of SO_2-adsorption on metal oxides incorporated in porous networks”. After graduation as “Diplom-Chemiker” (master degree) in Mai 2004, she stayed in the group of Johannes Lercher as a PhD student at the Tecnische Universität München. Her work was focused on the catalytic hydrothermal conversion of lignin.

9 List of publications

1. Roberts, V. M., Knapp, R., Lercher, J. A. „Catalytic conversion of diphenylether in supercritical water as a model compound for lignin hydrolysis”, 2008, in preparation
2. Roberts, V. M., Fendt, S., Lercher, J. A. “The influence of alkali carbonates on hydrolysis of benzyl phenyl ether in subcritical water”, 2008, in preparation
3. Roberts, V. M., Unkelbach, G., Schweppe, R., Lercher, J.L., 2008, “Elaboration of an optimized work up procedure for the BCD process”, in preparation
4. Roberts, V. M., Lercher, J. A., 2008, “On the mechanism of base catalyzed depolymerization of lignin“, ready for submission to J. Am. Chem. Soc.
5. Roberts, V. M., Stein, V., Lercher, J. A., 2008, “Boric acid as a capping agent to suppress oligomerization reactions during hydrothermal lignin treatment”, ready for submission to Angew. Chem. Int. Ed.

10 Oral and poster presentations

1. ERA Chemistry Workshop, “Ether hydrolysis as key reaction to utilize lignin”, April 2008 in Krakow, Poland
   V. M. Roberts, J. A. Lercher, oral presentation
2. Europacat 8, “Catalytic conversion of diphenyl ether in supercritical water as a model compound for lignin hydrolysis”, August 2007 in Turku, Finland
   V. M. Roberts, R. T. Knapp, J. A. Lercher, poster presentation
3. Jahrestreffen Deutscher Katalytiker, “ZrO_2 supported K_2CO_3 for the conversion of diphenyl ether in supercritical water“, March 2007 in Weimar, Germany
   V. M. Roberts, J. A. Lercher, poster presentation